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Photochemical Generation of Bis(phosphine)palladium and Bis(phosphine)platinum Equivalents

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Ultraviolet irradiation of oxalato bis(tertiary phosphine) complexes of platinum(II) and palladium(II), $Pt(C_2O_4)L_2$ and $Pd(C_2O_4)L_2$, results in the reductive elimination of the oxalate ligand as CO_2 and the production of the reactive intermediates PtL_2 and PdL_2. These 14-electron fragments bind ligands such as olefins, perfluoroethylene, acetylenes, and trialkylphosphines to yield zerovalent metal complexes. Substrates such as alkyl, allyl, and aryl halides, organosilanes, alcohols, allyl acetate, and hydrogen undergo oxidative addition reactions to yield platinum(II) or palladium(II) derivatives. Noteworthy is the synthesis of the sterically unhindered dihydride *trans*-$PtH_2(PEt_3)_2$ by this procedure and the clean generation of the reactive olefin complexes $Pt(C_2H_4)(PEt_3)_2$, $Pd(C_2H_4)[P(n\text{-}Bu)_3]_2$, and $Pd(C_2H_4)$(diphos) in solution.

Introduction

The stability and reactivity of tertiary phosphine complexes of platinum(0) and palladium(0), ML_n, vary widely with the steric and electronic properties of the phosphine ligands L and the coordination number *n*, that ranges from 2 to 4.[1-6] Fourteen-electron complexes, ML_2, are stable only if L is so sterically demanding that approach to the metal center is hindered.[3-5] The bulk of such ligands attenuates the reactivity of these compounds. For example, the crowded complex $Pt[P(t\text{-}Bu)_3)]_2$ does not react with dioxygen, molecular hydrogen, or methanol; as L becomes smaller [e.g., L = $P(t\text{-}Bu)_2Ph$, $P(c\text{-}Hx)_3$, $P(i\text{-}Pr)_3$], the reactivity of PtL_2 toward small molecules increases.[5-8] Relatively unhindered PtL_2 complexes, where L is a small phosphine ligand, have not been observed and should be highly reactive. For example, one phosphine can dissociate from $Pt(PEt_3)_4$ to give the 16-electron species $Pt(PEt_3)_3$, but further dissociation to produce spectroscopically observable quantities of $Pt(PEt_3)_2$ does not occur. In some cases,[6,9] reactive PtL_2 species have been implicated as intermediates in the reactions of platinum(0) complexes PtL_3, PtL_4, and PtL_2L', where L′ is an unsaturated ligand such as an olefin or an acetylene. As L becomes smaller, the tendency for PtL_2 to form by ligand dissociation drastically decreases.[1-6] For zerovalent tertiary phosphine complexes of Ni(0), Pd(0), and Pt(0), the ease of thermal ligand dissociation to produce coordinately unsaturated species follows the order Ni(0) >> Pt(0) > Pd(0). Consequently, it would be desirable to develop alternative methods of generating PtL_2 and PdL_2 fragments. Electronically, the ML_2 species are isolobal with the exceptionally reactive fragment methylene. Photochemical techniques have proved useful for the generation of carbenes in organic media. Now consider a photochemical approach for the production of the isolobal platinum and palladium equivalents.

It has been recognized that ultraviolet irradiation of transition-metal oxalate complexes leads to irreversible fragmentation of the oxalate dianion to two molecules of carbon dioxide, with concomitant transfer of two electrons to two metal centers.[10] The behavior of tris(oxalato)cobalt(III) exemplifies the majority of systems studied, wherein a stable metal +2 oxidation state forms upon one-electron reduction of the complex ion. Each photochemical event leads to the reduction of two metal centers by the sequence of reaction shown in eq 1 and 2.[10] In the

$$\mathrm{Co(C_2O_4)_3{}^{3-}} \xrightarrow[\mathrm{H_2O}]{h\nu} \mathrm{Co^{2+}(aq)} + 2\mathrm{C_2O_4{}^{2-}} + \text{“}\mathrm{C_2O_4{}^{-}\cdot}\text{”} \qquad (1)$$

$$\text{“}\mathrm{C_2O_4{}^{-}\cdot}\text{”} + \mathrm{Co(C_2O_4)_3{}^{3-}} \rightarrow \mathrm{Co^{2+}(aq)} + 3\mathrm{C_2O_4{}^{2-}} + 2\mathrm{CO_2} \qquad (2)$$

case of platinum(II) and palladium(II) oxalates, transfer of one electron to the metal would produce the relatively unstable +I oxidation state, whereas transfer of two electrons (either simultaneously or in rapid succession) yields the more stable zerovalent state. The net photochemical reaction should proceed as in eq 3. Blake and

$$\mathrm{M(C_2O_4)L_2} \xrightarrow{h\nu} \mathrm{ML_2} + 2\mathrm{CO_2} \qquad (3)$$

Nyman[11a] found that platinum(0) complexes could be isolated from photochemical reactions of $Pt(C_2O_4)(PPh_3)_2$; however, the characterization of several products was later questioned.[11b] Addison et al.[11c] showed that irradiation of the rhodium(III) oxalate complexes $Rh(C_2O_4)X(py)_3$ (X

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(1) Maltesta, L.; Cenini, S. "Zerovalent Compounds of Metals"; Academic Press: New York, 1974.

(2) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543–3544.

(3) (a) Green, M.; Howard, J. A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 3–4. (b) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006–1009.

(4) (a) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850–5858. (b) Immirzi, A.; Musco, A. *J. Chem. Soc., Chem. Commun.* **1974**, 400–401.

(5) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134–2140.

(6) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776–785.

(7) Abbreviations: Me = methyl; Et = ethyl; Ph = phenyl; *i*-Pr = isopropyl; c-Hx = cyclohexyl; *t*-Bu = *tert*-butyl; *n*-Bu = *n*-butyl; diphos = bis(1,2-diphenylphosphino)ethane; LAH = lithium aluminum hydride.

(8) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 107–110.

(9) (a) Halpern, J.; Weil, T. A. *J. Chem. Soc., Chem. Commun.* **1973**, 631–632 and references therein. (b) Pearson, R. G.; Rajaram, J. *Inorg. Chem.* **1974**, *13*, 246–247.

(10) (a) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970. (b) Adamson, A. W.; Waltz, W. L.; Zinato, E.; Watts, D. W.; Fleischauer, P. D.; Lindholm, R. D. *Chem. Rev.* **1968**, *68*, 541–585.

(11) (a) Blake, D. M.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5359–5364. (b) Blake, D. M.; Leung, L. M. *Inorg. Chem.* **1972**, *11*, 2879–2883. (c) Addison, A. W.; Gillard, R. D.; Sheridan, P. S.; Tipping, L. R. H. *J. Chem. Soc., Dalton Trans.* **1974**, 709–716.

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Table I. Platinum(II) and Palladium(II) Oxalate Infrared Band Assignments[a]

compound	ν_a(C=O)	ν_s(C=O)	ν_s(C–O) + ν(C–C)	δ_s(O–C=O) + δ_s(Pt–O)	medium
$Pt(C_2O_4)(PEt_3)_2$, 1	1704 vs	1681 s, 1670 sh	1366 s	792 m	CH_2Cl_2
	1697 vs	1680 vs, 1663 s	1359 vs	790 m	Nujol
$Pt(C_2O_4)(PPh_3)_2$, 2[b]	1710 s	1675 s	1350 s	790 s	Nujol
$Pt(C_2O_4)(SEt_2)_2$, 3	1703 vs	1672 vs	1350 vs	797 m	Nujol
$Pt(C_2O_4)(PMe_3)_2$, 4	1703 vs	1679 vs	1363 s	790 m	CH_2Cl_2
$Pt(C_2O_4)[P(n\text{-}Bu)_3]_2$, 5	1699 vs	1680 vs, 1669 s	1355 vs	790 m	Nujol
$Pt(C_2O_4)(SEt_2)[P(i\text{-}Pr)_3]$, 6	1703 vsl	1680 vs	1350 vs	790 s	Nujol
$Pt(C_2O_4)(SEt_2)[P(c\text{-}Hx)_3]$, 7	1705 vs	1677 s	1367 s	796 m	CH_2Cl_2
$Pd(C_2O_4)$(diphos)	1675 m	1658 vs	1370 s	782 m	KBr or Nujol
$Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$	1695 s	1670 vs, 1650 s	1352 vs	*c*	KBr or Nujol

[a] Based on the normal coordinate analysis (in-plane vibrations) of ref 24. Band positions in cm^{-1}. vs = very strong; s = strong; m = medium; sh = shoulder. [b] Reference 11. [c] Several peaks occurred in this region. One was at 780 cm^{-1}.

= Cl, Br; py = pyridine) caused two-electron reduction to the corresponding rhodium(I) species $RhX(py)_3$.

We have examined the photochemical reactions of (oxalato)bis(triethylphosphine)platinum(II) in detail and of several related platinum and palladium derivatives. Our observations point to formation of a highly reactive ML_2 species. In addition, we have found photochemical reactions of these complexes can be exploited to prepare compounds containing the ML_2 moiety. The oxalate starting materials are particularly convenient in this regard, since they are indefinitely stable in the absence of UV light; irradiation produces an ML_2 species under mild conditions in the absence of strongly competing ligands, and carbon dioxide is the only side product. Portions of this work have been communicated.[12]

Experimental Section

Materials. High purity acetonitrile and methanol were obtained from Burdick and Jackson and maintained and transferred under nitrogen. Benzene-d_6 (Merck) was dried over sodium/benzophenone and trap-to-trap distilled on a high-vacuum line. Hydrogen (99.999%), ethylene (C.P.), and chloromethane (C.P.) were purchased from Matheson. Tetrafluoroethylene, trimethylsilane, and triethylsilane were obtained from PCR. Phosphine ligands were purchased from Strem. The solvent *n*-hexane (99%, Aldrich) was distilled from lithium aluminum hydride. Silver oxalate (*Caution*! detonates upon heating) was prepared from $AgNO_3$ and $K_2C_2O_4$ in water.

Spectra. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. Solution spectra were recorded in matched 0.1-mm CaF_2 or NaCl cells. Fourier transform NMR spectra were recorded on a JEOL FX90Q (^1H 89.6 MHz, ^{31}P 36.3 MHz, ^{19}F 84.3 MHz, ^{13}C 22.5 MHz), a JEOL FX270 (^1H 269.7 MHz, ^{31}P 109.2 MHz, ^{13}C 67.8 MHz), or Nicolet 200 (^{31}P 80.99 MHz, ^{19}F 188.23 MHz) spectrometer. The notation $\{^1H\}$ indicates broad-band noise decoupling of the hydrogen nuclei. Selective decoupling of hydrogen nuclei at the resonance frequency of the triethylphosphine protons while observing the ^{31}P spectrum was done at low decoupler power, and this allowed observation of splittings of phosphine resonances by hydride ligands. In general, pulse parameters were chosen to prevent saturation effects and to ensure accurate integration of the NMR spectra. In some cases a software-controlled gated pulse sequence that suppressed nuclear Overhauser enhancement was used to increase integration accuracy. Chemical shifts are positive in the direction of increasing frequency with the exception of ^{19}F shifts that are in parts per million upfield from CCl_3F. ^1H chemical shifts were measured by using the solvent resonance (arising from incomplete deuteration) relative to Me_4Si at 0 ppm; ^{31}P chemical shifts were measured relative to the deuterium resonance of the solvent using the internal frequency lock of the spectrometer so that the resonance from a capillary of 85% H_3PO_4 centered in a 10-mm NMR tube containing that deuterated solvent appeared at 0 ppm at 30 °C. (No chemical shift corrections were made for spectra recorded at other temperatures.) ^{19}F chemical shifts used internal C_2F_4 (δ 132.84) as a standard.

