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Associative Reactions of Dihydridobis(trimethylphosphine)platinum(II). Molecular Structures of (Diphenylacetylene)bis(trimethylphosphine)platinum and Hydridotris(trimethylphosphine)platinum(II) Tetraphenylborate

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Olefinic and acetylenic ligands such as diphenylacetylene, ethylene, *tert*-butylethylene, and *trans*-stilbene displace H_2 from $PtH_2(PMe_3)_2$ to form zerovalent π complexes. The complex $Pt(PhC{\equiv}CPh)(PMe_3)_2$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$, $a = 9.508$ (2) Å, $b = 13.524$ (4) Å, $c = 16.124$ (4) Å, and $V = 2073.5$ Å^3. Refinment of 2040 unique observations $>3\sigma(I)$ led to $R = 0.043$ and $R_w = 0.056$. The complex adopts a nearly square-planar geometry, with Pt–P distances of 2.262 (4) and 2.284 (4) Å, Pt–C distances of 2.06 (1) and 2.04 (1) Å, and a C–C distance of 1.29 (2) Å for the bound acetylenic moiety. The reaction between *tert*-butylethylene and $PtH_2(PMe_3)_2$ follows a second-order rate law first order in olefin and platinum complex, with $k = (1.95 \pm 0.24) \times 10^{-3}$ M^{-1} s^{-1} at 21 °C. Hydrogenation of the unsaturated substrate does not occur, which agrees with theoretical predictions for a five-coordinate platinum hydride intermediate. Allyl chloride oxidatively adds to $PtH_2(PMe_3)_2$ to produce $Pt(C_3H_5)(PMe_3)_2^+$, isolated as the BPh_4^- salt. The family of substrates $HMPh_3$ (M = Si, Ge, and Sn) undergo oxidative addition reactions to yield *cis*-$PtH(SiPh_3)(PMe_3)_2$, and *cis,trans,cis*-$PtH_2(MPh_3)_2(PMe_3)_2$ for M = Ge and Sn. The reaction between methanol and $PtH_2(PMe_3)_2$ produces $[Pt(PMe_3)_2(\mu\text{-}H)_2Pt(PMe_3)_2H][OCH_3]$, and on addition of $NaBPh_4$, $[PtH(PMe_3)_3][BPh_4]$ precipitates. The compound $[PtH(P(CH_3)_3)_3][B(C_6H_5)_4]$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.011$ (2) Å, $b = 12.948$ (3) Å, $c = 26.699$ (4) Å, $\beta = 92.15$ (2)°, $V = 3458.2$ Å^3, and $Z = 4$ at $T = 296$ (1) K. Refinement of the structure led to $R_w = 0.048$ for 4325 unique reflections with $I > 3\sigma(I)$. The $PtH[P(CH_3)_3]_3^+$ species adopts a square-planar geometry. The Pt–P bond trans to hydrogen of 2.324 (1) Å is longer than the other two Pt–P bonds by 0.030 Å, demonstrating that hydride ligand has a greater trans influence than trimethylphosphine. The P–Pt–Pt angles of 100.69 (6) and 100.56 (6)° open up from 90° to accommodate the bulk of the phosphine ligands.

Introduction

In recent years sterically unhindered platinum dihydrides PtH_2L_2 (L = PMe_3, PEt_3) have been isolated and found to be much more reactive[2,3] than related compounds containing bulky phosphine ligands.[4-13] Such complexes may be involved as intermediates in the catalysis of alkene hydrogenation,[13] nitrile and olefin hydration,[14] alcoholysis,[15] hydrosilation,[16] and the water gas shift reaction.[17] Oxidative addition and reductive elimination of H_2 from sterically unhindered dihydrides has been the subject of experimental[18] and theoretical studies,[19] since these reactions model the behavior of hydrogen on platinum surfaces. These systems have played an important role in the development of an understanding of C–H activation and reductive elimination of C–H and C–C bonds.[20] Reductive elimination of hydrogen from PtH_2L_2 generates the highly reactive PtL_2 species, a precursor for the synthesis of other platinum complexes.[21,22a] The complexes $PtH_2(PEt_3)_2$ and $PtH_2(PMe_3)_2$ are stable only under a hydrogen atomosphere and reductively eliminate H_2 under nitrogen when in solution or in the solid state.[3,6] This paper examines reactions of the PMe_3 derivative in detail to define its reactivity. In particular we were interested in the competition between H_2 dissociation[18] to generate

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$Pt(PMe_3)_2$ vs associative attack at platinum in the substitution and oxidative addition reactions of these complexes.

Experimental Section

General Procedures. Reactions were carried out by using standard Schlenk techniques under an atmosphere of prepurified nitrogen or hydrogen. Unless noted, all procedures were performed at ambient temperature. Reactions monitored by NMR spectroscopy were contained in NMR tubes sealed with septum caps and flushed with nitrogen. Usually a 5-mm NMR tube containing a deuteriated solvent was inserted into a 10-mm NMR tube containing the sample to provide an external standard.

Materials. Hydrogen (99.999%) and deuterium (CP grade) were obtained from Liquid Carbonics. Ethylene (CP grade) was obtained from Matheson. Tetrahydrofuran (Mallinkrodt) was dried over potassium benzophenone ketyl and distilled under nitrogen. *n*-Hexane (Aldrich, 99%) was distilled from lithium aluminium hydride. Substrates were obtained from Aldrich or Mallinkrodt and were used as received. Deuterated solvents acetone-d_6 (MSD isotopes), benzene-d_6, and toluene-d_8 (Aldrich) and tetrahydrofuran-d_8 (Cambridge isotopes) were used without purification.

Physical Measurements. Solution IR spectra were recorded with a Perkin-Elmer 1320 or an IBM FTIR 32 spectrometer. Liquid samples were placed in 0.1-mm CaF_2 cells that were flushed with nitrogen before use. Solid samples were prepared as KBr disks or Fluorolube mulls in a glovebox. Fourier transform NMR spectra were recorded with Nicolet 1280[23] and General Electric QE-300 ^1H NMR spectrometers or a Nicolet 200 (^{31}P, 80.99 MHz). The notation $\{^1H\}$ denotes broad-band noise decoupling of the hydrogen nuclei. Selective decoupling of only phosphine protons was done by decreasing the decoupler power and broad-band modulation. All chemical shifts are positive in the direction of increasing frequency. Proton chemical shifts were referenced to Me_4Si at 0.0 ppm, and ^{31}P chemical shifts were referenced to the deuterium resonance of solvent by using the internal frequency lock of the spectrometer so that the resonance from a capillary of 85% H_3PO_4, centered in a 10-mm NMR tube containing the deuteriated solvent, appeared at 0.0 ppm at 20 °C.

Preparation of $PtH_2(PMe_3)_2 \cdot C_{10}H_8$ (1). This compound was prepared according to procedures described previously.[3] The following modifications were made to the synthesis of the *cis*-$PtCl_2(PMe_3)_2$ precursor: 1.9 equiv of PMe_3 were added to a stirred solution of *cis*-$PtCl_2(SEt_2)_2$[24a] in CH_2Cl_2 under nitrogen. The resulting white powder was filtered and washed with Et_2O. The $PtCl_2(PMe_3)_2$ was dried in vacuo for 16 h. If further purification was necessary, the compound was recrystallized from DMF or CH_3CN.

