

mp 241°. *Anal.* Calcd for  $C_{60}H_{50}Cl_4S_2As_2Pd_2$ : C, 53.79; H, 3.76; Cl, 10.58; S, 4.79. Found: C, 53.6; H, 3.6; Cl, 10.8; S, 4.8.  $\Lambda_M$  in nitromethane solution is  $119 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at 25° and a  $10^{-3} M$  concentration.

$\{[Pd(SC_6H_5)Br_2]As(C_6H_5)_4\}_2$ .—This complex was prepared by a metathetical reaction starting from the chloride analog in acetone with a large excess of LiBr. After 1 hr the red crystals were filtered off, washed with acetone, and dried; yield, 95%; mp 240°. *Anal.* Calcd for  $C_{60}H_{50}Br_4S_2As_2Pd_2$ : C, 47.49; H, 3.32; Br, 21.06; S, 4.22. Found: C, 47.6; H, 3.4; Br, 21.2; S, 4.2.  $\Lambda_M$  in nitromethane solution is  $127 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at 25° and a  $10^{-3} M$  concentration.

$\{[Pd(SC_6H_5)Cl_2]N(CH_3)_4\}_2$ .—This yellow-orange compound was prepared in the same way as  $\{[Pd(SC_6H_5)Cl_2]As(C_6H_5)_4\}_2$  by reaction of  $[Pd(SC_6H_5)Cl]_n$  with  $N(CH_3)_4Cl$ ; yield, 80%; mp >270°. *Anal.* Calcd for  $C_{20}H_{34}N_2Cl_4S_2Pd_2$ : C, 33.30; H, 4.75; N, 3.88; Cl, 19.66; S, 8.89. Found: C, 33.2; H, 4.6; N, 4.0; Cl, 20.0; S, 9.1.  $\Lambda_M$  in nitromethane solution is  $142 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at 25° and a  $10^{-3} M$  concentration.

$\{[Pd(SC_6H_5)Br_2]N(C_2H_5)_4\}_2$ .—This red-orange compound was prepared in the same way as  $\{[Pd(SC_6H_5)Cl_2]As(C_6H_5)_4\}_2$  by reaction of  $[Pd(SC_6H_5)Br]_n$  with  $N(C_2H_5)_4Br$ ; yield, 87%; mp >270°. *Anal.* Calcd for  $C_{28}H_{50}N_2Br_4S_2Pd_2$ : C, 33.25; H, 4.98; N, 2.77; Br, 31.60; S, 6.34. Found: C, 33.2; H, 4.6; N, 2.8; Br, 31.5; S, 6.2.  $\Lambda_M$  in nitromethane solution is  $150 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at 25° and a  $10^{-3} M$  concentration.

$\{[Pd(SC_6H_5)(diphos)]SnCl_3\}_2$ .—A 320-mg sample of  $Pd(SC_6H_5)(diphos)Cl$  suspended in methanol-ether (1:1) was treated with an excess of  $SnCl_2$  under stirring. Within 3 hr a yellow precipitate was formed. It was filtered off, washed with methanol and ether, and dried; yield, 85%; mp 215°. *Anal.* Calcd for  $C_{64}H_{58}Cl_6S_2P_4Sn_2Pd_2$ : C, 45.81; H, 3.48; Cl, 12.67; S, 3.82. Found: C, 45.3; H, 3.4; Cl, 12.9; S, 3.9.

For some of these compounds the analytical values are not in close enough agreement with calculated values owing to their difficult purification caused by their low solubility in most common organic solvents.

**Molecular Weights and Conductivity Measurements.**—A Mechrolab thermoelectric molecular weight apparatus was used in all cases. An LKB Type 3216 B conductivity bridge was employed for conductivity measurements with a cell of  $K = 0.0098$ .

**Infrared Spectra.**—Infrared spectra were recorded in the region 4000–250  $\text{cm}^{-1}$  with a Perkin-Elmer Model 621 instrument and with a Beckman IR-11 instrument in the region 400–140  $\text{cm}^{-1}$ . From 4000 to 1300  $\text{cm}^{-1}$  hexachlorobutadiene mulls and NaCl plates were used; from 1700 to 250  $\text{cm}^{-1}$  Nujol mulls and CsI plates were used. Nujol mulls and thin polythene sheets were used from 400 to 140  $\text{cm}^{-1}$ . Calibration was performed against either polystyrene film or a water vapor rotational spectrum. Accuracy is believed to be better than  $\pm 2 \text{ cm}^{-1}$  in the range 4000–400  $\text{cm}^{-1}$  and  $\pm 1 \text{ cm}^{-1}$  in the range 400–150  $\text{cm}^{-1}$ .