Irradiations were performed by using the output of a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled quartz jacket.

The IR parameters of oxalate complexes are given in Table I, and the ^{31}P NMR parameters of compounds appear in Table II. Microanalyses were performed by Galbraith Laboratories or Mic Anal.

Preparation of (Oxalato)bis(triethylphosphine)platinum(II). Method A. In a typical preparation, a mixture of *cis*-$PtCl_2(PEt_3)_2$[13] (7.6 g, 15 mmol) and $K_2C_2O_4 \cdot H_2O$ (7.1 g, 38 mmol) was heated with stirring in methanol (90 mL) and water (60 mL) until all solids dissolved and then further heated approximately 10 min. Concentration of the warm solution by rotary evaporation to one-third the original volume and cooling for several hours produced off-white crystals of $Pt(C_2O_4)(PEt_3)_2$, 1, that were collected, washed with warm water (2 × 20 mL), and dried under vacuum for 12 h. The complex (7.2 g) was recrystallized by dissolving in dichloromethane, filtering, and slowly adding anhydrous diethyl ether. Small white crystals of 1 formed over several hours at 25 °C, after which time the solution was cooled to −10 °C for 16 h. The crystals (6.6 g, 84% yield) were collected on a fine frit, washed with diethyl ether, and vacuum dried 1 h. Anal. Calcd for $C_{14}H_{30}O_4P_2Pt$: C, 32.37; H, 5.82; P, 11.93; Pt, 37.56. Found: C, 32.38; H, 5.76; P, 11.98; Pt, 37.80.

The reaction between $K_2C_2O_4 \cdot H_2O$ and *cis*-$PtCl_2(PPh_3)_2$[14] produced a mixture of starting complex and $Pt(C_2O_4)(PPh_3)_2$, 2, that were not separated. Only starting materials were recovered from the analogous reactions between *cis*-$PtCl_2(PMe_3)_2$, *trans*-$PtCl_2[P(c\text{-}Hx)_3]_2$, *cis*-$PtCl_2(SEt_2)_2$, or $PtCl_2$(1,5-cyclooctadiene) and potassium oxalate.

(Oxalato)bis(diethyl sulfide)platinum(II). Method B. Silver oxalate was prepared in subdued room light by slowly adding an aqueous solution of $AgNO_3$ (20.0 g, 118 mol) to a saturated aqueous solution of $K_2C_2O_4 \cdot H_2O$ (10.5 g, 57.0 mmol). The white powdery precipitate of $Ag_2C_2O_4$ (*Caution*! detonates on heating) was collected on a fine frit, washed with water, ethanol, and diethyl ether, then dried under vacuum for 24 h in the dark, and stored at 0 °C in the absence of light; yield 16.7 g, 54.9 mmol (96%). The following procedure is an adaptation of the procedure described by Almeida et al.[15a] for the preparation of complexes $Pt(C_2O_4)[P(OR)_3]_2$. Silver oxalate (4.8 g, 16 mmol) was added to a solution of *cis*-$PtCl_2(SEt_2)_2$[15b] (6.0 g, 13 mmol) in dichloromethane (50 mL) in a 125-mL Erlenmeyer flask with a stir bar. The flask was capped and wrapped in aluminum foil to completely exclude light, and the solution was stirred for 12 h at 25 °C. The solution was filtered in subdued light to remove silver chloride, which was washed with dichloromethane. The combined filtrate and washings were concentrated to approximately 5–10 mL, diethyl ether (ca. 10 mL) was added slowly, and the mixture was cooled to −20 °C. After 4 h, yellow crystals of $Pt(C_2O_4)(SEt_2)_2$,

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(12) Paonessa, R. S.; Trogler, W. C. *Organometallics* **1982**, *1*, 768–770.

(13) Parshall, G. W. *Inorg. Synth.* **1970**, *12*, 26–33.

(14) Hartley, F. R. *Organomet. Chem. Rev. A* **1970**, *6*, 119–137.

(15) (a) Almeida, J. F.; Azizian, H.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *210*, 121–133. (b) Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1960**, *6*, 211–215.

Table II. $^{31}P\{^1H\}$ NMR Parameters for Platinum Phosphine Complexes[a]

		P_A		P_B			
no.	compound	chem shift, ppm	$^1J_{PtP}$, Hz	chem shift, ppm	$^1J_{PtP}$, Hz	$^2J_{P_AP_B}$	solvent[b]
1	$Pt(C_2O_4)(PEt_3)_2$	4.8	3522				$CDCl_3$
2	$Pt(C_2O_4)(PPh_3)_2$	7.7	3770				$CDCl_3$
4	$Pt(C_2O_4)(PMe_3)_2$	−27.8	3546				$MeOH/C_6D_6$
5	$Pt(C_2O_4)[P(n\text{-}Bu)_3]_2$	−4.1	3476				THF/C_6D_6
6	$Pt(C_2O_4)(SEt_2)[P(i\text{-}Pr)_3]$	27.2	3613				$CDCl_3$
7	$Pt(C_2O_4)(SEt_2)[P(c\text{-}Hx)_3]$	16.4	3593				$CDCl_3$
8	$Pt(C_2O_4)(SEt_2)(PEt_3)$	4.9	3610				$CDCl_3$
9	$Pt(C_2O_4)(SEt_2)(PPh_3)$	2.8	3857				$CDCl_3$
10	$Pt(C_2H_4)(PEt_3)_2$	20.4	3519				C_6D_6
11	$Pt(C_2F_4)(PEt_3)_2$	15.4 m	2425				C_6D_6
12	$Pt(PEt_3)_3$	30.5	4207				C_6D_6
13	$Pt(CO)_2(PEt_3)_2$	−8.9	3230				C_6D_6
14	*trans*-$PtMeCl(PEt_3)_2$	15.4	2814				C_6D_6[c]
15	*trans*-$PtH(OMe)(PEt_3)_2$	24.8	2804				$MeOH/C_6D_6$
16	*cis*-$PtH(SiEt_3)(PEt_3)_2$	19.1 d	2392	22.8 d	1432	16.4	toluene-d_8[d]
17	*trans*-$PtPhCl(PEt_3)_2$	13.7	2791				CH_3CN/C_6D_6
18	*trans*-$PtH_2(PEt_3)_2$	27.7	2764				acetone-d_6[d]
18	*cis*-$PtH_2(PEt_3)_2$	18.9	1984				acetone-d_6[d]
19	*trans*-$PtMeI(PEt_3)_2$	10.5	2728				$CDCl_3$
20	*cis*-$PtH(SiMe_3)(PEt_3)_2$	18.9 d	2352	22.3 d	1416	16.4	toluene-d_8[d]
21	[*trans*-$PtH(MeOH)(PEt_3)_2$]BF_4	27.4	2704				$MeOH/C_6D_6$
22	$Pt(C_2O_4)(PEt_3)_3$	1.1 t	3318	19.2 d	2415	19.9	CH_2Cl_2[e]
23	$[Pt_2H_2(\mu\text{-}H)(PEt_3)_4]BPh_4$	19.9	2574				acetone-d_6
24	$[Pt_2H(\mu\text{-}H)_2(PEt_3)_4]BPh_4$	20.8 t	2741	24.2 t	2540		acetone-d_6
25	$PtH(PEt_3)_3^+$	12.0 t	2018	15.2 d	2459	19.9	CH_3CN/C_6D_6[e]
26	$PtCl(PEt_3)_3^+Cl^-$	10.4 t	3478	19.2 d	2246	19.9	CH_2Cl_2[e]

[a] Spectral lines are singlets unless otherwise noted; d = doublet, t = triplet, m = multiplet. All lines are surrounded ^{195}Pt satellites. [b] Recorded at 30 °C unless otherwise noted. Mixed solvents are approximately 3:1 (v/v). [c] 10 °C. [d] −30 °C. [e] −50 °C.

3, had formed. Additional diethyl ether was added, and after 16 h at −30 °C the crystals (5.4 g, 87% yield) were collected rapidly without warming, washed with diethyl ether (10 mL), and dried under vacuum. Anal. Calcd for $C_{10}H_{20}O_4PtS_2$: C, 25.91; H, 4.35; S. 13.84. Found: C, 25.76; H, 4.41; S, 13.70.

(Oxalato)bis(triethylphosphine)platinum(II) and (Oxalato)bis(triphenylphosphine)platinum(II). Method C. Complex **3** (5.0 g, 11 mmol) was suspended in benzene (120 mL), in which it partially dissolved at 25 °C, triethylphosphine (4.2 mL, 28 mmol) was added (under nitrogen), and the mixture was heated to reflux for 1.5 h, during which time the yellow color faded and a white precipitate of **1** formed identical with that prepared by method A above. This product was collected by filtration under nitrogen, washed with 10 mL of deaerated diethyl ether containing 0.1 mL of PEt_3, followed by a washing with diethyl ether (2 × 10 mL), and dried under vacuum; yield 4.9 g, 9.4 mmol (87%).

Addition of 2 equiv of PPh_3 to a solution of **3** in $CDCl_3$ cleanly and quantitatively produced **2**, as seen by ^{31}P NMR spectroscopy. A synthetic scale reaction (1.03 g of $Pt(C_2O_4)(SEt_2)_2$ and 1.20 g of PPh_3) in 10 mL of CH_2Cl_2 yielded a white solid upon adding Et_2O. The precipitate was collected and recrystallized from CH_2Cl_2–Et_2O for a yield of 1.43 g (80%). The infrared spectrum of the complex was identical with that of $Pt(C_2O_4)(PPh_3)_2$ prepared by Blake and Nyman's route.[11a] Anal. Calcd for $C_{38}H_{30}O_4P_2Pt$: C, 56.52; H, 3.71. Found: C, 56.26; H, 3.79.

(Oxalato)bis(trimethylphosphine)platinum(II), (Oxalato)bis(triethylphosphine)platinum(II), and (Oxalato)bis(tri-*n*-butylphosphine)platinum(II). Method D. In a typical preparation, **2** (2.5 g, 3.1 mmol) was suspended in dichloromethane solution (15 mL) under nitrogen, and trimethylphosphine (0.8 mL, ca. 8 mmol) was slowly added with a syringe. (*Caution*! trimethylphosphine is volatile, pyrophoric, and of unknown toxicity. It should be handled with care in a well-ventilated hood.) As trimethylphosphine was added, **2** was initially taken up into solution and $Pt(C_2O_4)(PMe_3)_2$, **4**, subsequently precipitated as a white solid. An intermediate mixed $Pt(C_2O_4)(PMe_3)(PPh_3)$ complex could be detected by ^{31}P NMR spectroscopy. Diethyl ether (20 mL) was added, the solid was collected, suspended in 10 mL of dichloromethane containing three drops of PMe_3, 10 mL of diethyl ether was added, and **4** was collected by filtration, washed with diethyl ether, and dried (74% yield). Anal. Calcd for $C_8H_9O_4P_2Pt$: C, 22.07; H, 4.16. Found: C, 22.32; H, 4.10. Complex **1** and $Pt(C_2O_4)[P(n\text{-}Bu)_3]_2$, **5**, were prepared similarly.

