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Multistep Cyclometalation of Solid *trans*-Dichloro[3,3′-oxybis[((diphenylphosphino)methyl)-benzene]]platinum(II)

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A solid complex of a new trans-spanning bis(phosphine) ligand, *trans*-dichloro[3,3′-oxybis[((diphenylphosphino)methyl)benzene]]platinum(II), *trans*-$PtCl_2$(PoP), I, undergoes thermolysis at ca. 250 °C with evolution of 2 mol of HCl to form a doubly cyclometalated complex, [3,3′-oxybis[((diphenylphosphino)methyl)benzen]ato(2−)-$C^2,C^{2'},P,P'$]platinum(II), Pt(PoP-2H), II. Deuterium labeling in different positions (Chart I) shows that during thermolysis, approximately one ortho hydrogen of the phosphino phenyl groups is replaced by a H_A proton (Chart I). This rearrangement is interpreted by a sequence of cyclometalation steps (Figure 5), one of which leads to an intermediate four-membered metallacycle. The reacting solid was investigated by thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), partly with on-line mass spectral monitoring of the gaseous reaction product, by heating X-ray powder diffraction, and by optical microscopy. The results indicate that a short-lived fluid phase is involved when the reaction is carried out under optimal conditions.

Introduction

Cyclometalations have rapidly become familiar reactions in organometallic chemistry, and this fast growing field has been reviewed several times in the last few years.[3-6] In most of the known examples, an organic molecule is coordinated via an aromatic or aliphatic carbon that has lost a hydrogen atom and via a second donor atom to form one five-membered or, less commonly, a four-membered chelate ring. In some presently less abundant examples, tetradentate ligands are formed in reactions that may be visualized as a sequence of two consecutive cyclometalation steps.

An apparent limitation to such sequential cyclometalations arises when additional rearrangement steps are required for structural reasons. Such limitations will appear even more severe if the cyclometalation steps are irreversible, e.g. in those cases where volatile reaction products (HCl, CH_4, or others) are continuously removed from the reaction mixture. This paper shows that no such limitations exist in the reaction I → II (Figure 1) where a doubly cyclometalated product is formed in high yield from the solid starting material. This transformation requires a trans to cis rearrangement of two phosphorus donor atoms at some stage of the reaction.

The success of this reaction raises the following questions: "what chemical mechanisms can accommodate this complicated sequence of steps?" and "which physical state of the reaction mixture is able to accommodate this process in the absence of solvent?". This paper accordingly presents the results of a series of deuterium-labeling experiments to elucidate the nature of some intermediates of this transformation as well as experiments designed to characterize intermediate physical states of the reacting material.

Experimental Section

Physical Methods. ^1H and ^{31}P NMR spectra were measured at ambient temperature on a Bruker HX90 instrument in the FT mode at 90 and 36.43 MHz relative to internal Me_4Si and external H_3PO_4 standards, respectively. IR spectra were recorded on a Beckman IR 4250 instrument to ±5 cm^{-1}. Mass spectra were run on a Hitachi Perkin-Elmer RMV 6M instrument at probe temperatures between 130 and 200 °C and at an acceleration voltage of 4.2 kV. In the elemental analyses of deuterated samples, H and D were determined as H_2O and the theoretical values were

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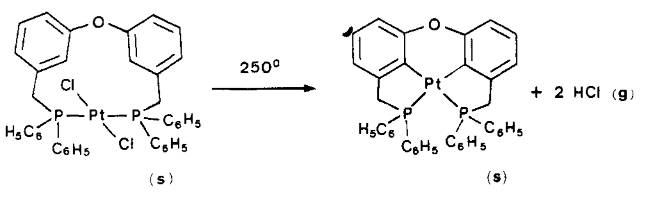

trans - $PtCl_2$(PoP), I

Pt(PoP - 2 HCl), II

Figure 1. Thermal dehydrohalogenation of *trans*-$PtCl_2$(PoP) (I) to Pt(PoP-2H) (II).

determined on this basis. Molecular masses were determined by vapor pressure osmometry. Thermal analyses were carried out on 20-mg samples of I on a Mettler thermoanalyzer TA-1 or on a Perkin-Elmer thermogravimetric system TGS-2 either statically in air or under streaming nitrogen (1.9 dm^3/h, heating rate 10 °C/min to 230 °C and then 1 °C/min to 300 °C). Thermoanalysis coupled to mass spectroscopy was performed on a Mettler TM 1 thermobalance coupled to a Balzers Quadrupole QMG 101 mass spectrograph system via a steel capillary.[7] A Perkin-Elmer differential scanning calorimeter DSC-2 was used in the DSC measurements. Heating X-ray powder photographs were taken on a "Nonius" Guinier-Lenné camera,[8] using Cu K_α radiation. The heating rates were varied for all methods used: 1–5 °C/min in TG, DTA, and DSC and 0.5 °C/h–1 °C/min in X-ray diffraction.

Materials and Preparations. All commercial chemicals used were of purum, puriss. or analytical grade. 3,3′-Oxybis[(bromomethyl)benzene] was prepared as described.[9] Chlorobis(pentadeuteriophenyl)phosphine was prepared from benzene-d_6 (>99% D) according to Horner et al.:[10] yield 29–42% based on benzene-d_6. Bis(pentadeuteriophenyl)phosphine was prepared from the chlorophosphine by $LiAlH_4$ reduction:[11] bp 77–79 °C (0.03–0.05 torr); yield 62%; ^1H NMR (1 ± 1)% aromatic proton intensity relative to the P–H proton intensity; IR (cm^{-1}) ν_{C-D} and ν_{P-H} at 2270 (br). Bis(2,6-dideuteriophenyl)phosphine was prepared according to Parshall et al.[12] from triphenylphosphine and deuterium gas (>99.5% D) by using $RuHCl[P(C_6H_5)_3]_3$ catalyst.[12,13] Tris(3,4,5-trideuteriophenyl)phosphine was prepared from (perdeuteriotriphenyl)phosphine[14] and hydrogen gas by using perdeuterated Ru catalyst. The corresponding labeled diphenylphosphines were prepared by reductive cleavage with sodium.[15]

3,3′-Oxybis[(methoxycarbonyl)benzene]. 3,3′-Oxybis[(carboxy)benzene][16] (0.5 g, 1.94 mmol) was suspended in thionyl chloride (8 mL) and heated under reflux (1 h) until the solution became homogeneous. Excess thionyl chloride was evaporated (0.01 torr, 12 h, 20 °C). The residue of solid dicarboxylic acid dichloride was converted into the dimethyl ester as its direct reduction to the diol proved unsatisfactory. It was thus treated (3 h) with pyridine (1 mL) and methanol (30 mL). Crystals of the ester precipitated (300 mg) that were recrystallized once from methanol–benzene and once from methanol alone: mp 126–127 °C; 130 mg (23%); IR (cm^{-1}) 1725, 1715 ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 7.5–7.6 (m, 8 H), 3.46 (s, 6 H). Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.92. Found: C, 67.07; H, 4.98.

