isomer ratios are absolutely constant[10] for some 11 leaving groups, a fact which contrasts sharply with the acid hydrolysis results reported in Table I. Indeed, the product ratios for the OH^--catalyzed reactions of pentaamminecobalt(III) species, defined not only by total anion competition[1] but also by ratios of linkage isomers[10,41,42] as well as geometric and optical isomers,[1,4,32] are generally less leaving-group sensitive compared to their "spontaneous" and "induced" aquation counterparts. In this light it does not seem unreasonable to discuss the substitution processes in terms of transient five-coordinate species that exist for lifetimes sometimes shorter and sometimes longer than the diffusion times associated with anion transferral (including the leaving group) between the solvation shell of the complex and the bulk solution.

Acknowledgment. Financial support from the Australian Research Grants Scheme is gratefully acknowledged. We are also indebted to Mrs. J. McKeon for assistance with some of the competition experiments.

---

(41) Jackson, W. G.; Randall, M. L.; Sargeson, A. M.; Marty, W. *Inorg. Chem.* **1983**, *22*, 1013.
(42) Jackson, W. G.; Fairlie, D. P.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 197.

Contribution from the Department of Chemistry,
University of Missouri—St. Louis, St. Louis, Missouri 63121

Preparation and Substitution Reactions of (Diphosphine)platinum(II) Carboxylate Complexes

Gordon K. Anderson* and Gregg J. Lumetta

Received September 18, 1986

$[Pt(OCOPh)_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane), [Pt(mal)(dppe)] (mal = malonate), and [Pt(mal)(dppm)] (dppm = bis(diphenylphosphino)methane) are prepared by treatment of $[PtCl_2(dppe)]$ or $[PtCl_2(dppm)]$ with AgOCOPh or $Ag_2(mal)$. $[Pt(OCOPh)_2(dppe)]$ reacts with P-*n*-Bu_3 to yield $[Pt(OCOPh)(P\text{-}n\text{-}Bu_3)(dppe)]^+$, which subsequently reacts with chlorinated solvents to produce $[PtCl(P\text{-}n\text{-}Bu_3)(dppe)]^+$. Analogously, [Pt(mal)(dppe)] gives $[PtCl(L)(dppe)]^+$ when treated with P-*n*-Bu_3, PEt_3, or $PMePh_2$. In the case of L = P-*n*-Bu_3 the intermediate $[Pt^+(OCOCH_2COO^-)(P\text{-}n\text{-}Bu_3)(dppe)]$ is observed spectroscopically at low temperature and may be protonated with $HClO_4$. The ease of substitution of dicarboxylate or diphosphine ligands is investigated by allowing $[Pt(O^\frown O)(P^\frown P)]$ ($O^\frown O$ = C_2O_4, mal; $P^\frown P$ = dppe, dppm) to react with P-*n*-Bu_3. [Pt(mal)(dppm)] reacts with 2 molar equiv of P-*n*-Bu_3 or $PMePh_2$ to give ion-paired species of the form $[Pt(L)_2(dppm)][mal]$.

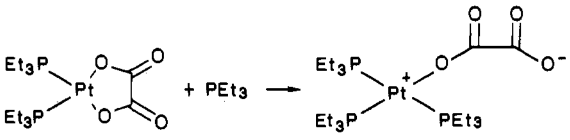
Introduction

Halide substitutions by neutral ligands in complexes of the type $[PtCl_2(P^\frown P)]$ ($P^\frown P$ = diphosphine) have been reported by Davies et al.,[1] and we have recently described a detailed spectroscopic study of the reactions of $[PtCl_2(P^\frown P)]$ complexes with tertiary phosphines.[2] Information about the substitution chemistry of (diphosphine)platinum carboxylate complexes is scant, however. Many of the substitution reactions of platinum(II) carboxylate complexes containing monodentate ligands are presented in the literature in terms of their synthetic utility. Paonessa et al.,[3] for example, have reported that the triphenylphosphine ligands in $[Pt(C_2O_4)(PPh_3)_2]$ may be displaced by more nucleophilic ligands such as PMe_3, PEt_3 or P-*n*-Bu_3, (eq 1). Similarly, diethyl sulfide

$$[Pt(C_2O_4)(PPh_3)_2] + 2L \rightarrow [Pt(C_2O_4)L_2] + 2PPh_3 \qquad L = PMe_3,\ PEt_3,\ P\text{-}n\text{-}Bu_3 \tag{1}$$

is readily displaced from $[Pt(C_2O_4)(SEt_2)_2]$ by treatment with PEt_3 or PPh_3,[3] and $[Pt(OCOMe)_2(SEt_2)_2]$ is converted to $[Pt(OCOMe)_2(PPh_3)_2]$ by treatment with triphenylphosphine.[4]

In each of the above examples it is the neutral ligand that is displaced, while the carboxylate ligand remains coordinated, but Paonessa et al. have described a reaction in which a carboxylate ligand is displaced from the platinum center.[3] When a CH_2Cl_2 solution of $[Pt(C_2O_4)(PEt_3)_2]$ is treated with excess PEt_3 an associative exchange of PEt_3 occurs, and a species of the form $[Pt(C_2O_4)(PEt_3)_3]$ is observed at low temperature (eq 2).