(Diethyl sulfide)(oxalato)(triisopropylphosphine)platinum(II) and (Diethyl sulfide)(oxalato)(tricyclohexylphosphine)platinum(II). Method E. When method C was followed by using triisopropylphosphine, $Pt(C_2O_4)[P(i\text{-}Pr)_3](SEt_2)$, **6**, was isolated in 70% yield. Anal. Calcd for $C_{20}H_{42}O_4P_2Pt$: C, 33.77; H, 5.86; P. 5.81; S, 6.01. Found: C, 34.27; H, 5.97; P, 5.87; S, 6.07. Heating **6** to 80 °C in chloroform in the presence of excess $P(i\text{-}Pr)_3$ failed to effect further reaction. The complex $Pt(C_2O_4)[P(c\text{-}Hx)_3](SEt_2)$, **7**, was prepared similarly in 81% yield. Anal. Calcd for $C_{24}H_{43}O_4PPtS$: C, 44.10; H, 6.63; P, 4.74; S, 4.90. Found: C, 44.31; H, 6.77; P, 4.88; S, 4.91. The compound $Pt(C_2O_4)(PEt_3)(SEt_2)$, **8**, was observed by ^{31}P NMR spectroscopy to form from the addition of 1 equiv of PEt_3 to a solution of **3** in $CDCl_3$ but was not isolated. Addition of a second equivalent of PEt_3 converted **8** to **1**. Analogous behavior was observed with triphenylphosphine, that initially yielded $Pt(C_2O_4)(PPh_3)(SEt_2)$, **9**.

Photochemical Reactions of $Pt(C_2O_4)(PEt_3)_2$, 1. Solutions of **1** were prepared in 10-mm NMR tubes, sealed with septum caps, and deaerated by nitrogen purge. Substrates were then added through syringe needles under nitrogen. In some cases, NMR tubes were blown onto ground glass joints and evacuated on a high-vacuum line; solvents and liquid or gaseous substrates were then transferred in under vacuum, and the tubes were flame sealed. Total pressure above solutions at 25 °C was usually slightly greater than 1 atm. Typically, 20–40 mg of **1** (0.04–0.08 mmol) was dissolved in 1.5 mL of acetonitrile, followed by addition of 0.5 mL of benzene-d_6. In reactions with methanol or dichloromethane, these solvents were substituted for acetonitrile. These solutions were kept in the dark at ambient temperature for several hours, and then NMR spectra were recorded to verify that thermal reactions had not taken place. The tubes were then placed in a water-cooled aluminum block and irradiated. The samples were removed periodically and their $^{31}P\{^1H\}$ (and in some cases ^1H, $^{13}C\{^1H\}$, or ^{19}F) NMR spectra were recorded. After partial conversion to products, the samples were again maintained in the dark at ambient temperature for a period of time, and then their NMR spectra were recorded to check for thermal reactions. The products of these reactions, **10**–**16**, and their yields (as determined by $^{31}P\{^1H\}$ NMR spectroscopy) are given in Scheme II. The NMR spectral parameters of the products are given in Table II. The preparation and spectra of the following compounds have been reported previously: 10,[16] 12,[2,8] 13,[17] 14,[18,19] 17.[19] Characterization of other products is described below.

Determination of Carbon Dioxide Evolved from $Pt(C_2O_4)(PEt_3)_2$ upon Irradiation. A solution of 1 (130 mg, 0.25 mmol) in acetonitrile (6 mL) was degassed by three freeze–pump–thaw cycles in a quartz vessel. This sample was irradiated for 8 h, after which time the evolved carbon dioxide was collected into a known volume using a Toepler pump. No noncondensable (liquid nitrogen) gases were collected. The amount of CO_2 evolved was found to be 0.18 ± 0.01 mmol (assuming ideal gas law behavior). The platinum-containing residue was dissolved in dichloromethane so that the total volume of solution was 4.0 mL. The IR absorbance of the 1366 cm^{-1} band of 1 in an aliquot of this solution was compared with the absorbance of 1 in a CH_2Cl_2 solution of known concentration, and it was calculated that 0.082 ± 0.01 mmol of 1 had reacted, so that 2.2 ± 0.2 mol of CO_2/mol of 1 were liberated.

Irradiation of $Pt(C_2O_4)(PEt_3)_2$ in the Solid State. A Nujol mull of 1 between a pair of NaCl plates was irradiated with a 450-W Xe arc lamp, causing the mull to turn brown. The IR spectrum of this mull showed the disappearance of the oxalate bands of 1 and the appearance of a signal for free CO_2 at 2330 cm^{-1}.

Photochemical Synthesis of (Tetrafluoroethylene)bis(triethylphosphine)platinum, $Pt(C_2F_4)(PEt_3)_2$, 11. A solution of 1 (0.20 g, 0.38 mmol) in deaerated acetonitrile (12 mL) and benzene (8 mL) saturated with tetrafluoroethylene was irradiated in a quartz Schlenk tube while stirred magnetically. The conversion of 1, as determined from the decrease in absorbance of the IR band at 1703 cm^{-1}, was 50% complete after 1 h of irradiation and 90% complete after 3 h, at that time irradiation was stopped. The solution had warmed slightly and was clear, pale yellow. Removal of the solvent under vacuum produced a solid residue that when extracted with hot *n*-hexane (1 × 6 mL, 1 × 3 mL) yielded a yellow solution that was filtered, concentrated to 5 mL, and allowed to cool to ambient temperature and then to −78 °C for 8 h. The off-white crystals of 11 that formed were collected, washed with cold *n*-hexane at −78 °C, and dried under a stream of nitrogen; yield: 0.11 g, 0.21 mmol (54% based on 1). Anal. Calcd for $C_{14}H_{30}F_4Pt$: C, 31.64; H, 5.69; F, 14.30; P, 11.66. Found: C, 31.72; H, 5.61; F, 14.16; P, 11.87.

Photochemical Synthesis of Ethylenebis(triethylphosphine)platinum, $Pt(C_2H_4)(PEt_3)_2$, 10, and *trans*-Dihydrobis(triethylphosphine)platinum, *trans*-$PtH_2(PEt_3)_2$, 18. In a typical preparation, a deaerated, ethylene-saturated solution of 1 (1.2 g, 2.3 mmol) in acetonitrile (25 mL) and benzene (15 mL) was irradiated in a quartz-walled Schlenk tube with stirring. The vessel was connected to a mineral oil bubbler to release CO_2 pressure, and a slow stream of ethylene was passed over the solution. Heat must be dissipated from the solution by a stream of cold air or by immersing the assembly in cold water. When approximately 80–90% of 1 had reacted (as judged from the decrease in the IR absorbance at 1703 cm^{-1}), the irradiation was halted. The $^{31}P\{^1H\}$ NMR spectrum of an aliquot of this clear orange-yellow solution showed that 10 had formed cleanly from 1. Reactions of 10 could then be carried out in situ, or else 10 was isolated and handled as follows.

Removal of the solvent under vacuum caused some darkening of the solution and left an air-sensitive, red-brown oily residue that was placed under 1 atm of ethylene. Extraction with benzene, followed by filtration to remove unreacted 1, yielded a dark orange-red solution of 10, from which the solvent was again removed under vacuum. To the resultant oil were added *n*-hexane (10 mL) and lithium aluminum hydride (LAH) (0.1 g), and the mixture was stirred under 1 atm of ethylene for 8 h at 25 °C. As the LAH scavenged impurities such as acetonitrile and water, the oil was gradually extracted into solution. (If LAH was not added, the oil formed a gummy residue that was immiscible with *n*-hexane.) The hexane solution was filtered through Celite, and evaporation of the solvent yielded 10 as an impure red-brown oil. Alternatively, concentrating the solution and cooling to −90 °C produced orange crystals of 10 from which the mother liquors were removed by syringe, but the crystals melted above approximately −20 °C. A third alternative was found to be most convenient. Bubbling hydrogen through the *n*-hexane solution of 10 for 15 min, followed by cooling to −30 °C, produced brown crystals of *trans*-$PtH_2(PEt_3)_2$, *trans*-18, that were recrystallized from *n*-hexane under hydrogen to yield *trans*-18 as analytically pure off-white crystals. These are indefinitely stable under 0.5 atm of hydrogen (37% isolated yield, based on 1). Anal. Calcd for $C_{12}H_{32}P_2Pt$: Pt, 45.01; P, 14.29; C, 33.25; H, 7.44. Found: Pt, 44.98; P, 14.55; C, 32.74; H, 7.21. Treatment of solutions of 18 with a stream of ethylene displaces H_2 and quantitatively regenerates a pale yellow solution of 10 that was then used in situ: $Pt(C_2H_4)$: ^1H NMR δ 2.24 (br, $^2J_{PtH}$ = 58 Hz (C_6D_6, 10 °C)).

Reactions of $PtH_2(PEt_3)_2$, 18. These experiments were carried out in NMR tubes containing solutions of 18 under a hydrogen atmosphere and monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Unless otherwise noted, products formed quantitatively from 18 (based on $^{31}P\{^1H\}$ NMR spectral changes) at ambient temperatures and reactions were complete within a few minutes. Products were identified from their NMR and IR spectral parameters, the values of which are given above for 10, 11, PtL_3, 13, and 16; values were previously reported for PtH_2L_3,[2] $PtHIL_2$,[20] $PtH(O_2CH)L_2$,[21] 23,[21] and 24.[21]

Reaction of $PtH_2(PEt_3)_2$ with D_2. The $^{31}P\{^1H\}$ and ^1H NMR spectra of a toluene-d_8 solution of 18 under 1 atm of D_2 revealed a gradual disappearance of the hydride resonances of *trans*-18 accompanied by a broadening of the lines and a slight upfield shift in the peak positions. These latter two phenomena indicate the formation of *trans*-$PtHD(PEt_3)_2$, 18-d_1; the broadening arises from H–D coupling, and the line shift results from a small deuterium isotope effect on the chemical shift. Simultaneously the $^{31}P\{^1H\}$ NMR signal for 18 is seen under high resolution to split into a multiplet wherein the outer lines gradually increase in intensity. This behavior is consistent with the presence of overlapping signals from 18-d_0 (singlet), 18-d_1 (1:1:1 triplet), and 18-d_2 (1:3:4:3:1 quintet), where the splittings arise from $^2J_{PD}$. When conversion to 18-d_2 is complete, as shown by the complete disappearance of the hydride signal in the ^1H NMR spectrum, the $^{31}P\{^1H\}$ NMR signal for 18-d_2 is seen as a 1:3:4:3:1 quintet. The value $^2J_{PD}$ = 2.7 Hz is in excellent agreement with the value predicted from $^2J_{PH}$ and the gyromagnetic ratios of hydrogen and deuterium [$(^2J_{PH})\gamma_D/\gamma_H$ = 2.8 Hz].

Catalytic H/D Exchange Reactions. An atmosphere of H_2 and D_2 (1 atm, 28 mL) was placed over a stirred, thermostated (25 °C) solution of 18 (6 mg, 0.14 mmol) in degassed benzene (1.5 mL) and shielded from room light. Aliquots of gas (0.5 mL) were periodically withdrawn by syringe, and the relative amounts of H_2, HD, and D_2 were determined by gas chromatography. A plot of $\ln\{(HD_\infty - HD_0)/(HD_\infty - HD_t)\}$ vs. t was linear, where HD_∞ is the fraction of HD present at equilibrium, HD_0 is the fraction present initially (from incomplete deuteration of D_2), and HD_t is the fraction at time t. The value of HD_∞ = 0.430 was calculated from the equilibrium constant[22] at 25 °C for $H_2 + D_2 \rightleftharpoons 2HD$ (K = 3.28) and agrees well with the value of HD_t at long times (HD_t = 0.424, t = 410 min).

In a similar reaction, a toluene-d_8 solution of 18, excess Et_3SiH, and excess D_2 were placed in a 10-mm NMR tube. The formation of Et_3SiD was indicated by the gradual decrease in intensity of the SiH resonance relative to the $SiEt_3$ resonances in the ^1H NMR spectrum. Gas chromatographic analyses of the gas phase revealed large quantities of H_2 and HD.

Gas Chromatographic Analysis of Mixtures of H_2, D_2, and HD. Analysis was performed by a modification of the method

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(16) (a) Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Inorg. Chem.* **1981**, *20*, 1312–1314. (b) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318–325.

(17) Chini, P.; Longoni, G. *J. Chem. Soc. A* **1970**, 1542–1546.

(18) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705–716.

