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Preparation, Characterization, and Reactivity of the *cyclo*-Metallosilane $[(C_6H_5)_3P]_2\overline{Pt[Si(C_6H_5)_2]_3Si}(C_6H_5)_2$[1a]

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Treatment of 1,4-dihydridooctaphenyltetrasilane, $H_2Si_4(C_6H_5)_8$, with bis(triphenylphosphine)ethyleneplatinum(0), $[(C_6H_5)_3P]_2PtC_2H_4$, affords the first example of a transition metal incorporated into a silicon ring, $[(C_6H_5)_3P]_2\overline{Pt[Si(C_6H_5)_2]_3Si}(C_6H_5)_2$. Infrared and ultraviolet spectroscopic examinations are reported and compared with similar data recorded for $[(C_6H_5)_3P]_2PtC_2H_4$, $Si_4(C_6H_5)_8$, and $Si_5(C_6H_5)_{10}$. Attempts at several alternate methods of synthesis are discussed as well as reaction of the *cyclo*-metallosilane with Br_2 and H_2.

Introduction

Our interest in incorporating a transition metal into a *cyclo*-silane, to yield a *cyclo*-metallosilane, originates in the report that $Si_5(CH_3)_{10}$, decamethyl-*cyclo*-pentasilane, forms a radical ion in which electron delocalization occurs.[2] Therefore, perhaps a *cyclo*-metallosilane system could be prepared in which intramolecular electron delocalization takes place where the metal functions as the reducing agent and the catenated silane as the electron acceptor. Our initial studies have involved platinum because of our prior experience with Pt–Si systems.[3]

When one considers possible routes toward formation of Pt–Si bonds, both the reaction of haloplatinum complexes with alkali metal–silyl species and oxidative addition of hydridosilanes to low coordination number–oxidation state platinum complexes have merit. Both routes have been successful for the formation of Pt–Si bonds, e.g., $[(C_6H_5)_3P]_2Pt[Si(C_6H_4CF_3)_3]_2$ from $[(C_6H_5)_3P]_4Pt$ and the corresponding hydridosilane,[4] *cis*-$[(C_6H_5)_3P]_2Pt(SiCl_2CH_3)_2$ from $[(C_6H_5)_3P]_2PtC_2H_4$ and the hydridosilane,[5] and *cis*-$[(C_6H_5)_2P]PtHSi(C_6H_5)_3$ from $(C_6H_5)_3SiLi$ and *cis*-$Cl_2Pt[P(C_6H_5)_3]_2$.[6] In this last case, complication arose in that the source of the PtH moiety is unknown. Other examples of employed methods for Si–Pt bond formation include platinum chloride with silyl mercurials[7] and hydridosilanes with hydridoplatinum complexes.[8] The reported examples of catenated silicon bonded to a transition metal have involved syntheses in which a halosilane was treated with a transition metal–alkali metal salt: π-$C_5H_5(CO)_3MSi_2(CH_3)_5$ (M = Cr, Mo, W),[9] $[(CH_3)_3Si]_3SiMn(CO)_5$,[10] and π-$C_5H_5(CO)_2Fe[Si(CH_3)_2]_2CH_3$.[11] The only report of a *cyclo*-metallopolysilane has been our preliminary disclosure.[1a]

Experimental Section

Equipment. Chemical reactions and procedures were followed as previously described[12] while molecular weight determinations were carried out with a Model 301A vapor pressure osmometer manufactured by Mechrolab Inc. Individual samples were dissolved in benzene or chloroform, and results were obtained from a calibration curve determined from standard solutions of benzil ($C_6H_5COCOC_6H_5$, mol wt 201.2) dissolved in the respective solvents. Melting points were determined on a Mel-Temp melting point apparatus equipped with a 0–500 °C range thermometer. Samples were placed in Kimax-51 capillary tubes ((1.6–1.8) × 100 mm).

Analyses. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. and Galbraith Laboratories, Inc., Knoxville, Tenn.