(2)

In this paper we report the preparation of some platinum(II) carboxylate complexes containing diphosphine ligands and their substitution reactions. The latter are complicated by reaction of the substitution products with chlorinated solvents, and these secondary reactions are discussed also. A preliminary account of part of this work has appeared.[5]

Results and Discussion

The platinum(II) oxalate and malonate complexes are prepared by the reaction of $[PtCl_2L_2]$ (L_2 = dppe, dppm) with 1 molar equiv of the appropriate silver(I) salt in CH_2Cl_2 solution, and they have been characterized by elemental analysis and infrared and $^{31}P\{^1H\}$ NMR spectroscopy. The data for the oxalate complexes have been reported previously.[6]

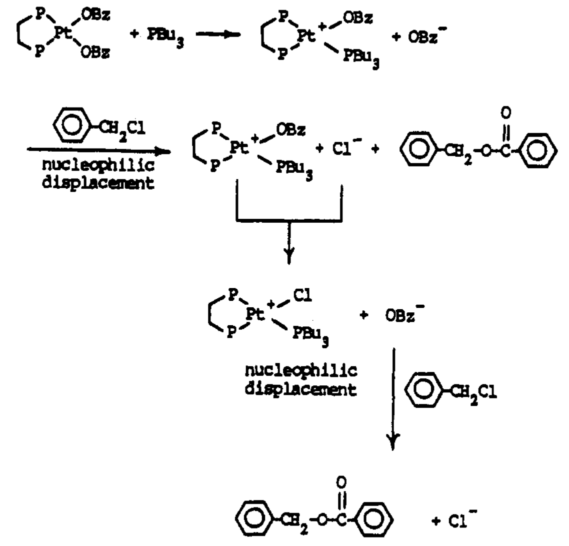
The infrared spectra of the oxalate complexes are characteristic of oxalate bound to the metal to form a five-membered ring.[3,7] The malonate complexes exhibit similar infrared spectra, for which band assignments are based on those reported previously.[8] Very broad absorptions appear at 1650 cm^{-1} for [Pt(mal)(dppe)] and 1640 cm^{-1} for [Pt(mal)(dppm)], and their shapes suggest that they are composites of several overlapping bands. These are

---

(1) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299.
(2) Anderson, G. K.; Lumetta, G. J. *Inorg. Chem.*, in press.
(3) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647.
(4) Kuyper, J. *Inorg. Chem.* **1979**, *18*, 1484.
(5) Anderson, G. K.; Lumetta, G. J. *Inorg. Chim, Acta* **1986**, *118*, L9.
(6) Anderson, G. K.; Lumetta, G. J. *J. Organomet. Chem.* **1985**, *295*, 257.
(7) Fujita, J.; Martell, A. E.; Nakamoto, K. *J. Chem. Phys.* **1962**, *36*, 324, 331.
(8) Schmelz, M. J.; Nakagawa, I.; Mizushima, S.; Quagliano, J. V. *J. Am. Chem. Soc.* **1959**, *81*, 289.

0020-1669/87/1326-1291$01.50/0

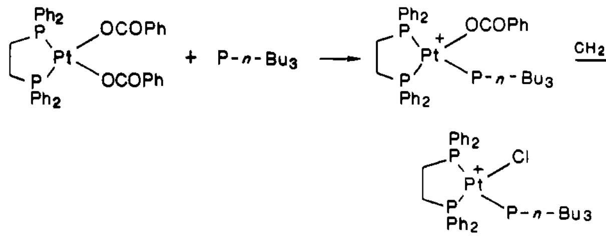
Scheme I



assigned to the O–C–O antisymmetric stretches, whereas the O–C–O symmetric stretch is observed at 1357 cm^{-1} for each complex. The –CH$_2$– rocking vibration may be seen at 930 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra of the oxalate and malonate complexes are very similar to those of the corresponding chlorides, suggesting that chelated oxalate and malonate ligands have trans influences similar to that of the chloride ligand.[9] The dppe complexes exhibit a downfield shift of the ^{31}P resonance relative to that of the free ligand, whereas the dppm complexes exhibit a large shift to higher field. These observations are typical for phosphorus atoms that are incorporated into five- or four-membered chelate rings, respectively.[10]

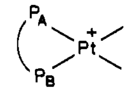
The complex [Pt(OCOPh)$_2$(dppe)] is prepared by reaction of [PtCl$_2$(dppe)] with 2 molar equiv of AgOCOPh in CH$_2$Cl$_2$ solution. It exhibits ν(C=O) and ν(C—O) bands in its infrared spectrum at 1625 and 1337 cm^{-1}, respectively. In its $^{31}P\{^1H\}$ NMR spectrum the one-bond platinum–phosphorus coupling constant is 100 Hz larger than that in [Pt(mal)(dppe)].

When a CH$_2$Cl$_2$ solution of [Pt(OCOPh)$_2$(dppe)] is treated with 1 molar equiv of P-*n*-Bu$_3$ and allowed to stand for 24 h, two species are observed in the $^{31}P\{^1H\}$ NMR spectrum, each of which exhibits a pattern consistent with its formulation as a square-planar complex containing three magnetically inequivalent phosphorus atoms. After 7 days only one species remains, which is identified as the [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ cation.[2] The chloride ligand here must be derived from the CH$_2$Cl$_2$ solvent. The other species, which is apparently the initial product of the reaction, is identified as [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$. This cation is the sole platinum-containing product when the reaction is performed in CH$_3$CN. Removal of the acetonitrile, followed by addition of CH$_2$Cl$_2$ results in complete conversion to [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ within 24 h. Thus, when a CH$_2$Cl$_2$ solution of [Pt(OCOPh)$_2$(dppe)] is treated with 1 molar equiv of P-*n*-Bu$_3$, the initial product is that obtained by displacement of one benzoate ligand, but this reacts with the solvent to give the chloroplatinum(II) complex (eq 3).



(3)

Table I. $^{31}P\{^1H\}$ Data^a for [PtX(L)(P⌒P)]$^+$ Complexes



X	Cl^b	OBz^c	Cl	Cl^b	Cl	Cl
L	P-*n*-Bu$_3$	P-*n*-Bu$_3$	PMePh$_2$	PEt$_3$	P-*n*-Bu$_3$	PMePh$_2$
P⌒P	dppe	dppe	dppe	dppe	dppm	dppm
$\delta(P_A)$	53.2	52.3	52.6	53.3	−49.7	−50.8
$\delta(P_B)$	42.8	31.0	44.9	42.6	−50.3	−51.4
$\delta(P_C)$	8.3	11.6	8.3	15.6	8.3	5.6
$^1J_{PtP_A}$	2255	2390	2366	2275	1867	1941
$^1J_{PtP_B}$	3551	3474	3480	3545	3042	3006
$^1J_{PtP_C}$	2281	2434	2342	2293	2312	2359
$^2J_{P_AP_B}$	*d*	*d*	6	*d*	66	66
$^2J_{P_BP_C}$	15	18	17	16	−9	−9
$^2J_{P_AP_C}$	368	356	389	370	396	408

^{a}Coupling constants are given in hertz. All spectra were recorded for CDCl$_3$ solutions, except were otherwise noted. ^{b}Recorded for CH$_2$Cl$_2$ solution. ^{c}Recorded for CH$_3$CN solution. ^{d}Not observed.