(19) Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700–2704.

(20) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979.

(21) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038–1048.

(22) Farkas, A. "Orthohydrogen, Parahydrogen, and Heavy Hydrogen"; Cambridge University Press: London, 1935; p 176.

of Shipman,[23] using packing material (100/120 mesh) prepared according to their directions in a 6 ft × 1/8 in. o.d. aluminum column immersed in liquid nitrogen, followed by a 6 in. × 1/8 in. o.d. stainless steel column filled with copper(II) oxide (60/80 mesh) and maintained at 550 °C with the aid of high-temperature heating tape. Analysis of a standard mixture of H_2 and D_2 showed that no detector response correction factor was required, within experimental error. Excellent resolution of H_2, HD, and D_2 mixtures was achieved by using samples of 0.5–2 mL at 1 atm. Relative concentrations were determined from electronically integrated peak areas.

Preparation of *trans*-$Pt(CH_3)X(PEt_3)_2$ (19, X = I; 14, X = Cl). A solution of **10** was prepared by irradiating **1** (0.15 g, 0.29 mmol) in deaerated acetonitrile (10 mL) and benzene (6 mL) saturated with ethylene. After 90% conversion of **1** to **10** (4.5 h irradiation), iodomethane was added (0.4 mL, 6 mmol), causing immediate gas evolution. After 5 min at 25 °C, the solvent, ethylene, and excess CH_3I were removed under vacuum to leave a bright orange oil which was dried under vacuum (10^{-3} torr, 2 h). Extraction into *n*-hexane (2 mL), followed by filtration and cooling, produced yellow crystals in **19** in 53% yield. The complex was identified by its NMR spectral parameters (Table II) (lit.[19] δ_P 10.8 ($^1J_{PtP}$ = 2753 Hz)) and its mass spectrum (*m/e* 573).

Complex **14** was prepared similarly by saturating a solution of **10** in benzene-d_6 with chloromethane and heating to 70 °C for 1 h. The product was not isolated but was identified by its NMR spectral parameters (Table II) (lit.[19] δ_P 16.2 ($^1J_{PtP}$ = 2821 Hz)).

Preparation of *cis*-$PtH(SiR_3)(PEt_3)_2$ (20, R = Me; 16, R = Et). Addition of excess Me_3SiH or Et_3SiH to a solution of **11** in toluene-d_8 at 25 °C cleanly produced, respectively, **20** and **16**, identified by their NMR spectra. Removal of the solvent and excess silane under vacuum left **16** and **20** as brown oils which slowly decomposed. The IR spectrum of **20**, immediately after isolation as an oil, contained a strong signal for the Pt–H stretch at 2035 cm^{-1}, that gradually decreased in intensity as the sample decomposed. ^{1}H NMR: Pt–H, **16**, δ −2.29, (dd, $^2J_{PH}{}^{cis}$ = 23 Hz, $^2J_{PH}{}^{trans}$ = 154 Hz, $^1J_{PtH}$ = 942 Hz); **20**, δ −2.03 (dd, $^2J_{PH}{}^{cis}$ = 22 Hz, $^2J_{PH}{}^{trans}$ = 154 Hz, $^1J_{PtH}$ = 972 Hz (toluene-d_8, −30 °C)).

Preparation of *trans*-$PtH(OMe)(PEt_3)_2$, 15, from [*trans*-$PtH(MeOH)(PEt_3)_2]^+BF_4^-$, 21. Addition of 1 equiv of sodium methoxide in methanol to a solution of **21** (prepared by the reaction of silver tetrafluoroborate and *trans*-$PtHCl(PEt_3)_2$ in methanol under nitrogen, followed by filtration to remove silver chloride) at −20 °C produces **15**.

Irradiation of *trans*-$Pt(Me)Cl(PEt_3)_2$, 14. A solution of **14**, prepared by the reaction of CH_3Cl with **10**, was irradiated in a 10-mm NMR tube under conditions used for irradiation of **1**, and the $^{31}P\{^1H\}$ NMR spectrum was periodically recorded. The platinum-containing products, as seen by $^{31}P\{^1H\}$ NMR spectroscopy, were identical with the secondary photoproducts that appeared in the photoconversion of **1** to **14** and were formed in the same ratios in both cases but were not investigated further.

Preparation of (Bis(diphenylphosphino)ethane)(oxalato)palladium(II), $Pd(C_2O_4)$(diphos). To a suspension of $PdCl_2$(diphos) (2.97 g, 5.16 mmol) in 90 mL MeOH was added excess AgC_2O_4 (3.54 g, 1.17 mol). The suspension was stirred in a foil wrapped flask and brought to reflux for 12 h. A black-green suspension was removed by filtration in subdued light, and the solvent was then removed from the filtrate under reduced pressure to yield a yellow solid. This solid was recrystallized twice from hot MeOH/diethyl ether and dried under vacuum to provide white $Pd(C_2O_4)$(diphos) (2.37 g, 4.00 mmol) in 77% yield: $^{31}P\{H\}$ NMR (Me_2SO-d_6) δ 60.5 (s). Anal. Calcd for $C_{52}H_{24}O_2P_2Pd$: C, 56.72, H, 4.08. Found: C, 55.64, H, 4.15.

Preparation of (Oxalato)bis(tri-*n*-butylphosphine)palladium(II), $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$. A suspension of *trans*-$PdCl_2[P(n\text{-}Bu)_3]_2$ (1.02 g, 1.76 mmol) and $Ag_2C_2O_4$ (90.4 g, 3.10 mmol) in 80 mL of CH_2Cl_2 was prepared in a flask wrapped in foil and stirred for 24 h. After filtration approximately half of the solvent was removed under reduced pressure. Anhydrous ether was added, and the resulting precipitate was recrystallized from CH_2Cl_2/Et_2O to give the white product $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$ (0.92 g, 1.52 mmol) in 85% yield: $^{31}P\{^1H\}$ NMR (Me_2SO-d_6) δ 27.2 (s). Anal. Calcd for $C_{26}H_{54}O_4P_2Pt$: C, 52.16; H, 9.02. Found: C, 52.03; H, 9.21.

Table III. Electronic Absorption Spectral Features of Bis(phosphine)platinum(II) and -palladium(II) Oxalates in CH_3CN

complex	absorptns, nm	molar extinction coeff, × 10^3
$Pt(C_2O_4)(PEt_3)_2$	286	0.75
	258	3.1
	236	8.3
	206	23
$Pt(C_2O_4)(PPh_3)_2$	326	3.5
	237	49
$Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$	335	0.79
	299	2.5
	252	12
$Pd(C_2O_4)$(diphos)	337	2.4
	300 sh	5
	244	24

Photochemical Preparation of (Bis(diphenylphosphino)ethane)(dimethyl acetylenedicarboxylate)palladium, Pd(COOMeC≡CCOOMe)(diphos). Under N_2, $Pd(C_2O_4)$(diphos) (0.102 g, 0.17 mmol) was suspended in 10 mL of CH_3CN in a quartz Schlenk tube, equipped with a stir bar, and sealed with a septum cap. An excess of dimethyl acetylenedicarboxylate (0.05 mL, 4.0 × 10^{-2} mol) was added by syringe. The suspension was cooled in an ice water bath and stirred while being irradiated for 1 h (unfiltered 450-W Hanovia medium-pressure mercury arc lamp). The solid dissolved, and the solution turned red. All solvent was removed under reduced pressure. The resulting red solid was recrystallized twice from CH_2Cl_2/MeOH to provide the yellow product Pd(COOMeC≡CCOOMe)(diphos) (0.024 g, 0.038 mmol) in 22% yield: IR (KBr pellet) 1815 (C≡C), 1680 cm^{-1} (C=O); $^{31}P\{^1H\}$ NMR (CH_3CN/C_6D_6) δ 47.0 (s). Anal. Calcd for $C_{32}H_{30}O_4P_2Pd$: C, 59.36; H, 4.63. Found: C, 58.92; H, 4.85.

Photochemical Preparation of (η^3-Allyl)(bis(diphenylphosphino)ethane)palladium Hexafluorophosphate, [(η^3-C_3H_5)Pd(diphos)]PF_6. To $Pd(C_2O_4)$(diphos) (0.18 g, 0.31 mmol) suspended in 10 mL of CH_3CN was added allyl acetate (1.5 mL, 1.39 × 10^{-2} mol). Irradiation for 30 min gave a yellow solution. After the volume of solution was reduced to approximately 2 mL, a solution of NH_4PF_6 (0.20 g, 1.2 × 10^{-3} mol) in 7 mL of EtOH was added. Cooling to −20 °C for 10 h gave the white precipitate [(η^3-allyl)Pd(diphos)]PF_6. The filtrate was removed by syringe, and the solid was washed twice with EtOH and twice with diethyl ether, recrystallized from CH_2Cl_2/Et_2O, and dried under vacuum (yield 0.16 g, 75%): IR (KBr pellet) 1480, 1440 cm^{-1}; $^{31}P\{^1H\}$ NMR (Me_2SO-d_6) δ 52.1 (s); ^{1}H NMR (Me_2SO-d_6) (η^3-C_3H_5), δ 6.0 (m), 5.0 (b), 3.7 (b). Anal. Calcd for $C_{29}H_{29}P_2Pd$: C, 50.42; H, 4.20. Found: C, 50.13; H, 4.10.

Photochemical Preparation of (η^3-Allyl)bis(tri-*n*-butylphosphine)palladium Tetraphenylborate, {(η^3-C_3H_5)Pd[P(*n*-Bu)$_3$]$_2$}BPh_4. In a quartz Schlenk flask (under N_2) equipped with a stir bar and containing 0.217 g (0.36 mmol) of $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$ was added 7 mL of distilled CH_3CN, 3 mL of distilled C_6D_6 and 3 mL of allyl acetate (degassed). The solution was irradiated for 45 min whereupon the solution turned yellow. Solvent was removed under reduced pressure, and the residue was then dissolved in 10 mL of distilled MeOH. After filtration (under N_2) into a two-neck round-bottom flask equipped with a stir bar, a solution of 0.145 g (0.42 mmol) of $NaBPh_4$ in 20 mL of degassed H_2O was slowly added. A white solid forms that was collected by filtration. Recrystallization from CH_2Cl_2/Et_2O yielded the title product (32%) as white crystals: ^{1}H NMR (η^3-C_3H_5), δ 5.50 (m), 4.37 (m), 3.21 (m); $^{31}P\{^1H\}$ NMR δ 9.11. Anal. Calcd for $C_{27}H_{32}P_2Pd$: C, 70.29; H, 9.14; P, 7.11. Found: C, 69.86; H, 9.03; P, 7.14.

Absorption Spectral Features of Pt(II) and Pd(II) Oxalates. The photoreactions described require irradiation with λ ≤ 313 nm since the metal complex absorption bands are centered in the UV spectral region (Table III). Mechanistic details of the primary photoprocess will be explored in the future by flash photolysis. At present the best working hypothesis would be to

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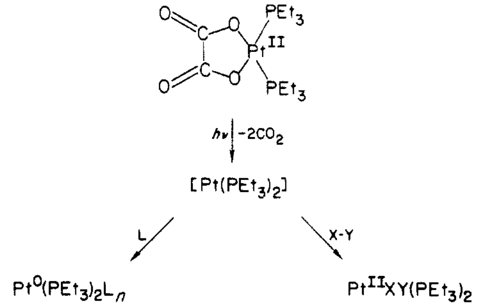
[23] Shipman, G. F. *Anal. Chem.* **1962**, *34*, 877–878.

