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Photochemical reactions of diphosphineplatinum(II) oxalate complexes

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Abstract

Irradiation at 254 nm of CH_3CN/C_6H_6 or PhCN solutions of $[Pt(C_2O_4)(dppe)]$ produces 2 equiv. of CO_2, and in the presence of PhCl or PhI yields $[PtX_2(dppe)]$ (X = Cl, I). With CO or PhC≡CPh the products are $[Pt(CO)_2(dppe)]$ or [Pt(PhC≡CPh)(dppe)], but in the latter case extended photolysis yields [PtPh(C≡CPh)(dppe)]. Photolysis in the presence of H_2 gives a mixture of the $[Pt_2H_3(dppe)_2]^+$ and $[Pt_3H_3(dppe)_3]^+$ cations. Simple elimination of CO_2 does not occur in all cases, as illustrated by the formation of $[Pt(CO_2Me)_2(dppe)]$ when $[Pt(C_2O_4)(dppe)]$ is photolyzed in the presence of methanol. Photochemical reactions of the related complexes $[Pt(C_2O_4)L_2]$ (L_2 = dppm, dcpe) are also described.

Introduction

The production of a reactive $Pt(PR_3)_2$ fragment has been achieved either electrochemically [1] or by photolysis of the corresponding oxalate complex [2,3]. Such fragments add neutral ligands, such as an alkene or alkyne, and undergo oxidative addition with such reagents as methyl iodide or dihydrogen. The work of Trogler and co-workers, in particular, has elucidated the mechanism of formation of a $Pt(PEt_3)_2$ species from the oxalate complex [3]. Photolysis of $[Pt(C_2O_4)(PEt_3)_2]$ in CH_3CN/C_6H_6 solution results in elimination of 2 equiv. of CO_2 and the *in situ* formation of the $Pt(PEt_3)_2$ fragment.

It has been suggested by Hoffmann that a bent d^{10}, 14-electron ML_2 fragment should be more reactive than a linear one [4], so it seemed to us that photolysis of an oxalato(diphosphine)platinum complex would be a convenient source of such a bent ML_2 species. Indeed, while this work was in progress, Whitesides demonstrated that a Pt(dcpe) fragment (dcpe = 1,2-bis(dicyclohexylphosphino)ethane), formed by thermolysis of $[PtH(CH_2CMe_3)(dcpe)]$, is reactive towards the oxidative addition of C–H bonds [5]. More recently, photolysis of $[Pt(OCH_2CH_2O)(dppe)]$ and related glycolates has been shown to generate the Pt(dppe) intermediate [6].

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Electrochemical reduction of complexes of the type $[PtX_2L_2]$ (X = halide; L_2 = diphosphine) has also been shown to be a viable method for producing non-linear ML_2 fragments as reaction intermediates [7,8].

We have shown previously that the reactions of $[Pt(C_2O_4)(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) and $[Pt(C_2O_4)(dppm)]$ (dppm = bis(diphenylphosphino)methane) with phenylacetylene occur thermally, rather than photochemically [9], and we have described some substitution reactions of these oxalate compounds [10]. In this paper we describe some photochemical reactions of $[Pt(C_2O_4)L_2]$ (L_2 = dppe, dcpe, dppm), in which we show that, at least in certain cases, the reactions of the PtL_2 fragment are complicated by the presence of free CO_2.

Results and discussion

The oxalate complexes are prepared by treating the corresponding dichloro compound with a slight excess of silver(I) oxalate and, following filtration and precipitation, the products are obtained as air-stable, white or yellow solids [9]. They are only sparingly soluble in dichloromethane or chloroform, and insoluble in benzene or toluene. Their infrared spectra are characterized by two or three strong absorptions in the range 1660–1710 cm^{-1} and another at approximately 1350 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra of $[Pt(C_2O_4)L_2]$ (L_2 = dppe, dmpe, dcpe; L = $Ph_2PCH_2CH_2OMe$) exhibit a single resonance flanked by satellites with one-bond Pt–P coupling constants of 3600–3700 Hz. A smaller value is observed for $[Pt(C_2O_4)(dppm)]$, as expected.

We have used two solvent systems for the photochemical reactions, namely acetonitrile/benzene (3:1), as used by Trogler, or benzonitrile. The oxalate complexes are more soluble in the latter. Even so, their limited solubility means that long reaction times are necessary. When $[Pt(C_2O_4)(dppe)]$ is photolyzed at 254 nm in CH_3CN/C_6H_6 solution, trapping of the gaseous products reveals that 2 equiv. of CO_2 (identified by an absorption at 2343 cm^{-1} in its infrared spectrum) are generated, as found by Trogler for the $[Pt(C_2O_4)(PEt_3)_2]$ system [3]. A Pt(dppe) fragment is presumably formed also.