When [Pt(OCOPh)$_2$(dppe)] is treated with 1 molar equiv of P-*n*-Bu$_3$ in benzyl chloride, [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ is the only platinum-containing species present after 24 h. The byproduct in this case is benzyl benzoate, which has been identified by thin-layer chromatography and ^{1}H NMR spectroscopy (see Experimental Section). In this case it is likely that the chloride ion is produced by attack of the benzoate ion on benzyl chloride in the classical S$_N$2 sense (Scheme I). Indeed, reaction of ammonium benzoate with PhCH$_2$Cl, in the presence of 18-crown-6, also produces benzyl benzoate. Dichloromethane, however, does not react with free carboxylate ions, and chloride ion abstraction from CH$_2$Cl$_2$ is likely to be mediated by the platinum center.

We have studied the relative rates of chloride abstraction from CH$_2$Cl$_2$, CHCl$_3$, and CCl$_4$ by treating solutions of [Pt(OCOPh)$_2$(dppe)] in these solvents, to which acetone-d_6 had been added as an internal lock, with P-*n*-Bu$_3$. As mentioned above, in CH$_2$Cl$_2$ solution both [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$ and [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ are observed after 24 h. Surprisingly, after a similar time, only [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$ is observed in chloroform solution. The reaction is much faster in CCl$_4$ solution, however, with both complexes being detected after 20 min; [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$ is no longer present after 24 h. The reaction is not clean, though, with several unidentified products being formed, as well as extensive oxidation of P-*n*-Bu$_3$.

Platinum(II) complexes containing chelated dicarboxylate ligands also form [PtCl(L)(P⌒P)]$^+$ species when treated with tertiary phosphines in chlorinated solvents, but the rate of formation of the chloride complex is much greater than it is for [Pt(OCOPh)$_2$(dppe)]. Complexes of the type [Pt$^+$(OCO(CH$_2$)$_n$COO$^-$)(L)(P⌒P)] (n = 0, 1), which would be formed upon initial displacement of one end of the dicarboxylate ligand, cannot be observed at ambient temperature. $^{31}P\{^1H\}$ NMR data for all the [PtCl(L)(P⌒P)]$^+$ complexes prepared in this manner are compiled in Table I. In each case the data are identical with those for the complexes obtained by treatment of [PtCl$_2$(P⌒P)] with L.[2] It should be noted that these complex cations are not always the exclusive products of the reactions of the dicarboxylate complexes with tertiary phosphines (vide infra).

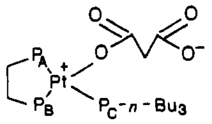
The reaction of [Pt(mal)(dppe)] with P-*n*-Bu$_3$ in chlorinated solvents to form [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ is quite clean, so this system was studied in greater detail. When P-*n*-Bu$_3$ (approximately 2 molar equiv) is allowed to mix with a CDCl$_3$ solution of [Pt(mal)(dppe)] at −60 °C, the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of a new platinum-containing species that displays resonances characteristic of a square-planar complex containing three magnetically inequivalent phosphorus atoms (Table II). This species is believed to be [Pt$^+$(OCOCH$_2$COO$^-$)(P-*n*-Bu$_3$)(dppe)], in which one of the carboxylate groups has been displaced by P-*n*-Bu$_3$. Consistent with this assignment is the chemical shift of phosphorus atom B ($\delta(P_B)$ 30.5), which is similar to that in [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$ but significantly different from that in the analogous chloro-

---

[9] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

[10] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Table II. $^{31}P\{^1H\}$ NMR Data[a] for $[Pt^+(OCOCH_2COO^-)(P\text{-}n\text{-}Bu_3)(dppe)]$ and $[Pt(OCOCH_2COOH)(P\text{-}n\text{-}Bu_3)(dppe)][ClO_4]$



	unprotonated[b]	protonated[c]
$\delta(P_A)$	50.6	57.2
$\delta(P_B)$	30.5	38.2
$\delta(P_C)$	12.8	10.1
$^1J_{PtP_A}$	2339	2108
$^1J_{PtP_B}$	3467	3704
$^1J_{PtP_C}$	2419	2223
$^2J_{P_AP_B}$	6	5
$^2J_{P_BP_C}$	17	18
$^2J_{P_AP_C}$	353	305

[a] Coupling constants are given in hertz. [b] Recorded for $CDCl_3$ solution. [c] Recorded for CD_3CN solution.

