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Preparation, Spectroscopic Properties, and Reactivity of *trans*-Hydridoaryl and *trans*-Hydridomethyl Complexes of Platinum(II)

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trans-Hydridomethyl and *trans*-hydridoaryl complexes of platinum(II), *trans*-$PtH(R)L_2$, have been made by three general methods: (1) reaction of hydroxo complexes *trans*-$Pt(OH)RL_2$ with methanol ($R = C_6H_5$, L = P-*t*-Bu_2Me, P-*t*-$BuMe_2$, PEt_3, PPh_3; $R = CH_3$, L = P-*i*-Pr_3); (2) treatment of chloro or *N*-acetamido complexes *trans*-$PtXRL_2$ (X = Cl, $NHCOCH_3$) with methanolic sodium methoxide or with methanolic or ethanolic sodium borohydride ($R = C_6H_5$, L = P-*t*-Bu_2Me, P-*t*-$BuMe_2$, PPh_3, P-*i*-Pr_3; $R = CH_3$, $L = PPh_3$); (3) treatment of labile solvento salts *trans*-$[PtR(solv)L_2]BF_4$ (solv = methanol or acetone) with sodium methoxide or sodium borohydride ($R = C_6H_5$, L = PPh_3, PEt_3, PMe_3; $R = CH_3$, $L = PPh_3$). The use of methanol (method 1) or of sodium methoxide (methods 2 and 3) depends on the formation of thermally unstable methoxo complexes *trans*-$Pt(OCH_3)RL_2$, two of which ($R = C_6H_5$, $L = PEt_3$; $R = CH_3$, $L = PPh_3$) have been isolated in an impure state and identified spectroscopically. In two cases, the product from $NaBH_4$ reduction is contaminated with a thermally unstable trihydridoplatinum(IV) complex $PtH_3(R)L_2$ ($R = C_6H_5$; L = PEt_3, PMe_3). In contrast with the behavior of the corresponding cis isomers, reductive elimination of RH from *trans*-$PtH(R)L_2$ occurs only at elevated temperature, stability to heat and air being greater for complexes containing bulky phosphines. Loss of benzene from *trans*-$PtH(C_6H_5)(PEt_3)_2$ is facilitated by CO and inhibited by triethylphosphine. Dimethyl acetylenedicarboxylate inserts into the Pt–H bond of *trans*-$PtH(C_6H_4$-*p*-$Br)(PEt_3)_2$ to give the σ-vinyl complex *trans*-$Pt[Z$-$C(CO_2Me){=}CH(CO_2Me)](C_6H_4$-*p*-$Br)(PEt_3)_2$, but olefins such as ethylene, diethyl maleate, and acrylonitrile do not react. Acetonitrile reacts with *trans*-$PtH(C_6H_5)(PMe_3)_2$ to give benzene and *trans*-$PtH(CH_2CN)(PMe_3)_2$ as the main products, probably via an intermediate platinum(IV) oxidative-addition product, and trimethyltin hydride oxidatively adds to *trans*-$PtH(C_6H_5)(PEt_3)_2$ at −78 °C to give a thermally unstable platinum(IV) complex, $PtH_2(C_6H_5)(SnMe_3)(PEt_3)_2$, as a mixture of two isomers, identified by their ^1H and ^{31}P NMR spectra.

Introduction

Transition-metal complexes containing both hydride and σ-carbon-bonded ligands are of current interest since they are implicated as intermediates in homogeneously catalyzed hydrogenation of unsaturated hydrocarbons[1] and as the products of oxidative addition of C–H bonds to low-valent transition-metal complexes.[2] Although hydridoalkyl and hydridoaryl complexes of octahedral ruthenium(II) and osmium(II) in cis- and trans-isomeric forms were described almost 20 years ago,[3] remarkably few platinum(II) compounds of this class were known when we began our work. Most are of the type *trans*-$PtH(R)L_2$, in which the σ-bonded group is strongly electron withdrawing, e.g.: $L = PPh_3$, $R = CF_3$,[4] $C(CN)_3$,[5] CH_2CN,[6,7] $(CH_2)_3CN$;[6,8] $L = P(cy)_3$, $R = C_6F_5$, 1,3,5-$C_6H_2F_3$, 1,3-$C_6H_3F_2$; $L = PEt_3$, $R = C_6F_5$.[9] Compounds lacking electron-withdrawing substituents in the alkyl group include the (trimethylsilyl)methyl and phenyl derivatives ($L = PEt_3$; $R = CH_2SiMe_3$,[10] C_6H_5[11]), which were not isolated in a pure state, and the 1-cyclohexenyl complex ($L = PPh_3$; $R = C_6H_9$).[12] The only stable *cis*-hydridoalkyl complexes of platinum(II) contain electron-withdrawing alkyl groups and bidentate bis(tertiary phosphines) and bis(tertiary arsines), e.g. *cis*-$PtH(R)L_2$ ($R = CF_3$, L_2 = *cis*-$Ph_2PCH{=}CHPPh_2$;[4] $R = CH_2CN$, L_2 = *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$[7]). The complexes of this type that lack an electron-withdrawing substituent, e.g. those with $L = PPh_3$, $R = CH_3$, C_2H_5, $CH_2CH{=}CH_2$, C_6H_5, undergo rapid reductive elimination of RH even at −25 °C and have been characterized by NMR spectroscopy.[13] We reported in a preliminary communication[14] that monomeric hydroxo complexes of platinum(II) containing σ-methyl or σ-phenyl groups are useful precursors to the corresponding hydrido complexes, and we give full details of our work in this paper. Meanwhile an alternative synthesis of complexes of the type *trans*-$PtH(R)L_2$ has been described.[15] In the following paper[16] we report a systematic study of the variation of the spectroscopic parameters of *trans*-hydridoaryl complexes with the nature of the aryl group.

Experimental Section

IR spectra were measured on a PE457 instrument in Nujol mulls, KBr disks, or CH_2Cl_2 solutions, ^1H NMR spectra were recorded on Varian HA-100 or Jeol FX-60 instruments with Me_4Si or CH_2Cl_2 as internal reference, and $^{31}P\{^1H\}$ NMR spectra were recorded at 24.3 MHz on a modified Bruker 322S instrument with 85% H_3PO_4 as external reference. The ^1H NMR spectrum of an equimolar mixture of *trans*-$PtH(C_6H_5)(PEt_3)_2$ and trimethyltin hydride was recorded in CD_2Cl_2 at −78 °C on a Bruker HFX-270 instrument. Melting points and decomposition points were measured in open capillaries. Microanalyses (Table I) were performed by the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University. Solvents were AR grade and were degassed by passage of nitrogen. AR methanol was dried by distillation from magnesium methoxide and was stored under nitrogen over 3-Å molecular sieves. Reactions were carried out under nitrogen, and while most of the complexes were air

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Table I. Analytical Data and Melting Points for *trans*-PtH(R)L$_2$ Complexes

complex	mp, °C	calcd % C	calcd % H	found % C	found % H
PtH(C_6H_5)(P-*t*-Bu$_2$Me)$_2$[a]	166-168	48.55	8.15	48.55	8.1
PtH(C_6H_5)(P-*t*-BuMe$_2$)$_2$	125	42.4	7.1	42.4	6.9
PtH(C_6H_5)(PPh$_3$)$_2$[b]	170 (dec >125)	63.2	4.55	63.0	4.6
PtH(C_6H_5)(P-*i*-Pr$_3$)$_2$[c]	55-56 (dec >155)	48.55	8.15	48.4	8.2
PtH(C_6H_5)(PEt$_3$)$_2$	ca. 5	42.4	7.1	42.35	6.9
PtH(C_6H_4-*p*-Br)(PEt$_3$)$_2$[d]	78-80	36.7	6.0	37.2	6.2
PtH(C_6H_5)(PMe$_3$)$_2$	98-102 dec	33.9	5.7	33.8	5.7
PtH(CH_3)(PPh$_3$)$_2$	170 (dec >140)	60.4	4.7	60.0	4.9
PtH(CH_3)(P-*i*-Pr$_3$)$_2$	110 (dec >138)	42.9	8.7	42.7	8.45

[a] Mol wt (osmometry, CH_2Cl_2, 37 °C): calcd, 594; found, 592. [b] % P: calcd, 7.8; found, 8.5. [c] % P: calcd, 10.4; found, 10.7. [d] % Br: calcd, 13.6; found, 13.4.

stable when isolated, some required handling under nitrogen using conventional Schlenk-tube and syringe techniques.