Chemicals. Benzene, Certified ACS, Fisher Scientific Co., was dried over lithium aluminum hydride. **Chloroform,** Certified ACS, Fisher Scientific Co., was dried over calcium hydride and stored over Linde 4A molecular sieves. **Chloroform-*d*$_1$,** 99.8% + 1% TMS added, Diaprep Inc., was used as received. **Cyclohexane,** Matheson Coleman and Bell, was dried over lithium aluminum hydride and stored over Linde 4A molecular sieves. **Dichlorodiphenylsilane,** PCR, Inc., was used as received. **Ethanol,** 95%, Commercial Solvents Corp., was used as received. **Lithium,** wire, $^1/_8$-in. diameter, Research Organic/Inorganic Chemical Corp., was used as received. **Tetrahydrofuran,** Certified, Fisher Scientific Co., was dried over lithium aluminum hydride. **Hexachloroplatinic acid,** H_2PtCl_6, was prepared by stirring small pieces of platinum wire or foil in aqua regia.[13] **Potassium hexachloroplatinate,** K_2PtCl_6, was prepared from the above solution as described in the literature.[14] **Potassium tetrachloroplatinate,** K_2PtCl_4, was prepared as described in the literature.[15] **Octaphenyl-*cyclo*-tetrasilane,** $Si_4(C_6H_5)_8$, was prepared from dichlorodiphenylsilane and lithium as described in the literature.[16] After purification by Soxhlet extraction with hot toluene, a melting point range of 319–322 °C was obtained (lit. mp 321–323 °C). Anal. Calcd: C, 79.1; H, 5.5; Si, 15.4. Found: C, 79.0; H, 5.5; Si (by difference), 15.5. Infrared data: 3060 (w), 1960 (vw, b), 1880 (vw, b), 1815 (vw, b), 1585 (w), 1486 (m), 1430 (s), 1303 (w), 1260 (w), 1190 (w), 1160 (w), 1094 (s), 1025 (w), 998 (m), 970 (vw), 910 (vw), 845 (vw), 735 (vs), 700 (vs), 695 (vs, sh), 684 (m), 678 (m, sh), 618 (vw), 531 (m), 480 (s), 469 (s), 458 (w, sh), 445 (m), 425 (m), 420 (m), and 330 (vs) cm^{-1}. **1,4-Dilithiooctaphenyltetrasilane,** $Li_2Si_4(C_6H_5)_8$, was prepared from octaphenyl-*cyclo*-tetrasilane and lithium.[16] **Decaphenyl-*cyclo*-pentasilane,** $Si_5(C_6H_5)_{10}$, was prepared on a small scale as previously described.[17] Purification was effected by fractional crystallization with hexane from a benzene solution; mp 462–466 °C (lit. mp 466-470 °C). For larger scale syntheses, a somewhat less pure product could be obtained by modifying the reaction used in the synthesis of octaphenyl-*cyclo*-tetrasilane. To 300 ml of dry tetrahydrofuran under nitrogen, 8.0 g (1.1 mol) of clean, finely cut lithium wire was added. Next, 126 g (ca. 0.5 mol) of diphenyldichlorosilane was added dropwise with constant stirring. After the addition was complete, the mixture was allowed to stir vigorously under reflux for 40 h. The brown mixture was filtered in air and the crude solid purified in a manner analogous to that described by Gilman for the purification of $Si_5(C_6H_5)_{10}$.[18] After recrystallization from benzene 45 g (50%) of the pentamer was obtained; mp 451–456 °C. The infrared spectrum of $Si_5(C_6H_5)_{10}$ contains absorptions at 3040 (w), 1955 (w, b), 1885 (w, b), 1815 (w, b), 1770 (vw, b), 1650 (vw, b), 1580 (vw), 1565 (vw), 1480 (m), 1430 (s), 1305 (w), 1262 (w), 1192 (w), 1155 (w), 1092 (s), 1025 (w), 1000 (w), 972 (w), 915 (vw), 890 (vw), 850 (w), 735 (vs), 725 (m, sh), 699 (vs), 515 (w), 484 (s), 472 (s), 442 (w, sh), 434 (w, sh), 412 (m), 377 (m), 345 (s), 335 (m, sh), 331 (m, sh), and 325 (s) cm^{-1}. **1,5-Dilithiodecaphenylpentasilane,** $Li_2Si_5(C_6H_5)_{10}$, was prepared from decaphenyl-*cyclo*-pentasilane and lithium as previously described in the literature.[18] The course of the reaction could be followed in a manner analogous to that for $Li_2Si_4(C_6H_5)_8$. **Bis(triphenylphosphine)oxygenoplatinum,** $[(C_6H_5)_3P]_2PtO_2$, was prepared by oxidation of $[(C_6H_5)_3P]_4Pt$ as previously described in the literature.[19] **Bis(triphenylphosphine)ethyleneplatinum,** $[(C_6H_5)_3P]_2Pt(C_2H_4)$, prepared from $[(C_6H_5)_3P]_2PtO_2$ and ethylene, as described in the literature,[19] exhibited ir absorptions at 3055 (w), 1584 (w), 1475 (m), 1437 (m), 1431 (m), 1305 (vw), 1179 (m), 1158 (w), 1145 (s), 1095 (s, sh), 1090 (s), 1068 (w), 1025 (w), 995 (w), 970 (vw), 932 (vw), 920 (vw), 750 (m, sh), 744 (s), 720 (w), 693 (vs), 540 (m), 523 (s), 510 (vs), 451 (w, sh), 445 (w), 426 (m), and 409 (w) cm^{-1}. **Tetrakis(methyldiphenylphosphine)platinum(0),** $[CH_3(C_6H_5)_2P]_4Pt$, was prepared as described in the literature, fractionally crystallized from benzene with hexane; mp 150–153 °C (sealed tube); lit.[20] mp 152–154 °C. In the **attempted synthesis of bis(methyldiphenylphosphine)ethyleneplatinum(0)** oxidation of tetrakis(methyldiphenylphosphine)platinum(0), carried out in benzene, did not lead to the precipitation of a solid as in the synthesis of bis(triphenylphosphine)oxygenoplatinum; however, the ir spectrum of the solid isolated upon evaporation of the solution exhibited a broad absorbance in the 1200-cm^{-1} phosphorus–oxygen stretch region. Assuming that this solid might consist of a mixture of the anticipated dioxygen complex and methyldiphenylphosphine oxide, it was dissolved in ethanol and the solution saturated with ethylene. Addition of a small amount of sodium borohydride results in the evolution of a gas, darkening of the solution, and precipitation of elemental platinum. The mixture was filtered and the filtrate evaporated. The ir spectrum of the resulting solid showed no absorbances which could be attributed to an ethylene ligand. **Bis(triphenylphosphine)platinum(II) chloride,** $[(C_6H_5)_3P]_2PtCl_2$, was prepared from K_2PtCl_4 and triphenylphosphine as described in the literature.