Reaction between $PtH_2(PMe_3)_2$ and Ph_3MH (M = Si, Ge, Sn). A solution of $PtH_2(PMe_3)_2$ in THF was generated by reduction of *cis*-$PtCl_2(PMe_3)_2$ (0.2 g, 0.48 mmol) suspended in 10 mL of THF with 2 equiv of sodium naphthalide (0.25 M in THF) under a H_2 atmosphere. After filtration under hydrogen an excess (1–3 equiv) of the desired substrate was added, under a nitrogen atmosphere. The solution was stirred 0.5 h and hydrogen gas evolved. The solution was concentrated to 1–2 mL, and 4 mL of *n*-hexane was layered on top of the solution. Cooling to −30 °C for 2 h resulted in the formation of white crystals of *cis*-$PtH(SiPh_3)(PMe_3)_2$, yield 0.15 g, 51%, or *cis,trans,cis*-$PtH_2(GePh_3)_2(PMe_3)_2$, yield 0.16 g, 34%. For M = Sn, the solution was stirred 2 h at 0 °C and the golden brown product *cis,trans,cis*-$PtH_2(SnPh_3)_2(PMe_3)_2$ crystallized from the THF/hexane mixture over 0.5 h at room temperature, yield 0.10 g, 20%. The solution was removed by cannula, and the crystals were dried under a stream of N_2. Anal. Calcd for $C_{24}H_{34}P_2PtSi$: C, 47.44; H, 5.64. Found: C, 46.56; H, 5.81. Anal. Calcd for $C_{42}H_{50}P_2Ge_2Pt$: C, 52.70; H, 5.28. Found: C, 51.62; H, 5.36. Anal. Calcd for $C_{42}H_{50}P_2Sn_2Pt$: C, 48.04, H, 4.77. Found: C, 47.42; H, 4.90.

Reaction with Methanol To Yield $[PtL_2(\mu\text{-}H)_2PtL_2H][OCH_3]$ and Metathesis with $NaBPh_4$ To Yield $[PtHL_3][BPh_4]$. A solution of $PtH_2(PMe_3)_2$ was generated by reduction of 0.2 g of cis-$PtCl_2(PMe_3)_2$ with 2 equiv of sodium naphthalide in THF under a H_2 atmosphere. To the generated solution was added 5 mL (excess) of dry, degassed MeOH. The spectral parameters for the resulting complex were similar to those reported for $[Pt(PEt_3)_2(\mu\text{-}H)_2Pt(PEt_3)_2H^+]$.[22] $^{31}P\{^1H\}$ NMR: δ (P_A) −14.3 (t of t, $^1J_{Pt_A-P_A} = 2658$ Hz, $^2J_{Pt_B-P_A} = 32$ Hz), δ (P_B) −17.9 (t of t, $^1J_{Pt_B-P_B} = 2414$ Hz, $^2J_{Pt_A-P_B} = 24$ Hz, $^3J_{P_A-P_B} \approx 2$ Hz). The solution was concentrated to ~5 mL, and 0.10 g of $NaBPh_4$ (0.3 mmol) was added under a N_2 atmosphere. The resulting white precipitate of $[PtHL_3][BPh_4]$ was filtered and dried under vacuum, yield 0.15 g, 43%. Anal. Calcd for $C_{33}H_{48}PtBP_3$: C, 53.3; H, 6.5; P, 12.5. Found: C, 53.0; H, 6.5; P, 13.4. IR (fluorolube): ν_{Pt-H} 2070 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ −20.9 (t, $^2J_{P-P} = 22$ Hz, $^1J_{Pt-P} = 1905$ Hz), −22.5 (d, $^2J_{Pt-P} = 22$ Hz, $^1J_{Pt-P} = 2434$ Hz). ^1H NMR: δ −5.8 (d of t, $^2J_{P-H(trans)} = 164$ Hz, $^2J_{P-H(cis)} = 20$ Hz, $^1J_{Pt-H} = 869$ Hz).

Reaction between $PtH_2(PMe_3)_2$ and Olefins or Acetylenes. A solution of $PtH_2(PMe_3)_2$ was generated by reducing 0.2 g (0.48 mmol) of *cis*-$PtCl_2(PMe_3)_2$ with 2 equiv of sodium naphthalide (0.25 M solution in THF) under a H_2 atmosphere in THF. The solution was filtered under H_2, and the appropriate substrate was added under an N_2 atmosphere. Specific details follow.

Reaction with Ethylene To Yield $Pt(C_2H_4)(PMe_3)_2$. Ethylene gas was bubbled through the dihydride solution for 10 min, and the THF was removed in vacuo. A cold finger was inserted and the flask placed in a warm water bath under vacuum. Naphthalene sublimed away to leave a yellow oil. ^1H NMR (C_6D_6): δ 2.2 (s, $^2J_{Pt-H} = 52$ Hz). $^{31}P\{^1H\}$ NMR: δ −19.8 (s, $^1J_{Pt-P} = 3509$ Hz).

Reaction with Diphenylacetylene To Yield $Pt(PhC{\equiv}CPh)(PMe_3)_2$. To the generated solution of $PtH_2(PMe_3)_2$ in THF was added 0.086 g (0.48 mmol) of diphenylacetylene. Hydrogen gas was evolved, and the solution became dark yellow. After being stirred 0.5 h, the solution was concentrated to 2 mL and 4 mL of *n*-hexane was added. Cooling to −30 °C for 16 h produced orange crystals of the acetylene complex, yield 0.14 g, 52%. IR (THF): $\nu_{C\equiv C}$ 1720 cm^{-1}. ^1H NMR: $\delta(CH_3)$ 1.3 (d, $^2J_{P-H} = 9$ Hz, $^3J_{Pt-H} = 14$ Hz), $\delta(C_6H_5)$ 7.7 (m). $^{31}P\{^1H\}$ NMR: δ −29.4 ($^1J_{Pt-P}$ = 3232 Hz). Anal. Calcd for $C_{20}H_{28}P_2Pt$: C, 45.7; H, 5.3; P, 11.8. Found: C, 46.4, H, 5.9, P, 11.7.

Reaction with *tert*-Butylethylene To Yield $Pt(CH_2{=}CHCMe_3)(PMe_3)_2$. To a THF solution of $PtH_2(PMe_3)_2$ (0.1 g, 0.21 mmol) was added 0.1 mL (0.84 mmol) of *tert*-butylethylene, evolving hydrogen gas. $^{31}P\{^1H\}$ NMR: $\delta(P_A)$ −14.3 ($^2J_{P-P} = 58$ Hz, $^1J_{Pt-P} = 3537$ Hz), $\delta(P_B)$ −16.2 ($^2J_{P-P} = 58$ Hz, $^1J_{Pt-P} = 3059$ Hz). A complex with the same spectral data was generated independently by reduction of 0.2 g (0.48 mmol) of *cis*-$PtCl_2(PMe_3)_2$ with 2 equiv of sodium naphthalide in THF in the presence of 0.25 mL (1.92 mmol) of *tert*-butylethylene.