3,3′-Oxybis[(hydroxymethyl)benzene] and 3,3′-Oxybis[(hydroxydideuteriomethyl)benzene]. A solution of the above ester (290 mg, 1 mmol in anhydrous ether (30 mL) was stirred with lithium aluminum hydride (70 mg, 1.84 mmol) in a stoppered flask (5 days, 20 °C). The mixture was then treated with ice and hydrochloric acid. Extraction with chloroform (5 × 20 mL) and removal of solvent gave the solid diol (192 mg, 82%) that was recrystallized from chloroform–petroleum ether: mp 87–88 °C; IR (cm^{-1}) 3260 (ν_{O-H}); ^1H NMR ($CDCl_3$) δ 7.3–6.5 (m, 8 H), 4.65 (s, 4 H), 1.93 (s, br, 2 H). The deuterated compound was prepared by $LiAlD_4$ (>99% D) reduction (crude yield 94%, mp 87–88 °C after one recrystallization): IR (cm^{-1}) 3260 (ν_{O-H}), 3050 (ν_{C-D}). ^1H NMR residual signal at δ 4.65 integrates corresponding to >97% deuteration. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.48; H, 6.16. Calcd for $C_{14}H_{10}D_4O_3$: C, 71.77; H, 7.74. Found: C, 71.58; H, 6.08.

3,3′-Oxybis[(chlorodideuteriomethyl)benzene]. The above deuterated alcohol (2.93 g, 12.5 mmol) was heated with thionyl chloride (15 g, 55 mmol) in chloroform (50 mL) under reflux (2 h). The oil remaining after evaporation (10 torr, 80 °C) was treated with methanol–benzene (12 h) and evaporated to remove residual thionyl chloride. Chromatography (silica gel, benzene) gave 2.5 g (74%) of nearly pure product that was directly used in the ligand synthesis: IR no ν_{O-H} absorption.

3,3′-Oxybis[((diphenylphosphino)methyl)benzene-d_0, -d_4, -d_8, -d_{12},-d_{12}, -d_{20}, and d_{24}] (PoP-d_0, -d_4, -d_8, -d_{12}, -d_{20}, and -d_{24}; Chart I). All ligands were prepared according to the following procedure for PoP-d_0 from the appropriately labeled diphenylphosphines and 3,3′-oxybis[(halogenomethyl)benzene]. Diphenylphosphine (2.22 g, 11.9 mmol) and butyllithium (5.6 mL, 2.6 M, 11.7 mmol) were added from a syringe to deoxygenated, anhydrous tetrahydrofuran (50 mL) with stirring at 0 °C under nitrogen. 3,3′-Oxybis[(bromomethyl)benzene] (2.08 g, 5.84 mmol) in deoxygenated benzene (12 mL) was then added within 20 min. After the mixture was stirred at room temperature (30 min), the solvent was removed under reduced pressure at 20–40 °C. The residue was distributed between water and chloroform, and the water layer was discarded. The chloroform phase was evaporated in vacuo, and the remaining oil was kept at 10^{-3} torr overnight. Hot, deoxygenated ethanol (10 mL) was added, and the ligand crystallized at 0 °C on constant stirring: yield 2.7 g (80%); mp 87 °C. **PoP-d_0**: IR (cm^{-1}) 3080–3000 (ν_{C-H} aromatic), 2920 (ν_{C-H} aliphatic), 1255 (ν_{C-O}); ^1H NMR ($CDCl_3$) δ 7.9–6.6 (aromatic protons, 28 H), 3.2 (s, 4 H). Anal. Calcd for $C_{38}H_{32}OP_2$: C, 80.55; H, 5.69; P, 10.94. Found: C, 80.38; H, 5.70; P, 10.64. **PoP-d_8**: IR (cm^{-1}) 3065 (ν_{C-H} aromatic), 2920 (ν_{C-H} aliphatic), 2270 (ν_{C-D} aromatic), 1250 (ν_{C-O}); ^1H NMR (CD_2Cl_2) δ 7.35–6.60 (aromatic protons, 20 H), 3.35 (s, 4 H). Anal. Calcd for $C_{38}H_{24}D_8OP_2$: C, 79.44; H, 5.72. Found: C, 78.87; H, 5.54. **PoP-d_{12}**: ^1H NMR (CD_2Cl_2) δ 7.72–6.55 (aromatic protons, 16 H), 3.35 (s, 4 H). **PoP-d_{20}**: IR (cm^{-1}) 3060 (ν_{C-H} aromatic), 2940–2900 (ν_{C-H} aliphatic), 2270 (ν_{C-D} aromatic), 1260 (ν_{C-O}); ^1H NMR (CD_2Cl_2) δ 7.12 (t, $^3J_{H-H}$ = 7.8 Hz, 2 H), 6.85 (d, $^3J_{H-H}$ = 6.5 Hz, 2 H), 6.60 (d + s, 4 H), 3.40 (s, 4 H). Anal. Calcd for $C_{38}H_{12}D_{20}OP_2$: C, 77.82; H, 5.50; P, 10.56. Found: C, 77.82; H, 5.63; P, 10.40. The ligands PoP–d_4 and PoP–d_{24} were not crystallized and were used in situ to prepare the corresponding $PtCl_2$ complexes.

***trans*-Dichloro[3,3′-oxybis((diphenylphosphino)methyl)benzene-d_0, -d_4, -d_8, -d_{12}, -d_{20}, and -d_{24}]platinum(II) ($PtCl_2$(PoP-d_n)).** To a deoxygenated solution of *cis*-$PtCl_2(CH_3CN)_2$[15] (2 g, 5.75 mmol) in acetonitrile (2 mL)–toluene (200 mL) at 80 °C was added the appropriate PoP ligand, e.g., PoP-d_0 (3.2 g, 5.65 mmol). The temperature was kept at 80 °C (2 h) and then at 100 °C (2 h). The resulting clear yellow solution was evaporated to dryness. The residue was dissolved in the minimal amount of methylene chloride and chromatographed on Merck silica gel 60 (70–230 mesh), 4 × 40 cm, with benzene. The product was eluted as a fast moving yellow band, and it was recovered when the solvent was evaporated to dryness. Samples for elemental analysis were dried in vacuo (120 °C, 140 h): yield 4.09 g (87%). ***trans*-$PtCl_2$(PoP-d_n)**: Anal. Calcd for $C_{38}H_{32}OP_2Cl_2Pt$ (n = 0): C, 54.82; H, 3.87; M_r 833. Found: C, 54.63; H, 3.95; M_r (CH_2Cl_2) 853. Calcd for $C_{38}H_{28}D_4OP_2Cl_2Pt$ (n = 4): 54.54; H, 3.91. Found: C, 55.11; H, 4.16. Calcd for $C_{38}H_{24}D_8OP_2Cl_2Pt$ (n = 8): C, 54.36; H, 3.95. Found: C, 54.28; H, 4.04. Calcd for $C_{38}H_{20}D_{12}OP_2Cl_2Pt$ (n = 12): C, 54.04; H, 3.97. Found: C, 54.11; H, 3.99. Calcd for $C_{38}H_{12}D_{20}OP_2Cl_2Pt$ (n = 20): C, 53.52; H, 4.03; P, 8.31. Found: C, 53.59; H, 4.00; P, 8.47. Calcd for $C_{38}H_8D_{24}OP_2Cl_2Pt$ (n = 24): C, 53.27; H, 4.07. Found: C, 53.35; H, 3.95.