[21] The product obtained in this manner was exclusively the cis isomer and subsequent purification was effected by recrystallization from benzene. Ir data: 3050 (w), 1588 (w), 1570 (vw), 1483 (m), 1480 (m), 1440 (s), 1435 (s, sh), 1314 (w), 1188 (w), 1182 (vw), 1164 (w), 1155 (vw), 1103 (m), 1098 (s), 1090 (s), 1070 (w), 1028 (w), 1000 (w), 761 (m, sh), 756 (s), 745 (s), 717 (w), 704 (s), 697 (vs), 690 (s, sh), 617 (vw), 551 (s), 530 (vw), 518 (s), 500 (s), 465 (w), 440 (w), 420 (w), 317 (m), and 292 (m) cm^{-1}. **Bis(methyldiphenylphosphine)platinum(II) chloride,** $[(CH_3)(C_6H_5)_2]_2PtCl_2$, (2 equiv) was added to a dry Schlenk flask in a drybox to prevent oxidation of the phosphine to the phosphine oxide. The reaction flask was removed from the drybox and, while purging it with nitrogen, a water solution of K_2PtCl_4 (1 equiv) was added. The flask was sealed and placed on an automatic shaker until the color of the water solution remained constant. The mixture was than filtered in air and the precipitate was washed with water and allowed to dry in air. As in the triphenylphosphine case, only the cis isomer of $[CH_3(C_6H_5)P]_2PtCl_2$ was obtained as indicated by the white color of the solid (the trans isomer is yellow).[22] Further purification was effected by fractional crystallization with hexane from an ethanol solution; mp 253–261 °C dec (lit.[23] mp 253–268 °C dec); yield 84%. Ir data: 3060 (w), 1584 (w), 1570 (w), 1478 (m), 1440 (s), 1310 (w), 1289 (w), 1190 (vw), 1177 (w), 1100 (s), 1070 (w), 1023 (vw), 993 (w), 970 (vw), 920 (vw), 903 (m), 890 (s), 840 (w), 750 (m), 742 (w), 735 (m), 720 (s), 706 (w), 695 (s), 682 (m), 521 (s), 510 (s), 495 (s), 480 (s), 457 (s), 450 (m, sh), 410 (w), 372 (w), 312 (s), and 290 (s) cm^{-1}. **1,4-Dibromooctaphenyltetrasilane,** $1,4\text{-}Br_2Si_4(C_6H_5)_8$, was prepared from octaphenylcyclotetrasilane and bromine as previously reported in the literature.[17] The product was purified by fractional crystallization with hexane from a benzene solution; mp 207–210 °C (lit.[17] mp 205–209 °C). Ir data: 3060 (w), 1950 (vw, b), 1879 (vw, b), 1807 (vw, b), 1760 (vw, b), 1650 (vw, b), 1582 (vw), 1558 (vw), 1480 (m), 1425 (s), 1302 (w), 1260 (w), 1180 (w, b), 1155 (m), 1105 (s, sh), 1097 (s), 1065 (m), 1027 (w), 998 (m), 975 (vw), 851 (w), 804 (vw), 738 (vs), 698 (vs), 620 (vw), 565 (vw), 525 (s), 481 (vs), 465 (vs), 460 (vs, sh), 422 (s), 380 (s), 351 (m), 330 (w), and 300 (vs) cm^{-1}. **1,4-Dihydridooctaphenyltetrasilane,** $H_2Si_4(C_6H_5)_8$, was prepared according to a literature modification.[24] A THF solution (50 ml) of 4.0 mmol of $1,4\text{-}Li_2Si_4(C_6H_5)_8$ was added dropwise from an addition funnel to an N_2-purged flask containing 10 ml of 1 N hydrochloric acid. When the addition was complete, the contents of the flask were evaporated to dryness on a rotary flash evaporator. The white solid residue was dissolved in ca. 5 ml of chloroform (in air), and hexane was added until the solution became cloudy. Cooling the sample overnight at 0 °C results in the precipitation of 1.7 g (57%) of 1,4-dihydridooctaphenyltetrasilane. The product was further purified by recrystallization from chloroform–hexane; mp 160–162 °C (lit. mp 161–162 °C). The proton NMR spectrum in chloroform-d_1 consisted of an unsymmetrical singlet near 7.1 ppm and a sharp singlet at 5.02 ppm downfield from internal TMS. (19.3:1, calcd 20:1). The ir spectrum of 1,4-dihydridooctaphenyltetrasilane contains absorptions at 3060 (w), 3040 (w), 2108 (s), 1958 (vw, b), 1886 (vw, b), 1815 (vw, b), 1581 (w), 1480 (m), 1427 (s), 1300 (w), 1260 (w), 1189 (w), 1155 (w), 1115 (m, sh), 1098 (s), 1025 (w), 996 (w), 970 (vw), 840 (vw, sh), 790 (s), 757 (s), 735 (s, sh), 730 (s), 720 (vs), 694 (vs), 600 (vw, sh), 510 (w), 468 (m), 460 (m, sh), 420 (w), 375 (w), 345 (vw), 290 (m), and 280 (w, sh) cm^{-1}. **1,5-Dihydridodecaphenylpentasilane,** $H_2Si_5(C_6H_5)^{10}$, was prepared in 70% yield in a manner analogous to $H_2Si_4(C_6H_5)_8$, i.e., acid hydrolysis of $1,5\text{-}Li_2Si_5(C_6H_5)_{10}$; mp 143–145 °C (lit.[24] mp 147–148 °C). The proton NMR spectrum in chloroform-d_1 consisted of an unsymmetrical singlet near 7.0 ppm and a sharp singlet at 4.86 ppm downfield from internal TMS (24:1, calcd 25:1). Ir data: 3060 (w), 3040 (w), 2110 (s), 1960 (vw, b), 1884 (vw, b), 1820 (vw, b), 1581 (vw), 1568 (w), 1481 (m), 1428 (s), 1300 (w), 1311 (w), 1190 (w), 1158 (w), 1100 (s), 1028 (w), 998 (w), 793 (s), 760 (s), 740 (s), 732 (vs), 725 (vs), 698 (vs), 515 (w), 478 (m, sh), 470 (s), 462 (s, sh), 433 (w, sh), 420 (m), 378 (m), 345 (m), 293 (s), and 280 (w, sh) cm^{-1}.