Reaction with Allyl Chloride To Yield $[Pt(C_3H_5)(PMe_3)_2]^+$. To the generated solution of $PtH_2(PMe_3)_2$ in THF was added 0.04 mL (0.48 mmol) of allyl chloride. The pale yellow solution became colorless, and gas was evolved. Then 0.16 g (0.48 mmol) of $NaBPh_4$ was added, and a small amount of NaCl precipitated from solution. The solution was filtered, and 5 mL of *n*-hexane was added to precipitate white crystals that were filtered and washed with MeOH to remove unreacted $NaBPh_4$, yield 0.22 g, 52%. ^1H NMR (acetone-d_6): $\delta(CH_3)$ 1.8 (d, $^2J_{P-H} = 12$ Hz, $^3J_{Pt-H} = 34$ Hz), $\delta(CH_2)$ 2.8, 4.3 (d, $^3J_{H-H} = 6$ Hz), $\delta(CH)$ 5.0 (quintet, $^3J_{H-H} = 6$ Hz), $\delta(C_6H_5)$ 6.8, 7.0, 7.4 (m). $^{31}P\{^1H\}$ NMR: δ −23.5 ($^1J_{Pt-P} = 3726$ Hz). Anal. Calcd for $C_{33}H_{43}P_2BPt$: C, 56.0; H, 6.1. Found: C, 55.6; H, 6.5.

Kinetic Studies. Isolated *trans*-$PtH_2(PMe_3)_2 \cdot C_{10}H_8$ was dissolved in THF to a known concentration under H_2. Desired amounts of *tert*-butylethylene were added to solutions of the dihydride in Schlenk tubes placed in a thermostated bath under an N_2 atmosphere. At timed intervals, aliquots were withdrawn by syringe and transferred into 0.1-mm path length CaF_2 liquid sample cells. The atmosphere was exchanged frequently to prevent the buildup of H_2 in the reaction flask. Cells were flushed with nitrogen before use and placed in an IBM 32 FTIR spectrometer. The reaction was followed by monitoring the decrease in absorbance of the Pt–H stretch at 1720 cm^{-1}. For measurement below 20 °C, the IR cells were precooled by flushing with nitrogen that was passed through a cooling oil in an N_2/pentane slush bath at −130 °C.

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Table I. Crystal and Refinement Parameters

	$Pt(PhC{\equiv}CPh)(PMe_3)_2$	$[PtH(PMe_3)_3][BPh]_4$
formula	$PtC_{20}H_{28}P_2$	$PtC_{33}H_{48}BP_3$
fw	525.48	743.57
cryst dimens, mm	0.82 × 0.24 × 0.21	0.8 × 0.3 × 0.4
cryst sys	orthorhombic	monoclinic
a, Å	9.508 (2)	10.011 (2)
b, Å	13.525 (4)	12.948 (3)
c, Å	16.124 (4)	26.699 (4)
β, deg		92.15 (2)°
V, Å^3	2073.5 (9)	3458.2
space group	$P2_12_12_1$	$P2_1/n$
Z	4	4
D_{calcd}, g/cm^3	1.69	1.43
F_{000}	1023	1469
μ(Mo kα), cm^{-1}	69.89	42.5
trans(max)/trans-(min)		0.494/0.999
diffractometer	Nicolet R3μ	Enraf-Nonius CAD4
radiatn	Mo Kα (λ = 0.71069), graphite monochromated	Mo Kα (λ = 0.71069), graphite monochromated
temp, °C	23	23
$2\theta_{max}$, deg	55.0	50.0
reflecns $>3\sigma(I)$	2040	4325
no. of var	104	343
R	0.043	0.037
R_w	0.056	0.048
largest peak in final diff map, e/Å^3	2.4 (near Pt)	0.52 (near Pt)

Crystal Data Collection and Refinement. Clear crystals of $C_{33}H_{48}PtBP_3$ were grown from an acetone solution. A parallelopiped crystal was cut from a larger crystal and mounted on a glass fiber in a random orientation. Final lattice parameters were determined from 24 strong reflections of Mo Kα radiation in the range $6 < \theta < 20$ on an Enraf-Nonius CAD-4 diffractometer. A total of 6778 reflections were measured by the ω–θ scan technique of which 6083 were unique. The intensities of three reflections measured every 60 min as a check on crystal and electronic stability remained constant within experimental error throughout data collection. The data reduction, structure solution, refinement, and all the other calculations were performed by using the Enraf-Nonius SDP/VAX package.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 42.5 cm^{-1} for Mo Kα radiation. An empirical absorption correction, based on a series of ψ-scans, was applied to the data. Relative transmission coefficients ranged from 0.494 to 0.999 with an average value of 0.779. No decay correction was applied. Intensities of equivalent reflections were averaged, and the agreement factors for the averaging of 546 observed and accepted reflections was 3.1% based on intensity and 2.3% based on F_o. Details of data collection and structural refinement are given in Table I.

From the systematic absences of $h0l$ ($h+l = 2n + 1$), $0k0$ ($k = 2n + 1$), $00l$ $l = 2n + 1$, and $h00$ ($h = 2n + 1$) and from the refinement the space group was determined to be $P2_1/n$. The structure was solved by using the Patterson heavy-atom method to obtain the position of the Pt atom, and then with successive difference Fourier syntheses the remaining non-hydrogen atoms were located. Refinement was done by using the full-matrix least-squares methods with 4325 reflections based on $I > 3\sigma(I)$. During the refinement anisotropic thermal parameters were applied for all non-hydrogen atoms. Atom positions and isotropic thermal parameters for H atoms were fixed. Positions for 35 of the 48 hydrogen atoms were obtained from successive difference Fourier syntheses, and the locations of the remaining hydrogen atoms were calculated. Attempts failed to locate the H atom bound to Pt in a final difference Fourier done after the refinement converged. Positional parameters for $HPt[P(CH_3)_3]_3^+$ are given in Table II and bond lengths and key angles in Table III.

Table II. Table of Positional Parameters for $PtH[P(CH_3)_3]_3^+$ and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Pt	0.42509 (2)	0.24264 (2)	0.12997 (1)	3.190 (5)
P(1)	0.2137 (2)	0.1703 (2)	0.1352 (1)	3.68 (4)
P(2)	0.5563 (2)	0.1069 (1)	0.1561 (1)	3.37 (4)
P(3)	0.3701 (2)	0.4122 (1)	0.1154 (1)	3.98 (4)
C(1)	0.1284 (9)	0.2160 (8)	0.1893 (4)	7.1 (2)
C(2)	0.1932 (8)	0.0315 (6)	0.1419 (4)	6.6 (3)
C(3)	0.0970 (7)	0.1951 (6)	0.0828 (3)	4.7 (2)
C(4)	0.5383 (7)	−0.0203 (5)	0.1296 (3)	4.3 (2)
C(5)	0.7336 (7)	0.1292 (6)	0.1493 (4)	6.5 (3)
C(6)	0.5449 (1)	0.0901 (7)	0.2224 (4)	6.6 (2)
C(7)	0.4486 (8)	0.4664 (7)	0.0618 (4)	7.1 (3)
C(8)	0.2003 (7)	0.4600 (6)	0.1079 (4)	5.3 (2)
C(9)	0.4362 (9)	0.4886 (7)	0.1660 (4)	7.8 (3)

[a] B = Equivalent isotropic thermal parameter.