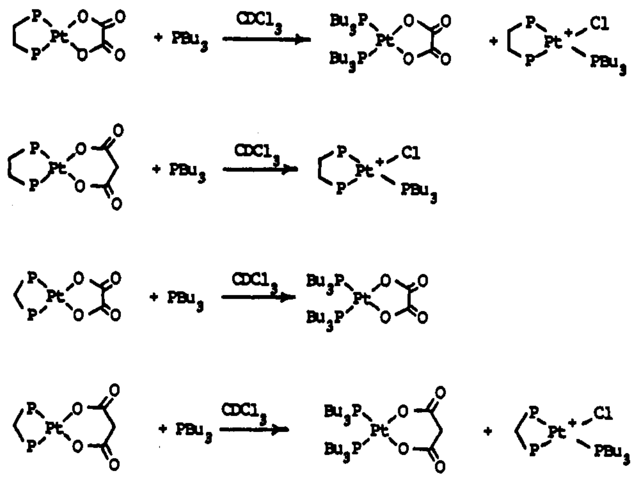
platinum(II) complex. Further support for this assignment comes from the $^{13}C\{^1H\}$ NMR spectrum, which displays two carbonyl resonances at 175.7 and 172.1 ppm due to the two different carbonyl carbons of the monodentate malonate ligand. A third peak at 173.6 ppm is believed to be due to the organic product resulting from reaction with $CDCl_3$, since a small amount of $[PtCl(P\text{-}n\text{-}Bu_3)(dppe)]^+$ is produced during acquisition of the $^{13}C\{^1H\}$ NMR spectrum. Indeed, after the solution is allowed to stand for 48 h, the $^{13}C\{^1H\}$ NMR spectrum, recorded at ambient temperature, exhibits a single resonance in the carbonyl region at 173.0 ppm. The $^{31}P\{^1H\}$ NMR spectrum at this stage indicates that complete conversion to $[PtCl(P\text{-}n\text{-}Bu_3)(dppe)]^+$ has occurred.

We cannot exclude the possibility that $[Pt(mal)(P\text{-}n\text{-}Bu_3)(dppe)]$ is a five-coordinate complex, but the chemical shifts and coupling constants observed in its $^{31}P\{^1H\}$ NMR spectrum are remarkably similar to those found in $[Pt(OCOPh)(P\text{-}n\text{-}Bu_3)(dppe)]^+$, providing support for its formulation as a four-coordinate, square-planar complex. The reactivity of the complex toward chlorinated solvents and the fact that it is not formed in other solvents (vide infra) precludes high-temperature NMR studies that might distinguish between these two structures.

To our knowledge, there have been no previous reports of directly observable monodentate malonate ligands. There are isolated reports of transition-metal complexes containing monodentate oxalate ligands, including the low-temperature detection of $[Pt(C_2O_4)(PEt_3)_3]$ mentioned above. This species exhibits two carbonyl resonances in its $^{13}C\{^1H\}$ NMR spectrum at 173.4 and 168.6 ppm.[3] Cooper et al.[11] have reported the synthesis of *trans*-$[Co(C_2O_4)(NO_2)(en)_2]$, which also displays two carbonyl peaks at δ(C) 178.3 and 170.1. Furthermore, monodentate oxalate and malonate ligands have been proposed as intermediates in several reactions, but most of these involve protonation of the free end of the dicarboxylate ligand.[12]

In an attempt to avoid reaction of $[Pt^+(OCOCH_2COO^-)(P\text{-}n\text{-}Bu_3)(dppe)]$ with chlorinated solvents, $[Pt(mal)(dppe)]$ was treated with 1 molar equiv of P-*n*-Bu_3 in CD_3CN solution, but a very complicated $^{31}P\{^1H\}$ NMR spectrum was obtained. A similar result was found when acetone-d_6 was employed as solvent. On the other hand, when $[Pt(mal)(dppe)]$ is treated with P-*n*-Bu_3 in acetonitrile solution, followed by the addition of excess $HClO_4$, the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of one predominant platinum-containing species. The resonances are typical of a $[PtX(L)(dppe)]^+$ complex but are considerably different from those of $[Pt^+(OCOCH_2COO^-)(P\text{-}n\text{-}Bu_3)(dppe)]$, and the spectrum has been tentatively assigned to the protonated species $[Pt(OCOCH_2COOH)(P\text{-}n\text{-}Bu_3)(dppe)]^+$ (Table II). The infrared spectrum of the oil, which is obtained upon solvent evaporation, exhibits two very broad absorptions at 1735 and 1665 cm^{-1}, and ν(OH) might be assigned to any of the bands at 3445, 3365, and 3220 cm^{-1}. Definitive ^1H and $^{13}C\{^1H\}$ NMR spectra could not be obtained, and repeated attempts to crystallize the compound have not met with success. It is interesting that the reaction of $[Pt(mal)(dppe)]$ with P-*n*-Bu_3 and $HClO_4$ in acetonitrile produces one predominant platinum-containing species, whereas in the absence of $HClO_4$ a complicated array of products is obtained, none of which has been identified unequivocally. When $HClO_4$ is later added to such a mixture, $[Pt(OCOCH_2COOH)(P\text{-}n\text{-}Bu_3)(dppe)]^+$ is indeed formed as the major platinum-containing product, but other species are also present, none of which has been identified.

Scheme II



When the substitution reactions are carried out in $CDCl_3$ solution, complexes of the type $[PtCl(L)(P\frown P)]^+$ are usually produced, but in general these are not the only products of such reactions. The best characterized series of reactions is that with P-Bu_3, and the reactions of the various (dicarboxylato)platinum(II) complexes with this ligand are summarized in Scheme II. A comparison of the reactivities of $[Pt(C_2O_4)(dppe)]$ and $[Pt(mal)(dppe)]$ suggests that the malonate ligand is more readily displaced than the oxalate. In both cases $[PtCl(P\text{-}n\text{-}Bu_3)(dppe)]^+$, which is formed subsequent to displacement of one end of the dicarboxylate ligand, is observed, but the reaction of $[Pt(C_2O_4)(dppe)]$ produces a significant amount of $[Pt(C_2O_4)(P\text{-}n\text{-}Bu_3)_2]$, indicating a strong tendency for the oxalate ligand to remain coordinated to platinum.