Synthesis of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ by Oxidative Addition. Bis(triphenylphosphine)ethyleneplatinum(0) (1.0 mmol) was dissolved in ca. 5 ml of dry benzene maintained at 35 °C with stirring. A benzene solution (10 ml) of an equimolar quantity of 1,4-dihydridooctaphenyltetrasilane was slowly added. Immediately the solution bubbled vigorously and became more intensely orange, and a precipitate formed. After the last addition, the mixture was permitted to stir until the evolution of gas ceased, and then the flask was cooled to room temperature. The reaction mixture was filtered in air followed by the addition of hexane to the filtrate to precipitate 0.073 mmol of the bright yellow solid, $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$. The gas evolved during the course of the reaction was fractionated through a −126 °C trap (methylcyclopentane slush) and characterized as ethylene by comparison of its ir spectrum to that of an authentic sample. The evolved noncondensable gas, assumed to be H_2, was measured and the observed $H_2{:}C_2H_4$ molar ratio was found to be 1:1. Anal. Calcd for $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$: C, 69.7; H, 4.8; Pt, 13.5; P, 4.3; Si, 7.7. Found: C, 69.6; H, 4.8; Pt, 13.3; P, 4.7; Si (by difference), 7.6. The compound melts at 180 °C with decomposition to a red-brown solid and to a black solid above 230 °C. The low solubility of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ prevented a molecular weight determination. Ir data: 3050 (w), 1580 (w), 1475 (m), 1431 (m), 1425 (m), 1270 (vw), 1178 (w), 1152 (vw), 1112 (vw, sh), 1095 (s), 1060 (vw, sh), 1023 (w), 955 (w), 968 (vw), 845 (w), 746 (m), 740 (m, sh), 735 (m), 720 (w), 703 (vw), 698 (s, sh), 678 (s), 529 (s), 507 (s), 490 (m), 475 (s), 455 (w), 450 (w), 424 (w), 417 (w, sh), and 368 (m) cm^{-1}.