Scheme I. Preparation of Platinum(II) Oxalate Complexes

	method	L
A	*cis*-$PtCl_2L_2 + K_2C_2O_4 \rightarrow Pt(C_2O_4)L_2 + 2KCl$	PEt_3
B	*cis*-$PtCl_2L_2 + Ag_2C_2O_4 \rightarrow Pt(C_2O_4)L_2 + 2AgCl$	SEt_2
C	$Pt(C_2O_4)(SEt_2)_2 + 2L \rightarrow Pt(C_2O_4)L_2 + 2SEt_2$	PEt_3, PPh_3
D	$Pt(C_2O_4)(PPh_3)_2 + 2L \rightarrow Pt(C_2O_4)L_2 + 2PPh_3$	PMe_3, PEt_3, $P(n\text{-}Bu)_3$
E	$Pt(C_2O_4)(SEt_2)_2 + L \rightarrow Pt(C_2O_4)(SEt_2)L + SEt_2$	PEt_3, PPh_3, $P(i\text{-}Pr)_3$, $P(c\text{-}Hx)_3$

Scheme II. Photochemical Reactions of $Pt(C_2O_4)(PEt_3)_2$



compd	L	*n*	% yield (% convers)
10	C_2H_4	1	91 (96)
11	C_2F_4	1	95 (90)
12	PEt_3	1	90 (95)
13	CO	2	95 (65)

compd	X	Y	geom	% yield (% convers)
14	Me	Cl	trans	88 (23), 45 (93)
15	MeO	H	trans	67 (75)
16	Et_3Si	H	cis	82 (68), 59 (93)
17	Ph	Cl	trans	42 (80)

assign the lowest energy intense absorption features to ligand to metal charge-transfer (LMCT) transitions as well as to phosphine-localized absorptions. It is likely that the oxalate to M(II) LMCT transition is responsible for the photoreduction process.

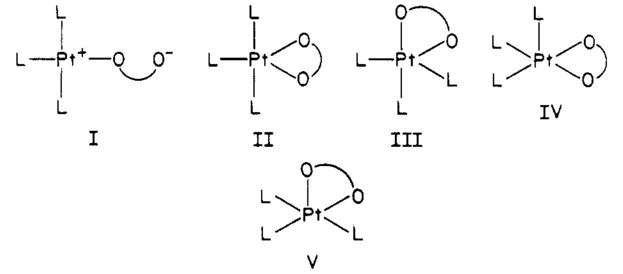
Results and Discussion

Preparation and Properties of Platinum(II) Oxalate Complexes. The reactions used to prepare the oxalate complexes are shown in Scheme I. The first two methods involve conversion of the corresponding dichloro complex to the oxalate, while the latter three rely on replacement of diethyl sulfide or triphenylphosphine from platinum(II) oxalate complexes. Methods C and D appear to be generally useful for preparing oxalate complexes $Pt(C_2O_4)L_2$ wherein L is a small trialkylphosphine ligand ($L = PMe_3$, PEt_3, $P(n\text{-}Bu)_3$). However, when bulkier phosphines such as triisopropylphosphine and tricyclohexylphosphine were employed, it is only possible to substitute one diethyl sulfide ligand (method E), to produce $Pt(C_2O_4)(SEt_2)L$ ($L = P(i\text{-}Pr_3)$ (**6**), $P(c\text{-}Hx)_3$ (**7**)). Apparently, the size of these ligands prevents substitution by a second bulky ligand. Both diethyl sulfide ligands could be displaced from **3** by triphenylphosphine, a ligand of intermediate size. The presence of oxalate bound to platinum and palladium to give a five-membered ring (as shown for **1** in Scheme II) was confirmed by the observations of IR signals (Table I) characteristic of this mode of oxalate bonding.[24] The $^{31}P\{^1H\}$ NMR spectra are also consistent with the assigned structures. The relatively large values of $^1J_{PtP}$ reflect the low trans influence of the oxalate ligand, as expected for oxygen donor ligands.[25]

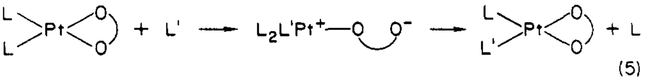
Free triethylphosphine exchanges with triethylphosphine coordinated to **1** by an associative mechanism, as generally found for platinum(II) substitution reactions[26] and demonstrated in this case by the $^{31}P\{^1H\}$ NMR spectra of solutions of **1** with and without excess triethylphosphine present. Without excess ligand, the NMR signals of **1** are sharp at 30 °C, but addition of triethylphosphine causes the resonances of **1** and free triethylphosphine (δ −18.7) to broaden considerably (width at half-height = 80–100 Hz) but to remain distinct. This behavior is characteristic of associative exchange. Upon cooling this solution to −50 °C, complete conversion of **1** to a new species, **22**, occurs. The $^{31}P\{^1H\}$ NMR spectrum of **22** at −50 °C is sharp and consists of a doublet and a triplet (each with ^{195}Pt satellites) in a 2:1 ratio, indicating a third triethylphosphine ligand is bound to **1**. This behavior is reversible and can be cycled by varying the temperature, indicating a temperature-dependent association equilibrium of the sort shown in eq 4. The temperature behavior indicates both

$$Pt(C_2O_4)(PEt_3)_2 + PEt_3 \overset{K}{\rightleftharpoons} \underset{\mathbf{22}}{Pt(C_2O_4)(PEt_3)_3} \qquad (4)$$

ΔH and ΔS are negative for the reaction as written and $K << 1$ at 25 °C. Five possible structures for **22** are diagrammed below, based on square-planar (I), trigonal-bipyramidal (II and III), and square-pyramidal (IV and V) geometries. To distinguish among these structures, we



recorded the $^{13}C\{^1H\}$ NMR spectra of **1** at low temperature with and without excess PEt_3 present. The oxalate carbons of **1** appear as a single sharp line at δ 165.1 (−30 °C, no PEt_3 present). In complex **22**, however, the two oxalate carbons are inequivalent (δ 168.6, 173.4, −90 °C, $[PEt_3]/[\mathbf{1}] = 5$), ruling out structures II and IV. Support for structure I comes from the similarity of the Pt–P and P–P coupling constants of **22** and of $PtCl(PEt_3)_3{}^+Cl^-$ (Table II). Structure I is reminiscent of $[PtXL_3]^+X^-$ intermediates proposed in the "double displacement" mechanism for the isomerization of PtX_2L_2 catalyzed by L.[26] Substitution of ligands in these platinum oxalate complexes may proceed by an analogous mechanism, wherein one oxygen of the oxalate ligand may be temporarily displaced by the incoming ligand (eq 5). The substitution mechanism we


(5)

propose is an attractive alternative to that suggested[27] for ligand exchange and catalytic phosphine oxidation in $Pt(O_2)L_2$ systems. For the latter complexes, an interme-

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[24] (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds, Third Edition"; Wiley: New York, 1978; pp 233–236. (b) Fujita, J.; Martell, A. E.; Nakamoto, K. *J. Chem. Phys.* **1962**, *36*, 324–331. (c) *Ibid.*, 331–338.

[25] Appelton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

[26] (a) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions"; Wiley: New York, 1967; Chapter 5. (b) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185–215. (c) Van der Poel, H.; Van Koeten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941–2950. (d) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356–1365. (e) De Renzi, A.; Panunzi, A.; Saporito, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1977**, *107*, 549–554. (f) Tau, K. D.; Meek, D. W. *J. Organomet. Chem.* **1977**, *139*, C83–C86.

[27] Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337–8339.

diate of structural type IV was preferred; however, the authors point out that the NMR data do not rule out other structures, such as I. Indeed, the formation of the active oxidant HO_2^- in the catalysis solution[27] is better explained by protonation of an intermediate of type I than by protonation of one of type IV. We have performed NMR studies with ^{17}O-labeled dioxygen complexes that were prepared according to the literature procedure.[27] Unfortunately the ^{17}O NMR resonances were too broad to be observed at −65 °C.

Photochemical Reactions of $Pt(C_2O_4)(PEt_3)_2$, 1. Complex 1 is stable in the absence of UV irradiation. No decomposition occurs after 26 h in refluxing toluene, while slow decomposition takes place in refluxing xylene. Ultraviolet irradiation ($\lambda \leq 313$ nm) triggers the release of 2 equiv of carbon dioxide from 1 and produces a highly reactive platinum species that we propose to be the 14-electron compound $Pt(PEt_3)_2$ or a weak complex with solvent (see below). This species can be trapped by irradiating 1 in the presence of substrates that either coordinate or oxidatively add to $Pt(PEt_3)_2$ to produce a series of platinum(0) and platinum(II) compounds containing the $Pt(PEt_3)_2$ moiety (Scheme II). Irradiation of 1 in the presence of donor and acceptor ligands L produces platinum(0) compounds $Pt(PEt_3)_2L_n$ ($n = 1, 2$), while in the presence of substrates XY that can undergo oxidative addition, platinum(II) complexes $PtXY(PEt_3)_2$ form. We did not observe intermediates in these reactions in the $^{31}P\{^1H\}$ NMR spectra. For example, successive $^{31}P\{^1H\}$ NMR spectra of solutions of 1 irradiated under an ethylene atmosphere reveal clean conversion of 1 to $Pt(C_2H_4)(PEt_3)_2$, **10**. Reaction of 1 does not occur in the absence of UV irradiation, neither initially nor after partial photochemical conversion. In some cases further reaction of a product was observed, because of its photochemical or thermal instability under the reaction conditions. The other platinum oxalate complexes **2**–**9** released CO_2 upon irradiation in CH_2Cl_2 solvent. Although these reactions were not studied in detail, it establishes the generality of the photochemical process.

Irradiation of 1 in solution, in the absence of substrates that trap the $Pt(PEt_3)_2$ moiety, leads to reaction with the solvent or rearrangement of $Pt(PEt_3)_2$ to $Pt(PEt_3)_3$ and platinum metal. An analogous reaction has been observed when $Pt(PPh_3)_2$ was generated in situ by reductive elimination of methane from *cis*-$PtH(Me)(PPh_3)_2$.[28] Irradiation of 1 in dichloromethane caused the solution to turn pale yellow, and the $^{31}P\{^1H\}$ NMR spectrum revealed the presence of at least five platinum-containing products, out of which *cis*-$PtCl_2(PEt_3)_2$ and *trans*-$PtHCl(PEt_3)_2$ were identified (eq 6).[29] Irradiation of $Pt(PPh_3)_2(C_2O_4)$ produces the cis dichloride in substantial quantities when irradiated in CH_2Cl_2.

$$Pt(C_2O_4)(PEt_3)_2 \xrightarrow[CH_2Cl_2]{h\nu} \textit{cis}\text{-}PtCl_2(PEt_3)_2 + \textit{trans}\text{-}PtHCl(PEt_3)_2 + ... \quad (6)$$

Irradiation of 1 in methanol/C_6D_6 produces the novel, labile complex *trans*-$PtH(OCH_3)(PEt_3)_2$, **15**. Such compounds have been proposed as intermediates in the dehydrogenation of alcohols to aldehydes by $Pt(PR_3)_2$ complexes, that react with alcohols to produce platinum(II) dihydrides (eq 7).[5]

$$Pt(PR_3)_2 + RCH_2OH \rightarrow \textit{trans}\text{-}PtH_2(PR_3)_2 + RC(O)H \quad (7)$$

Complex **15** gradually reacts in solution to form the platinum(II) dimer[21] $Pt_2H_2(\mu\text{-}H)(PEt_3)_4^+$, **23**. This reaction probably involves initial formation of *trans*-$PtH_2(PEt_3)_2$ accompanied by loss of formaldehyde.[21] Complex **15** could not be isolated because of its lability, but its identity could be determined from spectral parameters. The $^{31}P\{^1H\}$ NMR spectrum of **15** is a singlet with ^{195}Pt satellites ($^1J_{PtP}$ = 2804 Hz). When only the PEt_3 hydrogens are decoupled, each line in the ^{31}P NMR spectrum splits into a doublet, indicating the presence of a single hydride ligand in a complex of the type *trans*-$PtHX(PEt_3)_2$. This is confirmed by examination of the ^1H NMR spectrum that contains a hydride resonance (δ −23.76) split into a 1:2:1 triplet ($^2J_{PH}$ = 15.4 Hz) surrounded by ^{195}Pt satellites ($^1J_{PtH}$ = 1309 Hz). A broad signal for coordinated methoxide can be seen at δ 2.87, with ^{195}Pt satellites separated by $^3J_{PtH}$ = 56 Hz. A broad signal for methoxide also appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 53.0, but no couplings were resolved. As further confirmation of its identity, we generated **15** by the reaction between sodium methoxide and [*trans*-$PtH(CH_3OH)(PEt_3)_2]BF_4$, **21**.