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## Iodonium Salts of Complex Anions. I. The Self-Phenylation of Diphenyliodonium Salts of Bis(dithiooxalato)palladate(II) and -platinate(II)<sup>1</sup>

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The diphenyliodonium salts of the dithiooxalates of palladium(II) and platinum(II),  $((C_6H_5)_2I)_2[M(S_2C_2O_2)_2]$ , were isolated in a study of the phenylating effect of this cation on complex anions. This new ligand reaction was studied in both the solid state and in solution. At 150° in the solid state the products are the polymeric thiophenolates of palladium(II) and platinum(II), palladium also undergoing reduction to the metal to a considerable extent. These mercaptides were found to be soluble in molten triphenylphosphine and were briefly characterized in this solvent. In pyridine solution  $(pyH)_2[Pd(S_2C_2O_2)_2]$  and 2-, 3-, and 4-phenylpyridines were the principal products while the platinum complex gave  $[Pt(S_2C_2O_2)(py)_2]py$  and  $(pyH)[Pt(S_2C_2O_2)(S_2C_2O_2C_6H_5)(py)_2]$ . A radical mechanism is proposed for the reactions on the basis of the isolated products.

### Introduction

The reactions of coordinated ligands have been a subject of considerable study in the last few years. Our interest in this area has prompted us to investigate the arylation of coordinated ligands by a new reagent for this field, the diphenyliodonium ion,  $(C_6H_5)_2I^+$ .

This cation has several interesting features which make it suited to such a study. Many of its salts are easily precipitated from aqueous solution and these salts have built-in reactivity; the cation is the attacking species, the complex anion is the substrate, and

no solvent is required. The alternation of cation and anions in the crystal lattice ensures a precise stoichiometry and also eliminates the need for any other ions in the system. In addition, these salts are generally more soluble in organic solvents than are the corresponding alkali metal salts and so provide a wider range of possible reaction conditions for solution studies.

There have been a number of reports of arylation by the diphenyliodonium ion of simple nucleophiles like iodide<sup>2</sup> and chloride.<sup>3</sup> These reactions proceed *via* a nucleophilic substitution of iodobenzene by the simple

(1) (a) Presented to the Graduate School of the University of Connecticut by G. E. H. in partial fulfillment of the requirements for the Ph.D. degree. (b) Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

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(3) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

anion. With other systems such as 1,3-indanedione,<sup>4</sup> triphenylphosphine,<sup>5</sup> or mercury<sup>6</sup> the products indicate a radical mechanism takes place.

When Hartmann and Meyer<sup>7</sup> first synthesized the diphenyliodonium ion, they isolated the dichromate and the hexachloroplatinate(IV) salts as well as a number of other derivatives. Other reports involving metal complex anions have dealt with the use of diphenyliodonium salts in gravimetric analysis.<sup>8-10</sup> However, with the exception of the work by this group<sup>11</sup> on  $\text{PtCl}_4^{2-}$ , no complexes have been subjected to a study of arylation by the diphenyliodonium ion.

This paper deals with the phenylation of bis(dithiooxalato)platinate(II), **1**, and -palladate(II), **2**, by diphenyliodonium ion, both in the solid state and in solution.

### Experimental Section

**General Information.**—Infrared absorption spectra of most compounds were taken of mineral oil mulls between cesium bromide plates and were run on a Perkin-Elmer 137 Infracord and a Beckman IR-5A CsBr spectrophotometer from 4000 to 290  $\text{cm}^{-1}$ . Thin layer chromatographic plates were prepared from Brinkman Silica Gel-GF.

**Preparation of Potassium Bis(dithiooxalato)metalate(II) (Metal = Platinum or Palladium).**—The method of Cox, *et al.*,<sup>12</sup> was used with one modification: saturated solutions of the reagents were used in order to improve the yield.

**Preparation of Diphenyliodonium Chloride.**—The method of Beringer, *et al.*,<sup>3</sup> was used, but only the first crop from the recrystallization was retained since subsequent crops were found to contain  $\text{NH}_4\text{HSO}_4$ ; mp 228.5° dec; lit.<sup>3</sup> mp 228° dec.