Attempted Synthesis of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ by Salt Elimination. In vacuo, *cis*-$[(C_6H_5)_3P]_2PtCl$ (in THF) was treated with an equimolar quantity of $1,4\text{-}Li_2Si_4(C_6H_5)_8$ in THF. While constant stirring was maintained, the silane was rapidly added to the platinum complex and the reaction mixture was allowed to reflux for several hours. The solvent was distilled from the flask under reduced pressure, benzene added, and the mixture filtered in air. The resulting gray solid was determined to be a mixture of octaphenyl-*cyclo*-tetrasilane and lithium chloride based on infrared data and the formation of a heavy white precipitate with silver nitrate solution. Hexane was added to the orange benzene filtrate until a yellow precipitate formed. The infrared spectrum of this precipitate somewhat resembled that of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ but in addition possessed a very strong absorption between 1200 and 1000 cm^{-1}, attributable to a major siloxane impurity. Attempts to purify the product by recrystallization from benzene–hexane as well as by high-pressure liquid chromatography were unsuccessful based on the persistence of the broad ir absorption.

Attempted Synthesis of $[CH_3(C_6H_5)_2P]_2PtSi_4(C_6H_5)_8$ by Salt Elimination. In vacuo, *cis*-$[CH_3(C_6H_5)_2P]_2PtCl_2$ (in THF) was treated with an equimolar quantity of 1,4-dilithiooctaphenyltetrasilane in THF. When the addition was complete, the reaction mixture was allowed to reflux, and over a period of several hours the color changed from yellow to dark orange. When the color appeared to remain constant, the THF was distilled from the flask and dry benzene added. The white precipitate, consisting mostly of octaphenyl-*cyclo*-tetrasilane and lithium chloride, was removed by filtration under an inert atmosphere. In a glovebag filled with dry nitrogen, dry hexane was added to the filtrate until it just turned cloudy. After 1 h, the mixture was filtered and the precipitate determined to be octaphenyl-*cyclo*-tetrasilane by its ir spectrum. Subsequent crystallizations of the filtrate with hexane yielded a yellow product whose ir spectrum indicated the presence of silane as well as platinum–phosphine species. The crude product was chromatographed on a high-pressure liquid chromatography column, eluted with 6% ethanol in chloroform. A pale yellow solid was isolated which retained the broad ir absorption in the 1000–1200-cm^{-1} region. Anal. Calcd for $[CH_3(C_6H_5)_2P]_2PtSi_4(C_6H_5)_8$: C, 67.1; H, 5.0; Pt, 14.7; P, 4.7; Si, 8.5. Found: C, 56.8; H, 5.0; Pt, 10.3; P, 6.3; Si, 3.6.

Attempted Synthesis of $[CH_3(C_6H_5)_2P]_2PtSi_4(C_6H_5)_8$ by Oxidative Addition. Tetrakis(methyldiphenylphosphine)platinum(0) (0.25 mmol) was treated with 1,4-$H_2Si_4(C_6H_5)_8$ (0.25 mmol) in a manner analogous to that described for the triphenylphosphine derivatives. During the course of the reaction hydrogen was evolved (0.20 mmol) and methyldiphenylphosphine was later detected by its distinctive odor. Work-up of the reaction mixture resulted in the isolation of 40 mg (12%) of a yellow solid. The infrared spectrum of the solid possessed several weak but discernible bands in the 600–250-cm^{-1} region which could be attributed to the presence of a polysilane on platinum. However, attempts to purify this solid by fractional crystallization from benzene–hexane apparently resulted in decomposition as evidenced by disappearance of the polysilane ir bands. Also isolated during the attempted recrystallization was octaphenyl-*cyclo*-tetrasilane, characterized by its ir spectrum. Anal. Calcd for $[CH_3(C_6H_5)_2P]_2PtSi_4(C_6H_5)_8$: Pt, 14.7; P, 4.7; mol wt 1323. Found: Pt, 11.7; P, 5.8; mol wt 1154.