Thermal Cyclometalation Reactions on *trans*-$PtCl_2$(PoP-d_n). In a typical preparation, finely crystallized *trans*-$PtCl_2$(PoP-d_0) (73 mg, 0.086 mmol) was placed at the bottom of

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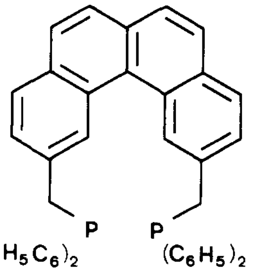
a Schlenk tube and covered with a quartz wool plug. A slow stream of nitrogen was passed through the tube via a gas inlet tube. The bottom of the tube was slowly heated to 250 ± 10 °C (2 h) and then to 270 °C (2 h). After this treatment, the remaining off-white powder was recrystallized from methylene chloride–petroleum ether to give colorless crystals (62 mg, 94%). **Pt(PoP-2H,*d*$_0$)**: Anal. Calcd for $C_{38}H_{30}OP_2Pt$: C, 60.07; H, 3.98; P, 8.15; M_r 760. Found: C, 60.35; H, 4.12; P, 8.03; M_r (CH_2Cl_2) 771. **Pt(PoP-2H,*d*$_4$)**: Anal. Calcd for $C_{38}H_{26}D_4OP_2Pt$: C, 59.70; H, 4.02. Found: C, 59.62; H, 4.22. **Pt(PoP-H-D,*d*$_7$)**: Anal. Calcd for $C_{38}H_{23}D_7OP_2Pt$: C, 59.53; H, 4.04. Found: C, 59.45; H, 4.09. **Pt(PoP-2H,*d*$_{12}$)**: Anal. Calcd for $C_{38}H_{18}D_{12}OP_2Pt$: C, 59.15; H, 4.09. Found: C, 58.70; H, 3.83. **Pt(PoP-H-D,*d*$_{19}$)**: Anal. Calcd for $C_{38}H_{11}D_{19}OP_2Pt$: C, 58.60; H, 4.14. Found: C, 58.36; H, 3.96. **Pt(PoP-H-D,*d*$_{23}$)**: Anal. Calcd for $C_{38}H_7D_{23}OP_2Pt$: C, 58.22; H, 4.19. Found: C, 57.63; H, 4.16.

Attempted Cyclometalation of *trans*-PtCl$_2$ (PoP) in Solution. Portions of the complex (20–100 mg) were heated under reflux or to a maximal temperature of 150 °C for hours to days while nitrogen was bubbled through the solutions. Enough solvent was used to ensure complete dissolution of the solid. The following solvents were used: decahydronaphthalene, dioxane, chlorobenzene, pyridine, and 1,3-dimethylisoquinoline. In no case were detectable amounts of II formed and most of the starting material was recovered. Further experiments were done to study the solution reactivity of I at temperatures where solid I would be converted into 2. A sample of I was heated to 250 °C in decahydronaphthalene in a sealed tube that was contained in an autoclave. A metallic mirror formed, indicating extensive decomposition of the starting material and/or the pyrolysis product. In this experiment, any HCl evolved cannot escape from the system so further experiments were done in solvents with boiling points >250 °C. Samples of I were heated to 250 °C in triethylene glycol and triethylenetetramine, respectively, while a stream of nitrogen was passed through the solution. Darkening of the solutions occurred at >200–220 °C within a few minutes, and extensive decomposition of the complex was suggested by the appearance of a fine, black precipitate. No II was detected in the residue left after these solvents were distilled under reduced pressure.

Results and Discussion

The Structures of Reactant I and Product II and the Reaction Stoichiometry. The new ligand PoP, owing to its "bite" of 11 atoms, is capable of spanning trans positions when acting as a bidentate ligand in square-planar complexes. The presence of two 1,3-disubstituted phenyl rings in the ligand backbone reduces its flexibility such as to favor the formation of a 12-membered trans-chelate ring. Indeed, space-filling models suggest greater strain and nonbonded interactions in a cis chelate than in a trans chelate. The structure of PoP resembles that of the less readily accessible ligand 2,11-bis((diphenylphosphino)methyl)benzo[c]phenanthrene, III,[17] the main difference being the greater flexibility of the PoP backbone.



III

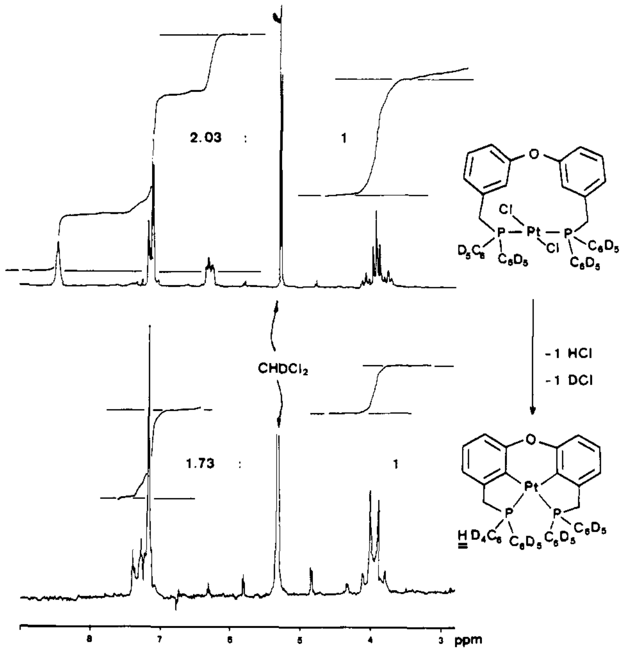


Figure 2. ^{1}H NMR spectra of *trans*-PtCl$_2$(PoP-d_{20}) and of Pt(PoP-H-D,d_{19}) at 90 MHz in CD_2Cl_2. Chemical shifts in δ units, relative to internal Me_4Si.

The configuration of the main product (87%) of the reaction between PoP and *cis*-PtCl$_2$(CH$_3$CN)$_2$, viz., the trans monomer I, is deduced from its ^{1}H and ^{31}P NMR spectra: the ^{1}H NMR spectrum (Figure 2 shows the analogous spectrum of *trans*-PtCl$_2$(PoP-d_{20})) features a three-line pattern with Pt satellites ($|^3J_{Pt-H}|$ = 28.4 Hz) for the methylene protons. Such patterns have been observed previously[17,18] and are considered to be due to "virtual" coupling ($|^2J_{P-H} + {}^4J_{P-H}|$ = 9 Hz) characteristic of two P donors in trans position. The aromatic protons appear as three complex patterns (δ 6.25–6.45 (2 H), 7.1–7.25 (4 H), and 7.25–7.6 (20 H) and one moderately broad signal at low field (δ 8.30 (2 H)). The latter is assigned to the H_A protons, and their observed deshielding is characteristic of the monomeric trans-spanning and cis chelations of the ligand as it is not observed in any of the known polymeric species.[19] An appreciable deshielding effect is also observed in analogous trans chelate complexes of III.[17] The ^{31}P NMR shift (δ 16.5 (CDCl$_3$)), and the Pt coupling ($|^1J_{Pt-P}|$ = 2610 Hz) are also consistent with a *trans*-PtP$_2$Cl$_2$ central coordination unit.[18,20] The asserted trans structure is also consistent with the IR spectrum (one ν_{Pt-Cl} at 343 cm^{-1}, no band at this position in the analogous bromo compound).