The preparation of platinum(II) chloro, hydroxo, and *N*-acetamido complexes has been described.[17,18] The previously unreported complex *trans*-PtCl(C_6H_5)(P-*i*-Pr$_3$)$_2$ was made by reaction of an excess of P-*i*-Pr$_3$ with PtCl(C_6H_5)(1,5-COD)[19] and was recrystallized from *n*-hexane as colorless crystals, mp 118 °C: IR (Nujol) 274 cm^{-1} (ν(PtCl)); ^{1}H NMR (CD_2Cl_2) δ 1.21 (q, 36, $|{}^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})|$ = 14 Hz, ^3J(HH) = 7 Hz, PCH*Me*$_2$), 2.3 (m, 6, PC*H*Me$_2$), 6.5-8 (m, 5, C_6H_5). Anal. Calcd for $C_{24}H_{47}ClP_2Pt$: C, 45.9; H, 7.5; Cl, 5.6. Found: C, 46.3; H, 7.65; Cl, 5.5.

The complex *trans*-PtBr(C_6H_4-*p*-Br)(PEt$_3$)$_2$ was prepared by oxidative addition of *p*-dibromobenzene to Pt(PEt$_3$)$_4$.[16] The following preparations of hydridoalkyl and hydridoaryl complexes are representative of the methods used.

(1) *trans*-Hydridomethylbis(triisopropylphosphine)platinum(II), *trans*-PtH(CH_3)(P-*i*-Pr$_3$)$_2$, from the Corresponding Hydroxo Complex. A suspension of *trans*-Pt(OH)(CH_3)(P-*i*-Pr$_3$)$_2$ (0.043 g, 0.08 mmol) in dry methanol (5 mL) was stirred for 3 h at room temperature. The colorless crystals that deposited were filtered off under nitrogen and dried in vacuo, giving *trans*-PtH(CH_3)(P-*i*-Pr$_3$)$_2$ (0.023 g, 55%).

The complexes Pt(OH)(C_6H_5)L$_2$ (L = P-*t*-Bu$_2$Me, P-*t*-BuMe$_2$) reacted with methanol to give the corresponding hydrido complexes, identified by their characteristic ^{1}H NMR spectra.

(2) *trans*-Hydridophenylbis(triphenylphosphine)platinum(II), *trans*-PtH(C_6H_5)(PPh$_3$)$_2$, from the Corresponding Hydroxo Complex. A suspension of *trans*-Pt(OH)(C_6H_5)(PPh$_3$)$_2$ in dry methanol was heated to 65 °C. The solid dissolved rapidly to give a pale yellow solution from which colorless crystals precipitated over a 30-min period. After the mixture was cooled to room temperature, the solid was collected by filtration, washed with methanol, and identified by ^{1}H NMR and IR spectroscopy as pure *trans*-PtH(C_6H_5)(PPh$_3$)$_2$.

(3) *trans*-Hydridophenylbis(di-*tert*-butylmethylphosphine)platinum(II), *trans*-PtH(C_6H_5)(P-*t*-Bu$_2$Me)$_2$. A suspension of *trans*-PtCl(C_6H_5)(P-*t*-Bu$_2$Me)$_2$ (0.628 g, 1 mmol) in dry methanol (40 mL) was treated with sodium methoxide (0.15 g, 2.8 mmol), and the mixture was heated under reflux with stirring for 2 h. The solvent was evaporated under reduced pressure, and the residue was extracted with *n*-hexane (25 mL) and water (10 mL). The *n*-hexane layer was separated, filtered through activated charcoal, and dried (Na_2SO_4), and the solvent was evaporated to yield a colorless solid. Recrystallization from dichloromethane/methanol gave *trans*-PtH(C_6H_5)(P-*t*-Bu$_2$Me)$_2$ as colorless needles (0.44 g, 74%).

(4) *trans*-Hydridomethylbis(triphenylphosphine)platinum(II), *trans*-PtH(CH_3)(PPh$_3$)$_2$. A suspension of *trans*-Pt(CH_3)(NHCOCH$_3$)(PPh$_3$)$_2$ (0.069 g, 0.09 mmol) in methanol (5 mL) containing sodium methoxide (0.015 g, 0.28 mmol) was stirred and heated under reflux for 1 h. The solution was allowed to cool to room temperature, and the colorless solid was collected by filtration under nitrogen. After the solid was dried in vacuo, the yield of *trans*-PtH(CH_3)(PPh$_3$)$_2$ was 0.048 g (75%).

(5) *trans*-Hydridophenylbis(triphenylphosphine)platinum(II), *trans*-PtH(C_6H_5)(PPh$_3$)$_2$. A suspension of *trans*-PtCl(C_6H_5)(PPh$_3$)$_2$ (0.208 g, 0.25 mmol) in methanol (20 mL) was heated to 60 °C and treated with AgBF$_4$ (0.049 g, 0.25 mmol) dissolved in the minimum volume of methanol. The mixture was stirred vigorously for 2 h, AgCl was removed by filtration, and the filtrate was treated with solid sodium methoxide (0.02 g). When the mixture was warmed to 65 °C for 30 min, colorless crystals formed rapidly. After the solution had been allowed to cool to room temperature, the solid was filtered off, washed with methanol, and dried. Recrystallization from dichloromethane/methanol gave colorless crystalline *trans*-PtH(C_6H_5)(PPh$_3$)$_2$ (0.16 g, 80%).

(6) *trans*-Methoxomethylbis(triphenylphosphine)platinum(II), *trans*-Pt(OCH_3)(CH_3)(PPh$_3$)$_2$, and Its Conversion into *trans*-PtH(CH_3)(PPh$_3$)$_2$. A mixture of *trans*-PtI(CH_3)(PPh$_3$)$_2$ (0.21 g, 0.25 mmol) and AgBF$_4$ (0.048 g, 0.25 mmol) in benzene (15 mL) and methanol (5 mL) was stirred at ca. 40 °C or 2 h. After the AgI had been removed by filtration and washed with dichloromethane (10 mL), the combined filtrate and washings were evaporated to dryness. The resulting white solid was suspended in dry methanol (15 mL), and sodium methoxide (0.02 g, 0.37 mmol) was added with stirring. The colorless crystals that formed within a few minutes were filtered, washed successively with water and methanol, and dried in vacuo. The complex was identified as impure *trans*-Pt(OCH_3)(CH_3)(PPh$_3$)$_2$ on the basis of its ^{1}H NMR spectrum in CD_2Cl_2: δ -0.33 (t with ^{195}Pt satellites, PtCH$_3$, ^3J(PH) = 6.3 Hz, ^2J(PtH) = 72 Hz), 2.51 (s with ^{195}Pt satellites, OCH$_3$, ^3J(PtH) = 25 Hz).

The solid was suspended in dry methanol and heated under reflux with stirring for 2 h. After being allowed to cool to room temperature, the solution was filtered and the solid was dried in vacuo. It was identified as impure *trans*-PtH(CH_3)(PPh$_3$)$_2$ by its ^{1}H NMR and IR spectra.

(7) *trans*-Methoxophenylbis(triethylphosphine)platinum(II), *trans*-Pt(OCH_3)(C_6H_5)(PEt$_3$)$_2$, and Its Conversion into *trans*-PtH(C_6H_5)(PEt$_3$)$_2$. Reaction of *trans*-PtCl(C_6H_5)(PEt$_3$)$_2$ with AgBF$_4$ in acetone and treatment of the resulting salt with NaOCH$_3$ as described by Coulson[20] gave impure *trans*-Pt(OCH_3)(C_6H_5)(PEt$_3$)$_2$ as a pale yellow oil. ^{1}H NMR: (C_6D_6) δ 3.80 (s with ^{195}Pt satellites, OCH$_3$, ^3J(PtH) = 27 Hz); (CD_2Cl_2) δ 3.51 (^3J(PtH) = 26 Hz). Attempted purification of this product led to rapid decomposition to dark, oily products. ^{1}H NMR spectra in C_6D_6 showed that *trans*-PtH(C_6H_5)(PEt$_3$)$_2$ was one of the species present.

