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### Preparation of Tertiary Phosphine-Olefin Complexes of Platinum(0): A Convenient Synthesis of Ethylenebis(triethylphosphine)platinum(0)<sup>1</sup>

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Presently available synthetic routes to complexes of trialkylphosphines with platinum(0) involve starting materials which are not readily available,<sup>4-6</sup> difficult isolations,<sup>7</sup> and manipulations of air-sensitive materials.<sup>4-8</sup> The more convenient of these preparations entail displacement of cyclooctadiene from bis(cyclooctadiene)platinum(0), but this compound is prepared only in moderate yield (40–60%) by an inconvenient reaction.<sup>9</sup> One of the simplest members of the class of platinum(0)–phosphine complexes, ethylenebis(triethylphosphine)platinum(0) (**1**) has not been reported. We wish to report a convenient, high-yield preparation of **1** by thermal decomposition of the air-stable, crystalline complex diethylbis(triethylphosphine)platinum(II). The generality of this thermal decomposition reaction as a route to platinum(0)–phosphine complexes is examined briefly.

#### Experimental Section

**General Information.** Proton NMR spectra were recorded on a Bruker WM-250 instrument. <sup>1</sup>H/<sup>31</sup>P NMR spectra were obtained at 36.4 MHz on a modified Bruker HFX-90 or Jeol FX-90Q spectrometer. <sup>31</sup>P chemical shifts, in parts per million, are relative to external 85% phosphoric acid (downfield shifts positive). Mass spectra were recorded on a Varian MAT-44 spectrometer. Olefins were removed from cyclohexane by treatment with concentrated H<sub>2</sub>SO<sub>4</sub>, and the cyclohexane was washed with saturated NaHCO<sub>3</sub>, dried over P<sub>4</sub>O<sub>10</sub>, and distilled under argon. Toluene-*d*<sub>8</sub> was passed through a 1 × 2 cm column of activated alumina and degassed by freeze-pump-thaw cycles. Ether was distilled under argon from sodium benzophenone dianion. Welding grade argon was used for inert-atmosphere work without further purification. Compounds were stored in a desiccator at –10 °C.

**Diethyl- and dipropylbis(triethylphosphine)platinum(II)** were prepared by modifications of literature methods.<sup>10,11</sup>

**Dicyclobutylbis(triethylphosphine)platinum(II).** Special care was needed in preparing the thermally unstable dicyclobutyl and dicyclopentyl compounds. In an argon-flushed 100-mL flask was suspended 0.50 g (1.3 mmol) of dichloro(1,5-cyclooctadiene)platinum(II)<sup>10</sup> ((COD)PtCl<sub>2</sub>) in 40 mL of ether. To this mixture was added 10 mL of 0.53 M (5.3 mmol) cyclobutylmagnesium chloride by syringe at –50 °C. The solution was allowed to warm to –20 °C over 2 h and stirred at this temperature for 6 h. The entire reaction

Table I. Platinum(0) Complexes Prepared by Thermal Decomposition of L<sub>2</sub>Pt<sup>II</sup>R<sub>2</sub>

complex	dec temp, °C (t, h)	yield, %	δ ( <sup>31</sup> P)	J <sub>Pt,P</sub> , Hz
(Et <sub>3</sub> P) <sub>2</sub> Pt(ethylene) <sup>a</sup>	118 (0.5)	100 <sup>c</sup>	20.6	3551
(Me <sub>3</sub> P) <sub>2</sub> Pt(ethylene) <sup>b</sup>	118 (1.2)	>70 <sup>d</sup>	–19.5 <sup>e,f</sup>	3435 <sup>e,f</sup>
(Et <sub>3</sub> P) <sub>2</sub> Pt(propylene) <sup>a</sup>	80 (10.0)	>80 <sup>d</sup>	21.1, 18.5	3767, 3279 <sup>g</sup>
(Et <sub>3</sub> P) <sub>2</sub> Pt(cyclobutene) <sup>a</sup>	40 (4.0)	95 <sup>d</sup>	20.1	3418
(Et <sub>3</sub> P) <sub>2</sub> Pt(cyclopentene) <sup>a</sup>	35 (1.0)	75 <sup>e</sup>	<i>e</i>	<i>e</i>
(Ph <sub>3</sub> P) <sub>2</sub> Pt(cyclobutene) <sup>b</sup>	35 (0.5)	40 <sup>d</sup>	34.2	3604
(DMPE) <sub>2</sub> Pt <sup>b</sup>	182 (20.0)	95 <sup>d</sup>	–8.1	3724

<sup>a</sup> Cyclohexane was the solvent for decompositions. <sup>b</sup> Toluene was the solvent for decompositions. <sup>c</sup> Determined by treatment with methyl iodide. <sup>d</sup> Estimated from NMR peak heights. <sup>e</sup> Rapid exchange of R<sub>3</sub>P groups was observed in the <sup>31</sup>P NMR spectrum at room temperature. <sup>f</sup> At –45 °C. <sup>g</sup> J<sub>P,P</sub> = 66 Hz.