The greater lability of the malonate ligand is also displayed in the reactions of $[Pt(C_2O_4)(dppm)]$ and $[Pt(mal)(dppm)]$. When the former is treated with P-*n*-Bu_3, the only platinum-containing product is that which results from dppm displacement, namely $[Pt(C_2O_4)(P\text{-}n\text{-}Bu_3)_2]$, but the analogous reaction of $[Pt(mal)(dppm)]$ yields both $[PtCl(P\text{-}n\text{-}Bu_3)(dppm)]^+$ and $[Pt(mal)(P\text{-}n\text{-}Bu_3)_2]$. This trend is in keeping with the notion that six-membered chelate rings are less thermodynamically stable than analogous five-membered ones. Also, infrared studies of oxalate and malonate complexes have suggested there is greater ionic character in the M–O bonds of the latter.[8] Thus it is to be expected that the M–O bonds in the malonate complexes should be more easily cleaved.

The reactions depicted in Scheme II also indicate that dppm is more readily displaced than dppe, which is in keeping with the greater thermodynamic stability of five-membered chelate rings relative to their four-membered analogues.

We have also investigated the reactivity of $[Pt(mal)(dppe)]$ toward tertiary phosphines of differing nucleophilicities. No reaction occurs with PPh_3, even when a large excess of the ligand is employed, but when a $CDCl_3$ solution of $[Pt(mal)(dppe)]$ is treated with $PMePh_2$, complete conversion to $[PtCl(PMePh_2)$-

---

(11) Cooper, J. N.; Pennell, C. A.; Johnson, B. C. *Inorg. Chem.* **1983**, *22*, 1956.

(12) Banerjea, D.; Chaudhuri, S. D. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2985. Kruszyna, H. G.; Milburn, R. M. *Inorg. Chem.* **1971**, *10*, 1578. Damrauer, L.; Milburn, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 6481. Frank, M. J.; Huchital, D. H. *Inorg. Chem.* **1972**, *11*, 776. Rowan, N. S.; Milburn, R. M.; Dasgupta, T. P. *Inorg. Chem.* **1976**, *15*, 1477.

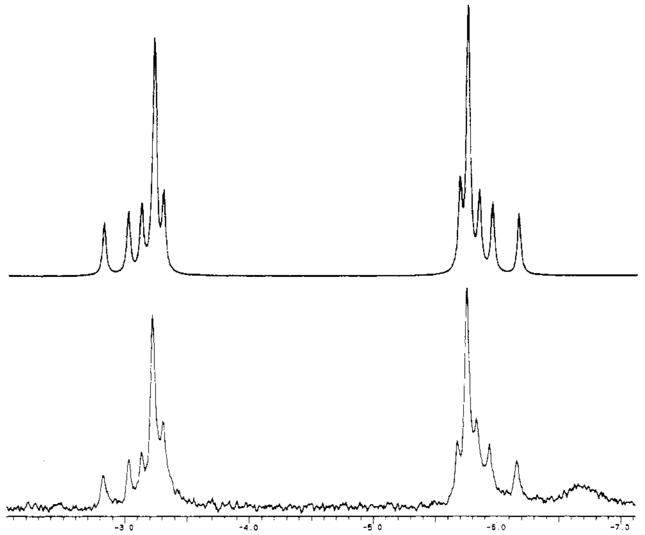
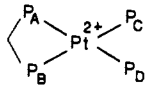


Figure 1. Calculated and experimental $^{31}P\{^1H\}$ NMR spectra of [Pt$(PMePh_2)_2$(dppm)][mal]. The region of the spectrum shown is that for the $PMePh_2$ resonances, with the dppm region being similar.

Table III. $^{31}P\{^1H\}$ NMR Data[a] for $[Pt(L)_2(dppm)]^{2+}$ Complexes



complex	$\delta(P_{A,B})$ ($^1J_{PtP_{A,B}}$) $\delta(P_{C,D})$ ($^1J_{PtP_{C,D}}$)	J_{AB} J_{AC} (J_{BD}) J_{AD} (J_{BC}) J_{CD}
$[Pt(PMePh_2)_2(dppm)][mal]$	−47.6 (1848)	35.4
	−4.5 (2293)	−18.0
		323.0
		22.6
$[Pt(PMePh_2)_2(dppm)]Cl_2$	−36.7 (2085)	59.6
	−6.7 (2604)	−20.9
		337.1
		19.2
[Pt(P-*n*-$Bu_3)_2$(dppm)][mal][b]	−41.9 (1846)	32.4
	−2.0 (2250)	−16.9
		321.4
		21.2
[Pt(P-*n*-$Bu_3)_2$(dppm)]Cl_2	−38.2 (2032)	55.1
	−9.2 (2609)	−22.1
		327.1
		21.2

[a] Coupling constants are given in hertz. Spectra were recorded for $CDCl_3$ solutions, except where otherwise noted. [b] Recorded in CD_3CN.

(dppe)]$^+$ takes place. Likewise, $[PtCl(L)(dppe)]^+$ complexes are formed when [Pt(mal)(dppe)] is reacted with PEt_3 or P-*n*-Bu_3 in $CDCl_3$ or CH_2Cl_2 solution. Thus ligands of moderate nucleophilicity are required to displace the malonate ligand from platinum(II); $PMePh_2$ is sufficiently nucleophilic for this purpose, but PPh_3 is not.

When a $CDCl_3$ solution of [Pt(mal)(dppm)] is treated with 2 molar equiv of $PMePh_2$, a species is formed whose $^{31}P\{^1H\}$ NMR spectrum consists of an AA′XX′ pattern, with ^{195}Pt satellites, which has been analyzed[13] and computer simulated (Figure 1). (To obtain a satisfactory correlation between the experimental and simulated spectra it is necessary that J_{AC} (Table III) be negative.) This species is different from that obtained by treatment of $[PtCl_2(dppm)]$ with 2 molar equiv of $PMePh_2$,[2] and the spectroscopic parameters for both products are listed in Table III. We suggest that in the present instance the malonate is ion-paired with the $[Pt(PMePh_2)_2(dppm)]^{2+}$ cation. To show that it is the malonate complex, and not the chloride, which is ion-paired, we have attempted to obtain the $[Pt(PMePh_2)_2(dppm)]^{2+}$ cation as its perchlorate salt. When a CH_2Cl_2 solution of $[PtCl_2(dppm)]$ is treated with 2 molar equiv of $PMePh_2$, followed by excess $AgClO_4$, a white precipitate is obtained after filtration and ether addition. This white solid is a mixture of $[PtCl(PMePh_2)_3]ClO_4$ and $[Pt(PMePh_2)_2(dppm)][ClO_4]_2$, and the $^{31}P\{^1H\}$ NMR spectroscopic parameters for the latter are identical with those for $[Pt(PMePh_2)_2(dppm)]Cl_2$. This suggests that the chloride complex is not ion-paired.