A similar procedure starting with *trnas*-PtCl(C_6H_5)(PMe$_2$Ph)$_2$ gave an impure brown oil containing ca. 65% *trans*-Pt(OCH_3)(C_6H_5)(PMe$_2$Ph)$_2$, as estimated by integration of the ^{1}H NMR spectrum. ^{1}H NMR (CD_2Cl_2): δ 3.4 (s with ^{195}Pt satellites, OCH$_3$, ^3J(PtH) = 26 Hz). Attempted recrystallization from *n*-pentane at low temperatures did not give a pure product.

(8) *trans*-Hydridophenylbis(triethylphosphine)platinum(II), *trans*-PtH(C_6H_5)(PEt$_3$)$_2$. A solution of *trans*-PtCl(C_6H_5)(PEt$_3$)$_2$ (0.272 g, 0.5 mmol) in dry methanol (5 mL) was treated with AgBF$_4$ (0.097 g, 0.5 mmol) in dry methanol (2 mL). The mixture was stirred for 10 min at room temperature, and the precipitated AgCl was filtered off under nitrogen and washed with two 2-mL portions of methanol. The combined filtrate and washings were cooled to -40 °C, and solid NaBH$_4$ (0.019 g, 0.5 mmol) was added in several portions. After ca. 5 min, a white solid precipitated, which dissolved with evolution of gas as the temperature was allowed to rise to ca. 20 °C over 30 min. The pale yellow solution was evaporated to dryness at ca. 20

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°C, and the oily solid residue was extracted with three 10-mL portions of *n*-pentane. The extract was filtered through Celite and evaporated to give *trans*-$PtH(C_6H_5)(PEt_3)_2$ as a colorless oil in almost quantitative yield. Recrystallization from isopentane (3 mL) at −78 °C gave colorless needles (0.14 g, 55%), which were separated by decantation of the mother liquor at −78 °C and dried in vacuo while the temperature was allowed to rise slowly. The solid melted at ca. 5 °C to a colorless oil that still contained solvent as shown by elemental analysis. Pumping at room temperature caused the oil to darken. An analytical sample was finally obtained by allowing the crystals to just melt, pumping at 10^{-5} mm/<10 °C, and then analyzing immediately, the sample being handled under nitrogen.

In some preparations the crude product contained up to ca. 10% of an impurity that was identified as ***trans-mer*-trihydridophenylbis(triethylphosphine)platinum(IV)**, $PtH_3(C_6H_5)(PEt_3)_2$, on the basis of its spectroscopic properties: IR (thin film) 1780 (br) cm^{-1} (ν(PtH) for *trans*-HPtH); ^1H NMR (C_6D_6) δ −13.22 (br tt, PtH trans to C_6H_5, $^1J(PtH) = 598$ Hz, $^2J(PH) = 15$ Hz, $^2J(HH, cis) = 3.7$, $^4J(HH$, *o*-$C_6H_5) =$ ca. 2 Hz), −9.48 (dt, PtH, $^1J(PtH) = 701$ Hz, $^2J(PH) = 14.7$ Hz, $^2J(HH, cis = 3.7$ Hz); $^{31}P\{^1H\}$ NMR (toluene, −50 °C) δ 5.5 ($^1J(PtP) = 1917$ Hz). This complex could not be separated from *trans*-$PtH(C_6H_5)(PEt_3)_2$ but decomposed more rapidly than the latter.

(9) *trans*-Hydrido(*p*-bromophenyl)bis(triethylphosphine)platinum(II), *trans*-PtH(C_6H_4-*p*-Br)(PEt_3)$_2$. A solution of $AgBF_4$ (0.49 g, 0.25 mmol) in methanol (5 mL) was added dropwise to a solution of *trans*-PtBr(C_6H_4-*p*-Br)$(PEt_3)_2$ (0.167 g, 0.25 mmol) in dichloromethane (3 mL). After removal of AgBr by filtration, the colorless solution was cooled to −50 °C and solid $NaBH_4$ (0.095 g, 0.25 mmol) was added to one portion. The white precipitate that formed initially dissolved with effervescence as the solution was allowed to warm to room temperature over ca. 30 min. Solvents were removed by evaporation, and the residue was extracted with *n*-hexane (10 mL). After concentration and cooling to −30 °C, colorless needles of *trans*-PtH(C_6H_4-*p*-Br)$(PEt_3)_2$ (0.115 g, 78%) were obtained.

(10) *trans*-Hydridophenylbis(trimethylphosphine)platinum(II), *trans*-$PtH(C_6H_5)(PMe_3)_2$. This was prepared similarly to the analogous PEt_3 compound by addition of $NaBH_4$ (ca. 0.015 g) to a solution prepared from *trans*-$PtCl(C_6H_5)(PMe_3)_2$ (0.153 g, 0.33 mmol) and $AgBF_4$ (0.065 g, 0.33 mmol) in dichloromethane/methanol. The resulting pale brown solution was evaporated to dryness, and the solid residue was extracted briefly with dichloromethane (7 mL). The solution was filtered, treated with methanol (7 mL), concentrated in vacuo, and cooled to −50 °C. The colorless crystals that separated were filtered at −78 °C, washed with methanol, and dried in vacuo to give 0.079 g (56%) of *trans*-$PtH(C_6H_5)(PMe_3)_2$. An analytically pure sample was obtained by recrystallization from ether/*n*-pentane.

The crude product obtained by extraction of the original solid residue with *n*-hexane was contaminated with a small amount of a compound having IR bands at 1978 and 1765 cm^{-1}, in addition to the band due to *trans*-$PtH(C_6H_5)(PMe_3)_2$ at 1926 cm^{-1}. The impurity is believed to be *trans-mer*-$PtH_3(C_6H_5)(PMe_3)_2$. When a *n*-hexane solution of the mixture was cooled, the mother liquor was enriched in the platinum(IV) complex but the complex could not be obtained in a pure state owing to its rapid decomposition and the small quantities in which it was formed.

(11) *trans*-Hydridophenylbis(*tert*-butyldimethylphosphine)platinum(II), *trans*-PtH(C_6H_5)(P-*t*-Bu_2Me)$_2$. To a solution of *trans*-$PtCl(C_6H_5)$(P-*t*-Bu_2Me)$_2$ (0.055 g, 0.1 mmol) in absolute ethanol (5 mL) was added $NaBH_4$ (0.02 g, 0.53 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure, and the residue was extracted with *n*-hexane (5 mL) and water (5 mL). The *n*-hexane layer was separated, filtered through activated charcoal, dried (Na_2SO_4), and evaporated to give *trans*-$PtH(C_6H_5)$(P-*t*-Bu_2Me)$_2$ quantitatively as colorless crystals.

Thermal Decomposition of *trans*-PtH(C_6H_5)(PEt_3)$_2$ in Various Solvents. (1) Cyclohexane. When a solution of *trans*-$PtH(C_6H_5)(PEt_3)_2$ in C_6H_{12} or C_6D_{12} was heated in a sealed NMR tube at 65 °C, it decomposed within 1 h, forming platinum metal, benzene, and three phosphorus-containing species, which showed singlets with ^{195}Pt satellites in their $^{31}P\{^1H\}$ NMR spectra. The major product was $Pt(PEt_3)_3$ (δ_P 41.8, $^1J(PtP) = 4224$ Hz; lit.[21] δ_P 42.2, $^1J(PtP) = 4231$ Hz in *n*-heptane). The unidentified minor products had δ_P 21.3, $^1J(PtP) = 3550$ Hz and δ_P 14.4, $^1J(PtP) = 2830$ Hz, peak heights being in the ratio 16:3:2, respectively.

(2) *n*-Decane. In this solvent there was an induction period of nearly 1 h at 70 °C, then the solution rapidly turned black. Benzene was identified by GC/MS and by ^1H NMR spectroscopy.