**Preparation of Diphenyliodonium Bis(dithiooxalato)platinate(II) (1).**—A solution of 1.24 g of  $(\text{C}_6\text{H}_5)_2\text{I}^+\text{Cl}^-$  in 150 ml of water was added dropwise to 1.00 g of  $\text{K}_2\text{Pt}(\text{S}_2\text{C}_2\text{O}_4)_2$  in an equal volume of water. The red-orange precipitate was filtered and washed with water, ethanol, and ether; yield, 1.88 g (97%). It dissolved readily in dimethylformamide, dimethyl sulfoxide, and pyridine; it was slightly soluble in a number of solvents. Its infrared spectrum was the sum of the spectra of the starting materials. The electronic spectrum in DMF solution was the same that of  $\text{K}_2\text{Pt}(\text{S}_2\text{C}_2\text{O}_4)_2$ , exhibiting five peaks ( $\lambda_{\text{max}}$  (m $\mu$ ), log  $\epsilon$ ): 466, 3.75; 436, 3.89; 419, 3.84; 340, 3.45; 225, 3.68. *Anal.* Calcd for  $\text{C}_{28}\text{H}_{20}\text{I}_2\text{PtS}_4\text{O}_8$ : C, 33.7; H, 2.01; S, 12.8; Pt, 19.5. Found: C, 33.40; H, 1.98; S, 12.48; Pt, 19.36.

**Preparation of Diphenyliodonium Bis(dithiooxalato)palladate(II) (2).**—This compound was prepared analogously to the platinum(II) complex, **1**, in 74% yield. The infrared spectrum was identical with that of **1** and the solubility was similar. *Anal.* Calcd for  $\text{C}_{28}\text{H}_{20}\text{I}_2\text{PdS}_4\text{O}_8$ : C, 37.0; H, 2.20; Pd, 11.9; S, 14.1. Found: C, 37.25; H, 2.21; Pd, 11.50; S, 14.20.

**Preparation of Bis(benzenethiolo)platinum(II).**—Two grams of  $\text{K}_2\text{PtCl}_4$  was suspended in 80 ml of warm dimethylformamide and 25 ml of warm water was added to dissolve most of the solid. To this solution was added 1.10 ml of benzenethiol. The solution was filtered, heated 2 hr on a steam bath, and cooled. Filtration followed by washing with dimethylformamide, hot water, acetone, and ether produced 1.52 g (75%) of the canary yellow

compound. Champ and Fauconnier claimed this compound was yellow-green,<sup>13</sup> but we found a green material to be produced as a by-product only when the reaction is done in aqueous solution. *Anal.* Calcd for  $\text{C}_{12}\text{H}_{10}\text{PtS}_2$ : C, 34.9; H, 2.42; S, 15.5; Pt, 47.2. Found: C, 34.41; H, 2.69; S, 15.58; Pt, 47.40. The solid was completely insoluble in most common solvents but could be dissolved in molten triphenylphosphine to give a yellow solution.

**Preparation of Bis(benzenethiolo)palladium(II).**—The method of Karasev and Kakovskii<sup>14</sup> was used. *Anal.* Calcd for  $\text{C}_{12}\text{H}_{10}\text{PdS}_2$ : Pd, 32.7. Found: Pd, 32.9. Infrared spectrum and solubility properties were identical with the analogous platinum compound. The red solid dissolved in triphenylphosphine to give a yellow solution.

**Solid-State Reaction of 1 and 2 in Vacuo.**—Into a 50-ml flask was placed 4.50 g of **1**. The flask was fitted with a distilling head, condenser, and vacuum line fraction collector. The flask was immersed in an oil bath at 50° and the temperature was raised about 3°  $\text{min}^{-1}$ ; the pressure was 0.08 Torr. At 146° the pressure reached 3.7 Torr when the first drop of iodobenzene distilled over. At 148° the pressure climbed quickly to 7.2 Torr and then dropped. Further temperature increase caused no change in pressure. The brown residue was insoluble in all solvents but triphenylphosphine.

The solid-state reaction *in vacuo* was also allowed to take place in the source of an AEI MS-12 mass spectrometer by placing a few milligrams of **1** into the cooled source and running the spectrum when the source temperature reached 160°. Peaks appeared at  $m/e$  (relative intensity, strongest peak = 100) 205 (5), 204 (73), 186 (20), 185 (7), 127 (7), 78 (7), 77 (100), 76 (7), 75 (5), 74 (12), 60 (41), 51 (46), 50 (32), 39 (5), 32 (17), 28 (27).