When $[Pt(C_2O_4)(dppe)]$ is photolyzed in either solvent system in the presence of C_6H_5Cl, CH_2Cl_2 or $CHCl_3$, the only product observed is $[PtCl_2(dppe)]$ (δ(P) 41.8, ^1J(Pt,P) = 3611 Hz). This is likely to arise by initial oxidative addition of the C–Cl bond to the Pt(dppe) fragment, but further reaction takes place under the photolysis conditions. Indeed, irradiation of a solution of [PtClPh(dppe)] also produces the dichloro complex. Photolysis of $[Pt(C_2O_4)(dppe)]$ in the presence of iodobenzene yields $[PtI_2(dppe)]$ (δ(P) 46.7, ^1J(Pt,P) = 3384 Hz). Similarly, $[Pt(C_2O_4)(dppm)]$ reacts with chloro- or iodobenzene to give $[PtCl_2(dppm)]$ (δ(P) −64.2, ^1J(Pt,P) = 3049 Hz) or $[PtI_2(dppm)]$ (δ(P) −69.3, ^1J(Pt,P) = 2870 Hz), respectively. Photolysis of $[Pt(C_2O_4)(PEt_3)_2]$ in the presence of PhCl or MeCl generates a complex of the type *trans*-$[PtClR(PEt_3)_2]$ [3].

When a CH_3CN/C_6H_6 solution of $[Pt(C_2O_4)(dppe)]$ is photolyzed under 1 atm of carbon monoxide, a single species is formed, identified by its $^{31}P\{^1H\}$ NMR and infrared spectra as $[Pt(CO)_2(dppe)]$ (δ(P) 22.6, ^1J(Pt,P) = 3066 Hz; ν(CO) 2012w, 1989s, 1943s cm^{-1}). $[Pt(CO)_2(dcpe)]$ (δ(P) 45.8, ^1J(Pt,P) = 2911 Hz) and $[Pt(CO)_2(Ph_2PCH_2CH_2OMe)_2]$ (δ(P) −10.0, ^1J(Pt,P) = 3190 Hz) are produced analogously. In contrast, [Pt(C_2O_4)(dmpe)] decomposes on irradiation and, with CO, [Pt(C_2O_4)(dppm)] gives a complex mixture of products.

When a CH_3CN/C_6H_6 solution of [Pt(C_2O_4)(dppe)] is irradiated in the presence of diphenylacetylene, [Pt(PhC≡CPh)(dppe)] is obtained as the major product. It was identified by comparison of its ^{31}P NMR parameters with those of a sample prepared by a reported method ($\delta(P)$ 48.7, $^1J(Pt,P) = 3115$ Hz) [11]. (The authors of ref. 11 incorrectly reported the ^{31}P NMR parameters as $\delta(P)$ 31.0, $^1J(Pt,P) = 2262$ Hz. When we repeated their synthesis of [Pt(dppe)(PhC≡CPh)], the product exhibited a resonance at 48.7 ppm, $^1J(Pt,P) = 3125$ Hz.) A similar treatment of [Pt(C_2O_4)(dppm)] yields [Pt(PhC≡CPh)(dppm)] ($\delta(P)$ -18.6, $^1J(Pt,P) = 2278$ Hz). On prolonged photolysis of [Pt(C_2O_4)(dppe)]/PhC≡CPh in benzonitrile, however, a second species is formed. The latter was found to have ^{31}P NMR parameters identical to those of [Pt(C≡CPh)Ph(dppe)] ($\delta(P)$ 39.7, $^1J(Pt,P) = 1540$ Hz, $\delta(P)$ 43.6, $^1J(Pt,P) = 2510$ Hz), formed by the reaction of [PtClPh(dppe)] with (PhC≡C)$SnMe_3$. Thus in the photochemical reaction with PhC≡CPh some activation of the C–Ph bond occurs. Conversely, in the synthesis of [Pt(C≡CPh)Ph(dppe)], a small amount of [Pt(PhC≡CPh)(dppe)] is formed, presumably by reductive elimination followed by coordination of PhC≡CPh (eq. 1).