Table III. Bond Lengths (Å) and Key Bond Angles (deg) in $PtH[P(CH_3)_3]_3^+$

Pt–P(1)	2.324 (1)	P(2)–C(4)	1.799 (6)
Pt–P(2)	2.287 (1)	P(2)–C(5)	1.814 (6)
Pt–P(3)	2.294 (1)	P(2)–C(6)	1.792 (8)
P(1)–C(1)	1.804 (8)	P(3)–C(7)	1.800 (8)
P(1)–C(2)	1.818 (7)	P(3)–C(8)	1.813 (6)
P(1)–C(3)	1.819 (7)	P(3)–C(9)	1.783 (3)
P(1)–Pt–P(2)	100.69 (6)	P(2)–Pt–P(3)	156.76 (5)
P(1)–Pt–P(3)	100.56 (6)		

A pale orange crystal of $C_{20}H_{28}PtP_2$ with dimensions of 0.82 × 0.24 × 0.21 mm was mounted on a glass fiber. Data collection was performed with Mo Kα radiation (λ = 0.71073 Å) on a Nicolet R3μ computer-controlled (microvax II) diffractometer. The SHELEXTL PLUS software routine was used for structure solution and refinement.[24] The space group selected from the sysematic absences $h00$ ($h = 2n$), $0k0$ ($k = 2n$), and $00l$ ($l = 2n$) was $P2_12_12_1$. A total of 2802 reflections were collected, of which 2040 > $3\sigma(I)$ were used in the refinement. As a check on crystal and electronic stability three reflections were measured once every 150 reflections. The intensities of these standards remained constant within experimental error throughout data collection. An analytic absorption correction was applied to the data, with the faces indexed as (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (011), and (0$\bar{1}\bar{1}$).

The structure was solved with the automated Patterson of SHELEXTL PLUS, which located the Pt and phosphorus atoms. Remaining non-hydrogen atoms were located after a cycle of refinement from the difference Fourier map. The phenyl moieties were refined as rigid groups. The structure was refined with full-matrix least-squares methods, and the preferred enantiomorph led to a lower R factor (0.079 vs 0.068 with all non-hydrogen atoms). The H atoms were placed at idealized positions (the methyl H refined as a rigid group) and a secondary extinction correction applied. Only Pt and the two phosphorus atoms were refined with anisotropic thermal parameters. Analysis of the variance vs reflection parity, sin θ, F_o, and Miller index showed no unusual trends. Final crystal and refinement parameters are given in Table I, positional parameters in Table IV, and bond distances and angles in Table V. Structure factor tables and tables of least-squares planes, H-atom positions, and anisotropic thermal parameters are available as supplementary material.

Results and Discussion

Oxidative Addition of Group 14 Hydrides. The synthesis of complexes containing platinum and the group 14 elements has been investigated extensively because of their relevance to homogeneous hydrosilation catalysis. Methods for their synthesis include the reaction between platinum(0) compounds and the derivatives R_3MH[25,26] or

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Table IV. Positional Parameters and U(eq) for $Pt[C_2(C_6H_5)_2][P(CH_3)]_2$

	x	y	z	U(eq),[a] Å^2
Pt	−4956 (1)	−1459 (1)	−6338 (1)	30 (1)
P(1)	−6768 (4)	−2561 (3)	−6230 (2)	36 (1)
P(2)	−3602 (4)	−2169 (3)	−7327 (2)	42 (1)
C(1)	−5145 (16)	−351 (9)	−5472 (7)	35 (3)
C(2)	−3967 (13)	−249 (10)	−5859 (8)	31 (3)
C(3)	−6001	7	−4775	39 (3)
C(4)	−7442	165 (9)	−4871 (5)	48 (4)
C(5)	−8244	492	−4201	66 (5)
C(6)	−7606	660	−3434	62 (5)
C(7)	−6166	502	−3338	66 (5)
C(8)	−5363	175	−4009	44 (3)
C(9)	−2756	413	−5854	35 (3)
C(10)	−2864 (8)	1336 (7)	−5473 (6)	42 (3)
C(11)	−1723	1983	−5481	60 (5)
C(12)	−472	1708	−5870	63 (5)
C(13)	−363	785	−6251	63 (5)
C(14)	−1505	138	−6243	42 (3)
C(15)	−6299 (26)	−3678 (18)	−5708 (15)	90 (7)
C(16)	−8245 (26)	−2180 (21)	−5617 (16)	96 (8)
C(17)	−7660 (24)	−3049 (18)	−7104 (13)	77 (6)
C(18)	−2956 (21)	−1287 (15)	−8106 (12)	65 (5)
C(19)	−1983 (19)	−2720 (15)	−6924 (12)	59 (5)
C(20)	−4201 (26)	−3145 (18)	−8008 (15)	84 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Bond Lengths (Å) and Angles (deg) in $Pt[C_2(C_6H_5)_2][P(CH_3)_3]_2$[a]

Pt–C2	2.04 (1)	Pt–P2	2.262 (4)
Pt–C1	2.06 (1)	Pt–P1	2.284 (4)
		C1–C2	1.29 (2)
C2–Pt–C1	36.7 (5)	C3–C1–Pt	143.9 (10)
C1–Pt–P1	110.9 (4)	C9–C2–Pt	149.1 (9)
C2–Pt–P2	110.2 (4)	C3–C1–C2	144.7 (12)
P2–Pt–P1	101.9 (1)	C9–C2–C1	138.5 (12)

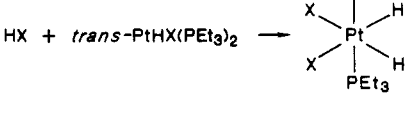
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

the reaction between platinum halides and R_3MLi[27] or $(Me_3M)_2Hg$.[28] Platinum dihydrides containing bulky phosphine ligands add to group 14 hydrides to generate platinum(II) complexes as in eq 1.[29,30] Such reactions are

$$trans\text{-}PtH_2L_2 + R_3MH \rightarrow trans\text{-}PtH(MR_3)L_2 + H_2 \quad (1)$$

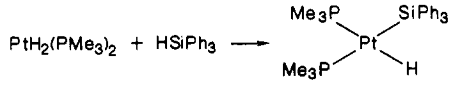
$$L = PCy_3,\ P(i\text{-}Pr)_3;\ R = Ph, H;\ M = Si, Ge, Sn$$

believed to proceed by oxidative addition involving a six-coordinate platinum(IV) intermediate.[27-29,31] Six-coordinate platinum dihydrides have been isolated from the oxidative addition of hydrogen halides to *trans*-$PtHX(PEt_3)_2$ (X = Cl, Br, I),[31] eq 2. These hydrides generally assume the *cis,cis,trans*-$PtH_2X_2L_2$ structures.



(2)

Compound 1 reacts with an excess of Ph_3MH to evolve hydrogen gas. No reaction occurs with Ph_3CH. The reaction with triphenylsilane produces *cis*-$PtH(SiPh_3)(PMe_3)_2$ (**2**), eq 3, similar to the reaction between trimethylsilane and $PtH_2(PEt_3)_2$.[21] When M = Ge or Sn, however, the reaction with **1** produces the six-coordinate platinum(IV) dihydrides **3a** and **3b**, eq 4. The composition of these dihydrides is confirmed by elemental analysis and the structure deduced (vide infra) by ^1H and ^{31}P NMR spectroscopy. Complexes **3a** and **3b** are stable in the solid state for several months but decompose in solution. The ^{31}P NMR spectra of solutions aged for several hours show 20–50% contamination with a single new platinum(II) compound. $^{31}P\{^1H\}$ NMR: from **3a**, δ −19.4 (J_{Pt-P} = 2492 Hz); from **3b**, δ −27.2 (J_{Pt-P} = 2282 Hz, J_{P-Sn} = 178 Hz). Selective decoupling of the phosphine protons in the NMR spectra shows that these compounds contain no hydride ligand, which suggests decomposition to $Pt(MPh_3)_2(PMe_3)_2$ occurs, where M = Ge and Sn. The oxidative addition of two trimethylstannane molecules to a bis(phosphine)platinum center to give a six-coordinate platinum dihydride has been postulated previously in the formation of $Pt(diphos)(SnMe_3)_2$;[28] however, a six-coordinate Pt(IV) intermediate was never isolated. Presumably the small basic PMe_3 ligand helps stabilize the six-coordinate species we observe.