The unprecedented reactivity of the photogenerated $Pt(PEt_3)_2$ species is demonstrated by its immediate cleavage of the carbon–chlorine bond of chlorobenzene at 15 °C to give *trans*-$Pt(Ph)Cl(PEt_3)_2$, **17** (Scheme II). Formation of **17** from $Pt(PEt_3)_3$ (**12**) takes place over 15 min at 111 °C,[2] possibly by dissociation of a triethylphosphine ligand to generate small quantities of $Pt(PEt_3)_2$. In contrast, the sterically hindered 14-electron complex $Pt[P(c\text{-}Hx)_3]_2$ reacts with chlorobenzene slowly over 4 days at ambient temperature to form[3b] *trans*-$Pt(Ph)Cl[P(c\text{-}Hx)_3]_2$.

Triethylsilane reacts with $Pt(PEt_3)_2$ to yield an oxidative addition product with cis geometry, in contrast to the trans geometry that we observed for most other substrates. The cis configuration may be electronically favored, since it places the hydride and triethylsilyl ligands, which are highest in the trans influence series, in positions opposite the phosphine ligands.[25] This arrangement has been found[30] for related complexes *cis*-$PtH(SiR_3)(PPh_3)_2$. Using the bulky tricyclohexylphosphine ligand, one obtains *trans*-$PtH(SiH_3)[P(c\text{-}Hx)_3]_2$; steric effects probably dictate the trans geometry.[31]

The photoreaction of 1 with hydrogen is quite interesting. Our initial expectation was that $PtH_2(PEt_3)_2$ would form by oxidative addition of H_2 to $Pt(PEt_3)_2$, eq 8; similar behavior is seen for bulky PtL_2 complexes.[5] Instead, $[Pt_2H(\mu\text{-}H)_2(PEt_3)_4]HCO_2$, **24**, is the sole product. We subsequently discovered that **18** and carbon dioxide react in polar solvents to form **24** by the sequence of eq 9 and 10,[21] and therefore believe that **18** forms initially as in eq. 8.

$$Pt(C_2O_4)(PEt_3)_2 + H_2 \xrightarrow{h\nu} PtH_2(PEt_3)_2 + 2CO_2 \quad (8)$$

$$PtH_2(PEt)_2 + CO_2 \rightarrow \textit{trans}\text{-}PtH(O_2CH)(PEt_3)_2 \quad (9)$$

$$PtH_2(PEt_3)_2 + \textit{trans}\text{-}PtH(O_2CH)(PEt_3)_2 \rightarrow \underset{\mathbf{24}}{[Pt_2H_3(PEt_3)_4]HCO_2} \quad (10)$$

Given the propensity of PtL_2 to react with alcohols, it is likely that the initial study[11] of day long photoreactions of $Pt(C_2O_4)(PPh_3)_2$ in ethanol solvent proceeded through

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(28) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

(29) The compounds *cis*-$PtCl_2(PEt_3)_2$ (δ_P 8.7 ($^1J_{PtP}$ = 3500 Hz)) and *trans*-$PtHCl(PEt_3)_2$ (δ_P 22.9 ($^1J_{PtP}$ = 2715 Hz)) were identified by comparison with NMR spectra of authentic samples, prepared by the literature method.[13]

(30) Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1972**, *43*, C5–C6.

(31) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *J. Chem. Soc., Dalton Trans.* **1978**, 1167–1170.

hydrido alkoxy and other hydride intermediates. In preliminary studies we found the PPh_3 complex to be bothersome due to the formation of red intractable products during photolysis. Reactions of the alkylphosphine derivatives proceeded much more cleanly. The reactivity of photogenerated ML_2 with alcohols also explains the initial report[11] that $Pd(C_2O_4)$(diphos) forms palladium mirrors upon irradiation. By contrast we observe (vide infra) relatively clean photoreactions of $Pd(C_2O_4)$(diphos) and $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$ in Me_2SO or CH_3CN solvent. Indeed, if one adds methanol to these latter two solvents, a black colloid forms during photolysis that we assume is Pd metal. By analogy to the PtL_2 system it seems likely that PdL_2 adds HOR to produce $Pd(H)(OR)L_2$. Rapid β-hydride abstraction[32] then yields PdH_2L_2. We infer that PdH_2L_2 is not stable and decomposes to yield Pd metal. One should note that PdH_2L_2 compounds are unknown in contrast to the PtH_2L_2 systems. Irradiation of $Pd(C_2O_4)$(diphos) and $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$ in Me_2SO or CH_3CN under H_2 leads to decomposition, in contrast to the stable hydrides that form when Pt analogues are irradiated in the presence of H_2.[21]

Solutions of 1 in deaerated acetonitrile or acetonitrile–benzene turn dark brown upon irradiation, and a complex mixture of products appears in the $^{31}P\{^1H\}$ NMR spectrum. Some of these are secondary photoproducts, since they do not form directly from 1 but only appear at long irradiation times. The major primary photoproduct is the cation $PtH(PEt_3)_3^+$, **25**, identified from its distinctive $^{31}P\{^1H\}$ NMR spectrum.[2] Evaporation of the solvent from these photoproduct solutions leaves a dark brown viscous oil. When dissolved in toluene-d_8, this oil was seen by ^{31}P NMR spectroscopy to contain $Pt(PEt_3)_3$, **12**, as the major component. Complex **12** is known to react reversibly with protic species such as water and alcohols to form cation **25**;[2,33] however, spectroscopically observable quantities of

$$\underset{\mathbf{12}}{Pt(PEt_3)_3} + ROH \rightarrow \underset{\mathbf{25}}{[PtH(PEt_3)_3]RO} \qquad (11)$$

25 only form in the presence of large excesses of these protic species.[33] We examined the behavior of **12** in solutions of acetonitrile (that generally contains traces of water) and found it was indefinitely stable under nitrogen. When an excess of water was added, complete conversion of **12** to **25** occurred. If, instead of water, carbon dioxide was added to the solution, we found to our surprise that **12** was again completely converted to **25**. Similar behavior occurred in pyridine solvent. We believe that carbon dioxide scavenges hydroxide or alkoxide ion to produce bicarbonate or alkyl carbonates and this process drives eq 11 to the right. Although we did not investigate this behavior further, these results establish that any **12** formed from 1 under the photolysis condition (where CO_2 forms as a byproduct) would be present as **25**.

The yields of the photoreactions in Scheme II, as measured by NMR spectroscopy, are affected by the absorption characteristics, photosensitivity, and thermal stability of the products. For example, *trans*-$PtMeCl(PEt_3)_2$, (**14**) is photosensitive. Although it forms cleanly in the early stages of the photoreaction of 1 and chloromethane, UV irradiation gradually converts it to a mixture of unidentified secondary products. The product from irradiation of 1 in methanol, **15**, slowly decomposes in solution at ambient temperature in the dark. Its yield in solution can be improved substantially by using high light intensities to hasten photochemical conversion and low temperatures to retard decomposition.

Photochemical Syntheses of Complexes from $Pt(C_2O_4)(PEt_3)_2$, 1. Light-triggered fragmentation of the oxalate group of 1 can be exploited to prepare complexes containing $Pt(PEt_3)_2$. The principal side product, carbon dioxide, is usually inert under the reaction conditions. The highest overall yields for the photoreactions of 1, shown in Scheme II, occur in the production of platinum(0) products, since these are less susceptible to secondary photoreaction. The insolubility of 1 in hydrocarbon solvents requires that the photochemical reactions be carried out in acetonitrile/benzene mixtures. Because the platinum products are very soluble in most solvents, we removed the acetonitrile and benzene under vacuum and extracted the products with n-hexane or benzene. In this way, the new tetrafluoroethylene complex **11** was isolated in 54% yield. All of the complexes could be readily identified by NMR spectroscopy. The planar structure of the C_2F_4 complex was evident from the second-order effects in the ^{31}P and ^{19}F (Figure 1) NMR spectra. Differing cis and trans P–F couplings that are present in a planar complex produce an $AA'X_2X'_2$ spin system. The preparative procedure could not be used for **13** that decomposes in the absence of carbon monoxide. Platinum(II) products formed photochemically from 1 were often too photolabile to be synthesized in good yield by this method. One notable exception is the dimeric product **24** produced under hydrogen. Although dihydride **18** is light-sensitive, carbon dioxide scavenges **18** rapidly enough (eq 9 and 10) that significant photodecomposition does not occur. Dimer **24** is stable to UV light and can therefore be isolated in good yield (as the tetraphenylborate salt) as reported previously.[21]

Complex **10** is a useful synthetic precursor, since displacement of the ethylene ligand produces platinum(0) and platinum(II) complexes that contain $Pt(PEt_3)_2$. Irradiation of ethylene-saturated solutions of 1 in acetonitrile/benzene mixtures, as described in the Experimental Section, efficiently and cleanly produces clear yellow solutions of **10** on a scale of up to several grams. Complex **10** is thermally stable and decomposes only slowly under UV irradiation. It is important to dissipate heat from the solutions during irradiation. Failure to do so results in partial decomposition and the solutions turn dark reddish brown. Complex **10** is an orange liquid (mp <−20 °C) and difficult to isolate in an analytically pure form. In many cases this is not necessary, since it can be allowed to react in situ, and the desired product can then be isolated by removing the solvent under vacuum and extracting the product into n-hexane. This has generally proved successful for those products that do not decompose under vacuum. Very labile complexes such as **13**, **16**, **18**, and **20** decompose under vacuum, necessitating different procedures. When the acetonitrile/benzene solvent mixture is removed under vacuum from solutions of **10**, some decomposition occurs and **10** remains as a viscous, orange-brown oil. Extraction with benzene under ethylene followed by filtration removes the unreacted 1. If the benzene is evaporated under vacuum at this point, **10** remains again as an impure oil. Curiously, although **10** is very soluble in n-hexane, extraction with this solvent causes much of **10** to remain behind as a waxy substance that is soluble in benzene but insoluble in n-hexane. We suspected impurities such as residual acetonitrile and water (present as an impurity in the acetonitrile solvent) that are immiscible with n-hexane were causing this behavior. This problem was overcome

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[32] (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075–5084. (b) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110–2116.

[33] Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027–2038.

by adding lithium aluminum hydride to *n*-hexane and stirring the suspension above the oily residue of impure **10** for approximately 8 h at 25 °C under 1 atm of ethylene. Complex **10** does not react with LAH during this time, but LAH scavenges the impurities, and **10** dissolves completely in *n*-hexane. Filtration, concentration, and cooling to −90 °C produces orange crystals of **10** that melt above approximately −20 °C and form a dark orange viscous oil. Rather than handle this oil, we find it convenient to convert **10** to *trans*-**18** by bubbling hydrogen through the *n*-hexane solution of 10 for 15 min. Cooling then yields crystals of *trans*-**18**. Recrystallization from *n*-hexane produces analytically and spectroscopically pure *trans*-**18** that is indefinitely stable under a hydrogen atmosphere. Bubbling ethylene through a solution of **18** quantitatively regenerates **10**.