Similar treatment of **2** gave peaks at  $m/e$  204 (100), 186 (30), 183 (6), 127 (6), 110 (6), 78 (6), 77 (100), 76 (6), 75 (6), 74 (6), 60 (50), 51 (40), 50 (23), 39 (6), 38 (6), 32 (18), 28 (18), 18 (6).

**Solid-State Reaction in Diethylbenzene Slurry.**—Into a flask was placed 5.00 g of **1**, 100 ml of diethylbenzene, and a magnetic stir bar. The mixture was boiled and after heating at 150° for 0.5 hr the tan solid was filtered and washed with benzene, dimethylformamide, and ether; yield, 0.75 g (91%). This reaction was repeated several times; the analytical values are means of five separate analyses, followed by the standard deviations. *Anal.* Calcd for  $\text{C}_{37}\text{H}_{30}\text{OPt}_4\text{S}_8$ : C, 29.1; H, 1.97; Pt, 51.1; S, 16.8. Found: C, 28.7  $\pm$  0.5; H, 1.90  $\pm$  0.07; S, 16.0  $\pm$  0.7; Pt, 51.5  $\pm$  1.9. The atom ratio of sulfur to platinum is 1.9.

Infrared bands appeared at ( $\text{cm}^{-1}$ , intensity) 2070 (m), 1630 (w), 1580 (m), 1300 (w), 1270 (w), 1170 (w), 1150 (w), 1060 (w), 1010 (m), 995 (w), 830 (w), 730 (s), 680 (s), 500 (w), 477 (s), and 440 (w, br). This solid dissolved in ethylenediamine and molten triphenylphosphine but was insoluble in all common solvents and KCN solution. The powder did not diffract X-rays and was judged to be amorphous.

This solid was dissolved in triphenylphosphine at 100°, and attempts to separate the several components by addition of various solvents and by recrystallization were not successful. Preparative thin layer chromatography (0.75-mm silica gel plates eluted with toluene) gave four major bands each of which gave, after removal in ether, a thin layer chromatograph containing one or more spots other than its own. Thin layer chromatography of authentic  $\text{Pt}(\text{SC}_6\text{H}_5)_2$  dissolved in triphenylphosphine and diluted with benzene (0.25-mm plates eluted with toluene) gave the same results as did the residue above.

When heated in diethylbenzene slurry at 150° the palladium compound **2** also decomposed. About 50% (by weight) of the residue was metallic palladium. The infrared spectrum of the mixture had absorptions at 1570 (w), 1430 (s), 1290 (w), 1270 (w), 1160 (w, br), 1060 (w), 1010 (m), 995 (w), 900 (w, br), 825 (w), 730 (s), 678 (s), 475 (s), 435 (w, br), 344  $\text{cm}^{-1}$  (w, br).

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Thin layer chromatography of the triphenylphosphine-soluble fraction (toluene eluent) gave the same pattern as identically treated samples of both platinum (II) and palladium (II) benzene-thiolates, plus one additional band.

**Cryoscopy in Triphenylphosphine.**—The cryoscopic molecular weight of the residue from the thermal reaction of **1** was determined in triphenylphosphine as a function of the time that the sample was heated in this solvent. The melting point of triphenylphosphine is 79.5°; its cryoscopic constant is  $-12.0^\circ m^{-1}$  ( $\pm 0.5^\circ m^{-1}$ ).<sup>15</sup> Mixtures of triphenylphosphine and the residue were heated to 100° in a steam bath and then removed. On cooling, the solutions always supercooled despite vigorous stirring and the plateau temperature was recorded as well as the time the sample spent in the steam bath. The observed molecular weight climbed slowly from 408 after 11 min of heating to  $533 \pm 1$  after 74 min. Addition of more triphenylphosphine gave  $533 \pm 12$ . Heating for 2 min or longer at 150° gave  $441 \pm 25$ . The infrared spectrum of this mixture did not contain the 2070-cm<sup>-1</sup> band present before the triphenylphosphine treatment.