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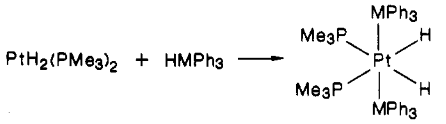
(3)



(4)

3a, M = Ge
b, M = Sn

NMR Spectra of Platinum Complexes of Silicon, Germanium, and Tin. The $^{31}P\{^1H\}$ NMR spectrum of *cis*-$PtH(SiPh_3)(PMe_3)_2$ exhibits two resonances arising from nonequivalent phosphorus nuclei coupled to one another (Table VI): δ −13.7 (d, $^2J_{P_AP_B}$ = 19 Hz, $^1J_{PtP_A}$ = 1723 Hz), δ 20.0 (d, $^2J_{P_AP_B}$ = 19 Hz, $^1J_{Pt-P_B}$ = 2210 Hz). The platinum–phosphorus coupling constants of about 2000 Hz identify this as a complex of Pt(II); the lower value of 1723 Hz for J_{PtP_A} shows P_A trans to the $SiPh_3$ ligand, which exhibits a higher trans influence than hydride.[32,33] The hydride region of the proton NMR spectrum exhibits a second-order doublet of doublets arising from coupling to phosphorus cis and trans to hydride [δ −3.0 (dd, $^2J_{PH(cis)}$ = 21 Hz, $^2J_{PH(trans)}$ = 164 Hz, $^1J_{PtH}$ = 892 Hz)] and resembles that of *cis*-$PtH_2(PMe_3)_2$.[2,3]

The complex *cis,trans,cis*-$PtH_2(GePh_3)_2(PMe_3)_2$ also exhibits a proton NMR spectrum similar to that of *cis*-$PtH_2(PMe_3)_2$. The second-order doublet of doublets at δ −10.4, with $^2J_{PH(cis)}$ = 22 Hz, $^2J_{PH(trans)}$ = 202 Hz, and $^1J_{PtH}$ = 709 Hz, suggests phosphines cis and trans to hydride. The phosphines must be equivalent, since the $^{31}P\{^1H\}$ NMR shows a singlet at δ −55.5 ($^1J_{PtP}$ = 1655 Hz). The low value of the platinum–phosphorus coupling constant resembles that found in other six-coordinate platinum(IV) dihydrides.[31,32] Selective decoupling of the phosphine (but

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Table VI. Spectral Parameters for Platinum-Group 14 Hydrides

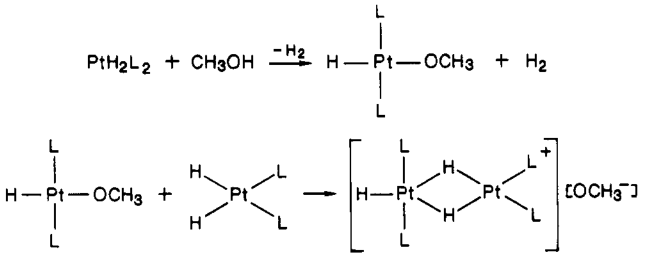
	^{31}P NMR				^{1}H NMR				
	P_A		P_B						
compound	δ	$^{1}J_{Pt-P}$, Hz	δ	$^{1}J_{Pt-P}$, Hz	δ	$^{1}J_{Pt-H}$, Hz	$^{2}J_{PH(cis)}$, Hz	$^{2}J_{PH(trans)}$, Hz	IR[d] ν_{Pt-H}, cm^{-1}
cis-$PtH(SiPh_3)(PMe_3)_2$[a]	−13.7	1723	−20.0	2210	−3.05 (dd)	892	21	164	2040
cis,trans,cis-$PtH_2(GePh_3)_2(PMe_3)_2$[b]	−55.5	1655			−10.35 (dd)	709	22	202	2140
cis,trans,cis-$PtH_2(SnPh_3)_2(PMe_3)_2$[c]	−60.9	1694	($^{2}J_{P-Sn}$ = 100 Hz)		−10.75 (dd)	649	11	180	2070

[a] Acetone-d_6, $^{2}J_{P_AP_B}$ = 19 Hz. [b] Toluene-d_8. [c] Benzene-d_6. [d] Fluorolube mull.

not hydride) protons in the ^{31}P NMR spectrum splits the resonance into a doublet of doublets consistent with two hydride ligands cis and trans to each phosphorus. The most reasonable structure for this compound is thus *cis,trans,cis*-$PtH_2(GePh_3)_2(PMe_3)_2$.

A second-order doublet of doublets also appears in the hydride region of *cis,trans,cis*-$PtH_2(SnPh_3)_2(PMe_3)_2$, with the added feature of ^{119}Sn satellites (Figure 1): δ −10.8 (dd, $^{2}J_{PH(cis)}$ = 11 Hz, $^{2}J_{PH(trans)}$ = 180 Hz, $^{1}J_{PtH}$ = 607 Hz, $^{2}J_{SnH}$ = 47 Hz). A singlet resonance in the $^{31}P\{^{1}H\}$ NMR spectrum at δ −60.9 confirms the presence of equivalent phosphine ligands. A six-coordinate structure is consistent with the low platinum–phosphorus coupling constant of 1694 Hz. Small tin–phosphorus coupling broadens the singlet near the base line. Selective decoupling of the phosphine protons results in splitting of the singlet into a doublet of doublets from coupling of each phosphine to cis and trans hydrides, with additional coupling to cis-^{119}Sn, $^{2}J_{PSn}$ ~ 100 Hz. The formulation most consistent with these spectral data is *cis,trans,cis*-$PtH_2(SnPh_3)_2(PMe_3)_2$.

Reaction between 1 and Methanol. Reaction of 1 with methanol produces the unsymmetrical dimer $[PtL_2(\mu-H)_2PtL_2H][OCH_3]$ in a reaction analogous to that of $PtH_2(PEt_3)_2$.[22a] The dimer structure was evident in the short- and long-range couplings between Pt and P in the ^{31}P NMR spectrum (see Experimental Section and ref 22a). Presumably this reaction proceeds by oxidative addition of methanol to produce the hydridomethoxyplatinum species, which then combines with 1 equiv of *cis*-1 as in eq 5.