$$\begin{tikzcd}
\mathrm{Pt(C_2O_4)(dppe) + PhC{\equiv}CPh} \arrow[dr] & \\
& \mathrm{Pt(PhC{\equiv}CPh)(dppe) + Pt(C{\equiv}CPh)Ph(dppe)} \\
\mathrm{PtClPh(dppe) + (PhC{\equiv}C)SnMe_3} \arrow[ur] &
\end{tikzcd} \tag{1}$$

When hydrogen gas is bubbled through a benzonitrile (or CH_3CN/C_6H_6) solution of [Pt(C_2O_4)(dppe)], no reaction takes place. When such a solution is irradiated, however, two species are formed, which have been identified as the $[Pt_2H_3(dppe)_2]^+$ and $[Pt_3H_3(dppe)_3]^+$ cations (Table 1) [12,13]. The nature of the anion in each case is uncertain but, by comparison with the results of Trogler [3b], formate seems most likely. When the irradiation is performed in DMSO solution,

Table 1

^1H and ^{31}P NMR parameters for the hydride complexes [a]

Complex	[PtH_2(dppe)]	$[Pt_2H_3(dppe)_2]^+$	$[Pt_3H_3(dppe)_3]^+$	$[Pt_2H_3(dcpe)_2]^+$
$\delta(H)$	-3.63 [b,c]	-2.76 [d]	-1.73 [d]	-2.63 [d,e]
$^1J(Pt,H)$	1110	498	383	479
$^2J(P,H)$	177 *trans* 14 *cis*	40	29	38
$\delta(P)$	47.0 [b]	59.4	57.3	84.4
$^1J(Pt,P)$	1895	2901	2817	2793
$^3J(Pt,P)$		164	111	149
$^4J(P,P)$		9	19	

[a] In CD_3CN, unless stated otherwise. [b] In DMSO-d_6. [c] Doublet of doublets. [d] Quintet. [e] In CD_3CN/C_6D_6.

the unstable [PtH_2(dppe)] has been detected. Irradiation of [Pt(C_2O_4)(dppm)] in the presence of H_2 gives a complex mixture of products, but with [Pt(C_2O_4)(dcpe)], the dimeric platinum hydride complex [Pt_2H_3(dcpe)$_2$]$^+$ is formed (Table 1) [13,14]. (The authors of ref. 13 suggest that the complex formulated as [Pt_2H_2(dcpe)$_2$] in ref. 14 is, in fact, the [Pt_2H_3(dcpe)$_2$]$^+$ cation.) Trogler has reported the formation of [$Pt_2H_3(PEt_3)_4$]O_2CH in the photolysis of [Pt(C_2O_4)(PEt_3)$_2$] in the presence of H_2 [3].

In each of the above reactions, the products may be accounted for in terms of the elimination of 2 equiv. of CO_2 and addition of the substrate to the Pt(dppe) fragment. The first indication that not all reactions are this simple came from the irradiation of [Pt(C_2O_4)(dppe)] alone in CH_3CN/C_6H_6. In this case two products were formed (δ(P) 33.0, ^1J(Pt,P) = 3489 Hz; δ(P) 36.0, ^1J(Pt,P) = 3140 Hz). The former was identified as [Pt(CO_3)(dppe)] by comparison of its NMR parameters with those of an authentic sample, prepared by reaction of [$PtCl_2$(dppe)] with Ag_2CO_3. The second species could not be isolated and remains unidentified. Photolysis of [Pt(C_2O_4)(dppe)] in benzonitrile solution yielded only one product (δ(P) 36.2, ^1J(Pt,P) = 3149 Hz), but it also decomposed on attempted isolation.

Further significance of the formation of the carbonate complex may be seen from the following observations. Irradiation of a benzonitrile solution of [Pt(CO_3)(dppe)] yields the same species (δ(P) 37.9, ^1J(Pt,P) = 3151 Hz) that is formed on photolysis of the oxalate complex. Also, the carbonate complex reacts thermally with carbon monoxide to give [Pt(CO)$_2$(dppe)] as the major product, the same product formed in the photolysis of [Pt(C_2O_4)(dppe)] in the presence of carbon monoxide (*vide supra*). Thus it appears that, either the oxalate complex itself can break down under photolysis into [Pt(CO_3)(dppe)] and CO, or the CO_2 formed initially (and identified in the infrared spectrum of a solution of [Pt(C_2O_4)(dppe)] after photolysis) is not simply lost from the system but can react with the coordinatively unsaturated platinum(0) species to generate [Pt(CO_3)(dppe)] and CO (*vide infra*).