There is a remarkable color difference between [Pt$(PMePh_2)_2$(dppm)][mal] and $[Pt(PMePh_2)_2(dppm)]Cl_2$, the former being bright yellow, whereas the chloride complex is almost colorless. Apparently this ion pairing slows the reaction of the malonate ligand with the chlorinated solvent; after the solution of $[Pt(PMePh_2)_2(dppm)][mal]$ is allowed to stand at ambient temperature for 4 weeks, however, the only platinum-containing species present are $[PtCl(PMePh_2)_3]^+$ and $[PtCl(PMePh_2)(dppm)]^+$. Treatment of a solution of $[Pt(PMePh_2)_2(dppm)][mal]$ with an 18-fold excess of NaCl in the presence of 18-crown-6 has no effect. Attempts to prepare the ion-paired malonate complex from $[Pt(PMePh_2)_2(dppm)]Cl_2$ by treatment with silver malonate led to mixtures of $[Pt(mal)(PMePh_2)_2]$, $[PtCl(PMePh_2)(dppm)]^+$ and $[PtCl(PMePh_2)_3]^+$. These suggest that the platinum–malonate interaction is quite robust and the ion-paired species can only be obtained where the malonate is originally coordinated to the metal.

A similar situation prevails when [Pt(mal)(dppm)] is treated with 2 molar equiv of P-*n*-Bu_3. An intense yellow coloration of the $CDCl_3$ solution ensues, and the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of [Pt(mal)(P-*n*-$Bu_3)_2$] and [Pt(P-*n*-$Bu_3)_2$(dppm)][mal]. The formation of the former is not surprising since it is also observed when [Pt(mal)(dppm)] is treated with 1 molar equiv of P-*n*-Bu_3. The spectroscopic parameters for [Pt(P-*n*-$Bu_3)_2$(dppm)][mal] and its chloride analogue are collected in Table III; again, there is ion pairing between the malonate and the [Pt(P-*n*-$Bu_3)_2$(dppm)]$^{2+}$ cation. The ion-paired malonate complex is also formed when [Pt(mal)(P-*n*-$Bu_3)_2$] is reacted with dppm. In $CDCl_3$ solution the resulting product mixture is identical with that obtained by treatment of [Pt(mal)(dppm)] with 2 molar equiv of P-*n*-Bu_3, but in CD_3CN solution [Pt(P-*n*-$Bu_3)_2$(dppm)][mal] is formed virtually quantitatively.

In summary, carboxylate ligands bound to (diphosphine)platinum(II) centers can be displaced by tertiary phosphines, and in chlorinated solvents, the ultimate products are chloroplatinum(II) species. Malonate ligands are more readily displaced than oxalates, and where diphosphine displacements occur, dppm is substituted with greater facility than dppe. When [Pt(mal)(dppm)] is treated with 2 molar equiv of $PMePh_2$ or P-*n*-Bu_3 the novel ion-paired species $[Pt(L)_2(dppm)][mal]$ are formed.

Experimental Section

The ligands dppe, dppm, P-*n*-Bu_3, PEt_3, $PMePh_2$, and PPh_3 were obtained from commercial suppliers and used as received. The complexes $[PtX_2(\overset{\frown}{P\ P})]$ ($X = Cl$ or $X_2 = C_2O_4$; $\overset{\frown}{P\ P}$ = dppe, dppm) were prepared according to previously reported procedures.[6,14]

NMR spectra were recorded on a JEOL FX-100 or Varian XL-300 spectrometer. ^{13}C chemical shifts are relative to Me_4Si (internal), and ^{31}P chemical shifts are relative to H_3PO_4 (external), more positive shifts representing deshielding. Spin simulation experiments were carried out by using the LAME program, which is included in the XL-300 software package. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

Preparation of [Pt(mal)(dppe)]. To a CH_2Cl_2 solution (150 mL) of $[PtCl_2(dppe)]$ (0.54 g, 0.82 mmol) was added excess silver malonate (0.61 g, 1.93 mmol). The mixture was heated[15] in the absence of light for 72 h. After the mixture was filtered through activated charcoal, the resulting colorless solution was concentrated to 5 mL and ether was added. The white precipitate thus obtained was collected, washed with

---

(13) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1969; pp 88–127.

(14) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 3607.

(15) It should be noted that heating is not necessary for a successful synthesis. The reaction has been found to proceed satisfactorily at ambient temperature.

ether, and dried by suction (0.48 g, 85%). Anal. Calcd for $C_{29}H_{26}O_4P_2Pt$: C, 50.08; H, 3.78. Found: C, 49.50; H, 4.14. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ(P) 29.1, $^1J_{PtP}$ = 3665 Hz. IR (KBr pellet): 1650 (vs, br; ν_a(OCO)), 1357 (vs; ν_s(OCO)), 930 cm^{-1} (m; CH_2 rock).

The following complexes were prepared analogously.

[Pt(mal)(dppm)]. Anal. Calcd for $C_{28}H_{24}O_4P_2Pt$: C, 49.34; H, 3.56. Found: C, 48.67; H, 3.63. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ(P) –65.2, $^1J_{PtP}$ = 3091 Hz. IR (KBr pellet): 1640 (vs, br; ν_a(OCO)), 1357 (vs; ν_s(OCO)), 930 cm^{-1} (m; CH_2 rock).