mixture was passed through a 1 × 6 cm column of silica gel containing 5% activated charcoal at –78 °C. The solution thus obtained was treated with 0.40 mL (2.8 mmol) of triethylphosphine at 0 °C. After 15 min the ether was partially removed under reduced pressure. Adding methanol (5 mL) and cooling to –78 °C induced crystallization. The white precipitate was separated by filtration and recrystallized from ether–methanol to give 0.40 g (56%) of fine needles, mp 87–88 °C. <sup>31</sup>P NMR: δ = 6.3 (J<sub>Pt,P</sub> = 1647 Hz).

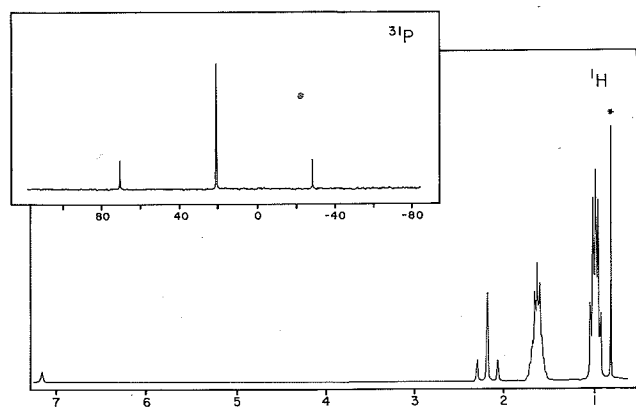
**Dicyclobutylbis(triphenylphosphine)platinum(II).** This compound was prepared by a procedure similar to that described for the triethylphosphine complex except as noted. Triphenylphosphine was added to the solution of (COD)Pt(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub> as a solution in a minimum volume of diethyl ether at 0 °C. The product precipitated directly from the ether solution without addition of methanol, giving 0.42 g (41%) of white needles, mp 87–97 °C dec. <sup>31</sup>P NMR: δ = 26.3 (J<sub>Pt,P</sub> = 1709 Hz).

**Dicyclopentylbis(triethylphosphine)platinum(II).** In a 250-mL round-bottomed flask was placed 0.50 g (1.3 mmol) of (COD)PtCl<sub>2</sub>. The flask was fitted with a stirring bar, sealed with a rubber septum, and flushed thoroughly with argon. Into the flask was transferred 100 mL of ether via cannula, and the mixture was cooled to –50 °C. To the stirred mixture was added by syringe 10.0 mL of 0.60 M cyclopentylmagnesium bromide in THF. The reaction mixture was stirred vigorously at –50 °C for 4 h, warmed slowly to –20 °C, and stirred for an additional 4 h. The reaction was quenched by addition of 10 mL of 20% methanol in water by syringe. The ether layer was decanted via cannula into a 100-mL flask and the ether removed at –20 °C under reduced pressure to a volume of ca. 10 mL. Cold methanol (30 mL) containing 1.00 mL (0.810 g, 6.86 mmol) of triethylphosphine was added to this solution. The solution was stirred for 3 h at –20 °C during which time a white crystalline solid precipitated. The solution was further concentrated at reduced pressure, cooled to –30 °C, and filtered rapidly on a coarse frit. The product was washed with two 3-mL portions of cold (–30 °C) methanol and dried in vacuo to give an off-white solid in 43% overall yield; mp 59–61 °C dec. <sup>31</sup>P NMR: δ = 9.0 (J<sub>Pt,P</sub> = 1616 Hz).

**General Decomposition Procedure.** Thermal decompositions of diethyl- and dipropylplatinum(II) complexes were carried out in sealed tubes by procedures analogous to that described below for the preparation of ethylenebis(triethylphosphine)platinum(0). Indistinguishable results have been obtained in serum-capped tubes under argon.<sup>12</sup> Cyclobutyl and cyclopentyl complexes were decomposed in serum-stopped test tubes under an argon atmosphere. <sup>31</sup>P NMR data for all new platinum(0) complexes are in Table I. Yields of platinum(0) complexes were determined either by measuring the yield of iodomethylbis(phosphine)platinum(II) obtained after reaction with methyl iodide or by estimating <sup>31</sup>P NMR peak heights relative to triethylphosphate internal standard. Comparable results were obtained by either method.