When [Pt(C_2O_4)(dppe)] is irradiated in the presence of methanol, a single product is formed (δ(P) 39.5, ^1J(Pt,P) = 1878 Hz; δ(H) 3.38 (s); ν(CO) 1680, 1640 cm^{-1}). This is identified as [Pt(CO_2Me)$_2$(dppe)], by comparison of its spectroscopic parameters with those reported by Bryndza [15], who prepared this complex by reaction of [Pt(OMe)$_2$(dppe)] with carbon monoxide. Again it is clear that photolysis of the oxalate complex does not proceed simply *via* elimination of 2 equiv. of CO_2, since oxalate is the most likely source of the CO needed to form the methoxycarbonyl species. (With [Pt(C_2O_4)(dcpe)] an analogous product is obtained (δ(P) 60.1, ^1J(Pt,P) = 1907 Hz), though less cleanly, but irradiation of a [Pt(C_2O_4)(dppm)]/MeOH solution gives a complex mixture of products.) In contrast, photolysis of [Pt(C_2O_4)(PEt_3)$_2$] in the presence of methanol gave the oxidative addition product, *trans*-[PtH(OMe)(PEt_3)$_2$] [3].

We believe there are two significant differences between the photochemical reactions of [Pt(C_2O_4)(dppe)], and related diphosphineplatinum(II) oxalate compounds, and [Pt(C_2O_4)(PEt_3)$_2$]. The first is that the diphosphine complexes are of considerably lower solubility, which necessitates the use of long reaction times. For the reactions with PhX, in particular, where the expected products undergo further photolysis to give [PtX_2(dppe)], the long reaction times preclude the observation of [PtXPh(dppe)]. The second, of course, is the *cis* arrangement of the phosphino groups in the Pt(dppe) fragment, although it is unclear how this affects the reactivity of the platinum center in the reactions we have studied. Whether it is a consequence of using diphosphine ligands or not, we have demonstrated that photolysis of platinum oxalate complexes does not proceed to give 2 equiv. of CO_2 in all cases, but that other modes of cleavage of the oxalate ligand are available.

There are also significant differences between the present photochemical studies and the thermal [5] or electrochemical [8] generation of non-linear PtL_2 fragments. The thermally induced reductive elimination of neo-pentane from $[PtH(CH_2CMe_3)(dcpe)]$ produces a Pt(dcpe) moiety which may be trapped by a suitable substrate or, in the absence of such a substrate, may insert into a C–H bond of the solvent [5]. The solubility of $[PtH(CH_2CMe_3)(dcpe)]$ in hydrocarbons allows these reactions to be carried out without competition from processes involving the solvent. Electrochemical reductions, on the other hand, necessitate the presence of a solvent/electrolyte system that may participate in the reaction. Although reduction of $[PtX_2L_2]$ (L_2 = dppe, dcpe, dcpp) in the presence of PhX or PhC≡CPh cleanly produces $[PtXPhL_2]$ or $[Pt(PhC{\equiv}CPh)L_2]$, reactions in the absence of such substrates tend to be less discriminate. The more flexible dcpp (dcpp = 1,3-bis(dicyclohexylphosphino)propane) ligand does permit selective insertion of the Pt(dcpp) fragment into the C–H bond of benzene, however [8]. Although it had been supposed that the CO_2 generated by photolysis of platinum oxalate compounds was an inert byproduct, and thus photolysis of $[Pt(C_2O_4)(dppe)]$ should have been a convenient source of the Pt(dppe) fragment, the present work indicates that this is not necessarily the case. The formation of CO in the reaction with methanol, and of coordinated carbonate in CH_3CN/C_6H_6, as well as the thermal reactions of the carbonate complex, represent unexpected processes which demonstrate the complexity of the system.

Experimental

NMR spectra were recorded on a Varian XL-300 spectrometer, operating in the FT mode. ^1H and ^{31}P chemical shifts are relative to the residual solvent resonance and external H_3PO_4, respectively, positive shifts representing deshielding. Infrared spectra were recorded on a Perkin–Elmer 783 spectrophotometer. Microanalyses were performed by Atlantic Microlab, Inc. Silver(I) oxalate was prepared from $AgNO_3$ and $K_2C_2O_4 \cdot H_2O$ according to a reported procedure [3c].