The thermal reaction I → II is accompanied by HCl evolution as shown by thermal analysis with on-line mass spectral monitoring of the gas phase that gave peaks at *m/e* 36 and 38 (natural abundance ratio, 3.09, found H^{35}Cl/H^{37}Cl, 3.21; Figure 3). Neither H_2 nor Cl_2 were detected among the gaseous reaction products. The proposed reaction stoichiometry (2 mol of HCl/mol of I) was confirmed by the weight loss as determined by thermogravimetry (1.95–2.16 mol of HCl/mol of I). In other experiments, the evolved HCl was absorbed in NaOH and titrated with AgNO$_3$ or HNO$_3$. These titrations are more precise and do not suffer from interference by sublimation

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[19] These are (*trans*-PtCl$_2$(PoP))$_2$ and (*cis*-PtCl$_2$(PoP))$_n$ (n > 2). Monomeric *cis*-PtCl$_2$(PoP) is not formed in detectable quantities by reacting Pt compounds with the ligand PoP: Kägi, St.; Marty, W., unpublished results.

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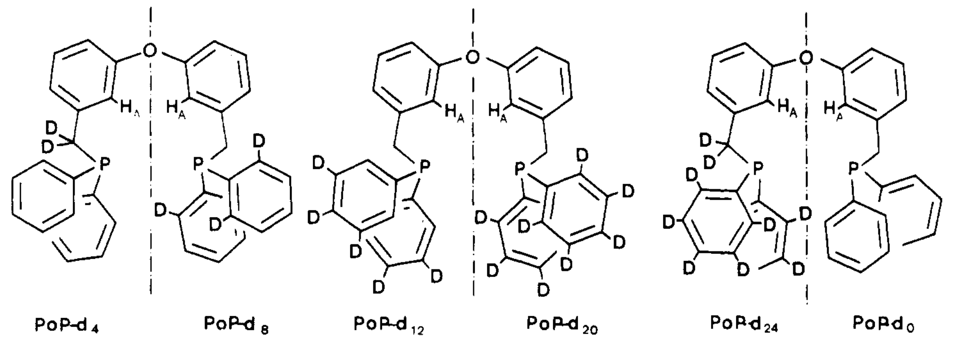
Chart I



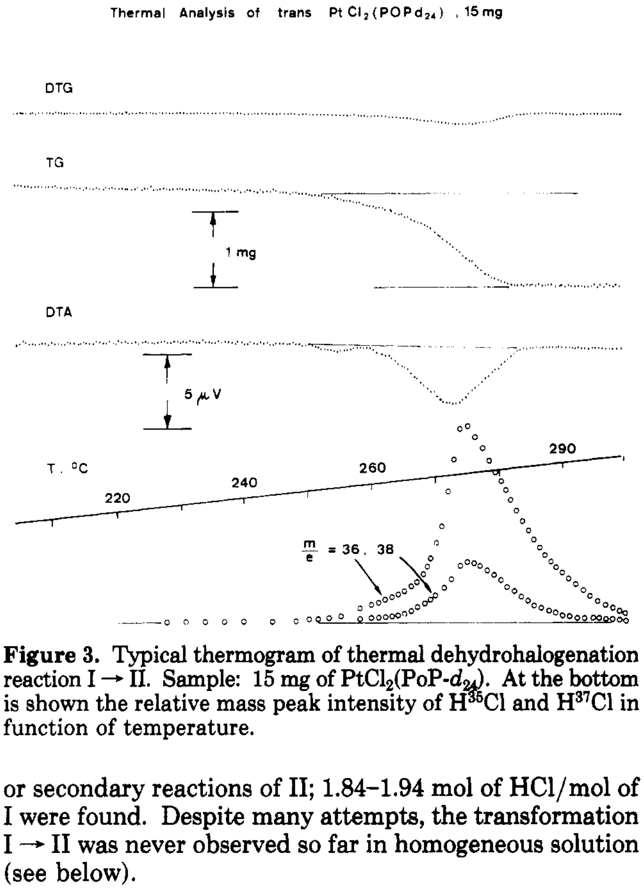
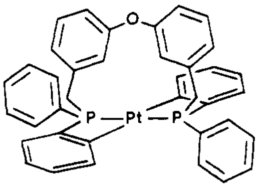


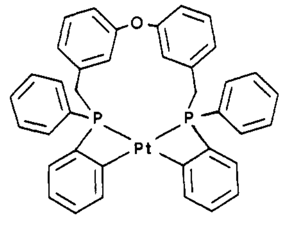
Figure 3. Typical thermogram of thermal dehydrohalogenation reaction I → II. Sample: 15 mg of PtCl$_2$(PoP-d_{24}). At the bottom is shown the relative mass peak intensity of H^{35}Cl and H^{37}Cl in function of temperature.

or secondary reactions of II; 1.84–1.94 mol of HCl/mol of I were found. Despite many attempts, the transformation I → II was never observed so far in homogeneous solution (see below).

The ^{1}H NMR spectrum of pyrolysis product II (Figure 2 shows the spectrum of the pyrolysis product of *trans*-PtCl$_2$(PoP-d_{20}), viz., Pt(PoP-H-D,d_{19})) shows a different, higher order pattern for the CH$_2$ protons and there is no low-field proton signal. The ^{31}P NMR chemical shift (δ 39.57) is consistent with the strong deshielding expected for the formation of five-membered chelate rings by cyclometalation.[21,22] The small coupling $|^2J_{Pt-P}|$ = 2067 Hz is consistent with σ-bonded carbon trans to the phosphorus nuclei such as in *cis*-Pt(C$_6$H$_5$)$_2$[P(C$_2$H$_5$)$_3$]$_2$ ($|^2J_{Pt-P}|$ = 1705 Hz[23]) and in *cis*-Pt(CH$_3$)$_2$(PoP) ($|^2J_{Pt-P}|$ = 1930 Hz[24]). Two alternative structures for the thermolysis product, viz., IV and V, are ruled out on the basis of the observed strong ^{31}P deshielding since formation of four-membered chelate rings by cyclometalation is expected to give a shielding effect.[21] Compound II reacts with bromine to form a tetrabromo compound: two bromine atoms are oxydatively added to Pt and another two substitute aromatic hydrogens in the backbone of the PoP ligand.[27] The X-ray molecular structure of this tetrabromoplatinum(IV) compound has been determined[32] and shows the same arrangement of PoP as proposed for II.



IV



V

Deuterium-Labeling Studies. The syntheses of the specifically deuterated PoP ligands d_4, d_8, d_{12}, d_{20}, and d_{24} (Chart I) involved the use of differently labeled diphenylphosphines and of 3,3′-oxybis[(chlorodideuteriomethyl)benzene], all of which were prepared following known methods outlined in the Experimental Section. As shown by appropriate blank experiments, our preparative method for *trans*-PtCl$_2$ (PoP-d_n) did not result in detectable loss or scrambling of deuterium. The pyrolysis experiment on *trans*-PtCl$_2$(PoP-d_{20}) was originally designed to provide an independent means of discriminating between structure II and IV/V. For the formation of II, two hydrogen atoms would be lost (as HCl), but formation of IV or V would require evolution of 2DCl. Rather than determining HCl and DCl in the gas evolved, the resulting complex may be analyzed for its deuterium content by ^{1}H NMR integration and by mass spectroscopical determination of its molecular mass.[25] In the case of *trans*-PtCl$_2$(PoP-d_{20}), the observed integral ratio (aromatic H: aliphatic H = 1.73, $\simeq$7:4) is almost exactly intermediate between that anticipated for direct loss of the two H$_A$ protons (6:4) and that for exclusive elimination of two deuterium atoms from the phosphino phenyl groups (8:4). Thus, *one hydrogen and one deuterium are lost from the*

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[26] In (H$_5$C$_6$)$_3$P, the coupling constants are $^3J_{P-H_2}$ = 7.5 Hz, $^4J_{P-H_3}$ = 1.4 Hz, and $^5J_{P-H_4}$ = 0.7 Hz: (a) Sørensen, S.; Jakobsen, H. J. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 248. (b) Radics, L.; Baitz-Gacs, E.; Neszmelyi, A. *Org. Magn. Res.* **1974**, *6*, 60.