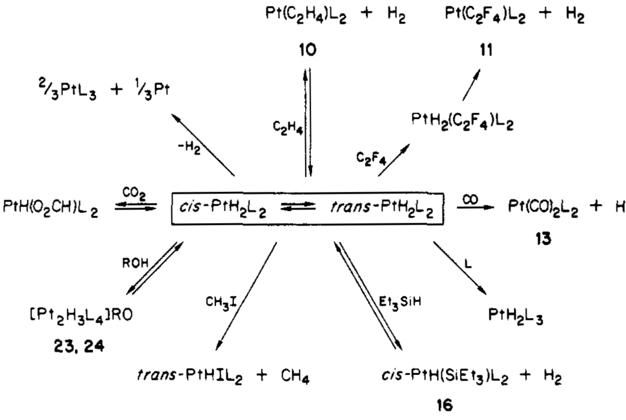
An interesting solvent effect is found for the photochemical formation of **10**. When conducted in mixtures of acetonitrile and benzene, this reaction cleanly produces **10**. In the absence of benzene, the yield of **10** decreases considerably and a number of unidentified sideproducts form, as shown by the $^{31}P\{^1H\}$ NMR spectrum. We have found the solubility of ethylene is approximately the same in benzene, acetonitrile, and mixtures of the two, so that this behavior cannot be caused by different concentrations of ethylene in these solvents.

It is possible that $Pt(PEt_3)_2$ forms weak complexes with solvents such as benzene and acetonitrile that have vacant π^*-orbitals. Isolable complexes form with the more electrophilic analogues trifluoroacetonitrile[34] and perfluorohexamethylbenzene.[35] Electron-withdrawing substituents lower the energy of the π^*-orbitals of these species, thereby strengthening metal-to-ligand π-back-bonding.

Some competitive thermal routes to $Pt(PEt_3)_2$ have appeared in recent years. The ethylene complex **10** has been prepared in solution by Nuzzo, McCarthy, and Whitesides[16a] by controlled thermolysis of *cis*-$Pt(C_2H_5)_2(PEt_3)_2$. Barker et al.[36] report $Pt_2(\mu\text{-COD})(PEt_3)_4$ is a convenient reagent to produce PtL_2; however, this complex requires prior preparation of $Pt(COD)_2$. Head[37] has claimed to generate **10** by reducing $PtCl_2(PEt_3)_2$ with sodium naphthalide under an ethylene atmosphere. No spectral properties were reported. The trans isomer of $PtH_2(PEt_3)_2$ has been previously isolated[5] in impure form from the reaction between $PtCl_2(PEt_3)_2$ and Na/Hg. Hydrocarbon solutions of *trans*-**18** have also been prepared[38] by the reaction between H_2 and $Pt(neopentyl)_2(PEt_3)_2$.

Properties of $PtH_2(PEt_3)_2$. The dihydride $PtH_2(PEt_3)_2$ is present in solution as an equilibrium mixture of cis and trans isomers. These species are readily identified by their ^{31}P (Table II) and ^1H NMR parameters. In the proton NMR spectrum the trans isomer exhibits a resonance δ −2.96 that is a triplet ($^2J_{P-H}$ = 18 Hz) due to splitting by the two phosphines that are cis to the hydrides. The cis isomer exhibits an AA′XX′ pattern centered at δ −3.56 with $^2J_{P_{cis}-H}$ = 24 Hz and $^2J_{P_{trans}-H}$ = 172 Hz. Platinum satellites are also observed for the cis (J_{Pt-H} = 1030 Hz) and trans (J_{Pt-H} = 790 Hz) isomers. When the triethylphosphine hydrogens are selectively decoupled in the ^{31}P NMR, then the ^{31}P resonance assigned (Table II) to the trans isomer splits into the expected triplet, while that assigned to the cis isomer is a partly resolved doublet of doublets. The equilibrium constant, K = cis/trans is small (0.03) in toluene solvent and significant (0.12) in acetone solution. When pure crystalline *trans*-**18** is dissolved in acetone (at 25 °C), the equilibrium between the cis and trans isomers is reached within 15 min. If less then the stoichiometric amount of C_2H_4 is added to a mixture of *cis*-**18** and *trans*-**18**, the cis isomer is selectively depleted and then equilibrium is restored on the time scale cited above.

Scheme III. Reactions of $PtH_2(PEt_3)_2$



The complexes *cis*-**18** and *trans*-**18** provide the first example of square-planar d^8 dihydride complexes to exhibit cis–trans isomerization. Prior to this study cis dihydrides of Pt had only been observed with chelating phosphines. Reductive elimination of H_2 from square-planar d^8 complexes has caught the attention of theorists in recent years.[39-41] Model calculations[41] on *cis* and *trans*-$PtH_2(PH_3)_2$ and the corresponding PMe_3 complex suggested that the cis and trans dihydrides may be of comparable thermodynamic stability although the cis isomer was still predicted to be quite unstable (by 23 kcal/mol) relative to the trans isomer. Present results suggest that the cis–trans energy difference is so small the solvent polarity (more polar solvents favor the polar cis isomer) can influence the relative amounts of cis and trans isomers at equilibrium.

Solutions of **18** under hydrogen in hydrocarbon solvents or in acetone are quite stable. (A solution in C_6D_6 under 0.5 atm of H_2 showed no signs of decomposition after 1 year at room temperature.) Under vacuum, these solutions decompose slowly to yield $Pt(PEt_3)_3$ and platinum metal. An investigation of the chemistry of **18** reveals much greater reactivity than that of more sterically hindered platinum(II) dihydrides. The reactions, displayed in Scheme III, proceed cleanly under mild conditions (25 °C, 1 atm of gases) and are complete within minutes.

Ligands that are π-acceptors such as CO, C_2H_4, and C_2F_4 readily displace H_2 from **18** to produce zerovalent compounds $Pt(PEt_3)_2L_n$ (L = C_2H_4, n = 1; L = C_2F_4, n = 1; L = CO, n = 2). The reactions of **18** with carbon monoxide or ethylene are complete within minutes, and no hydrogenation products were observed by ^1H NMR spectroscopy. Gas chromatographic analysis of the gas phase in the reaction with ethylene showed little or no ethane was produced. At much longer times (1 day), ethane was de-

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[34] Bland, W. J.; Kemmitt, R. D. W.; Moore, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1292–1295.

[35] Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31–32.

[36] Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Onak, T. P.; Siwapanyoyos, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1687–1692.

[37] Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637–1640.

[38] Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81–85.

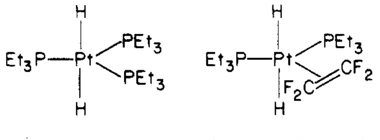
[39] Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867.

[40] Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. *Inorg. Chem.* **1982**, *21*, 2162–2174.

[41] (a) Noell, J. O.; Hay, P. J. *Inorg. Chem.* **1982**, *21*, 14–20. (b) Noell, J. O.; Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4578–4584.

tected above solutions of 18 under 0.5 atm of H_2 + 0.5 atm of C_2H_4, but this slow catalytic hydrogenation was not investigated further.

Addition of 1 equiv of triethylphosphine to a solution of *trans*-18 in toluene produces the known[2] five-coordinate adduct $PtH_2(PEt_3)_3$. The reaction of *trans*-18 with tetrafluoroethylene rapidly produces an intermediate adduct, $PtH_2(C_2F_4)(PEt_3)_2$, that loses H_2 over 0.5 h to form 11. The intermediate was not isolated, but its structure can be inferred from $^{31}P\{^1H\}$, ^1H, ^{19}F NMR, and IR spectroscopic data. The phosphines, hydrides, and fluorines are, respectively, chemically equivalent. The chemical equivalence of the fluorine atoms rules out insertion ($PtCF_2CF_2H$) and coupling (perfluoroplatinacyclopentane) products. The complex multiplet pattern in the $^{31}P\{^1H\}$ spectrum (δ 15.5 (m, $J_{P-F} \approx 27$, $^1J_{P-Pt} = 2425$ Hz)) very closely resembles that seen in the $^{31}P\{^1H\}$ NMR spectrum of $Pt(C_2F_4)(PEt_3)_2$ in which the C_2F_4 and PEt_3 ligands lie in the same plane; such agreement is reasonable if the phosphines and C_2F_4 are also coplanar in $PtH_2(C_2F_4)(PEt_3)_2$. The hydride resonance is an apparent seven-line multiplet (17-Hz spacing) at δ −9.86, separated by ^{195}Pt satellites ($^2J_{PtH} = 746$ Hz). The intermediate can be viewed formally either as a five-coordinate adduct of platinum(II) and C_2F_4 or as a six-coordinate complex of platinum(IV) in which $C_2F_4^{2-}$ occupies two coordination sites. The low value of $^1J_{PtP}$ suggests a pseudo-platinum(IV) compound, and this formulation is consistent with the strong π-electron-withdrawing power of tetrafluoroethylene. Finally, the low value of the platinum–hydride IR signal ($\nu_{PtH_2} = 1812$ cm^{-1}) is most reasonably assigned to the antisymmetric *trans*-H–Pt–H stretch. Related adducts between platinum(II) and electron-withdrawing olefin and acetylene ligands are known.[42]



When solutions of 18 in toluene are placed under an atmosphere of D_2, both *trans*-$PtHD(PEt_3)_2$ and *trans*-$PtD_2(PEt_3)_2$ form, along with H_2 and HD. If an excess of H_2 and D_2 are present, they are catalytically scrambled to produce an equilibrium mixture of H_2, HD, and D_2. The percentage of HD in the gas phase over a stirred benzene solution at 25 °C that contained 1 mol % *trans*-18 ([*trans*-18] = 0.009 M) was monitored as a function of time. Excellent first-order kinetic behavior for consumption of H_2 and D_2 and appearance of HD was observed over 3 half-lives as the isotopic distribution approach equilibrium. A statistical analysis[43] of the exchange kinetics reveals the turnover rate for the degenerate exchange $PtH_2L_2 + H_2 \rightarrow PtH_2L_2 + H_2$ (i.e., the gross turnover rate, regardless of isotope) is 1.6 ± 0.4 min^{-1} per platinum at 25 °C. The solutions remain homogeneous, and no induction period is observed; partial decomposition of 18 by introduction of oxygen results in a decrease in the rate of exchange. These observations, along with the demonstrated stability of 18 under the mild catalytic conditions, argue against the possibility that catalysis arises from unseen decomposition products. Similarly, Et_3SiH reacts reversibly with 18 to yield *cis*-$PtH(SiEt_3)(PEt_3)_2$ and H_2. If the reaction is carried out with an excess of Et_3SiH under a D_2 atmosphere, Et_3SiD forms catalytically. The reaction of 18 with methyl iodide immediately produces *trans*-$PtHI(PEt_3)_2$ and CH_4.

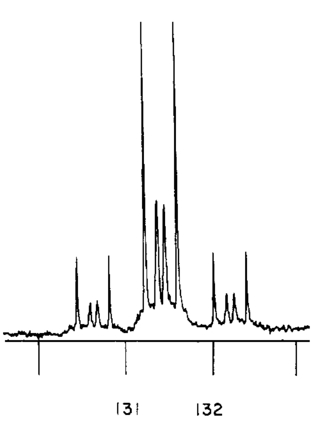


Figure 1. $^{19}F\{^1H\}$NMR spectrum (84.3 MHz) of $Pt(C_2F_4)(PEt_3)_2$ in C_6D_6 solvent at 30 °C. Chemical shifts are in parts per million upfield from CCl_3F.

Extension to Palladium Oxalate Systems. The complexes $Pd(C_2O_4)$(diphos) and $Pd(C_2O_4)_2[P(n\text{-}Bu)_3]_2$ were readily prepared from $Ag_2C_2O_4$ and the corresponding dichloro complexes. Both complexes liberate CO_2 (by IR) when irradiated in CH_2Cl_2 and produce $PdCl_2$(diphos) and $PdCl_2[P(n\text{-}Bu_3)]_2$ in nearly quantitative yield as judged by the changes in ^{31}P NMR spectra.