Reactions of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$. Pyrolysis. A sublimation apparatus containing 15 mg (0.01 mmol) of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ was slowly heated to 210 °C and allowed to remain at that temperature for 2 h under a dynamic vacuum. During this period the color of the solid changed from bright yellow to red-brown, and a condensable material was evolved. No solid was detected on the cold finger of the sublimator. The ir spectrum of the red-brown product was essentially the same as that of the starting material except for the disappearance of the 678-cm^{-1} peak. Absorptions in the 600–250-cm^{-1} region were basically unchanged. The condensable material was determined to be benzene, 0.0095 mmol, from its ir spectrum. When another sample of I was heated above 260 °C, the red-brown intermediate afforded a white solid which collected on the sublimator cold finger and a black residue. The ir spectrum of the white sublimate indicated it to be a mixture of triphenylphosphine, octaphenyl-*cyclo*-tetrasilane, and a trace amount of benzene. The ir spectrum of the black solid revealed only very weak absorptions in the 1200–250-cm^{-1} region, somewhat resembling those attributable to a P–C_6H_5 linkage. The solid did not change its appearance even at 500 °C.

Bromine Reaction. A 20-mg (0.014-mmol) sample of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$, stirred in 2 ml of benzene, was treated with a solution of 4.4 mg (0.028 mmol) of bromine in 2 ml of dry hexane. The reaction proceeded rapidly as evidenced by the immediate discharge of the bromine color following each addition. After 1-h reaction time, hexane was added dropwise to the mixture until no further precipitation occurred; filtration in air resulted in isolation of an isomer mixture of bis(triphenylphosphine)platinum(II) bromide, characterized by a comparison of its ir spectrum with those of other *cis*- and *trans*-bis(triphenylphosphine)platinum(II) halides. Anal. Calcd: Br, 18.2. Found: Br, 17.9. The yield was 11.7 mg (97.5%). The pale yellow filtrate was concentrated, and addition of hexane resulted in the precipitation of a white solid, characterized as 1,4-dibromooctaphenyltetrasilane by comparison of its ir spectrum with that of an authentic sample and by its melting point (found 202–206 °C, lit.[24] 205–209 °C); yield 2.5 mg (21%).

Attempted Reaction with Hydrogen. Hydrogen gas was bubbled through a mixture of 25 mg of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ stirred in THF. After 2 h, during which time additional THF was added as required, the THF was allowed to evaporate yielding a yellow solid. The solid was determined to be starting material.

Reaction of $[(C_6H_5)_3P]_2Pt(C_2H_4)$ with 1,5-Dihydridodecaphenylpentasilane, $H_2Si_5(C_6H_5)_{10}$. $[(C_6H_5)_3P]_2Pt(C_2H_4)$ (1.0 g, 1.3 mmol) was dissolved in ca. 5 ml of dry benzene and treated dropwise with 1.2 g (1.3 mmol) of 1,5-$H_2Si_5(C_6H_5)_{10}$ dissolved in benzene. The reaction mixture was heated at 35 °C for 1 h during which time H_2 and C_2H_4 were evolved and a light cloudy precipitate formed. The metallosilane reaction product was isolated following the procedure described for the analogous tetrasilane reaction and consisted of I, 140 mg. The ir spectrum of this product and its decomposition temperature were found to be identical with those of $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$. Anal. Calcd for $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$: Pt, 13.5; P, 4.3. Calcd for $[(C_6H_5)_3P]_2PtSi_5(C_6H_5)_{10}$: Pt, 12.0; P, 3.8. Found: Pt, 13.4; P, 4.7.

Results and Discussion

In an effort to prepare *cyclo*-platiniosilane species, our investigations have included treatment of *cis*-$[(C_6H_5)_3P]_2PtCl_2$ with 1,4-dilithiooctaphenyltetrasilane, $Li_2Si_4(C_6H_5)_8$. Formation of *cyclo*-metallopolysilane does not take place in this system; however, octaphenyl-*cyclo*-tetrasilane, $Si_4(C_6H_5)_8$, results. This finding is consistent with our previous experience involving α,ω-dilithiopolysilanes and chloride sources such as C_6H_5Cl or K_2PtCl_2. These systems usually result in *cyclo*-polysilane formation with the chloride source functioning as a lithium sink. In a similar fashion, treatment of *cis*-bis(methyldiphenylphosphine)platinum(II) chloride, $[CH_3(C_6H_5)_2P]_2PtCl_2$, with $Li_2Si_4(C_6H_5)_8$ affords $Si_4(C_6H_5)_8$.[25]

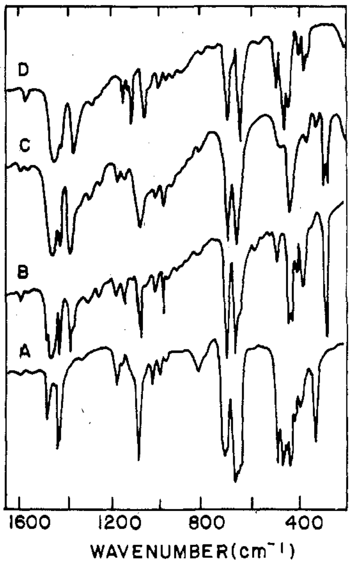

Figure 1. Infrared spectra of some *cyclo*-metallo related compounds: A, $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$; B, $Si_4(C_6H_5)_8$; C, $Si_5(C_6H_5)_{10}$; D, $[(C_6H_5)_3P]_2PtC_2H_4$.