(3) Methylcyclohexane. At 45 °C there was an induction period of 6 h. Most of the complex then decomposed over a period of 1 h, and the rest decomposed slowly over a further 5 h. As judged by their ^{31}P NMR spectra, the products appeared to be the same as those formed in cyclohexane and were formed in similar proportions.

(4) Cyclohexane Containing Triethylphosphine. When experiment 1 was repeated in the presence of 1 mol of triethylphosphine, the solution remained clear and no benzene could be detected after 1 h. The hydride resonance of the complex was still present although ^{31}P coupling was no longer observed.

Reaction of *trans*-PtH(C_6H_5)(PEt_3)$_2$ with CO. Carbon monoxide was bubbled through a solution of *trans*-$PtH(C_6H_5)(PEt_3)_2$ in *n*-hexane at room temperature. After 45 min the solution became pale yellow and then darkened to orange and finally red. Initially the solution showed IR ν(CO) bands at 1988 and 1947 cm^{-1}, probably due to $Pt(CO)_2(PEt_3)_2$ (lit.[22] 1973, 1931 cm^{-1} in THF). Subsequently these bands decreased in intensity and were replaced by strong bands at 1930 and 1766 cm^{-1} due to unidentified cluster compounds.

A similar experiment carried out in an NMR tube at −20 °C showed that benzene was formed within 20 min of continuous bubbling of CO.

Reaction of *trans*-PtH(C_6H_4-*p*-Br)(PEt_3)$_2$ with Dimethyl Acetylenedicarboxylate. A mixture of *trans*-PtH(C_6H_4-p-Br)$(PEt_3)_2$ (0.12 g, 0.2 mmol) and dimethyl acetylenedicarboxylate (30 μL, 0.25 mmol) in *n*-hexane was heated under reflux for 45 min. The colorless crystals that had begun to form within ca. 10 min were separated from the yellow mother liquor and washed by decantation with *n*-pentane. Recrystallization from dichloromethane/*n*-hexane gave colorless crystals of *trans*-Pt(C_6H_4-*p*-Br)$[C(CO_2Me){=}CH(CO_2Me)](PEt_3)_2$, mp 168 °C dec (0.05 g, 33%). Anal. Calcd for $C_{24}H_{41}BrO_4P_2Pt$: C, 39.5; H, 5.7; Br, 10.9. Found: C, 39.6; H, 5.75; Br, 11.2. IR (cm^{-1}, Nujol): 1712, 1700, 1202, 1163 (all s) (ester), 1571 m(C=C). ^1H NMR (CD_2Cl_2): δ 3.63, 3.65 (each s, 6, CO_2CH_3), 6.88 (t with ^{195}Pt satellites, 1, $^3J(PtH) = 72$, $^4J(PH) = 2.2$ Hz, $C\mathit{H}CO_2CH_3$). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 4.8 ($^1J(PtP) = 2771$ Hz).

Under similar conditions *trans*-PtH(C_6H_4-*p*-Br)$(PEt_3)_2$ did not react with acrylonitrile in refluxing *n*-hexane or methanol nor with diethyl maleate in refluxing toluene. No insertion product could be isolated from the attempted reaction of the hydride with acrylonitrile in refluxing methanol, though a small amount of $CH_3OCH_2CH_2CN$ was formed, as shown by ^1H NMR spectroscopy.

Results and Discussion

We have shown[12] that the cyclohexyne platinum(0) complexes $Pt(C_6H_8)L_2$ (L_2 = 2 PPh_3, dppe) differ markedly in their reactions with alcohols. When it is heated with methanol or ethanol, the triphenylphosphine derivative gives a hydrido(η^1-cyclohexenyl) complex, *trans*-$PtH(C_6H_9)(PPh_3)_2$, whereas the dppe derivative gives a methoxo complex, $Pt(OCH_3)(C_6H_9)$(dppe), which is thermally stable but is readily hydrolyzed to the corresponding hydroxo complex $Pt(OH)(C_6H_9)$(dppe). The hydride is probably formed by β elimination of the appropriate aldehyde from the thermally unstable alkoxo complexes *trans*-$Pt(OR)(C_6H_9)(PPh_3)_2$ (R = CH_3, C_2H_5).

In the light of these results, it is not surprising that when the hydroxo complexes *trans*-$Pt(OH)(C_6H_5)L_2$ (L = P-*t*-Bu_2Me, P-*t*-BuMe_2, and PEt_3) and *trans*-$Pt(OH)(CH_3)$(P-*i*-Pr_3)$_2$[17] are dissolved in methanol or aqueous methanol at room temperature the corresponding colorless, crystalline hydrido complexes *trans*-$PtH(C_6H_5)L_2$ and *trans*-$PtH(CH_3)$(P-*i*-Pr_3)$_2$ can be isolated in 50–60% yield. A similar reaction to give *trans*-$PtH(C_6H_5)(PPh_3)_2$ occurs when *trans*-$Pt(OH)(C_6H_5)(PPh_3)_2$ is heated under reflux in methanol. We have found a number of routes to the hydrido complexes that do not require prior isolation of the hydroxo complexes (Scheme I). Thus, when the complex *trans*-$PtCl(C_6H_5)$-

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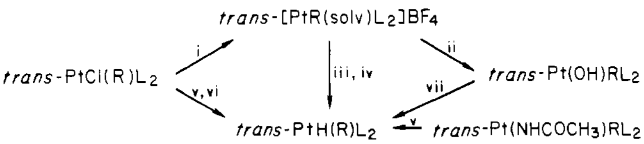
Scheme I. Preparation of *trans*-$PtH(R)L_2$[a]



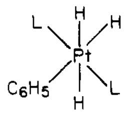
[a] Legend: (i) $AgBF_4$, solv = acetone or methanol; (ii) KOH(aq), solv = acetone; (iii) $NaOCH_3/CH_3OH$, 65 °C, solv = methanol, R = C_6H_5, CH_3, L = PPh_3; (iv) $NaBH_4$, solv = methanol, R = C_6H_5, L = PPh_3, PEt_3, PMe_3; (v) $NaOCH_3/CH_3OH$, 65 °C, R = C_6H_5, L = P-*t*-Bu_2Me, PPh_3, P-*i*-Pr_3, R = CH_3, L = PPh_3; (vi) $NaBH_4/CH_3OH$, R = C_6H_5, L = P-*t*-Bu_2Me; $NaBH_4/C_2H_5OH$, R = C_6H_5, L = P-*t*-$BuMe_2$; (vii) CH_3OH, 25 °C, R = C_6H_5, L = P-*t*-Bu_2Me, P-*t*-$BuMe_2$, PEt_3, R = CH_3, L = P-*i*-Pr_3; CH_3OH, 65 °C, R = C_6H_5, L = PPh_3.

$(PPh_3)_2$ is heated in benzene/methanol with a threefold excess of sodium methoxide, the hydrido complex *trans*-$PtH(C_6H_5)(PPh_3)_2$ is formed directly, and this method has also been used successfully to prepare the phenyl complexes containing P-*t*-Bu_2Me and P-*i*-Pr_3. Low yields of impure *trans*-$PtH(C_6H_5)(PPh_3)_2$ are obtained by this method owing to the poor solubility of the starting material, *trans*-$PtI(CH_3)(PPh_3)_2$, in the reaction medium; higher yields and purer product are obtained by employing the *N*-acetamido complex *trans*-$Pt(NHCOCH_3)(CH_3)(PPh_3)_2$.[18]