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[31] It may be possible that the reaction occurs in a liquid crystalline phase, but the present experiments do not provide specific evidence for this.

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starting material. The observed deviations (~±10%) are within the error. The mass spectrum of the pyrolysis product (M^+, *m/e* 778) is consistent with the NMR result; abstraction of 2HCl or 2DCl would require M^+ at *m/e* 777 or 779, respectively. Further confirmation of the *migration* of a proton into a phosphino phenyl group comes from the following observations. The ^{31}P NMR spectrum of the pyrolysis product indicates the presence of two chemically equivalent phosphorus nuclei so that any type of mixed four-membered/five-membered chelate ring structure is ruled out. On the basis of the above ring current argument that supports structure II, the loss of one hydrogen and one deuterium indicates a hydrogen migration from position A to a phosphino phenyl ring. The rearranged proton was observed as a doublet in the 360-MHz ^1H NMR spectrum (δ 8.09 (1.0 ± 0.1 H, $^3J_{P-H}$ = 11.7 Hz)). The large P–H coupling constant is indicative of an ortho proton.[26] The assignment of this coupling was checked by its $\{^{31}P\}^1H$ NMR spectrum which showed collapse of the original doublet into a single line.

Pyrolysis reactions on *trans*-$PtCl_2(PoP\text{-}d_8)$ and on *trans*-$PtCl_2(PoP\text{-}d_{12})$ were carried out as an independent check of the ortho regiospecificity in the postulated hydrogen migration to one phosphino phenyl group. In the former, the anticipated loss of an ortho deuterium was verified by ^1H NMR (integral ratio aromatic H:aliphatic H = 4.80. Substitution of one D by H requires a ratio of 19:4 = 4.75) and by mass spectroscopy (M^+, *m/e* 766. Pt(PoP-H-D, d_7) requires *m/e* 766). The dodecadeuterio compound did not react with substitution of deuterium by light hydrogen as expected for H_A being transferred into the ortho position of the phosphino phenyl group. (^1H NMR integral ratio aromatic H:aliphatic H = 3.51. Calculated ratio for the absence of isotopic rearrangement: 14:4 = 3.50. Mass spectrum: M^+, *m/e* 771. Pt(PoP-2H,d_{12}) requires *m/e* 771). Within experimental error, complete ortho regiospecificity of the hydrogen migration is obtained. Finally, possible participation in hydrogen exchange of the methylene group of the PoP ligand is ruled out by the observation that pyrolysis of *trans*-$PtCl_2(PoP\text{-}d_4)$ and of *trans*-$PtCl_2(PoP\text{-}d_{24})$ did not lead to an increase of the weak residual ^1H NMR signals for the deuterated methylene group in the products.

The pyrolysis of *trans*-$PtCl_2(PoP\text{-}d_0)$ was also carried out under an atmosphere of DCl (~1 atm) to see whether incorporation of deuterium is possible from the gaseous reaction product. The mass spectrum of the resulting product distinctly differs from that of Pt(PoP-2H) prepared under nitrogen. The most intense line of the M^+ pattern is shifted from *m/e* 759 to *m/e* 762, and a detailed analysis of the pattern intensities gave the best fit for an average degree of deuteration of 3.36 D/molecule and for an irregular distribution of d_n species (n = 0–8). Thus deuterium is incorporated from gaseous DCl, and this observation is interpreted below.

Analysis of Mass Spectral Intensity Patterns: Intermediate and Product Formation in the Gas Phase. The intensity patterns of the M^+ ions of the starting materials and of the pyrolysis products were calculated on the basis of the natural isotope abundances for Pt and Cl, whereas the contributions from the ligands were matched against the experimental spectra of the free ligands. The latter spectra show the effects of hydrogenation and dehydrogenation reactions and of incomplete isotopic purity in the case of deuterated species. The spectra of Pt(PoP-2H,d_n) (n = 0, 12) agree satisfactorily with those calculated on this basis (Table I). However, in all cases where loss of one HCl and one DCl is inferred, the agreement is not as good for all lines with *m/e* > (M^+ + 2) and *m/e* < (M^+ − 2), and possible reasons for these discrepancies will be discussed below.

The mass spectra of the *trans*-$PtCl_2(PoP\text{-}d_n)$ species provide a clue to possible intermediates in the transformation I → II in the gas phase. The stability of such intermediates may be judged from their relative pattern intensity. *trans*-$PtCl_2(PoP\text{-}d_0)$ shows its most intense pattern at *m/e* 795 (M^+ − HCl) and *m/e* 759 (M^+ − 2HCl). Agreement between observed and calculated isotope distribution patterns is good, suggesting no significant source of interference in these dehydrohalogenation reactions (Table I). A broad signal representing a metastable fragment occurred at *m/e* 725, arising from *m/e* (795 − 36) = 759, i.e., $[PtCl(PoP\text{-}H)]^+$ or $[HPtCl(PoP\text{-}2H)]^+$ producing $[Pt(PoP\text{-}2H)]^+$. Clearly, loss of one molecule of HCl leads to an intermediate that reacts directly to form the product in the gas phase reaction.

We now return to the discrepancies between observed and calculated isotope intensity patterns in the pyrolysis products formed with simultaneous HCl/DCl elimination. As suggested by the pyrolysis experiment in DCl atmosphere, these deviations may be due to to random loss of zero, one, or two DCl per molecule and a mixture of differently labeled species of the proper total composition could be formed. Even in the absence of excess hydrogen chloride, such scrambling could occur by a reversible HCl/DCl elimination–addition sequence in the physical state of the reacting system (see below). For comparison, the mass spectrum of *trans*-$PtCl_2(PoP\text{-}d_8)$ was studied. Here, the intense fragment corresponding to double dehydrohalogenation $[PtCl_2(PoP\text{-}d_8)\text{-}2HCl]^+$ occurs reproducibly at m/e 767, i.e., one unit higher than the mass peak of the solid-state pyrolysis product, $[Pt(PoP\text{-}H\text{-}D,d_7)]^+$. Thus, the mass spectrometer reaction does not involve a proton migration and follows a mechanism different of that of pyrolysis of the solid. The *isotope intensity distribution patterns* in Table I and Figure 4 show the following characteristics for the mass peaks of the pyrolysis products $[Pt(PoP\text{-}2H,d_n)]^+$ and $[Pt(PoP\text{-}H\text{-}D,d_7)]^+$ and the corresponding gas phase pyrolysis product peaks $[PtCl_2(PoP\text{-}d_n)\text{-}2HCl]^+$.

(i) There is good to reasonable agreement between $[Pt(PoP\text{-}2H,d_n)]^+$ and $[PtCl_2(PoP\text{-}d_n)\text{-}2HCl]^+$ for n = 0 and 12, i.e., where there is exclusive loss of HCl. These patterns all show a sharp drop in peak intensity between *m/e* $(M^+ - 1)^+$ and m/e $\leq (M^+ - 2)^+$ (where M stands also for the doubly dehydrohalogenated fragments of I).