**Reaction of 2 in Pyridine.**—Four grams of **2** and 132 ml of reagent grade pyridine were suspended together by vigorous stirring and heated. The solid all dissolved as the solution began to reflux. Within 2 min 1.30 g of  $(pyH)_2[Pt(S_2C_2O_2)_2]$  precipitated as yellow needles and was filtered from the hot solution. Cooling gave an additional 0.26 g (total 70%). An analytical sample was twice recrystallized from 0.10 M aqueous pyridine. *Anal.* Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>PdS<sub>4</sub>: C, 33.2; H, 2.37; N, 5.53; Pd, 20.9; S, 25.3. Found: C, 32.89; H, 2.42; N, 5.44; Pd, 20.8; S, 25.03. The infrared spectrum showed absorptions at 2800 (m, br), 2340 (w), 2000 (w), 1816 (vw), 1630 (w), 1565 (s), 1510 (m), 1470 (m), 1430 (w), 1370 (m), 1330 (w), 1300 (w), 1260 (w), 1240 (vw), 1190 (m), 1155 (vw), 1080 (s), 1050 (w), 1042 (w), 1012 (vw), 1004 (w), 940 (m), 872 (w), 745 (s), 678 (s), 602 (m), 568 (w), 513 (m), 417 (s), 401 (s), 323 cm<sup>-1</sup> (s).

To the pyridine filtrate was added slowly a solution of 13 g of NaOH in 25 ml of water. The organic layer was decanted into 200 ml of water and this was extracted repeatedly with ether. The extract was vacuum distilled to isolate the fraction at 140–150° and 15 Torr (0.79 g). Thin layer chromatography (chloroform eluent) of this fraction showed it to contain 2-, 3-, and 4-phenylpyridines as well as benzenethiol. Precipitation of the phenylpyridine picrates (0.63 g, 19% based on amount of **2** taken) eliminated the benzenethiol.

Authentic phenylpyridinium picrates were made by the method of Haworth, Heilbron, and Hey<sup>16</sup> and gave the following uncorrected melting points (literature value): 4 isomer, 197–199° (195–196°); 2 isomer, 176–178° (175–176°); 3 isomer, 162–163° (159–160, 162–164°<sup>17</sup>). Mixture melting points of these with the picrates of commercial 2- and 4-phenylpyridines (Eastman, vacuum distilled once) further confirmed their identity.

**Reaction of 1 in Pyridine.**—Three grams of **1** was dissolved in 200 ml of reagent grade pyridine, refluxed a few minutes, and concentrated at 55° and 15 Torr to about 15 ml. Earlier thin layer chromatographic experiments showed this reaction to be over within 2 min; no diphenyliodonium ion could be detected in the solutions. Cooling of the above solution produced 0.88 g of tiny orange and yellow crystals. Separation was achieved by hand picking the two types of crystals from a fresh preparation which had been cooled very slowly.

The orange compound is  $[Pt(S_2C_2O_2)(py)_2]py$ . The compound does not melt below 280° but decomposes around 200°. On standing, the solid loses pyridine and crumbles. *Anal.* Calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>PtS<sub>2</sub>: C, 36.9; H, 2.73; N, 7.61; S, 11.6; Pt, 35.3. Found: C, 36.77; H, 2.73; N, 7.38; S, 11.30; Pt, 35.13. Infrared absorption bands are observed at 3400 (w, br), 3000 (w), 2700 (w), 2100 (vw), 2000 (vw), 1930 (vw), 1870 (vw), 1710 (vw), 1620 (s), 1570 (s), 1480 (s), 1440 (s), 1410 (m), 1350 (m), 1300 (w, br), 1235 (m), 1210 (m), 1150 (m), 1058 (s),

1028 (m), 1015 (m), 1000 (w), 995 (m), 950 (w), 923 (s), 875 (m), 760 (s), 745 (m), 735 (w), 709 (m), 695 (s), 670 (w), 642 (w), 595 (w), 558 (m), 448 (m), 415 (m, br), 402 (m), 385 (m), 335 (m), 310 cm<sup>-1</sup> (w).

The yellow compound is less stable, giving off an odor like that of H<sub>2</sub>S. It is formulated as a pyridinium salt:  $(pyH)[Pt(S_2C_2O_2)(S_2C_2O_2C_6H_5)(py)_2]$ . *Anal.* Calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>PtS<sub>4</sub>: C, 40.0; H, 2.80; N, 5.60; S, 17.1; Pt, 26.0. Found: C, 39.7 ± 1.9; H, 2.74 ± 0.05; N, 5.56 ± 0.06; S, 17.50 ± 0.34; Pt, 26.9 ± 3.1. A sodium fusion test for halogen was negative showing the absence of the diphenyliodonium ion. The sample does not melt but becomes red at 150°, brown at 200°, and black at 250°. Molar conductance (cm<sup>2</sup> mol<sup>-1</sup> ohm<sup>-1</sup>) in dimethylformamide solution was 57 at 1.0 × 10<sup>-3</sup> M and 54 at 4.0 × 10<sup>-4</sup> M, lending support to the formulation as a 1:1 electrolyte. The infrared absorption spectrum showed bands at 3000 (w), 2500 (m, br), 2000 (m, br), 1625 (s), 1610 (s), 1560 (m), 1480 (m), 1440 (s), 1410 (m), 1350 (m), 1305 (w), 1238 (w), 1215 (m), 1200 (w), 1155 (w), 1062 (s), 1045 (s), 1020 (s), 1020 (m), 1015 (m), 1005 (m), 990 (m), 935 (w), 908 (m), 754 (s), 734 (s), 685 (s), 647 (m), 625 (m), 547 (m), 483 (w), 430 (w, br), 390 (m), 318 (s), 300 cm<sup>-1</sup> (w, br). Treating the filtrate from this reaction as before only 0.27 g (9%) of phenylpyridine picrates could be obtained.