- (1) Supported by the National Science Foundation, Grant CHE 7711282.
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- (3) National Science Foundation Predoctoral Fellow, 1978–1981.
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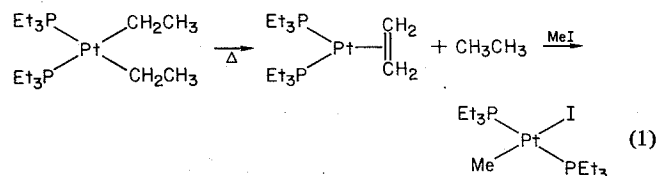
**Figure 1.** Ambient-temperature  $\{^1\text{H}\}^{31}\text{P}$  and 250-MHz  $^1\text{H}$  NMR spectra of (ethylene)bis(triethylphosphine)platinum(0) produced by thermal decomposition of diethylbis(triethylphosphine)platinum(II) in benzene- $d_6$  at 118 °C. The asterisk denotes ethane; the triplet at  $\delta = 2.2$  is due to coordinated ethylene.

**(Ethylene)bis(triethylphosphine)platinum(0).** Diethylbis(triethylphosphine)platinum(II) (100 mg, 0.204 mmol) was placed in a clean, dry, Pyrex tube which was then evacuated to 0.1 torr and flushed with argon: NMR tubes were used for much of this work. Dry, degassed cyclohexane (1 mL) was introduced by syringe. The tube was cooled (liquid nitrogen), evacuated (0.1 torr), sealed, allowed to warm to room temperature, and heated at 118 °C (oil bath) for 30 min. The resulting solution contained  $(\text{Et}_3\text{P})_2\text{Pt}^0\text{C}_2\text{H}_4$  as the only detectable phosphorus-containing species (Figure 1). The  $^1\text{H}$  NMR spectrum exhibits a single set of resonances for platinum-coordinated ethylene ( $\delta = 2.15$  ( $J_{\text{Pt,H}} = 55$  Hz)); free ethylene is not observed.

**Reaction of  $(\text{Et}_3\text{P})_2\text{Pt}^0\text{C}_2\text{H}_4$  with Methyl Iodide.** The tube was opened in an argon stream and treated with 0.1 mL (excess) of methyl iodide. After ca. 30 min the contents of the tube were poured onto a watch glass. Evaporation of the solvent and excess methyl iodide yielded 116.7 mg (100%) of off-white *trans*-iodomethylbis(triethylphosphine)platinum(II), identified by its melting point of 68–71 °C (lit.<sup>13</sup> mp 71.0–71.5 °C), mass spectrum ( $m/e$  573 [ $\text{M}]^+$ ), and  $^{31}\text{P}$  NMR spectrum (cyclohexane) [ $\delta = 10.1$  ( $J_{\text{Pt,P}} = 2778$  Hz), lit.<sup>14</sup>  $\delta = 9.4$  ( $J_{\text{Pt,P}} = 2754$  Hz)].

## Results and Discussion

Diethylbis(triethylphosphine)platinum(II) decomposes thermally in cyclohexane solution by  $\beta$ -hydrogen activation followed by reductive elimination of ethane (eq 1).<sup>15</sup> The



solution changes from colorless to dark orange over the course of the thermolysis. Free ethylene is not visible in the  $^1\text{H}$  NMR spectrum; the  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra<sup>16</sup> exhibit resonances which can be attributed to ethylenebis(triethylphosphine)platinum(0) (Figure 1). The orange color is apparently due

to an impurity,<sup>17</sup> although the solution behaves chemically and spectroscopically as though it were pure. When the solution is treated with methyl iodide, its orange color disappears, ethylene appears in the  $^1\text{H}$  NMR spectrum, and *trans*-iodomethylbis(triethylphosphine)platinum(II) is formed in quantitative yield. Compound 1 can be isolated as a dark orange oil by solvent removal. Attempted purification by low-temperature crystallization has led to less pure oils.

The generality of this method for preparing complexes having the structure  $\text{L}_2\text{Pt}^0(\text{olefin})$  has been explored (Table I). The procedure seems to tolerate alkyl and phosphine substitution, although the yield of (olefin)bis(phosphine)platinum(0) obtained depends on the nature of the olefin formed, the phosphine, and the temperature at which the thermolysis is carried out. (Cyclobutene)bis(triethylphosphine)platinum(0) can be prepared under the conditions described in Table I; the solution containing this compound is colorless. A labile cyclopentene complex of  $\text{L}_2\text{Pt}^0$  can be prepared from dicyclopentylbis(triethylphosphine)platinum(II) by decomposition at ambient temperature. At higher temperatures the olefin complex decomposes. Similarly, decomposition of dipropylbis(triethylphosphine)platinum(II) at 80 °C gives the propene complex. Under the more severe conditions for formation of 1 (118 °C, Table I), this olefin complex is a minor product; the reaction solution is dark brown and contains  $(\text{Et}_3\text{P})_3\text{Pt}^0$  as a major constituent.<sup>20</sup> Thus, the strongly coordinating ethylene, or an equivalent olefin, seems to be necessary for the stabilization of these bis(trialkylphosphine)platinum(0) moieties at higher temperatures. Compound 1 begins to disproportionate<sup>20</sup> at ca. 150 °C.