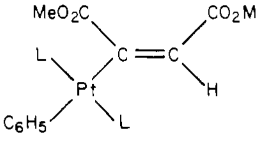
All these reactions undoubtedly proceed via the methoxo complexes *trans*-$Pt(OCH_3)RL_2$, and evidence for their intermediacy has been obtained in several cases. Addition of sodium methoxide or sodium hydroxide to a methanolic solution of *trans*-$[Pt(C_6H_5)(MeOH)(PEt_3)_2]BF_4$, generated in situ by treatment of *trans*-$PtCl(C_6H_5)(PEt_3)_2$ with $AgBF_4$ in methanol, gives a methoxo complex, *trans*-$Pt(OCH_3)(C_6H_5)(PEt_3)_2$, as reported by Coulson.[20] The ^1H NMR spectrum of the crude oily product exhibits values of $\delta(OCH_3)$ and $^3J(PtOCH_3)$ in agreement with those cited, but when the product is allowed to stand, the methoxyl resonance disappears and is replaced by a triplet at δ -6.67 (C_6D_6) due to the hydride proton of *trans*-$PtH(C_6H_5)(PEt_3)_2$. Similar behavior is observed in the corresponding PMe_2Ph system, although all attempts to isolate pure *trans*-$PtH(C_6H_5)(PMe_2Ph)_2$ by this or any of the other methods described in this paper were unsuccessful. Addition of $NaOCH_3$ to *trans*-$[Pt(CH_3)(CH_3OH)(PPh_3)_2]BF_4$ gives an immediate precipitate of impure *trans*-$Pt(OCH_3)(CH_3)(PPh_3)_2$, the ^1H NMR spectrum of which shows a singlet with ^{195}Pt satellites due to the methoxyl protons at δ 2.51 ($^3J(PtOCH_3)$ = 25 Hz) and a triplet with ^{195}Pt satellites due to Pt–CH_3 at δ -0.33 ($^3J(PH)$ = 6.3 Hz, $^2J(PtH)$ = 72 Hz). When it is heated in methanol, this compound decomposes to give impure *trans*-$PtH(CH_3)(PPh_3)_2$. Thermally stable methoxo complexes of the type *trans*-$Pt(OCH_3)RL_2$ have been obtained only when strongly electron-withdrawing groups R are present.[23]

Sodium borohydride can be used in place of sodium methoxide as a reducing agent in some of the preparations. For example, treatment of *trans*-$PtCl(C_6H_5)$(P-*t*-$Bu_2Me)_2$ with methanolic $NaBH_4$, or of *trans*-$PtCl(C_6H_5)$(P-*t*-$BuMe_2$) with ethanolic $NaBH_4$, gives good yields of the hydrides *trans*-$PtH(R)L_2$. Addition of $NaBH_4$ to the solvento cation *trans*-$[Pt(C_6H_5)(MeOH)(PEt_3)_2]^+$ in methanol below -40 °C precipitates colorless crystals, which dissolve with gas evolution on warming to ca. -15 °C. The crystals are stable under nitrogen at -40 °C but rapidly become oily and black in air at room temperature. Room-temperature workup of the reaction mixture gives *trans*-$PtH(C_6H_5)(PEt_3)_2$ in high yield. Attempts to measure the ^1H NMR spectrum of the intermediate have been thwarted by its thermal instability. Although decomposition occurred during the measurements, the IR spectra of Nujol mulls showed bands at ca. 2380, 1670, and 1260 cm^{-1} suggestive of the presence either of a η^2-tetrahydridoborate complex, e.g. $Pt(BH_4)(C_6H_5)(PEt_3)_2$ or of a borohydride salt such as $[Pt(C_6H_5)(MeOH)(PEt_3)_2]BH_4$.[24] Such a compound could react with methanol to give hydrogen and *trans*-$PtH(C_6H_5)(PEt_3)_2$. η^2-Tetrahydridoborate complexes of the later transition elements stabilized by bulky phosphines are known, e.g. *trans*-$MH(BH_4)L_2$ (M = Ni, Pd; L = $P(cy)_3$, P-*i*-Pr_3),[25] $IrH_2(BH_4)L_2$ (L = P-*t*-Bu_3, P-*t*-$BuMe_2$, P-*t*-Bu_2(*p*-MeC_6H_4)),[26] $RuH(BH_4)L_3$ (L = PPh_3, $PMePh_2$),[27,28] and $RuH(BH_4)$(ttp) (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$).[29]

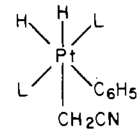
The ^1H NMR spectra of the crude products from $NaBH_4$ reduction of *trans*-$[Pt(C_6H_5)(MeOH)L_2]^+$ (L = PMe_3, PEt_3) occasionally showed the presence of ca. 10% of a second hydrido complex in addition to *trans*-$PtH(C_6H_5)L_2$. The triethylphosphine complex has been characterized on the basis of its IR spectrum and ^1H and $^{31}P\{^1H\}$ NMR spectra (see later) as the trihydridoplatinum(IV) complex *mer*-$PtH_3(C_6H_5)(PEt_3)_2$ (**1**), containing *trans*-PEt_3 ligands. These byproducts are thermally unstable and do not survive the recrystallization step needed to obtain pure *trans*-$PtH(R)L_2$.



1 (L = PEt_3)



2 (L = PEt_3)



3 (L = PMe_3)

All preparations of *trans*-$PtH(CH_3)$(P-*i*-$Pr_3)_2$ carried out with use of methanolic sodium methoxide or sodium borohydride as described above give a product contaminated with *trans*-PtH_2(P-*i*-$Pr_3)_2$, identified by comparison of its IR spectra (ν(PtH)) and ^1H NMR spectra (δ(PtH)) with those reported.[30,31] This byproduct presumably arises by methanolysis or hydrogenolysis of the Pt–CH_3 bond under the reaction conditions. The pure complex *trans*-$PtH(CH_3)$(P-*i*-$Pr_3)_2$ is best obtained either by the reaction between $Pt(OH)(CH_3)$(P-*i*-$Pr_3)_2$ and methanol at room temperature or by the reaction between *trans*-$PtHCl$(P-*i*-$Pr_3)_2$ and methylmagnesium bromide reported recently by Halpern and co-workers.[15]

All the *trans*-hydridophenyl complexes reported here are colorless, crystalline solids whose stability to heat, light, and air is markedly dependent on the nature of the tertiary phosphine. Melting points, approximate decomposition temperatures in air, and elemental analyses are given in Table I. The complexes of alkylphosphines are readily soluble in most common organic solvents including saturated hydrocarbons, whereas the triphenylphosphine complex is soluble in benzene but insoluble in *n*-hexane. The complex *trans*-$PtH(C_6H_5)$(P-*t*-$Bu_2Me)_2$ is particularly stable; it remains colorless and crystalline for many months in air and requires no precautions in handling and storage. In contrast, the triethylphosphine analogue is difficult to isolate pure owing to its high solubility

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Table II. Spectroscopic Data for Hydridoplatinum(II) Complexes *trans*-$PtH(R)L_2$[a]

complex	IR[b]	^1H NMR[c]				^{31}P NMR[d]	
	$\nu(PtH)$	$\delta(PtH)$	$^1J(PtH)$	$^2J(PH)$	$\delta(L)$ or $\delta(R)$[e]	$\delta(P)$	$^1J(PtP)$
$PtH(C_6H_5)(P\text{-}t\text{-}Bu_2Me)_2$	1956	−6.34	600	18.0	1.00 (t, PCH_3, "$J(PH)$" = 6.5, $^2J(PtH)$ = 33), 1.35 (t, P-*t*-Bu, "$J(PH)$" = 14)	49.6	2927
$PtH(C_6H_5)(P\text{-}t\text{-}BuMe_2)_2$	1992[f]	−6.83	640	18.3	nm	16.6	2803
$PtH(C_6H_5)(PPh_3)_2$	1890[g]	−5.71	600	18.3	7.2–7.9 (m, Ph)	31.0[h]	3120
$PtH(C_6H_5)(P\text{-}i\text{-}Pr_3)_2$	1968	−8.32	588	18.0	1.15 (q, $PCHCH_3$, "$J(PH)$" = 13), 2.16 (m, $PCHCH_3$)	55.9	3425
$PtH(C_6H_5)(PEt_3)_2$	1940[i]	−6.67[j]	648	19.0	1.05 (qn, PCH_2CH_3, "$J(PH)$" = 15), ca. 1.65 (m, PCH_2CH_3)	17.3[k]	2800
$PtH(C_6H_4\text{-}4\text{-}Br)(PEt_3)_2$	1952[l]	−6.85[m]	650	19.0	nm	17.0	2773
$PtH(C_6H_5)(PMe_3)_2$	1926	−5.74	678	20.6	1.13 (t, PCH_3, "$J(PH)$" = 6.5, $^2J(PtH)$ = 33)	−21.0	2710
$PtH(C_6H_5)(PMe_2Ph)_2$[n]	1945	−6.10	664	19.5	1.50 (t, PCH_3, "$J(PH)$" = 7, $^2J(PtH)$ = 38)	nm	nm
$PtH(CH_3)(PPh_3)_2$	1936[o]	−3.77	656	18.3	−0.41 (dt, $PtCH_3$, $^2J(PtH)$ = 52, $^3J(PH)$ = 5, $^3J(HPtCH)$ = 2.2), 7.2–7.9 (m, Ph)	nm	nm
$PtH(CH_3)(P\text{-}i\text{-}Pr_3)_2$	1927	−6.80[p]	648	17.1	−0.09[q] (dt, $PtCH_3$, $^2J(PtH)$ = 54, $^3J(PH)$ = 4.5, $^3J(HPtCH)$ = 2.4), 1.06 (q, $PCHCH_3$, "$J(PH)$" = 13), 2.20 (m, $PCHCH_3$)	nm	nm