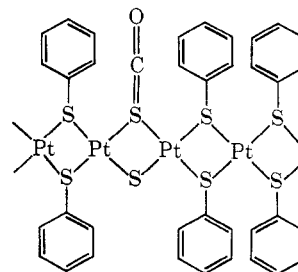
**Reaction of Tetrapropylammonium Bis(dithiooxalato)palladate-(II) in Pyridine.**—This compound was refluxed for 30 min in reagent grade pyridine and recovered unchanged.

**Photochemical Behavior of 1 in Methanol.**—From a solution of 0.70 g of **1** in 1.7 l. of methanol was obtained 0.10 g of impure Pt(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> by centrifuging the solution after exposure for 5 days in a 350-mμ irradiator. Infrared bands in the NaCl region appeared at 3400 (w), 1730 (w), 1620 (w), 1580 (w), 1160 (w), 1010 (w), 950 (w, br), 730 (m), 680 cm<sup>-1</sup> (w). *Anal.* Calcd for C<sub>12</sub>H<sub>10</sub>PtS<sub>2</sub>: Pt, 47.2. Found: Pt, 47.0. Thin layer chromatography of a triphenylphosphine solution of this compound corresponded with that of a similarly treated sample of authentic Pt(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. The filtrate from this reaction gave a negative test for the diphenyliodonium ion. Slight turbidity could be obtained on refluxing this solution, even in the dark.

## Results and Discussion

**Solid-State Reaction.**—Heating  $[(C_6H_5)_2I][Pt(S_2C_2O_2)_2]$ , **1**, to 146° produced within 1 min mainly Pt(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, an amorphous compound which only dissolves in strongly coordinating solvents such as triphenylphosphine or ethylenediamine. This reaction product was characterized by dissolution in triphenylphosphine and comparison of the thin layer chromatographs of the resulting triphenylphosphine adducts with those formed by a similarly treated authentic sample.

The impurities in the reaction product are as insoluble as the Pt(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, and, although the overall composition of the product was somewhat variable, the number of atoms of sulfur per atom of platinum was always 2. Thus, the thermal degradation product is best described as a defect polymer with every fourth platinum bonded to one bridging sulfide ligand and one bridging monothio carbon dioxide ligand



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The infrared spectrum of the solid residue had all the bands characteristic of  $\text{Pt}(\text{SC}_6\text{H}_5)_2$  and two additional bands at 2070 and 500  $\text{cm}^{-1}$ . Gaseous SCO is known to absorb at 2064 (CO stretch), 859 (CS stretch), and 524  $\text{cm}^{-1}$  (SCO bend).<sup>18</sup> The CS stretch in our compound may not be absent at all but instead hidden in the weak phenyl absorption at 830  $\text{cm}^{-1}$ .

Further evidence for the formation of SCO in this reaction is the presence of a mass 60 peak when the pyrolysis was allowed to take place in the source of a mass spectrometer.

One difficulty in working with mercaptide complexes is their insolubility, conferred by their polymeric nature. We have found molten triphenylphosphine to be an excellent solvent for the thiophenolates prepared in this work. This is undoubtedly due to the cleavage of the polymer and formation of lower molecular weight triphenylphosphine complexes. An added advantage to using this solvent is its large cryoscopic constant, enabling one to determine the molecular weight of the solute thus produced.

When the molecular weight of the reaction product was determined as a function of the duration of heating at 100° in triphenylphosphine, observed molecular weights climbed slowly from 408 (higher than the average of 381 per atom of platinum calculated for the defect polymer) to 533 after 1 hr and thereafter remained constant. However, heating to 150° reduced the apparent value to 441.