Pt(mal)(P-*n*-Bu$_3$)$_2$]. Anal. Calcd for $C_{27}H_{56}O_4P_2Pt$: C, 46.21; H, 8.06. Found: C, 45.73; H, 8.09. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ(P) –3.7, $^1J_{PtP}$ = 3548 Hz.

Preparation of Silver Benzoate. Ammonium benzoate (2.89 g, 20.8 mmol) was dissolved in water (200 mL), and an almost saturated aqueous solution of $AgNO_3$ (3.53 g, 20.8 mmol) was added dropwise. A white precipitate formed during the addition, and after all the $AgNO_3$ solution had been added, the flask was cooled in ice to complete the precipitation. The product was filtered, washed with cold water, cold ethanol and ether, and dried by suction (4.29 g, 90%).

Preparation of [Pt(OCOPh)$_2$(dppe)]. To a CH_2Cl_2 solution (150 mL) of [$PtCl_2$(cod)] (0.71 g, 1.89 mmol) was added dppe (0.75 g, 1.89 mmol), and the solution was stirred for 0.5 h. After addition of AgOCOPh (1.01 g, 4.41 mmol), the mixture was stirred in the absence of light for 72 h. After filtration the pale yellow solution was concentrated to 5 mL, and addition of hexane caused precipitation of a white solid, which was separated, washed with hexane, and dried by suction (1.59 g, 94%). Anal. Calcd for $C_{40}H_{34}O_4P_2Pt$: C, 57.48; H, 4.11. Found: C, 57.22; H. 4.31. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ(P) 31.8, $^1J_{PtP}$ = 3770 Hz. IR (KBr pellet): 1625 (ν(C=O)), 1337 cm^{-1} (ν(C—O)).

Reactions of [Pt(OCOPh)$_2$(dppe)] with P-*n*-Bu$_3$. (a) [Pt(OCOPh)$_2$(dppe)] (0.070 g, 0.083 mmol) was dissolved in CH_2Cl_2 (2.0 mL) in a 10-mm NMR tube. After the sample was purged with argon, P-*n*-Bu$_3$ (20.8 μL, 0.083 mmol) was added to the tube. After the sample was allowed to stand at ambient temperature overnight, the $^{31}P\{^1H\}$ NMR spectrum indicated the presence of [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$ and [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$.

(b) When [Pt(OCOPh)$_2$(dppe)] was treated with 1 molar equiv of P-*n*-Bu$_3$ in the manner described above, with CH_3CN as solvent, the $^{31}P\{^1H\}$ NMR spectrum indicated the presence of [Pt(OCOPh)(P-*n*-Bu$_3$)(dppe)]$^+$ only. The CH_3CN was evaporated and the residue was dissolved in CH_2Cl_2. After 24 h, [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ was the only species observable by $^{31}P\{^1H\}$ NMR spectroscopy.

(c) [Pt(OCOPh)$_2$(dppe)] (0.10 g, 0.12 mmol) was dissolved in $PhCH_2Cl$ (2.0 mL) in a 10-mm NMR tube. The tube was flushed with argon, and then P-*n*-Bu$_3$ (31.1 μL, 0.12 mmol) was added. After 24 h at ambient temperature the $^{31}P\{^1H\}$ NMR spectrum indicated that complete conversion to [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ had occurred.

Benzyl benzoate was identified in the reaction mixture by thin-layer chromatography. A double development of the silica gel plate was performed, with first pentane and then acetone used as eluent.

The reaction mixture was passed down a silica gel column, eluting with pentane to remove benzyl chloride and then acetone to obtain benzyl benzoate. Comparison of the ^1H NMR spectrum with that of an authentic sample confirmed the presence of benzyl benzoate: δ 5.36 (s, CH_2), 7.3–8.1 (m, C_6H_5).

Reaction of [Pt(mal)(dppe)] with P-*n*-Bu$_3$. A $CDCl_3$ solution of [Pt(mal)(dppe)] (0.021 g, 0.030 mmol) in a 5-mm NMR tube was purged with argon and cooled to –78 °C. P-*n*-Bu$_3$ (20 μL, 0.08 mmol) was introduced to the frozen solution, and the tube was immediately transferred to the NMR probe, which had been precooled to –60 °C. After 10 min the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra indicated the presence of [Pt$^+$(OCOCH$_2$COO$^-$)(P-*n*-Bu$_3$)(dppe)] and free P-*n*-Bu$_3$. When the tube was allowed to stand at ambient temperature for 48 h, complete conversion of the platinum complex to [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ occurred.

Reaction of [Pt(mal)(dppe)] with P-*n*-Bu$_3$ and HClO$_4$. To a CH_3CN solution (300 mL) of [Pt(mal)(dppe)] (0.058 g, 0.083 mmol) was added P-*n*-Bu$_3$ (31 μL, 0.12 mmol) under an argon atmosphere. After the mixture was stirred for 0.5 h, a solution of $HClO_4$ (20 mL of a 60% aqueous solution) in CH_3CN (20 mL) was added dropwise. The resulting colorless solution was stirred overnight, and then the solvents were evaporated. The residue was dissolved in CD_3CN, and the $^{31}P\{^1H\}$ NMR spectrum of this solution was consistent with the formulation of the product as [Pt(OCOCH$_2$COOH)(P-*n*-Bu$_3$)(dppe)]ClO$_4$. Attempts to crystallize this compound were unsuccessful. Addition of pentane to the CD_3CN solution did not lead to precipitation, and cooling to –10 °C for several weeks resulted only in the formation of an immiscible oil.

Reaction of [Pt(C$_2$O$_4$)(dppe)] with P-*n*-Bu$_3$. A $CDCl_3$ solution of [Pt(C_2O_4)(dppe)] (0.014 g, 0.020 mmol) in a 5-mm NMR tube was purged with argon, and then P-*n*-Bu$_3$ (5.0 μL, 0.020 mmol) was introduced, giving a pale yellow solution. The $^{31}P\{^1H\}$ NMR spectrum of this solution indicated the presence of [PtCl(P-*n*-Bu$_3$)(dppe)]$^+$ and [Pt(C_2O_4)(P-*n*-Bu$_3$)$_2$] (δ(P) –4.3, $^1J_{PtP}$ = 3530 Hz).