[a] Abbreviations: nm, not measured; t, triplet; dt, double triplet; q, quartet; qn, quintet; m, multiplet. [b] In Nujol, except where indicated. [c] In CH_2Cl_2 or CD_2Cl_2, except where indicated. Aromatic resonances C_6H_5Pt were multiplets in the range δ 6.8–8.0. Coupling constants (J) are in Hz. [d] In C_6H_6, except where indicated. [e] "$J(PH)$" = $|^2J(PH) + {}^4J(PH)|$ for P-CH_3 and $|^3J(PH) + {}^5J(PH)|$ for P–C–CH_3. [f] 1990, 1965 sh, 1925 cm^{-1} (KBr disk), 1953 cm^{-1} (CH_2Cl_2). [g] 1966 cm^{-1} (CH_2Cl_2). [h] In CH_2Cl_2. [i] Liquid film. [j] Lit.[11] δ −7.05, J = 648, 19 Hz ($(CD_3)_2CO$). [k] Lit.[11] δ 17.3, J = 2796 Hz ($(CD_3)_2CO$). [l] In acetone. [m] In C_6D_6. [n] Not purified. [o] 1968 cm^{-1} (CH_2Cl_2). [p] Lit.[15] δ −6.19, J = 641.8, 17.2 Hz ($C_6D_5CD_3$). [q] Lit.[15] δ 0.64, J = 52.7, 49, 2.3 Hz ($C_6D_5CD_3$).

and thermal instability. Colorless needles are obtained by crystallization from a concentrated solution in isopentane at −78 °C, but the compound liquefies at ca. 5 °C even under high vacuum. The liquid is not stable to air or light for more than a few hours at room temperature, but it is more stable in solution in benzene or *n*-pentane, where it can be stored for at least 24 h at room temperature in the absence of light. The solid complex is stable for long periods under nitrogen at −20 °C. The trimethylphosphine analogue *trans*-$PtH(C_6H_5)(PMe_3)_2$ is a colorless crystalline solid that is unstable in benzene or dichloromethane solution at room temperature.

The hydridomethyl complexes are more sensitive to air and light than the corresponding hydridophenyl complexes. Solid *trans*-$PtH(CH_3)(PPh_3)_2$ becomes yellow even under nitrogen at room temperature, and solutions in dichloromethane lose the characteristic $\nu(PtH)$ band on standing. The P-*i*-Pr_3 analogue can be stored under nitrogen at 0 °C for several months.

Spectroscopic data for the *trans*-$PtH(R)L_2$ complexes are summarized in Table II. The IR spectra in Nujol mulls or dichloromethane solution show an intense, broad band in the region 1900–2000 cm^{-1} assigned to $\nu(PtH)$. In several cases the band maximum shifts by 30–70 cm^{-1} to higher frequency from solid state to solution, e.g. for *trans*-$PtH(C_6H_5)(PPh_3)_2$ $\nu(PtH)$ is 1890 cm^{-1} in Nujol and 1966 cm^{-1} in dichloromethane cf. for *trans*-$PtH(C_6H_9)(PPh_3)_2$, 1940, 1855 cm^{-1} (KBr disk) and 1920 cm^{-1} (CH_2Cl_2)).[12] These values of $\nu(PtH)$ are lower than those observed for complexes of the type *trans*-$PtHClL_2$ (ca. 2100 cm^{-1}),[32,33] as expected on the basis of the high trans influence of phenyl and methyl groups. All the complexes show a singlet with ^{195}Pt satellites in their $^{31}P\{^1H\}$ NMR spectra, the magnitude of $^1J(PtP)$ being as expected for mutually trans phosphines in planar platinum(II) complexes. In agreement, the ^1H NMR spectra of complexes of methyl- and tert-butylphosphines show triplet resonances for the P–CH_3 or P–C–CH_3 groups. In the hydridophenyl complexes the hydride resonance consists of a broad 1:2:1 triplet with ^{195}Pt satellites, $^2J(PH)$ being 18–20 Hz and $^1J(PtH)$ = 600–700 Hz. These values are characteristically larger and smaller, respectively, than those observed for *trans*-$PtHXL_2$ complexes where X is an electronegative ligand of low trans influence, e.g. for X = Cl and L = PEt_3, $^2J(PH)$ = 14.5 Hz and $^1J(PtH)$ = 1276 Hz. In well-resolved spectra the broadness of the lines of the triplet can be seen to be due to coupling of the hydride proton with the ortho protons of the σ-phenyl ligand, each line itself being a 1:2:1 triplet with $^4J(HH) \approx 2$ Hz. In the hydridomethyl complexes the hydride resonance appears as a triplet of quartets with ^{195}Pt satellites owing to coupling with the Pt–CH_3 protons ($^3J(HH) \approx 2$ Hz); as expected, the methyl proton resonances are double triplets with ^{195}Pt satellites ($^3J(PH) \approx 5$ Hz, $^2J(PtH) \approx 53$ Hz). In both the hydridophenyl and hydridomethyl complexes the hydride resonance is at higher frequency (δ −3 to −8) than that in *trans*-$PtHClL_2$, e.g. δ −16.9 for L = PEt_3.

The spectroscopic evidence for the formulation of the byproduct in the reduction of *trans*-$[Pt(C_6H_5)(MeOH)(PEt_3)_2]^+$ as *mer*-$PtH_3(C_6H_5)(PEt_3)_2$ is as follows. The ^1H NMR spectrum shows two hydride resonances centered at δ −13.22 and −9.48 assigned respectively to H trans to C_6H_5 and H trans to H. The first is a broad triplet of triplets with ^{195}Pt satellites, this hydride being coupled to *two* equivalent hydride protons in addition to two ortho hydrogens of the σ-phenyl group and phosphorus, while the second is a triplet of doublets with ^{195}Pt satellites, these hydrides being coupled to the hydride trans to C_6H_5. Coupling constants are given in the Experimental Section. The $^{31}P\{^1H\}$ NMR spectrum in toluene at −50 °C shows a singlet with ^{195}Pt satellites at δ 5.5 ($^1J(PtP)$ = 1917 Hz), the magnitude of $^1J(PtP)$ being about 0.6 that for the platinum(II) complex *trans*-$PtH(C_6H_5)(PEt_3)_2$, as expected.[34] The IR spectrum of a thin film of crude *trans*-$PtH(C_6H_5)(PEt_3)_2$ containing $PtH_3(C_6H_5)(PEt_3)_2$ as an impurity exhibits a broad band at 1780 cm^{-1} assignable to $\nu(PtH)$ for the *trans*-H–Pt–H unit (cf. 1725 cm^{-1} for *trans*-$PtH_2(PEt_3)_2$);[31] the corresponding band for the *trans*-H–Pt–C_6H_5 unit is presumably obscured by the strong absorption due to the major component.