Thus, the initial molecular weight is higher than expected and becomes higher still, indicating that the number of molecules present in solution is decreasing. This can only happen if molecules leave the solution or if they combine to form dimers or oligomers. If the high values were due to molecules leaving the solution, reduction of the molecular weight on heating to higher temperature could not occur. An equilibrium must be achieved slowly at 100° between monomer and oligomer, giving an average molecular weight of 530. Heating to 150° shifts the equilibrium in favor of monomer and quickly cooling quenches a nonequilibrium system.

Since the infrared spectrum of this solution does not contain the 2070- $\text{cm}^{-1}$  band, the SCO is no longer present in this substance, presumably displaced from the coordination sphere by the donor solvent. The analysis on the residue (prior to triphenylphosphine treatment) indicates a certain amount of SCO to be present. Assuming this all to leave the solution, we recalculate the experimental molecular weight to be 423. This is higher than the average required for  $\text{Pt}(\text{SC}_6\text{H}_5)_{3/4}(\text{S})_{1/4}$  and still indicates significant monomer-oligomer equilibrium. Chromatographic results concurred with the idea that there were several components present in these solutions.

When  $[(\text{C}_6\text{H}_5)_2\text{I}]_2[\text{Pd}(\text{S}_2\text{C}_2\text{O}_2)_2]$ , **2**, was heated to 150° for a few minutes, it produced mainly palladium metal (76 mol %) and the rest of the product was  $\text{Pd}(\text{SC}_6\text{H}_5)_2$ . Although there was SCO present when the

reaction was run in a mass spectrometric source, there was no 2070- $\text{cm}^{-1}$  band in the infrared spectrum of the residue. We do not feel this absence to be particularly significant.

In summary, the solid-state arylation of  $\text{M}(\text{S}_2\text{C}_2\text{O}_2)_2^{2-}$  leads to the production of  $[\text{M}(\text{SC}_6\text{H}_5)_2]_n$ . At the temperatures employed for the reaction intermediate phenyl esters of the coordinated thioacid are not stable. The principal difference one observes between platinum(II) and palladium(II) is the extensive reduction of the latter.

**The Reaction in Pyridine.**—In pyridine solution two compounds are formed from **1**. The orange complex  $[\text{Pt}(\text{S}_2\text{C}_2\text{O}_2)(\text{py})_2]\text{py}$  contains both coordinated and uncoordinated pyridine, as deduced from infrared spectral evidence.<sup>19</sup> Also, slow loss of pyridine and crumbling of the crystals on standing is further evidence for lattice solvent.

From the work of Nakamoto and Fujita on S-bonded dithiooxalato complexes<sup>20</sup> other assignments could be made, with the interesting result that the strong carbonyl band was shifted from 1570 to 1620  $\text{cm}^{-1}$  in  $[\text{Pt}(\text{S}_2\text{C}_2\text{O}_2)(\text{py})_2]\text{py}$ . The two bands involving platinum-sulfur stretching were shifted to higher energy: the 435-420- and the 320- $\text{cm}^{-1}$  bands in  $\text{K}_2\text{Pt}(\text{S}_2\text{C}_2\text{O}_2)_2$  appear at 448 and 335  $\text{cm}^{-1}$  in the pyridine-substituted compound. Substitution of two pyridines for one dithiooxalato appears to allow the remaining sulfur atoms a greater share of the filled d orbitals of the metal, increasing the bond order between platinum and sulfur. The corresponding decrease in S-C bonding is compensated by increased O-C bond strength. Nakamoto has pointed out that the strength of an oxygen-metal bond in a series of oxalato complexes of different metal ions is reflected in the carbonyl stretching frequency.<sup>21</sup> This also appears to be true where the metal ion is the same and the substituents account for the different bond strengths.

The yellow compound from **1** and pyridine was not stable enough for thorough characterization, but it appears to be an ionic complex of a reaction intermediate:  $(\text{pyH})[\text{Pt}(\text{S}_2\text{C}_2\text{O}_2)(\text{S}_2\text{C}_2\text{O}_2\text{C}_6\text{H}_5)(\text{py})_2]$ . Because of the coincidence of free pyridine and monosubstituted benzene in the infrared spectrum, one cannot determine whether both pyridine molecules are coordinated. Even if the monophenylated dithiooxalato does not function in a bidentate fashion, there are too many groups present to satisfy the coordination requirements of Pt(II). Further work with this compound is certainly justified.