Thermal decomposition of diethyl[1,2-bis(dimethylphosphino)ethane]platinum(II) does not give a stable olefin complex. (Cyclobutene)bis(triphenylphosphine)platinum(0) can be prepared by this method but is contaminated by  $\text{L}_3\text{Pt}(0)$  and "LPt(0)" oligomers<sup>17</sup> which are significant coproducts. (Ethylene)bis(trimethylphosphine)platinum(0) forms in good yield, but, unlike 1, rapid intermolecular exchange of phosphine moieties is indicated by the  $^{31}\text{P}$  NMR spectrum at room temperature. We do not know if impurities are responsible for this behavior.

Thermal decomposition of  $\text{L}_2\text{PtR}_2$  complexes in the presence of added phosphine yields tris- and tetrakis(phosphine)platinum(0) complexes. Decomposition of diethylbis(triethylphosphine)platinum(II) in the presence of 1 equiv of triethylphosphine yields a bright yellow solution which contains free ethylene. Evaporation of solvent gives  $(\text{Et}_3\text{P})_3\text{Pt}^0$  as an orange oil. Thermolysis of diethyl[1,2-bis(dimethylphosphino)ethane]platinum(II) in toluene at 182 °C in the presence of dmpe gives  $(\text{dmpe})_2\text{Pt}^0$  as the only product.

Thermal decomposition of diethylbis(triethylphosphine)platinum(II) is a convenient, high-yield preparation of compound 1. The overall yield of 1 from dichloro(cyclooctadiene)platinum(II)<sup>10</sup> is 86%. As a precursor to platinum(II) compounds, 1 has the advantage over  $(\text{Et}_3\text{P})_3\text{Pt}^0$  that ethylene is the coproduct. The reaction can be used to generate other (olefin)bis(phosphine)platinum(0) complexes, but yields and purities may be lower than for 1.

**Registry No.** 1, 76136-93-1;  $(\text{Me}_3\text{P})_2\text{Pt}(\text{ethylene})$ , 69547-16-6;  $(\text{Et}_3\text{P})_2\text{Pt}(\text{propylene})$ , 76136-94-2;  $(\text{Et}_3\text{P})_2\text{Pt}(\text{cyclobutene})$ , 76136-95-3;  $(\text{Et}_3\text{P})_2\text{Pt}(\text{cyclopentene})$ , 76136-96-4;  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{cyclobutene})$ , 76136-97-5;  $(\text{DMPE})_2\text{Pt}$ , 25398-78-1;  $(\text{Et}_3\text{P})_2\text{PtEt}_2$ , 76189-28-1;

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(16) This coupling constant ( $J_{\text{Pt,P}}$ ) is typical of a platinum(0)–phosphine complex. See ref 4. The relatively large line width (8.5 Hz at 250 MHz) of the ethylene resonances in the  $^1\text{H}$  NMR spectrum may be due to unresolved P–H coupling. For  $(\text{Ph}_3\text{P})_2\text{PtC}_2\text{H}_4$ ,  $J_{\text{PH}} = J_{\text{PH}} = 3$  Hz; Cheng, P. T.; Cook, C. D.; Nyburg, S. C.; Wan, K. Y. *Inorg. Chem.* **1971**, *10*, 2210–2213. Differences in the rate of rotation around the platinum–olefin bond (perhaps due to steric differences between  $\text{Et}_3\text{P}$  and  $\text{Ph}_3\text{P}$ ) might contribute to differences in the line shapes for these two complexes: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(17) (Ethylene)bis(triphenylphosphine)platinum(0) is white;<sup>18</sup> the orange color may arise from an oligomerization<sup>19</sup> or from an equilibrium forming  $(\text{Et}_3\text{P})_3\text{Pt}^0$ .

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(Me<sub>3</sub>P)<sub>2</sub>PtEt<sub>2</sub>, 76136-98-6; (Et<sub>3</sub>P)<sub>2</sub>PtPr<sub>2</sub>, 76189-29-2; (Et<sub>3</sub>P)<sub>2</sub>Pt-(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>, 76156-55-3; (Et<sub>3</sub>P)<sub>2</sub>Pt(C<sub>3</sub>H<sub>9</sub>)<sub>2</sub>, 76136-99-7; (Ph<sub>3</sub>P)<sub>2</sub>Pt-(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>, 76137-00-3; (DMPE)PtEt<sub>2</sub>, 76137-01-4; (COD)PtCl<sub>2</sub>, 12080-32-9; *trans*-(Et<sub>3</sub>P)<sub>2</sub>Pt(Me)I, 18974-13-5; MeI, 74-88-4; cyclobutylmagnesium chloride, 76124-42-0; cyclopentylmagnesium bromide, 33240-34-5.