Not surprisingly, the complexes *trans*-$PtH(R)L_2$ are much more stable with respect to reductive elimination of RH than are the corresponding cis isomers. Thus, *trans*-$PtH(C_6H_5)(PPh_3)_2$ can be recovered unchanged from refluxing benzene

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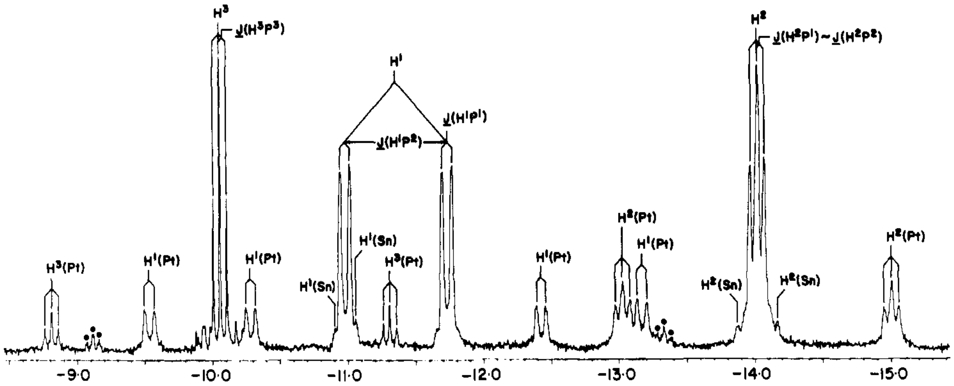

Figure 1. ^1H NMR spectrum at 270 MHz in the metal hydride region of a mixture of *trans*-$PtH(C_6H_5)(PEt_3)_2$ and $(CH_3)_3SnH$ in CD_2Cl_2 at −78 °C, showing the presence of adducts **4** and **5**. $H^n(Pt)$, $H^n(Sn)$ refer to the ^{195}Pt and $^{117,119}Sn$ satellites, respectively, of the H^n resonance, protons H^n being numbered as in **4** and **5**. Peaks marked ● arise from $PtH_3(C_6H_5)(PEt_3)_2$.

after 5 h, whereas *cis*-$PtH(C_6H_5)(PPh_3)_2$ decomposes at −25 °C. The triethylphosphine complex *trans*-$PtH(C_6H_5)(PEt_3)_2$ decomposes rapidly at 65 °C in C_6H_{12} or C_6D_{12} to give benzene, platinum metal, and $Pt(PEt_3)_3$ as the major metal complex, identified by ^{31}P NMR spectroscopy. Two other complexes are also formed in small amount, but they have not been identified. In methylcyclohexane at 45 °C, *trans*-$PtH(C_6H_5)(PEt_3)_2$ appears to be stable for ca. 6 h, then undergoes rapid decomposition over a period of ca. 1 h, and finally decomposes gradually over a further 5-h period. The products are the same as those in cyclohexane at 65 °C and are formed in similar proportions. The system does not seem to be particularly suitable for kinetic study, although the fact that decomposition in cyclohexane at 65 °C is repressed by triethylphosphine suggests that the first step may be dissociation of this ligand from the coordination sphere.[35] The ^1H NMR spectrum of *trans*-$PtH(C_6H_5)(PEt_3)_2$ at room temperature in the presence of triethylphosphine shows a broad singlet with ^{195}Pt satellites for the hydride resonance; i.e., ^{31}P coupling is removed as a consequence of rapid intermolecular exchange, presumably via the five-coordinate species $PtH(C_6H_5)(PEt_3)_3$. Since this intermediate does not readily eliminate benzene, it probably has the phenyl and hydride ligands in mutually trans sites, e.g. in a trigonal-bipyramidal structure containing equatorial triethylphosphine ligands. A similar structure has been suggested for the thermally unstable dihydride $PtH_2(PEt_3)_3$.[36]

In contrast with triethylphosphine, carbon monoxide causes rapid elimination of benzene from *trans*-$PtH(C_6H_5)(PEt_3)_2$, even at −20 °C. The initial product, $Pt(CO)_2(PEt_3)_2$, readily reacts further to give unidentified clusters containing bridging CO groups which are probably analogous to those reported for other tertiary phosphines.[37] It is noteworthy that both CO and tertiary phosphines cause rapid elimination of cyanoalkane from *trans*-$PtH(CH_2CH_2CH_2CN)(PPh_3)_2$, whereas *trans*-$PtH(CH_2CN)(PPh_3)_2$ is unaffected by these reagents.[8]

The Pt–H bond of the *trans*-$PtH(R)L_2$ complexes is surprisingly unreactive toward insertion of unsaturated molecules. In contrast with *trans*-$PtHX(PEt_3)_2$ (X = Cl, ONO_2), *trans*-$PtH(C_6H_5)(PEt_3)_2$ does not react with ethylene and the thermally more stable *p*-bromophenyl compound fails to react with diethyl maleate in refluxing toluene or with acrylonitrile in refluxing *n*-hexane. When the last reaction is carried out in methanol, some 2-methoxypropionitrile is formed, possibly as a result of reactions 1–3, initiated by reversible reaction of the hydride with an excess of methanol.

$$PtH(Ar)L_2 + CH_3OH \rightleftharpoons Pt(OCH_3)(Ar)L_2 + H_2 \quad (1)$$

$$Pt(OCH_3)(Ar)L_2 + CH_2{=}CHCN \rightarrow Pt[CH(CN)CH_2OCH_3](Ar)L_2 \quad (2)$$

$$Pt[CH(CN)CH_2OCH_3](Ar)L_2 + CH_3OH \rightarrow Pt(OCH_3)(Ar)L_2 + CH_3OCH_2CH_2CN \quad (3)$$

The highly electrophilic acetylene dimethyl acetylenedicarboxylate, $CH_3O_2CC_2CO_2CH_3$, reacts rapidly with *trans*-$PtH(C_6H_4\text{-}p\text{-}Br)(PEt_3)_2$ in refluxing hexane to give the product of insertion into the Pt–H bond, **2**. The vinylic proton resonance appears as a triplet with ^{195}Pt satellites at δ 6.88, showing that the phosphine ligands are mutually trans; this is confirmed by the appearance of a singlet with ^{195}Pt satellites in the $^{31}P\{^1H\}$ NMR spectrum. The magnitude of $^3J(PtH)$ for the vinylic proton, 72 Hz, indicates that the ester substitutents are mutually cis on the double bond.[38]

The trimethylphosphine complex *trans*-$PtH(C_6H_5)(PMe_3)_2$ loses benzene on heating with acetonitrile to give a compound identified spectroscopically as the hydrido(cyanomethyl) complex *trans*-$PtH(CH_2CN)(PMe_3)_2$. The IR spectrum shows strong bands at 2185 cm^{-1} ($\nu(CN)$) and 2018 cm^{-1} ($\nu(PtH)$), and in the ^1H NMR spectrum the hydride resonance appears as a triplet with ^{195}Pt satellites at −8.56 ($^2J(PH)$ = 20.7, $^1J(PtH)$ = 850 Hz). Similar data have been reported for *trans*-$PtH(CH_2CN)(PPh_3)_2$, viz. 2183 cm^{-1} ($\nu(CN)$), 2027 cm^{-1} ($\nu(PtH)$), and δ_H −7.32 ($^1J(PtH)$ = 746 Hz).[6,7] The reaction probably proceeds by initial oxidative addition of acetonitrile to give the dihydridoplatinum(IV) complex **3**, which subsequently eliminates benzene. Alternatively, reductive elimination of benzene could take place first to give a reactive $Pt(PMe_3)_2$ fragment, which than adds acetonitrile. The IR spectrum of the crude product also shows a weak band at 1570 cm^{-1}, which may arise from a small amount of $Pt(C_6H_5)(CH_2CN)(PMe_3)_2$ formed by loss of hydrogen from **3**, but owing to the small amount of material available purification was not attempted.

Since it is well-known that group 4 element hydrides undergo oxidative addition to platinum(II) complexes,[39] the re-

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(35) This is also the first step in the decomposition of dialkylbis(tertiary phosphine)platinum(II) complexes: McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403 and references cited therein.

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(37) Chatt, J.; Chini, P. *J. Chem. Soc. A* **1970**, 1538–1542.

(38) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667–2673.