(5)

Attempted metathesis of the dimer with sodium tetraphenylborate in acetone solvent unexpectedly cleaved the dimer, resulting in formation of $[PtH(PMe_3)_3][BPh_4]$ (4), whose molecular structure is given in Figure 2. Positional parameters for the atoms in the $PtH[P(CH_3)_3]_3^+$ moiety are given in Table II, with bond lengths and angles in Table III. No unusual bond lengths or angles occur in the tetraphenylborate counterion. The $PtH[P(CH_3)_3]_3^+$ species adopts a square-planar geometry, distorted slightly about the bulky phosphine ligands to minimize steric interactions. The Pt–P(1) bond (2.324 (2) Å) is longer than Pt–P(2) (2.287 (2) Å) or Pt–P(3) (2.294 (2) Å), which shows the trans influence of the hydride ligand exceeds that of trimethylphosphine. The structure can be compared to the triethylphosphine analogue $PtH[P(C_2H_5)_3]_3^+$, the only other sterically unhindered tris(phosphine)hydridoplatinum cation to be structurally characterized.[34] The P–Pt–P bond angles do not differ significantly, which suggests that triethylphosphine is not bulkier than trimethylphosphine in the plane of the molecule. The triethylphosphine analogue also exhibits the slight lengthening of the Pt–P bond trans to hydride. One surprising aspect of the structures is the similarity between the P–Pt–P bond angles of 100.69 (6) and 100.56 (7)° in HPt[P-

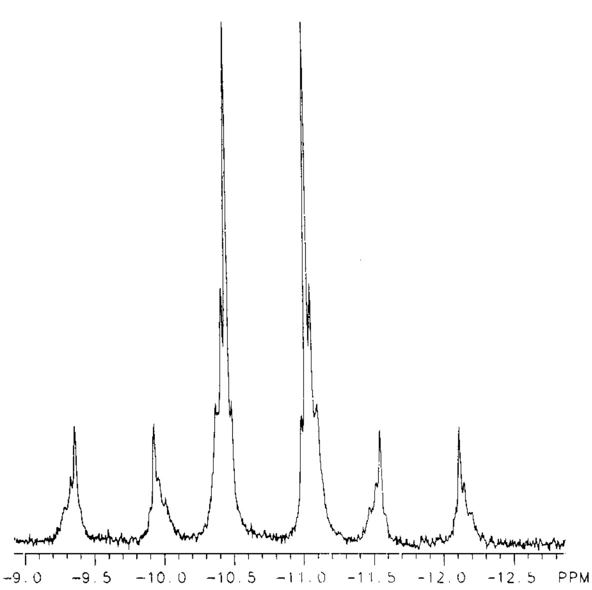


Figure 1. Hydride region of the ^{1}H NMR spectrum of *cis,trans,cis*-$PtH_2(SnPh_3)_2(PMe_3)_2$, **3b**, showing ^{119}Sn coupling to the hydride ligand.

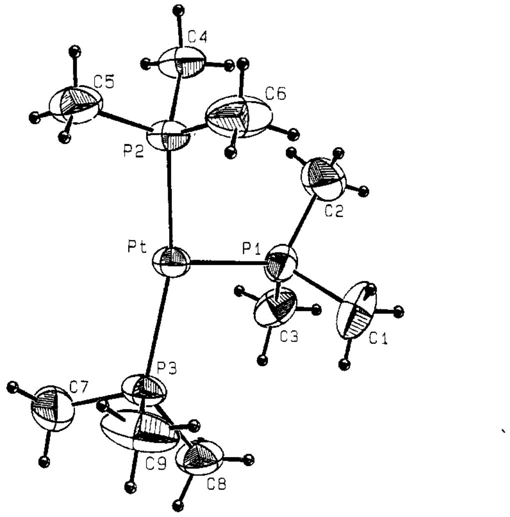


Figure 2. Thermal ellipsoid (50%) plot and atom numbering scheme showing the $PtH(PMe_3)_3^+$ fragment.

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Table VII. $^{31}P\{^1H\}$ NMR Spectral Data for $Pt(substrate)(PMe_3)_2$

substrate	δ(P)	$^1J_{Pt-P}$, Hz
CH_2CH_2[a]	-19.8	3509
$CH_2{=}CHC(CH_3)_3$[a]	-16.2, -14.3	3537, 3059
trans-PhCH=CHPh[a]	-20.0	3523
HC≡CH[a]	-20.4	3367
PhC≡CPh	-29.4	3232

[a] Solution generated by addition of olefin or alkyne to a THF solution of $PtH_2(PMe_3)_2$.

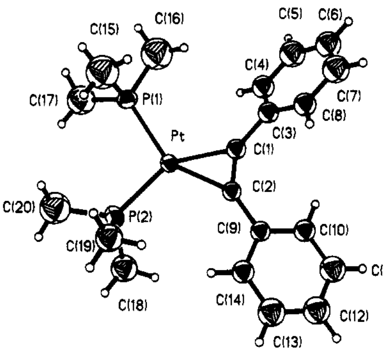

Figure 3. Thermal ellipsoid (50%) plot and atom numbering scheme for $Pt(PhC{\equiv}CPh)(PMe_3)_2$.

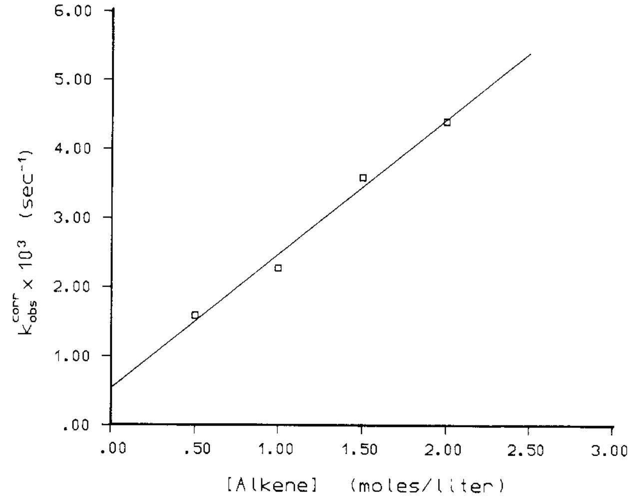

Figure 4. Plot of the dependence of k_{obsd}^{corr} on substrate concentration for the reaction between 1 and *tert*-butylethylene at 21 °C.

$(CH_3)_3]_3^+$ and of 100.1 (2) and 101.5 (2)° in $HPt[P(C_2H_5)_3]_3^+$. Ligand cone angles of 118° and 132° for $P(CH_3)_3$ and $P(C_2H_5)_3$, respectively,[35] suggest an appreciable steric difference. This difference influences the reactivity and cis–trans equilibria of square-planar complexes such as $PtH_2(PR_3)_2$[2,3] but apparently does not perturb the ground-state structure.

Reaction between $PtH_2(PMe_3)_2$, Alkenes, and Alkynes. In solution, 1 reacts with alkenes and alkynes to evolve hydrogen gas and form a π complex with substrate. No insertion products were detected. The lack of insertion reactions will be considered shortly. The characteristic phosphorus–platinum coupling constants of 3000–4000 Hz identify the complexes formed as zerovalent species.[32] Table VII contains the ^{31}P NMR parameters for the products of reaction between 1 and various alkenes and alkynes. According to the Dewar–Chatt–Duncanson model, the bonding in these complexes is intermediate between an alkene with a π bond to platinum and an alkane σ-bonded to the metal.[32]

The diphenylacetylene π complex (Figure 3) was characterized crystallographically (Tables IV and V) to provide a definitive structural determination on which to base the NMR characterization for the series of olefin and alkyne complexes. The structure exhibits a pseudo square-planar coordination sphere about Pt. There is only a 3.1° angle between the Pt, P1, P2, C1, C2 plane and the Pt, C1, C2 plane. The C1–C2 length of 1.29(2) Å resembles that found[36] in $Pt(C_2Ph_2)(PPh_3)_2$ of 1.32 (9) Å. The phenyl groups bend back on coordination with Pt–C1–C3 ≥ 143.9 (10)° and Pt–C2–C9 ≥ 149.1 (9)°. The phenyl groups align with 16.3° and 130.4° dihedral angles between their least-squares planes and that defined by Pt, C1, and C2.