Reaction of [Pt(C$_2$O$_4$)(dppm)] with P-*n*-Bu$_3$. To a CH_2Cl_2 solution of [Pt(C_2O_4)(dppm)] (0.015 g, 0.022 mmol) in a 10-mm NMR tube was added P-*n*-Bu$_3$ (5.4 μL, 0.022 mmol) under argon. After the solution was allowed to stand for 2 weeks, the $^{31}P\{^1H\}$ NMR spectrum indicated that [Pt(C_2O_4)(P-*n*-Bu$_3$)$_2$] was the only platinum-containing species in solution.

Reaction of [Pt(mal)(dppm)] with P-*n*-Bu$_3$. To a $CDCl_3$ solution of [Pt(mal)(dppm)] was added 1 molar equiv of P-*n*-Bu$_3$ under argon. After 1 week the $^{31}P\{^1H\}$ NMR spectrum indicated the presence of [PtCl(P-*n*-Bu$_3$)(dppm)]$^+$ and [Pt(mal)(P-*n*-Bu$_3$)$_2$].

Reaction of [Pt(mal)(dppm)] with PMePh$_2$. One molar equivalent of $PMePh_2$ was added to a $CDCl_3$ solution of [Pt(mal)(dppm)] under argon, and the solution was allowed to stand at ambient temperature for 1 week. The $^{31}P\{^1H\}$ NMR spectrum indicated the presence of [PtCl(PMePh$_2$)(dppm)]$^+$ and [Pt(mal)(PMePh$_2$)$_2$] (δ(P) –5.7, $^1J_{PtP}$ = 3688 Hz).

Reaction of [Pt(mal)(dppm)] with 2 equiv of PMePh$_2$. A $CDCl_3$ solution of [Pt(mal)(dppm)] (0.016 g, 0.023 mmol) was flushed with argon, and $PMePh_2$ (8.7 μL, 0.047 mmol) was introduced. The resulting bright yellow solution displayed a $^{31}P\{^1H\}$ NMR spectrum consistent with the formation of a species of the form [Pt(PMePh$_2$)$_2$(dppm)][mal]. After the mixture was allowed to stand for 4 weeks, a mixture of products was observed, including [Pt(mal)(PMePh$_2$)$_2$], [PtCl(PMePh$_2$)(dppm)]$^+$, and [PtCl(PMePh$_2$)$_3$]$^+$.

Reaction of [Pt(mal)(dppm)] with 2 equiv of P-*n*-Bu$_3$. Addition of P-*n*-Bu$_3$ (15.4 μL, 0.062 mmol) to a $CDCl_3$ solution of [Pt(mal)(dppm)] (0.021 g, 0.031 mmol), under argon, resulted in formation of a bright yellow solution. Spectroscopic examination of the solution revealed the presence of [Pt(mal)(P-*n*-Bu$_3$)$_2$] and a species of form [Pt(P-*n*-Bu$_3$)$_2$(dppm)][mal].

Reaction of [Pt(mal)(P-*n*-Bu$_3$)$_2$] with Dppm. [Pt(mal)(P-*n*-Bu$_3$)$_2$] (0.021 g, 0.029 mmol) and dppm (0.012 g, 0.031 mmol) were mixed under argon in a 5-mm NMR tube, and CD_3CN was added to give a bright yellow solution. The $^{31}P\{^1H\}$ NMR spectrum indicated that [Pt(P-*n*-Bu$_3$)$_2$(dppm)][mal] was the predominant species in solution. [Pt(mal)(P-*n*-Bu$_3$)$_2$] was also observed.

Acknowledgment. This work was supported by the Research Corp., Monsanto Co., a Missouri Research Assistance Grant, and the University of Missouri Weldon Spring Fund. Thanks are expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support and to Johnson Matthey for a generous loan of K_2PtCl_4. Funds from the National Science Foundation to the University of Missouri—St. Louis for the purchase of a NMR spectrometer and the assistance of the Washington University High Resolution NMR Facility, funded through NIH Biomedical Research Support Shared Instrument Grant 1 S10 RR02004 and a gift from Monsanto Co., are gratefully acknowledged.

Registry No. [Pt(mal)(dppe)], 105471-33-8; [PtCl$_2$(dppe)], 14647-25-7; [Pt(mal)(dppm)], 107134-97-4; [PtCl$_2$(dppm)], 52595-94-5; [Pt(mal)(PBu$_3$)$_2$], 105451-55-6; [PtCl$_2$(PBu$_3$)$_2$], 15076-72-9; [Pt(OCOPh)$_2$(dppe)], 105471-29-2; [PtCl$_2$(cod)], 12080-32-9; [Pt(OCOPh)(PBu$_3$)(dppe)]$^+$, 105471-31-6; [PtCl(PBu$_3$)(dppe)]$^+$, 105471-30-5; [Pt$^+$(OCOCH$_2$CO$_2$$^-$)(PBu$_3$)(dppe)], 105451-51-2; [Pt(OCOCH$_2$CO$_2$H)(PBu$_3$)(dppe)]ClO$_4$, 107134-98-5; [Pt(C_2O_4)(dppe)], 23604-03-7; [Pt(C_2O_4)(PBu$_3$)$_2$], 94929-02-9; [Pt(C_2O_4)(dppm)], 103636-92-6; [PtCl(PBu$_3$)(dppm)]$^+$, 107134-99-6; [PtCl(PMePh$_2$)$_3$]$^+$, 76740-64-2; [Pt(PBu$_3$)$_2$(dppm)][mal], 107135-01-3; [PtCl(PMePh$_2$)(dppm)]$^+$, 107147-88-6; [Pt(mal)(PMePh$_2$)$_2$], 107135-02-4.