Preparation and Characterization of Octaphenyl-*cyclo*-[bis(triphenylphosphine)]platinio(II)tetrasilane, $[(C_6H_5)_3P]_2Pt[Si(C_6H_5)_2]_3Si(C_6H_5)_2$. Treatment of bis(triphenylphosphine)ethyleneplatinum(0), $[(C_6H_5)_3P]_2PtC_2H_4$, with an equimolar quantity of 1,4-dihydridooctaphenyltetrasilane, $H_2Si_4(C_6H_5)_8$, results in the evolution of equal quantities of ethylene and dihydrogen, as well as formation of the bright yellow solid $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$ (I).

$$[(C_6H_5)_3P]_2PtC_2H_4 + HSi(C_6H_5)_2[Si(C_6H_5)_2]_2Si(C_6H_5)_2H$$
$$\rightarrow [(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8 + H_2 + C_2H_4$$

This synthesis affords the first example of a *cyclo*-silane incorporating a transition metal into a silicon ring. Additional characterization includes comparison of the ir spectrum of I with that of four- and five-membered *cyclo*-silanes as well as that for $[(C_6H_5)_3P]_2PtC_5H_4$, Figure 1. Absorptions in the region 1600–400 cm^{-1} are usually attributable to phenyl vibrations associated with P or Si.[26,27] With regard to polysilanes, both linear and cyclic, absorptions generally occur in the 400–250-cm^{-1} region which are sensitive to ring or chain size. Consequently, the *cyclo*-metallosilanes may be expected to exhibit unique absorptions as a result of ring size and, furthermore, silicon–silicon bond strengthening could result from Pt→Si $d\pi d\pi$ electron delocalization.

In the 400–250-cm^{-1} region, the expected absorptions are exhibited by all three *cyclo*-polysilanes while the absorptions near 400 cm^{-1} for $[(C_6H_5)_3P]_2PtC_2H_4$ have been assigned to coordinated olefin.[28] A predominant peak in this region is the strong absorption which occurs near 335 cm^{-1} in the case of $Si_4(C_6H_5)_8$ and $Si_5(C_6H_5)_{10}$ and is attributable to vibrations of the silicon–silicon bond.[18] In the case of the *cyclo*-metallosilane, the absorption which appears at 368 cm^{-1} is tentatively assigned to the Si–Si bond with an apparent high-energy shift of ca. 35 cm^{-1}. The explanation for this shift can best be rationalized in terms of the anticipated increase in Si–Si bond order.

Ultraviolet Spectroscopy. The uv spectral properties associated with *cyclo*-polysilanes have been reported and interpreted in terms of $\sigma \rightarrow \pi$ transitions with the σ state involving the electrons associated with the Si–Si bond while the π state is considered to arise from the overlapping 3d orbitals.[29] The ability of the σ state to exhibit nucleophilic character, in an intermolecular fashion, has recently been established with the isolation of adducts between permethylpolysilanes and tetracyanoethylene.[30,31]

When one examines the uv absorption spectrum of I and compares it to the spectra of other relevant species, it would appear that intramolecular charge transfer takes place in I. The relevant uv absorption data are as follows: *trans*-$(Bu_3P)_2PtCl_2$,[32] 3.800×10^4 cm^{-1}; $PtCl_4^{2-}$,[33] 1.77×10^4 cm^{-1} (ϵ 3), 2.1×10^4 cm^{-1} (ϵ 13), 2.5×10^4 cm^{-1} (ϵ 59), 3×10^4 cm^{-1} (ϵ 64), 3.79×10^4 cm^{-1} (ϵ 250), 4.6×10^4 cm^{-1} (ϵ 9580); *cis*-$[(C_6H_5)_3P]_2PtCl_2$,[25] 2.94×10^4 cm^{-1} (sh), 3.38×10^4 cm^{-1}; I, 3.73×10^4 cm^{-1} (ϵ 64 000), 3.39×10^4 cm^{-1} (ϵ 21 000), 3.07×10^4 cm^{-1} (ϵ 8600); $Si_5(CH_3)_{10}$,[29] 4.76×10^4 cm^{-1} (sh), 3.83×10^4 cm^{-1} (ϵ 1100), 3.68×10^4 cm^{-1} (ϵ 970); $Si_5(C_6H_5)_{10}$,[29] 3.98×10^4 cm^{-1} (ϵ 60 000).