Reaction between 1 and the hindered substrate *tert*-butylethylene proceeds readily in THF solvent at 20 °C to give the π-complex 5 (eq 6). The reaction may be

$$trans\text{-}PtH_2L_2 \underset{K}{\rightleftharpoons} cis\text{-}PtH_2L_2 \xrightarrow{k_{obs}^{corr}} \underset{5}{cis\text{-}Pt(olefin)L_2} + H_2 \qquad (6)$$

followed by monitoring the decrease in absorbance at 1720 cm^{-1} attributed to *trans*-1, k_{obsd}, in the infrared spectrum. It was determined previously[2] that tetrafluoroethylene reacts preferentially with *cis*-$PtH_2(PEt_3)_2$, to deplete the concentration of the cis isomer and shift the trans ⇌ cis equilibrium until all the dihydride reacts. The five-coordinate intermediate $PtH_2(C_2F_4)(PEt_3)_2$ was observed at low temperatures. No further mechanistic details of the H_2 displacement reaction have been reported. The absence of hydrogenation in the reaction of alkenes with the dihydride has not been explained. Even though the cis isomer may react with olefin, the decay of the *trans*-dihydride can be used to monitor the reaction since *cis–trans* isomerization occurs faster than the reaction with olefin.[37] According to the mechanism of eq 6, $k_{obsd}^{corr} = k_{obsd}(1 + 1/K)$. It was not possible to monitor the reaction by NMR spectroscopy because the dihydride resonances lie close to those of the olefin complex and are not resolved above -30 °C, where reaction occurs.

Under pseudo-first-order conditions of a large (10–40-fold) excess of *tert*-butylethylene, the reaction rate is independent of the concentration of 1 (0.1–0.3 M). The rate constant k_{obsd}^{corr} shows a first-order dependence on the concentration of substrate (Figure 4). The slope of the line, $(1.95 \pm 0.24) \times 10^{-3}$ M^{-1} s^{-1}, gives the second-order rate constant at 21 °C. The intercept, $(5.4 \pm 2) \times 10^{-4}$ s^{-1}, approaches zero within the error of the experiment. However, this value resembles that of 7.3×10^{-4} s^{-1} observed for the first-order reductive elimination of hydrogen from 1 at 21 °C,[18] which may imply that as the concentration of substrate approaches zero, the reductive elimination pathway becomes important and the reaction follows the rate law $(k_1 + k_2[olefin])[PtH_2L_2]$.

An Eyring plot of the temperature dependence of k_{obsd}^{corr} at high olefin concentration, where k_2 dominates, yields $\Delta H^{\ddagger} = 8.1 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -42 \pm 4$ cal/(mol K). The large negative value of $\Delta S^{\ddagger}$, together with the observed rate dependence on substrate concentration, conforms to an associative mechanism involving coordination of the olefin to an intact dihydride molecule in the transition state, followed by reductive elimination of hydrogen; eq 7. It was not possible to measure the phosphine dependence of the reaction rate since phosphine reacts with 1

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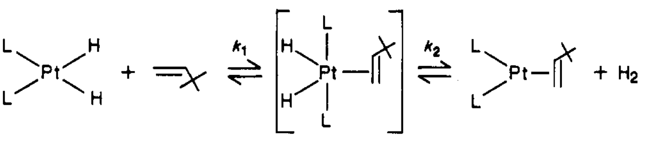
[35] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[36] Glanville, J. O.; Stewart, J. M.; Grim, S. O. *J. Organomet. Chem.* **1967**, *7*, 9.

[37] Spin saturation transfer studies in progress show that the rate constant for trans ⇌ cis isomerization is about 0.1 s^{-1} at -60 °C.



(7)

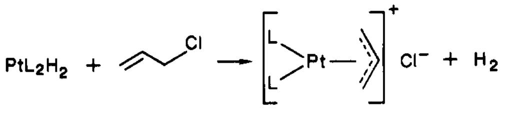
to produce the known five-coordinate species $PtH_2(PMe_3)_3$.[2] If *tert*-butylethylene is added to a solution of 1 under a H_2 atmosphere, the reaction reaches an equilibrium near 50% completion.

No hydrogenation of *tert*-butylethylene (<5%) is observed by gas chromatography analysis of the reaction products. Neither was the unhindered substrate ethylene hydrogenated by reaction with $PtH_2(PEt_3)_2$.[2] Theoretical studies[38,39] have postulated that insertion of alkenes and alkynes into a platinum–hydrogen bond occurs from a four-center transition state. Hoffmann and Thorn[38] predicted that insertion would not proceed from a five-coordinate species, since it would relax into a configuration unsuitable for insertion. Only after dissociation of a ligand to form a four-coordinate complex could insertion occur. The inability of 1 to hydrogenate olefins, in the five-coordinate intermediate or transition state, supports this hypothesis. Experimental studies of the insertion of alkynes into platinum hydrides such as *trans*-$PtHCl(PEt_3)_2$ in polar solvents suggest that insertion involves a four-coordinate intermediate formed by displacement of chloride by acetylene.[40,41]

Insertion of tetrafluoroethylene into the platinum–oxygen bond of $Pt(CH_3)(OCH_3)(DPPE)$ proceeds by an associative mechanism,[42] and the five-coordinate intermediate may be observed at low temperatures.[42] Other examples exist of coordination of tetrafluoroethylene to bis(phosphine)platinum(II) alkyl or hydride complexes before insertion into the platinum–carbon or platinum–hydrogen bond.[2,41] In an interesting study Clark et al.[43] show that activated acetylenes insert into the platinum–hydrogen bond of the sterically hindered dihydride $PtH_2(PCy_3)_2$ by an electron-transfer process involving a charge-transfer interaction between a Pt(II) radical cation and an acetylene radical anion. Analysis of the reaction products for the $PtH_2(PMe_3)_2$ system show no evidence of insertion to form a *trans*-PtH(alkenyl)$(PMe_3)_2$ species.

Because of the small size of the PMe_3 ligand, even bulky substrates may coordinate associatively to 1. Ethylene, acetylene, *trans*-stilbene, and diphenylacetylene react with 1 more rapidly than *tert*-butylethylene at 21 °C in THF, presumably by an associative mechanism since reductive elimination of hydrogen occurs slowly at this temperature.[18] The olefins tetracyanoethylene, tetramethylethylene, and tri- or tetraphenylethylene do not react with 1 even when heated to 40–50 °C under nitrogen. Under these conditions 1 decomposes via reductive elimination of hydrogen to give $Pt(PMe_3)_4$ and platinum metal. Evidently these substrates are too hindered to approach the platinum center.

Reaction between $PtH_2(PMe_3)_2$ and Allyl Chloride. A variation on the associative reaction between alkenes and the dihydride is the reaction with allyl chloride. Addition of an equivalent of allyl chloride to a solution of $PtH_2(PMe_3)_2$ in THF yields the π-allyl complex 6 according to eq 8. The ^{31}P NMR spectrum of this reaction shows 6 as

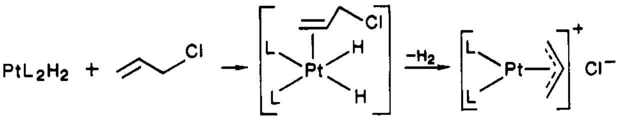


(8)

6

the only phosphorus-containing species in solution. The allyl complex can be obtained as an analytically pure white powder after metathesis with $NaBPh_4$.