(ii) In contrast with the calculated patterns, this intensity drop is not found in $[Pt(PoP\text{-}H\text{-}D,d_7)]^+$ and this may at first sight appear characteristic of the situation where there is loss of deuterium.

(iii) Surprisingly, this intensity drop is not found either in $[PtCl_2(PoP\text{-}d_8)\text{-}2HCl]^+$ despite the fact that formation of this fragment is not accompanied by loss of deuterium. This shows that lack of this intensity drop is linked with the presence of ortho deuterium in the phosphino phenyl groups and not necessarily with its abstraction. H/D randomization during pyrolysis that would give rise to a higher intensity of the $(M - 2)^+$ peak is therefore not a satisfactory explanation, and the origin of the $(M - 2)^+$ intensity discrepancy remains unknown. This problem does not, however, affect the mechanistic conclusions for the gas-phase dehydrohalogenation of the M^+ ion.

Mechanistic Interpretation. Chemical Mechanism. The observed migration of one hydrogen atom from position H_A into an ortho position of the phosphino phenyl groups in the course of five-membered metallacycle for-

Table I. Mass Spectra of *trans*-$PtCl_2(PoP\text{-}d_n)$ Species and Their Pyrolysis Products: Observed and Calculated Isotope Abundance Patterns for Selected Fragments[a]

(a) M^+ Ions

m^+/e	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851
$PtCl_2(PoP)$	...	...	58	84	*100*	73	64	27	19	7														
	(1.2)	(0.5)	(52.2)	(75.2)	(100)	(70.5)	(63.8)	(27.5)	(18.0)	(5.9)	(2.3)													
$PtCl_2(PoP\text{-}d_8)$									...	10	60	84	*100*	73	62	29	18	6	3	1				
									(2.5)	(9.9)	(59.6)	(82.0)	(100)	(71.3)	(60.4)	(26.0)	(16.6)	(5.0)	(2.1)	(0.5)				
$PtCl_2(PoP\text{-}d_{12})$													2, 6	6	52	79	*100*	78	67	34	20	9	4	...
													(1.1)	(3.5)	(48.3)	(74.7)	(100)	(78.8)	(68.9)	(34.8)	(21.8)	(8.2)	(3.4)	(1.0)

(b) M − HCl^+ Fragments

m^+/e	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813
$PtCl_2(PoP)$-HCl	81	100	*100*	59	44	13	6													
	(62.4)	(90.0)	(100)	(55.6)	(44.7)	(14.9)	(7.2)													
$PtCl_2(PoP\text{-}d_8)$-HCl							5	21	78	100	*95*	56	41	15	5	...				
							(3.1)	(12.2)	(72.7)	(97.4)	(100)	(56.6)	(42.2)	(13.8)	(6.8)	(1.7)				
$PtCl_2(PoP\text{-}d_{12})$-HCl											8	18	70	98	*100*	66	45	20	9	...
											1.3	(4.1)	(56.8)	(87.2)	(100)	(64.9)	(49.2)	(20.2)	(9.8)	(3.2)

(c) M − $2HCl^+$ Fragments (First Line) and M^+ of Solid Pyrolysis Product (Second Line)

m^+/e	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776
$PtCl_2(PoP)$				5	73	*100*	85	32	22	7													
	1	2	4	8	74	*100*	86	29	21	6	1												
			(1.6)	(7.0)	(69.0)	(100)	(89.1)	(29.5)	(20.6)	(7.0)	(1.3)												
$PtCl_2(PoP\text{-}d_8)$										5	10	23	76	*100*	84	37	22	9	3				
								3	7	17	37	82	*100*	3	42	22	9	3					
										(3.3)	(13.0)	(76.6)	(100)	(82.1)	(28.1)	(18.6)	(5.6)	(1.3)					
$PtCl_2(PoP\text{-}d_{12})$															7	14	64	*100*	98	52	29	14	5
																13	71	*100*	92	38	23	10	2.5
																(4.7)	(65.7)	(100)	(95.2)	(43.2)	(26.4)	(9.5)	(2.9)

[a] Calculated values in parentheses.

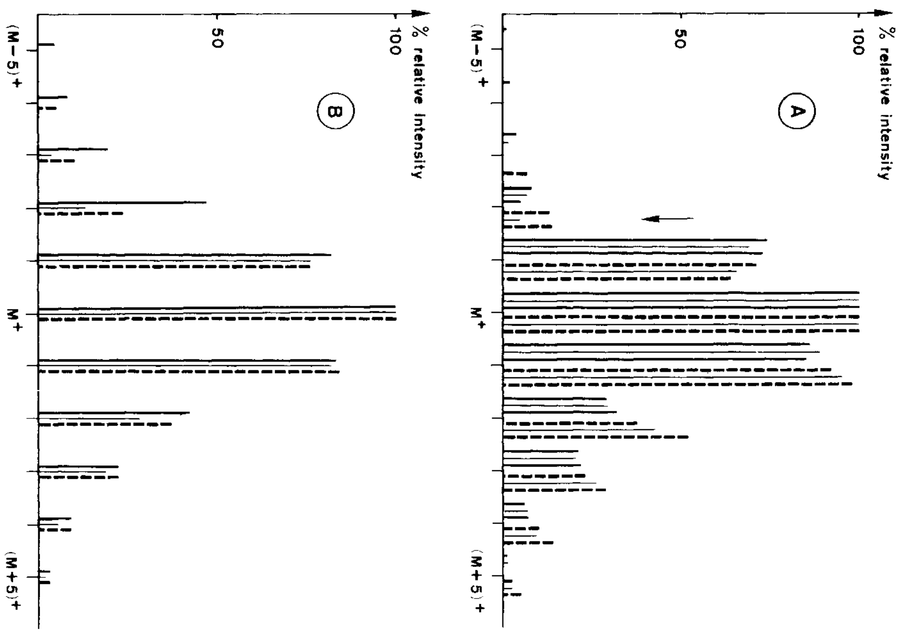

Figure 4. Isotope intensity distribution patterns for mass peaks and fragments arising from double dehydrohalogenation (both abbreviated by M^+): (A) observed pattern (—) for $[Pt(PoP\text{-}2H,d_0)]^+$ on left-hand side and for $[PtCl_2(PoP\text{-}d_0)\text{-}2HCl]^+$ on right-hand side (calculated pattern, thin middle lines); observed pattern (---) for $Pt(PoP\text{-}2H,d_{12})$ on left-hand side and for $[PtCl_2(PoP\text{-}d_{12})\text{-}2HCl]^+$ on right-hand side (calculated pattern, thin middle lines); (B) observed pattern (—) for $[Pt(PoP\text{-}H\text{-}D,d_7)]^+$; observed pattern for (---) for $[PtCl_2(PoP\text{-}d_8)\text{-}2HCl]^+$ calculated pattern, thin middle line). Note that there is *one mass unit difference in M^+* for the two observed patterns.

mation is unexpected and, to our knowledge unprecedented. It may be interpreted mechanistically as a sequence of two cyclometalation steps. (i) Formation of a four-membered metallacycle that is subsequently opened by the migrating H_A proton. (ii) The carbon from which the migrating proton originated becomes a donor atom in a five-membered metallacycle. Inspection of space-filling models suggests that the ortho positions of the phosphino phenyl groups are well buried inside the complex and that formation of a four-membered metallacycle is more likely than intermolecular metalation unless one phosphine donor is completely detached at some stage of the reaction. However, the exclusive formation of mononuclear pyrolysis product makes this an unlikely prospect. The deuterium scrambling in the pyrolysis under DCl of *trans*-$PtCl_2(PoP\text{-}d_0)$ suggests more than one act of formation of the four-membered metallacycle for any one act of product formation.