Preparation of $[Pt(C_2O_4)(dppe)]$

To a CH_2Cl_2 solution of $[PtCl_2(cod)]$ (1.06 g, 2.83 mmol) under an argon atmosphere was added dropwise a CH_2Cl_2 solution of dppe (1.13 g, 2.83 mmol). After all the dppe solution had been added, $Ag_2C_2O_4$ (1.07 g, 3.51 mmol) was introduced and the mixture was stirred in the dark for several days. Following filtration to remove AgCl and unreacted $Ag_2C_2O_4$, the filtrate was reduced to 10 ml, and ether was added to give an off-white precipitate. This was filtered, washed with ether, and dried by suction to give $[Pt(C_2O_4)(dppe)]$ (1.84 g, 95%). Anal. Found: C, 49.05; H, 3.71. $C_{28}H_{24}O_4P_2Pt$ calc.: C, 49.35; H, 3.55%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution): δ(P) 32.7, ^1J(Pt,P) = 3628 Hz. ν(CO) (KBr pellet) 1705, 1678, 1356 cm^{-1}.

The following complexes were prepared analogously: $[Pt(C_2O_4)(dppm)]$ (93% yield). Anal. Found: C, 48.49; H, 3.43. $C_{27}H_{22}O_4P_2Pt$ calc.: C, 48.58; H, 3.32%.

$^{31}P\{^1H\}$ NMR: δ(P) −63.7, $^1J(Pt,P) = 3081$ Hz. ν(CO) 1699, 1678, 1666, 1357 cm^{-1}.

$[Pt(C_2O_4)(dmpe)]$ (73%). Anal. Found: C, 22.82; H, 4.10. $C_8H_{16}O_4P_2Pt$ calc.: C, 23.09; H, 3.88%. $^{31}P\{^1H\}$ NMR: δ(P) 20.7, $^1J(Pt,P) = 3503$ Hz. ν(CO) 1700, 1678, 1660, 1370 cm^{-1}.

$[Pt(C_2O_4)(dcpe)]$ (59%). Anal. Found: C, 47.25; H, 6.76. $C_{28}H_{48}O_4P_2Pt$ calc.: C, 47.65; H, 6.86%. $^{31}P\{^1H\}$ NMR: δ(P) 58.2, $^1J(Pt,P) = 3534$ Hz.

$[Pt(C_2O_4)(Ph_2PCH_2CH_2OMe)_2]$ (100%). Anal. Found: C, 49.35; H, 4.62. $C_{32}H_{34}O_6P_2Pt$ calc.: C, 49.81; H, 4.44%. $^{31}P\{^1H\}$ NMR: δ(P) −0.2, $^1J(Pt,P) = 3717$ Hz. ν(CO) 1704, 1674, 1628, 1352 cm^{-1}.

$[Pd(C_2O_4)(dppe)]$ (60%) from $[PdCl_2(cod)]$, dppe and $Ag_2C_2O_4$. Anal. Found: C, 56.53; H, 4.62. $C_{28}H_{24}O_4P_2Pd$ calc.: C, 56.73; H, 4.08%. $^{31}P\{^1H\}$ NMR: δ(P) 57.5. ν(CO) 1699, 1674, 1665, 1360 cm^{-1}.

$[Pt(C_2O_4)(cod)]$ (32%) from the reaction of $[PtCl_2(cod)]$ with $Ag_2C_2O_4$. Anal. Found: C, 30.60; H, 3.15. $C_{10}H_{12}O_4Pt$ calc.: C, 30.70; H, 3.09%.

Preparation of [Pt(CO₃)(dppe)]

To a stirred solution of $[PtCl_2(dppe)]$ (0.201 g, 0.303 mmol) in CH_2Cl_2 (50 mL) was added Ag_2CO_3 (0.186 g, 0.673 mmol) under argon. The mixture was stirred in the dark for 48 h, then filtered. The precipitate was washed with CH_2Cl_2, and the combined filtrate was concentrated. Addition of hexane gave the product as an off-white solid. Anal. Found: C, 49.53; H, 3.74. $C_{27}H_{24}O_3P_2Pt$ calc.: C, 49.62; H, 3.70%. $^{31}P\{^1H\}$ NMR: δ(P) 32.6, $^1J(Pt,P) = 3539$ Hz. ν(CO) (C_6H_5CN solution) 1680 cm^{-1}.

Photochemical experiments

In a typical experiment the oxalate complex (approx. 100 mg) was suspended in CH_3CN/C_6H_6 (3:1) or C_6H_5CN (4 mL) and placed in a quartz tube. The appropriate reagent (in large excess) was introduced and the system was purged with argon and capped. Where the reagent was CO or H_2, the system was purged with the appropriate gas. Irradiation of samples with 254 nm radiation was accomplished using a Rayonet RS photochemical reactor. An aliquot was withdrawn after a given time, C_6D_6 was added as a lock solvent, and the solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy.

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