In the nonreactive solvents CH_3CN or Me_2SO, the putative PdL_2 species could be trapped with C_2H_4, C_2F_4, and PhC≡CPh to produce unstable solutions of the monoolefin or monoacetylene complexes. In the case of DMAD = dimethyl acetylenedicarboxylate, the complex Pd(DMAD)(diphos) could be isolated in analytically pure form. Palladium olefin and acetylene complexes are much less stable than their platinum analogues, and few have been prepared and even fewer isolated. Of note is the generation of $Pd(C_2H_4)$(diphos), $Pd(C_2F_4)$(diphos), $Pd(C_2H_4)[P(n\text{-}Bu)_3]_2$, and $Pd(C_2F_4)[P(n\text{-}Bu)_3]_2$. Although these complexes were only characterized by NMR, the formulation of the perfluoroethylene complexes is convincing since the P–F coupling pattern establishes that two phosphines are coupled to four fluorine atoms. The $^{31}P\{^1H\}$ NMR spectrum of $Pd(C_2F_4)$(diphos), prepared by photolysis of $Pd(C_2O_4)$(diphos) in C_2F_4 saturated Me_2SO-d_6, was an apparent quintet ($J_{P-F} = 50$ Hz) at δ 38.3. In the ^{19}F spectra a second-order doublet of doublets ($J_{P-F} \approx 48$ and 51 Hz) was found at δ 127.5. The $^{31}P\{^1H\}$ NMR spectrum of $Pd(C_2F_4)[P(n\text{-}Bu)_3]_2$, prepared similarly in CH_3CN/C_6D_6, yielded a complex multiplet at δ 4.5. Again the ^{19}F NMR spectrum exhibited a second-order doublet of doublets ($J_{P-F} \approx 39$ and 45 Hz) at δ 129.2. As for $Pt(C_2F_4)(PEt_3)_2$ (Figure 1) second-order $AA'X_2X'_2$ spectra arise from the magnetically inequivalent cis and trans P–F couplings expected in a square-planar complex. The ethylene complexes $Pd(C_2H_4)$(diphos) and $Pd(C_2H_4)[P(n\text{-}Bu)_3]_2$ were characterized by their $^{31}P\{^1H\}$ chemical shifts (δ 33.9 (s) and 5.7 (s), respectively) that were similar to the corresponding C_2F_4 derivatives. Furthermore for the $P(n\text{-}Bu)_3$ derivative exchange broadened resonances for free (δ 5.3) and coordinated (δ 2.9) ethylene were observed in the proton NMR spectra. It should be noted that solutions of the ethylene complexes decompose if the ethylene atmosphere is removed. Unstable solutions of the complexes Pd(PhC≡CPh)(diphos) and Pd(PhC≡CPh)$[P(n\text{-}Bu)_3]_2$ were tentatively characterized by singlet resonances in the $^{31}P\{^1H\}$ NMR spectra at δ 40.5 (Me_2SO-d_6)

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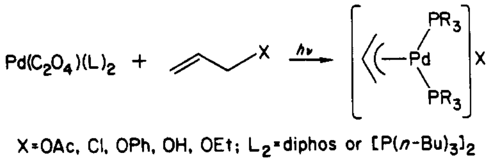
(42) (a) Uguagliati, P.; Baddley, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 5446–5452. (b) Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1970**, *9*, 2670–2675. (c) *Ibid.* **1971**, *10*, 18–25. (d) Davies, B. W.; Puddephatt, R. J.; Payne, N. C. *Can. J. Chem.* **1972**, *50*, 2276–2284.

(43) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanisms"; Wiley: New York, 1953; pp 178–179.

and δ 5.3 (CH_3CN/C_6D_6) when the respective oxalate complexes were irradiated in the presence of a fivefold excess of PhC≡CPh.

One of the more interesting reactions was the clean photochemical conversion of $Pd(C_2O_4)$(diphos) and $Pd(C_2O_4)[P(n\text{-}Bu)_3]$ into η^3-allyl complexes according to eq 12. When L = diphos, the photochemical reaction (X = Cl, OAc, OPh, OH, OEt in eq 12) proceeded to yield a singlet (δ 51.9) in the ^{31}P NMR spectra. For allyl chloride this initial product underwent secondary photolysis to produce $PdCl_2$(diphos), identified by comparison of its phosphorus chemical shift (δ 65.6) with that of an authentic sample. The allyl complex was isolated in analytically pure form by metathesis with NH_4PF_6. Analogous behavior was observed for the $P(n\text{-}Bu)_3$ derivative (X = Cl, OAc, OPh), and the allyl complex was isolated as the BPh_4^- salt. When similar reactions were attempted with the platinum oxalate system (L = diphos and PEt_3), a complex mixture of products was obtained.



(12)

The chemistry of PdL_2 differs from that of PtL_2 in several respects. We have mentioned the instability of the corresponding dihydride, PdH_2L_2, and the lack of well-defined chemistry with alcohol substrates. Qualitative observations suggest that the stability of olefin and alkyne complexes with PdL_2 is less than with PtL_2 analogues. One unusual contrast between the reactions of photogenerated PdL_2 and PtL_2 arises from their reactions with allyl chloride and other substituted allyls. For PdL_2 oxidative addition of the allyl derivative occurs in high yield according to eq 12. When similar reactions were attempted with PtL_2, the ^{31}P NMR spectra revealed a complex mixture of products. The ability of PdL_2 to react stoichiometrically with allyl substrates to form cationic allyl complexes is believed to be a key step in allylic alkylations that are catalyzed by Pd(0) phosphine complexes.[44] The reaction of eq 12 provides an experimental verification that this hypothesis is reasonable.

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Registry No. **1**, 81457-59-2; **2**, 23697-36-1; **3**, 94929-00-7; **4**, 94929-01-8; **5**, 94929-02-9; **6**, 94929-03-0; **7**, 94929-04-1; **8**, 94929-05-2; **9**, 94929-06-3; **10**, 76136-93-1; **11**, 53987-15-8; **12**, 39045-37-9; **13**, 76125-09-2; **14**, 13964-96-0; **15**, 81457-60-5; **16**, 80540-37-0; **17**, 13938-93-7; *trans*–**18**, 62945-61-3; *cis*-**18**, 61459-92-5; **18**-d_1, 94929-07-4; **18**-d_2, 94992-28-6; **19**, 18974-13-5; **20**, 94929-08-5; **21**, 84624-81-7; **22**, 94929-09-6; **23**, 94929-11-0; **24**, 81800-05-7; **25**, 48074-87-9; **26**, 72778-83-7; $Pd(C_2O_4)$(diphos), 94929-12-1; $Pd(C_2O_4)[P(n\text{-}Bu)_3]_2$, 94929-13-2; *cis*-$PtCl_2(PEt_3)_2$, 15692-07-6; *cis*-$PtCl_2(PPh_3)_2$, 15604-36-1; $Pt(C_2O_4)(PMe_3)(PPh_3)$, 94929-14-3; *trans*-$PtHCl(PEt_3e_2$, 16842-17-4; Pd(COOMeC≡CCOOMe)(diphos), 52585-44-1; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]PF_6$, 41449-73-4; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}BPh_4$, 94929-15-4; $PtH_2(PEt_3)_3$, 33937-25-6; $PtH_2(C_2F_4)(PEt_3)_2$, 80540-36-9; $Pd(C_2H_4)$(diphos), 94929-16-5; $Pd(C_2F_4)$(diphos, 94929-17-6; $Pd(C_2H_4)[P(n\text{-}Bu)_3]_2$, 94929-18-7; $Pd(C_2F_4)[P(n\text{-}Bu)_3]_2$, 94929-19-8; Pd(PhC≡CPh)(diphos), 94929-20-1; Pd(PhC≡CPh)$[P(n\text{-}Bu)_3]_2$, 94929-21-2; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OAc$, 94929-22-3; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]Cl$, 94929-23-4; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OPh$, 94929-24-5; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OH$, 94929-25-6; $[(\eta^3\text{-}C_3H_5)Pd(diphos)]OEt$, 94929-26-7; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}OAc$, 94929-27-8; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}Cl$, 94929-28-9; $\{(\eta^3\text{-}C_3H_5)Pd[P(n\text{-}Bu)_3]_2\}OPh$, 94929-29-0; $PdCl_2$(diphos), 19978-61-1; *cis*-$PtCl_2(SEt_2)_2$, 15442-57-6; *trans*-$PdCl_2[P(n\text{-}Bu)_3]_2$, 17523-47-6; $Pt(PEt_3)_2$, 66916-63-0; *trans*-$PtHI(PEt_3)_2$, 16971-06-5; $PtH_2(PEt)_3$, 94929-30-3; $PtH(O_2CH)(PEt_3)_2$, 81768-78-7; $Ag_2C_2O_4$, 533-51-7; C_2F_4, 116-14-3; C_2H_4, 74-85-1; Et_3SiD, 1631-33-0; CH_3I, 74-88-4; CH_3Cl, 74-87-3; Et_3SiH, 617-86-7; Me_3SiH, 993-07-7; COOMeC≡CCOOMe, 762-42-5; PhCl, 108-90-7; PhC≡CPh, 501-65-5; Pt, 7440-06-4; Pd, 7440-05-3; allyl acetate, 591-87-7; allyl chloride, 107-05-1; allyl phenoxide, 1746-13-0; allyl alcohol, 107-18-6; allyl ethoxide, 557-31-3.

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[44] (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393. (b) Godleski, S. A.; Gundlach, K. B.; Ho, H. Y.; Keinan, E.; Frolow, F. *Organometallics* **1984**, *3*, 21–28.

Synthesis of Aryl Phenyl and Heteroaryl Phenyl Selenides by Nickel(II)-Catalyzed Arylation of Sodium Benzeneselenoate

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The substitution of halogen on various aryl, pyridyl, and thienyl iodides or bromides by sodium benzeneselenolate is catalyzed by various complexes of nickel(II) bromide with chelating phosphine or nitrogen heterocycles. The most efficient catalyst is bis(bipyridyl)nickel(II) bromide. The reaction is regioselective and gives high yields of the corresponding aryl phenyl selenides, pyridyl phenyl selenides, and thienyl phenyl selenides.

A variety of synthetic routes to unsymmetrical diaryl selenides are available. They imply, however, high-energy σ complexes,[1] aryl radicals ($S_{RN}1$ mechanisms),[2] diazonium salts,[3] Grignard reagents[4] alkyllithium reagents,[4b] diarylmercurials,[4a] and, more recently, aryl selenocuprates[5] and (phenylseleno)dimethylsulfonium tetrafluoroborate.[6] The reagents or the intermediates involved are highly reactive, often not compatible with functional groups present in the

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[1] Agenas, L. B. In "Organic Selenium Compounds. Their Chemistry and Biology"; Klayman, D. L., Gunther, W. H. H., Eds.; Wiley: New York, 1973; p 190.

[2] Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667.

[3] Keimatsu, S.; Yokota, K. *J. Pharm. Soc. Jpn.* **1930**, *50*, 531.

[4] (a) Campbell, T. W.; McCullough, J. D. *J. Am. Chem. Soc.* **1945**, *67*, 1965. (b) Greenborg, B.; Goold, E. S.; Burlant, W. M. *J. Am. Chem. Soc.* **1956**, *78*, 4028.

[5] Osuka, A.; Ohmasa, N.; Susuki, H. *Synthesis* **1982**, 857.

[6] Gassman, P. G.; Miura, A.; Miura, T. *J. Org. Chem.* **1982**, *47*, 951.