The transformation I → II requires trans to cis isomerization of the phosphine donors in addition to hydrogen chloride elimination, most probably in several elementary steps. It is somewhere within this series of events that the inferred formation of a four-membered metallacycle must be placed. The following, additional observations enable us to propose a sequence for these steps. Solid *cis*-$PtCl_2(PoP)$ (prepared by HCl addition to $Pt(PoP\text{-}2H)$)

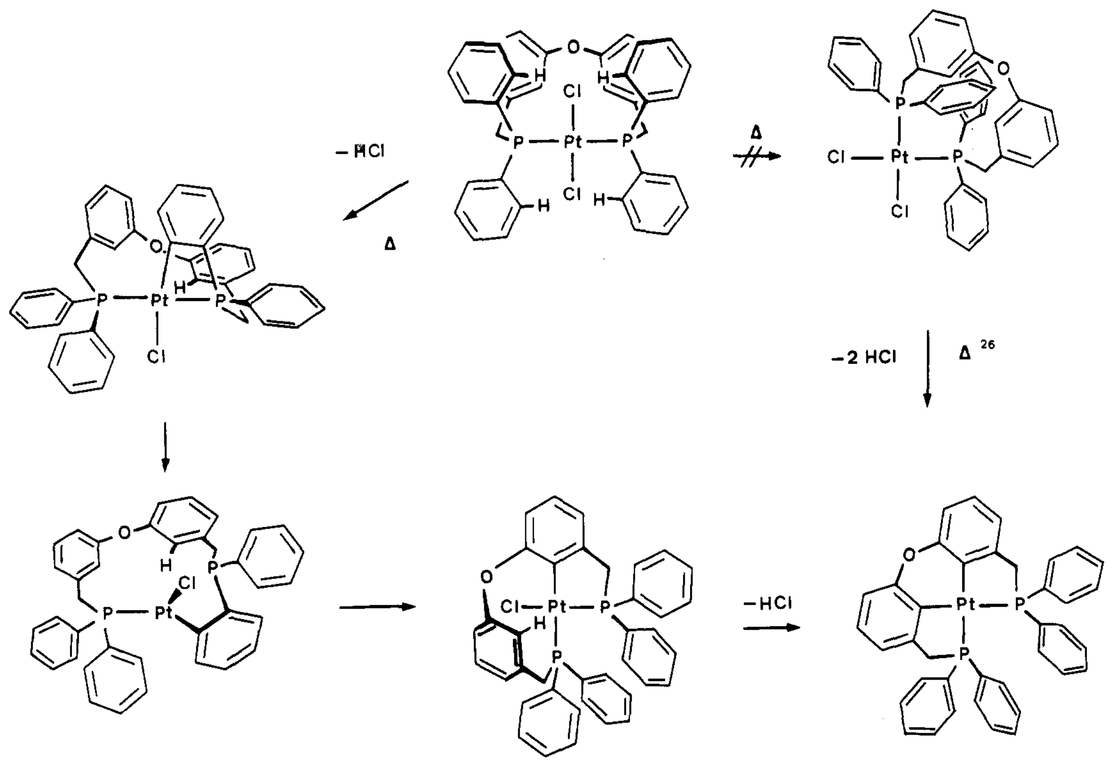

Figure 5. Proposed sequence of mechanistic steps in the thermal dehydrohalogenation of PtCl$_2$(PoP).

undergoes thermal dehydrohalogenation at ≳250 °C to form II. This isomer therefore fulfills important necessary conditions for being an intermediate in the sequence I → II. However, a pyrolysis experiment on appropriately deuterated *cis*-PtCl$_2$(PoP) showed the absence of proton migration.[27] From this, we conclude that *cis*-PtCl$_2$(PoP) is not a likely intermediate of the sequence since its formation would have to precede HCl elimination. This is inconsistent with the observed retention of deuterium in *cis*-PtCl$_2$(PoP) pyrolysis. Formation of the four-membered metallacycle with HCl elimination is therefore likely to precede or to accompany the trans–cis rearrangement process. We may interpret the formation of a four-membered metallacycle by speculating that its formation assists rearrangement of the phosphine donors. Once this metallacycle is formed, the adjacent phosphine donor may dissociate in order to relieve strain. In this loose arrangement, a first five-membered metallacycle can form while the P donors move into cis positions, and during this process, the proton released from the ligand backbone is inserted into the C–Pt bond of the phosphino phenyl group. In another series of experiments, samples of solid *trans*-PtCl$_2$(PoP-d_{20}) were heated to 250 °C and rapidly cooled. All these samples showed only the ^{31}P NMR resonances of I and II, and the ^{1}H NMR of recovered starting material showed no evidence for proton migration without dehydrohalogenation. Although these experiments are not particularly sensitive, they argue against the building up of significant concentrations of an intermediate and a fast, reversible proton migration as the initial step of the sequence. The proposed mechanism (Figure 5) accounts for all available information. We finally note that the reaction temperature, while common to the trans and cis isomers, is not very likely to indicate a common intermediate state for the two systems as also solid Pt(CH$_3$)$_2$(*o*-tolyl)$_2$PCH$_2$CH$_2$CH$_2$P(*o*-tolyl)$_2$ has been reported to undergo cyclometalation with methane evolution at ≳250 °C.[28]

Solid-State Investigation of the Pyrolysis Reaction. Physical Mechanism. In the course of this work it became ever more evident that the success of reaction I → II depended on a number of subtle variables. We did not vary the reaction conditions systematically beyond the variations described below, and we are therefore not sure whether there are no further variables of which we remain unaware. However, when strictly adhering to the procedures given in the Experimental Section, the preparation of II (from free ligand via I) worked reliably in the hands of several of us. All attempts to produce II in homogeneous solution were unsuccessful. The crystalline modification of I is critical; the crystalline powder obtained by rapid evaporation of the eluate from chromatography reproducibly gave II in >85% yield. On the other hand, samples of I from this source, when recrystallized from ethanol-containing solvent mixtures, gave crystals of essentially the same analytical composition and with identical spectra but with a slightly different X-ray powder diffraction pattern. They decomposed with some HCl evolution at 250 °C, leaving a brownish, glassy residue that was insoluble in the common solvents. The heating rate and the size of the crystals are also important:[29] fast heating (5–10 °C/min) or the use of finely powdered starting material led to complete melting and the product yield was greatly reduced.