Both $(Bu_2P)_2PtCl_2$ and $PtCl_4^{2-}$ have uv absorptions in the range 30 000–38 000 cm^{-1} but of relatively low intensity and these absorptions have been attributed to d–d transitions.[32,33] The spectrum of *cis*-$[(C_6H_5)_3P]_2PtCl_2$ was recorded as a mull; however no absorptions were recorded in the range 35 000–50 000 cm^{-1}. The intense absorption at 39 800 cm^{-1} for $Si_5(C_6H_5)_{10}$ has been attributed to a $\sigma \rightarrow \pi$ transition and is observed in both $Si(C_6H_5)_4$ and benzene. The intense absorption for I at 37 300 cm^{-1} is not present in the indicated Pt(II) complexes and is attributed to charge transfer from Pt filled d orbitals to a vacant conjugated 3d silicon MO.

Chemical Studies. Treatment of I with Br_2 is ideally described by

$$[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8 + 2Br_2 \rightarrow cis\text{-} + trans\text{-}[(C_6H_5)_3P]_2PtBr_2 + 1{,}4\text{-}Br_2Si_4(C_6H_5)_8$$

A 98% yield of platinum complexes was recovered while that of 1,4-dibromooctaphenyltetrasilane was 21%. In addition a yellow oil was obtained which could not be crystallized. Yellow oils have also been observed in analogous systems, i.e., cleavage of $Si_4(C_6H_5)_8$ by Br_2.

Dihydrogen was found not to react with I. This could be interpreted in terms of nonreactivity of I or oxidative cleavage of the Pt–Si bond by H_2 affording hydrido species followed by rapid dihydrogen elimination and Pt–Si bond re-formation.

Selective pyrolysis of I at 210 °C affords benzene while the accompanying residue decomposes at 280 °C to yield $(C_6H_5)_3P$ and $Si_4(C_6H_5)_8$. Formation of $Si_4(C_6H_5)_8$ apparently results as a consequence of reductive elimination from I while benzene arises from ortho proton exchange associated with two-coordinate Pt, $[(C_6H_5)_3P]_2Pt$. Similar benzene formations have been reported as a consequence of dissociation of SiF_4 from $[(C_6H_5)_3P]_2PtSiF_4$.[3]

Attempted Synthesis of Additional *cyclo*-Metallosilanes. Decaphenyl[bis(triphenylphosphine)]platinio(II)pentasilane, $[(C_6H_5)_3P]_2Pt[Si(C_6H_5)_2]_4Si(C_6H_5)_2$. Treatment of $[(C_6H_5)_3P]_2PtC_2H_4$ with 1,5-$H_2Si_5(C_6H_5)_{10}$ affords I rather than the expected $[(C_6H_5)_3P]_2PtSi_5(C_6H_5)_{10}$. A mechanism leading to formation of I may include removal of $Si(C_6H_5)_2$ from the metallocycles via a transition state involving Pt-coordinated diphenylsilene.

Octaphenyl[bis(methyldiphenylphosphine)]platinio(II)-tetrasilane. In an effort to prepare the methyldiphenylphosphine analogue of I, $[CH_3(C_6H_5)_2P]_4Pt$ was treated with $HSi(C_6H_5)_2[Si(C_6H_5)_2]_2Si(C_6H_5)_2H$. The failure to isolate a crystallizable *cyclo*-metallosilane from this reaction is presumably due to the stability of $[CH_3(C_6H_5)_2P]_4Pt$ in solution with regard to ligand dissociation and hence decreased tendency for the Pt to undergo hydrosilane oxidative addition.

Our studies are continuing on the preparation and reactivity of *cyclo*-metallosilanes with regard to reactivity changes as a consequence of metal employed, metal ligands, and specific moieties associated with silicon.

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Registry No. $[(C_6H_5)_3P]_2PtSi_4(C_6H_5)_8$, 58958-39-7; $[(C_6H_5)_3P]_2Pt(C_2H_4)$, 12120-15-9; *cis*-$[(C_6H_5)_3P]_2PtCl_2$, 15604-36-1; *cis*-$[CH_3(C_6H_5)_2P]_2PtCl_2$, 16633-72-0; $Si_4(C_6H_5)_8$, 1065-95-8; $Si_5(C_6H_5)_{10}$, 1770-54-3; 1,4-$Br_2Si_4(C_6H_5)_8$, 13529-76-5; 1,4-$H_2Si_4(C_6H_5)_8$, 18840-82-9; 1,5-$H_2Si_5(C_6H_5)_{10}$, 18849-09-7.

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