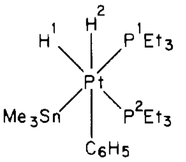
(39) Oxidative addition is often followed by reductive elimination and redistribution reactions: (a) Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1974**, *66*, 23–28. (b) Bentham, J.; Cradock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587–593. (c) Clemmit, A. F.; Glockling, F. *Ibid.* **1971**, 1164–1169. (d) Eaborn, C.; Pidcock, A.; Steele, B. R. *J. Chem. Soc., Dalton Trans.* **1975**, 809–813. (e) Glockling, F.; Pollock, R. J. I. *Ibid.* **1975**, 497–498. (f) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *Ibid.* **1978**, 1167–1170.

Table III. NMR Spectroscopic Data for Isomers of $PtH_2(C_6H_5)(SnMe_3)(PEt_3)_2$[a]

	complex 4				complex 5	
	$\delta(H^1)$	$\delta(H^2)$	$\delta(P^1)$	$\delta(P^2)$	$\delta(H^3)$	$\delta(P^3)$
	−11.3	−14.0	−13.0	−22.9	−10.1	−1.7
J(PH) (^{1}H) or J(PP) (^{31}P)	204 (H^1P^2) 18 (H^1P^1)	14	19.5	19.5	14	
J(PtH) or J(PtP)	780	535	1406	1670	674	1841
J(SnH) or J(SnP)	~40	45[b]	1762 (^{119}Sn) 1688 (^{117}Sn)	no	~40	140

[a] Abbreviation: no, not observed. [b] Obtained from $^1H\{^{31}P\}$ spectrum at 60 MHz.

action of *trans*-$PtH(C_6H_5)(PEt_3)_2$ with trimethyltin hydride was investigated. Equimolar quantities of the two reagents give a colorless solution in CD_2Cl_2 at −78 °C. The ^{1}H NMR spectrum in the metal–hydride region is very complicated (Figure 1), but the presence of two platinum(IV) complexes **4** and **5** can be inferred from this and from the $^{31}P\{^1H\}$ NMR spectrum; the data are collected in Table III. Complex **4** shows two hydride resonances at δ −11.3 and −14.0. The former has one large and one small ^{31}P coupling, showing that the hydride is trans to one PEt_3 ligand and cis to the other, while the lower frequency hydride resonance appears as a triplet owing to almost equal couplings with two mutually cis phosphines. Both resonances show satellites arising from coupling with ^{195}Pt and with the two tin isotopes (^{119}Sn, $I = {}^1/_2$, 8.58% abundance; ^{117}Sn, $I = {}^1/_2$, 7.61% abundance). The ligand arrangement deduced from these data is confirmed by the $^{31}P\{^1H\}$ NMR spectrum, which shows a pair of doublets (^2J(PP) = 19.5 Hz) due to the inequivalent PEt_3 ligands, each with ^{195}Pt satellites. The higher frequency signal arising from PEt_3 trans to Me_3Sn also has two distinguishable pairs of satellites due to coupling with ^{119}Sn (J(SnP) = 1762 Hz) and with ^{117}Sn (J(SnP) = 1688 Hz), the magnitudes of these coupling constants being similar to those observed in platinum(II) complexes of the type *cis*-$Pt(aryl)(SnMe_3)(PPh_3)_2$.[40] It is noteworthy that the magnitude of ^1J(PtP) for PEt_3 trans to Me_3Sn in **4**, 1406 Hz, is smaller than that for PEt_3 trans to H, 1670 Hz, which implies that Me_3Sn has an even larger trans influence than hydride. Complex **5** shows in its ^{1}H NMR spectrum a triplet with ^{195}Pt satellites at δ −10.1 due to equivalent hydride ligands which are cis to two phosphine ligands. The $^{31}P\{^1H\}$ NMR spectrum comprises a singlet due to the equivalent PEt_3 ligands together with satellites arising from coupling with ^{195}Pt (^1J(PtP) = 1841 Hz) and with ^{117,119}Sn (J(SnP) = 140 Hz). In both **4** and **5** the magnitudes of ^1J(PtH) and ^1J(PtP) resemble those of other hydridoplatinum(IV) complexes[41] and support the structural assignments. The ^{1}H NMR spectrum of the solution at −78 °C also shows peaks assignable to a small amount of *mer*-$PtH_3(C_6H_5)(PEt_3)_2$ (**1**). When it is warmed to room temperature, the solution turns yellow and gives a mixture of decomposition products, including benzene, tetramethyltin, and hexamethylditin, presumably resulting from a series of reductive elimination, redistribution, and Sn–C cleavage reactions, but the platinum-containing products could not be identified.



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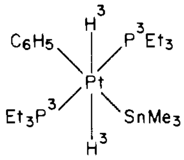

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Registry No. **1**, 90065-01-3; **2**, 90130-05-5; **3**, 90065-08-0; **4**, 90065-07-9; **5**, 90130-04-4; *trans*-$PtH(C_6H_5)(P\text{-}t\text{-}Bu_2Me)_2$, 90064-99-6; *trans*-$PtH(C_6H_5)(P\text{-}t\text{-}BuMe_2)_2$, 90065-05-7; *trans*-$PtH(C_6H_5)(PPh_3)_2$, 76188-93-7; *trans*-$PtH(C_6H_5)(P\text{-}i\text{-}Pr_3)_2$, 87635-50-5; *trans*-$PtH(C_6H_5)(PEt_3)_2$, 67891-26-3; *trans*-$PtH(C_6H_4\text{-}p\text{-}Br)(PEt_3)_2$, 90065-02-4; *trans*-$PtH(C_6H_5)(PMe_3)_2$, 76125-03-6; *trans*-$PtH(CH_3)(PPh_3)_2$, 76188-92-6; *trans*-$PtH(CH_3)(P\text{-}i\text{-}Pr_3)_2$, 76125-04-7; *trans*-$Pt(OCH_3)(CH_3)(PPh_3)_2$, 76125-08-1; *trans*-$Pt(OCH_3)(C_6H_5)(PEt_3)_2$, 60477-61-4; *trans*-$Pt(OCH_3)(C_6H_5)(PMe_2Ph)_2$, 90065-00-2; *trans-mer*-$PtH_3(C_6H_5)(PMe_3)_2$, 90065-03-5; $Pt(CO)_2(PEt_3)_2$, 76125-09-2; *trans*-$Pt(C_6H_4\text{-}p\text{-}Br)[C(CO_2Me){=}CH(CO_2Me)](PEt_3)_2$, 90065-04-6; *trans*-$PtH(C_6H_5)(PMe_2Ph)_2$, 90065-06-8; *trans*-$PtCl(C_6H_5)(P\text{-}i\text{-}Pr_3)_2$, 90065-09-1; $PtCl(C_6H_5)(1,5\text{-}COD)$, 51177-65-2; *trans*-$Pt(OH)(CH_3)(P\text{-}i\text{-}Pr_3)_2$, 76125-05-8; *trans*-$Pt(OH)(C_6H_5)(P\text{-}t\text{-}Bu_2Me)_2$, 76124-94-2; *trans*-$Pt(OH)(C_6H_5)(P\text{-}t\text{-}BuMe_2)_2$, 76124-95-3; *trans*-$Pt(OH)(C_6H_5)(PPh_3)_2$, 60399-83-9; *trans*-$PtCl(C_6H_5)(P\text{-}t\text{-}Bu_2Me)_2$, 76316-26-2; *trans*-$Pt(CH_3)(NHCOCH_3)(PPh_3)_2$, 41650-11-7; *trans*-$PtCl(C_6H_5)(PPh_3)_2$, 18421-49-3; *trans*-$PtI(CH_3)(PPh_3)_2$, 28850-19-3; *trans*-$PtCl(C_6H_5)(PEt_3)_2$, 13938-93-7; *trans*-$PtCl(C_6H_5)(PMe_2Ph)_2$, 27081-34-1; *trans*-$PtBr(C_6H_4\text{-}p\text{-}Br)(PEt_3)_2$, 90065-10-4; *trans*-$PtCl(C_6H_5)(PMe_3)_2$, 90065-11-5; $Pt(PEt_3)_3$, 39045-37-9; $AgBF_4$, 14104-20-2; C_6H_{12}, 110-82-7; *n*-decane, 124-18-5; methylcyclohexane, 108-87-2; dimethyl acetylenedicarboxylate, 762-42-5; acrylonitrile, 107-13-1; diethyl maleate, 141-05-9.

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