The reaction was investigated by the heating X-ray powder diffraction technique.[8] Figure 6 shows a typical run at a heating rate of 1 °C/min. The powder diffraction lines of I remain essentially unchanged up to ca. 250 °C. At very slow heating rates (0.5–2.5 °C/h) the reaction temperature was lowered to ca. 200 °C. Near these temperatures most of the lines fade gradually with new lines growing in. The overlapping of reactant and product lines indicates that there is always a solid phase (I and/or II) present at any temperature. There are no additional lines of an intermediate. The observed influence of the crystal modification and the heating X-ray powder pattern may suggest a genuine solid-state transformation. This possibility is, however, ruled out by observations made on the reacting complex under a hot-stage optical microscope. When a heating rate of 1 °C/min is used at or near 253

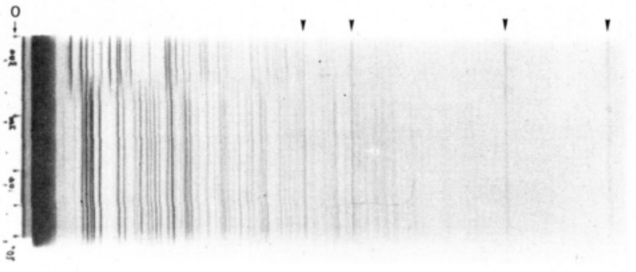

Figure 6. Heating X-ray powder diffraction diagram for thermal reaction I → II. Ordinate: temperature in °C; marks on left margin, 20, 100, 200, and 300 °C from bottom. Abscissa: $d = \lambda/2 \sin \theta$, Å. Arrows: calibration lines from internal Pt standard; from left to right, 2.265, 1.387, and 1.1826 Å; $\lambda = 1.5405$ Å.

°C larger crystals of the starting material showed the beginning of a melting process that gradually stopped during the transformation to leave the solid final product. In another experiment, larger crystals were heated to 254 °C at 1 °C/min for a short time to show melting at edges and corners. Heating was then interrupted for 30 min and then continued to higher temperature to cause once more partial melting on the surface of the crystals. Once the reaction was finished, no melting was observed on further heating below the melting point of II. The diffraction pattern of this product is identical with that of a molten (349 °C) and solidified sample. These results show that melting of the reactant is crucial to the reaction. The melt could act as a fluid reaction medium or, less likely, as a catalyst to trigger a solid-state transformation. The observation that some of the powder lines remain essentially unchanged during the reaction is not inconsistent with a melt as the reaction medium since the structures of I and II are similar enough to give rise to coincidence of some powder lines.

The pyrolysis reaction was finally investigated by thermal analysis (TG, DTG, DTA, and DSC). Figure 3 shows a typical run. There was up to 5.3% excess weight loss in the runs and this is explained by sublimation of II under atmospheric pressure as shown by the appearance of crystals of II outside the crucible. While only a single enthalpy effect and one burst of HCl formation are seen in the TG/DTA/MS experiments, two separate, though appreciably smaller enthalpy effects become apparent in the DSC runs, both of which are irreversible. These two peaks are not unambiguously assigned, but one possible interpretation is that in the first process melting occurs along with some chemical step, followed by another chemical reaction. This is supported by the observation that the starting material was never recovered unchanged after melting had taken place.

Attempted Dehydrohalogenation in Solution. Many attempts were made to carry out transformation I → II thermally in homogeneous solution. Solvents of quite different polarity and basicity (see Experimental Section) were used as well as different temperatures up to 150 °C. In every except one experiment (decahydronaphthalene at 250 °C), nitrogen was passed through the solutions to remove rapidly any HCl evolved. Under this range of conditions, a major part of the known cyclometalation reactions would occur but no reaction was observed in all above mentioned experiments.

In three different solvents (decahydronaphthalene, triethylenetetramine, and triethylene glycol), rapid and extensive decomposition of I was found in the temperature range 200–250 °C. We estimate that ca. 10% of II could have gone undetected in these experiments. These experiments are clearly not definitive, but they suggest that reaction I → II is more difficult to achieve in solution than by using solid I.

Conclusions. A novel and interesting concept in preparative chemistry begins to emerge from the present work. The mechanistic studies indicate that the transformation I → II is a complicated multistep sequence that has very little probability to occur via a topotactic[30] or more complex solid-solid transformation process. Indeed, a melting process (only detected by optical microscopy) accompanies the chemical changes and under optimal reaction conditions (i.e., a moderately slow heating rate, the proper crystalline phase, optimal crystal size), the molten phase must be highly unstable with respect to solid product II. This becomes apparent from the heating X-ray powder diffraction as well as from microscopical observations on intermediate-size reacting crystals. Such a short-lived molten phase allows for the extensive internal molecular motion required in the series of proposed mechanistic steps and yet it may not correspond to a homogeneous,[31] thermally equilibrated fluid phase (such as a homogeneous melt or solution); this potentially minimizes certain undesired side reactions, viz., intermolecular reaction with solvent or other solutes. At the same time, the high reaction temperature will ensure rapid transformation into products. The observation that reaction I → II is very difficult if not impossible to achieve in homogeneous solution lends support to the idea that such a highly unstable melt provides a unique reaction medium. The success of this reaction may be due to the following constellation of crucial events: a solid starting material is first transformed into a melt. Under ideal conditions, the lifetime of this melt is kept very short by its high reactivity and by rapid crystallization of the final product. While rapid reaction is favored by the high melting temperature, the last condition is fulfilled by the melting point difference between the starting material and the final product of ca. 100 °C. If a short lifetime of the melt is important, then isothermal heating at a temperature as close as possible to the melting point will give higher product yields than rapid, nonisothermal heating, and this has been confirmed by our experiments. Other factors important to the heat flow in the reacting system are the crystal size and modification of the starting material, both of which have been shown to influence the yield. Clearly, the conditions for a successful reaction in an unstable melt, as restrictive as they may appear, still allow for more molecular motion than a proper solid-state reaction and this reaction type seems therefore more widely applicable than the last.

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Registry No. I, 84369-28-8; II, 84393-87-3; PoP-d_0, 84369-34-6; PoP-d_4, 84369-35-7; PoP-d_8, 84393-93-1; PoP-d_{12}, 84369-36-8; PoP-d_{20}, 84369-37-9; PoP-d_{24}, 84369-38-0; *trans*-$PtCl_2$(PoP-d_4), 84369-29-9; *trans*-$PtCl_2$(PoP-d_8), 84369-30-2; *trans*-$PtCl_2$(PoP-d_{12}), 84369-31-3; *trans*-$PtCl_2$(PoP-d_{20}), 84369-32-4; *trans*-$PtCl_2$(PoP-d_{24}), 84369-33-5; Pt(PoP-2H,d_4), 84393-88-4; Pt(PoP-H-D,d_7), 84393-89-5; Pt(PoP-2H,d_{12}), 84393-90-8; Pt(PoP-H-D,d_{19}), 84393-91-9; Pt(PoP-H-D,d_{23}), 84393-92-0; *cis*-$PtCl_2(CH_3CN)_2$, 21264-32-4; 3,3′-oxybis[(methoxycarbonyl)benzene], 74302-26-4; 3,3′-oxybis[carboxybenzene], 15791-89-6; 3,3′-oxybis[benzenecarbonyl chloride], 19434-44-7; 3,3′-oxybis[(hydroxymethyl)benzene], 84369-39-1; 3,3′-oxybis[(hydroxydideuteriomethyl)benzene], 84369-40-4; 3,3′-oxybis[(chlorodideuteriomethyl)benzene], 84369-41-5; diphenylphosphine, 829-85-6; 3,3′-oxybis[(bromomethyl)benzene], 69484-03-3; chlorobis(pentadeuteriophenyl)phosphine, 72142-98-4; bis(pentadeuteriophenyl)phosphine, 72142-99-5; bis(2,6-dideuteriophenyl)phosphine, 84369-42-6; tris(3,4,5-trideuteriophenyl)phosphine, 84369-43-7.