Previous attempts to prepare this complex by oxidative addition of allyl chloride to the PtL_2 species generated photochemically from $Pt(C_2O_4)L_2$ ($L = PEt_3$) resulted in a complex mixture of products.[21] A mechanism for reaction, eq 9, involves precoordination of the alkene functionality followed by reductive elimination of hydrogen and oxidative addition of the coordinated allyl. Intermediate formation of the five-coordinate complex may inhibit the formation of side products generated in the oxidative addition of the free allyl chloride to highly reactive PtL_2. Irradiation of 6 does not cause decomposition of the complex; therefore secondary photolysis does not contribute to the decomposition observed in the photochemical addition of allyl chloride to $Pt(C_2O_4)L_2$.



(9)

Conclusion

The sterically unhindered dihydride $PtH_2(PMe_3)_2$ exhibits different reactivity from bulkier analogues. Sterically hindered platinum bis(phosphine) dihydride complexes generally reductively eliminate H_2 to generate PtL_2 as a reactive intermediate or insert unsaturated substrates into the Pt–H bond. Although H_2 will reductively eliminate from $PtH_2(PMe_3)_2$ the reaction occurs much slower than the associative reactions between it and olefinic, acetylenic, and oxidative addition substrates. These substrates react by associative attack at the platinum center. Platinum(IV) complexes are isolable intermediates in several oxidative addition reactions of these unhindered dihydrides. The small size and good donor properties[35] of the PMe_3 ligand probably account for these differences. While sterically hindered dihydrides such as $PtH_2(PCy_3)_2$ undergo insertion reactions with olefins and small molecules,[41,43,44] associative reactions that displace H_2 are a general feature of the chemistry of $PtH_2(PMe_3)_2$.

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Registry No. **1**, 80581-71-1; **2**, 111112-81-3; **3a**, 111112-80-2; **3b**, 111112-82-4; **4**, 111112-86-8; **5**, 111112-87-9; **6** (BPh_4 salt), 111112-89-1; *cis*-$PtCl_2(PMe_3)_2$, 15630-86-1; *cis*-$PtCl_2(SEt_2)_2$, 15442-57-6; Ph_3SiH, 993-07-7; Ph_3GeH, 2816-43-5; Ph_3SnH, 892-20-6; $[Pt(PMe_3)_2(\mu\text{-}H)_2Pt(PMe_3)_2H][OCH_3]$, 111112-84-6; $CH_2{=}CH_2$, 74-85-1; $Pt(C_2H_4)(PMe_3)_2$, 69547-16-6; $PhC{\equiv}CPh$, 501-65-5; $Pt(PhC{\equiv}CPh)(PMe_3)_2$, 75982-99-9; *tert*-butylethylene, 558-37-2; allyl chloride, 107-05-1.

Supplementary Material Available: Tables of least-squares planes, anisotropic thermal parameters, and bond distances and angles for $Pt(C_2Ph_2)(PMe_3)_2$ and $[PtH(PMe_3)_3][BPh_4]$ and a table of hydrogen coordinates for $Pt(C_2Ph_2)(PMe_3)_2$ and a table of positional parameters for $[PtH(PMe_3)_3][BPh_4]$ (21 pages); listings of structure factors (69 pages). Ordering information is given on any current masthead page.

Synthesis of Metallacarborane Clusters Derived from the Monocarbon Carborane $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$

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A single-crystal X-ray study of $9\text{-}Ph_3P\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ (I) has confirmed that the compound has a structure based on an 11-vertex nido cage geometry. Crystal data for I: space group $P2_1/n$; $Z = 4$; $a = 17.154$ (3) Å, $b = 11.999$ (2) Å, $c = 17.469$ (4) Å, $\beta = 108.2$ (1)°; $V = 3414.2$ Å^3. The structure was refined to a final $R = 0.061$ and $R_w = 0.073$ for the 2916 reflections having $F_o^2 > 3\sigma(F_o^2)$. The dimethyl sulfide analogue of I, $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$, has been shown to be a versatile ligand for transition metals. The reaction of $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ and $(\eta\text{-}C_5H_5)Co(CO)_2$ in refluxing toluene resulted in a complex mixture from which three metallacarborane products could be characterized. Compounds II and III were shown to be the isomeric sandwich complexes $7\text{-}(CH_3)_2S\text{-}2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_9$ and $12\text{-}(CH_3)_2S\text{-}2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_9$, respectively. Also isolated in trace amounts was the zwitterionic compound IV, $12\text{-}[(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4)]^+[2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_9]^-$. Reaction of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ and $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ gave $2\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}NiCB_{10}H_{10}$ (V), while reaction of the carborane with cobalt vapor and toluene gave $2\text{-}(\eta^6\text{-}C_6H_5CH_3)\text{-}1\text{-}[((CH_3)_3Si)_2CH]\text{-}2,1\text{-}CoCB_{10}H_{10}$ (VI). The sandwich structures of compounds of V and VI were confirmed by single-crystal X-ray crystallographic studies. Crystal data for V: space group $P\bar{1}$; $Z = 2$; $a = 8.856$ (1) Å, $b = 17.165$ (5) Å, $c = 8.647$ (1) Å, $\alpha = 103.14$ (1)°; $\beta = 114.51$ (1)°; $\gamma = 85.63$ (2)°; $V = 1164.5$ Å^3. The structure was refined to a final $R = 0.056$ and $R_w = 0.069$ for the 3726 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for VI: space group $P\bar{1}$; $Z = 2$; $a = 8.803$ (2) Å, $b = 18.007$ (5) Å, $c = 8.663$ (2) Å, $\alpha = 101.09$ (2)°, $\beta = 114.16$ (2)°, $\gamma = 83.07$ (2); $V = 1228.1$ Å^3. The structure was refined to a final $R = 0.087$ and $R_w = 0.096$ for the 2355 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We recently reported[1] that the dimethyl sulfide promoted reaction of bis(trimethylsilyl)acetylene with decaborane(14) gives, as one of the major products, the new monocarbon carborane $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$. From the spectroscopic data, the compound was proposed to have an 11-vertex nido-cage geometry, based on an icosahedron missing one vertex, with the dimethyl sulfide and bis(trimethylsilyl)methyl groups bound to the 9-boron and 7-carbon, respectively, on the open face. In addition, the ^1H NMR data indicated the presence of two boron–boron bridging hydrogens. We have now found that the dimethyl sulfide group can be readily displaced by triphenylphosphine and a single-crystal X-ray study of the resulting compound $9\text{-}Ph_3P\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ has confirmed the proposed structures of these carboranes.

It was also demonstrated[1] that under appropriate conditions the dimethyl sulfide and/or the two bridging hydrogens can be removed from $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$. For example, reaction of the compound with lithium triethylborohydride results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the *closo*-$RCB_{10}H_{10}^-$ anion, while thermolysis of the compound results in hydrogen loss and cage closure to give the isoelectronic neutral carborane *closo*-$RCB_{10}H_9{\cdot}SMe_2$. These results suggested that $9\text{-}(CH_3)_2S\text{-}7\text{-}[((CH_3)_3Si)_2CH]CB_{10}H_{11}$ might also function as a versatile transition-metal ligand similar to other known eleven-vertex monocarbon carboranes.[2] Thus, depending on whether the bridge protons and/or the dimethyl sulfide are removed from the cage either of the anions $RCB_{10}H_{10}^{3-}$

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