When the palladium compound **2** was refluxed in pyridine, it quickly precipitated the pyridinium salt  $(\text{pyH})_2[\text{Pd}(\text{S}_2\text{C}_2\text{O}_2)_2]$  in high yield. This was in striking contrast to the behavior of **1**, in which arylation of the solvent and its consequent production of pyridinium ions was only a side reaction and in which there was so little of the original complex ion remaining after arylation.

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tion that the insoluble pyridinium salt did not precipitate even when the solution was concentrated and cooled.

Roughly equal quantities of the three isomers of phenylpyridine were isolated from the filtrate of the reaction of **2** in pyridine, along with some benzenethiol. The same result was obtained for the platinum compound **1** except that the yield of phenylpyridines was much lower.

There are two important contrasts here. The first is the striking difference between the solution reactions of the platinum(II) and the palladium(II) complexes. With the former, primarily complex arylation occurs, the unstable partially phenylated  $[\text{Pt}(\text{S}_2\text{C}_2\text{O}_2)(\text{S}_2\text{C}_2\text{O}_2\text{-C}_6\text{H}_5)(\text{py})_2]$  being an intermediate step in the total phenylation and subsequent loss of one dithiooxalate from the platinum. On the other hand, the palladium complex undergoes very little sulfur phenylation, but predominantly solvent phenylation occurs. It should be mentioned that when the bis(dithiooxalato)palladate(II) ion is refluxed in pyridine in the absence of the diphenyliodonium ion, no change occurs; the phenomena we observe are indeed the result of diphenyliodonium reactions.

A second contrast in this work is that between the solution and solid-state experiments. In solution there is little tendency toward thiophenol formation, which of course predominates in the solid reaction. We feel that what actually happens in the solid is first the phenylation of coordinated dithiooxalate followed by a further reaction of the coordinated phenyl ester at the higher temperature of the solid reaction, giving the observed products.

**The Reaction Mechanism.**—A radical mechanism is warranted for the methanol solution reaction by its thermal or photoinduction, for the solid-state reactions by the large difference in reaction rate between 140 and 146°, as well as similarity of product obtained from methanol, and for the pyridine solution reactions by the production of all three phenylpyridines.<sup>17</sup>

In refluxing pyridine the solvent phenylation is a radical process, and we have assumed that here attack on the complex anion is also radical in nature. In view of our other results this is not unlikely. The drastic difference in behavior between **1** and **2** in solution must reflect a difference in the attractive forces between the complex and the reactive iodonium species. Here the course of the ligand reaction shows a pronounced dependence on the nature of the metal ion. This is indeed surprising considering the otherwise close similarity of palladium(II) and platinum(II).

In the solid-state reaction the observed products are consistent with a radical mechanism. However, no kinetic study was attempted and the details of the mechanism are unknown. We wish to emphasize that this is one of the very few ligand reactions studied in which a radical mechanism, rather than a nucleophilic substitution, is the apparent course.

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## Spectroscopic Studies of Alkyl Sulfoxide Complexes of Platinum(II) and Palladium(II)

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A number of sulfoxide complexes of platinum(II) and palladium(II) have been synthesized, and their infrared and proton magnetic resonance spectra indicate that sulfur is the donor atom. The Pt(II) complexes are of the type  $\text{PtCl}_2\text{L}_2$  (L = sulfoxide) and far-ir data suggest all have *cis* configurations except the diisopropyl sulfoxide complex. The Pd(II) complexes  $\text{PdCl}_2\text{L}_2$  are *trans* in the *solid* state but in solution most appear to revert to the halo-bridged binuclear structures  $\text{Pd}_2\text{Cl}_4\text{L}_2$ . The pmr spectra of the Pt(II) complexes have been analyzed, and the values of <sup>195</sup>Pt-H coupling constants have been rationalized in terms of preferred conformations about the C-S bonds. In suitable sulfoxides, *e.g.*, diethyl, it is clear that S coordination to Pt(II) or Pd(II) results in a significant increase in the degree of methylene proton inequivalence. Magnetic anisotropic effects in these d<sup>8</sup> square-planar structures are suggested to be responsible.

### Introduction

The isolation and characterization of metal complexes of dimethyl sulfoxide (DMSO) were reported<sup>2-4</sup> some

years ago, and it was recognized<sup>2</sup> and later demonstrated by spectroscopic<sup>2-4</sup> and X-ray studies<sup>3,5,6</sup> that while DMSO generally associated with metal ions through its oxygen atom, sulfur donation was favored

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