

Cis Dihydride Diphosphine Complexes of Platinum(II) and Their Dehydrogenation to Form Dimeric Platinum(0) Complexes. The Structure of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$

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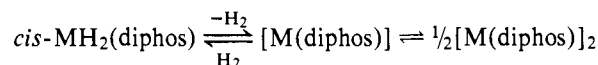
Abstract: A series of diphosphinedichloroplatinum(II) complexes, having bulky phosphine substituents, react with sodium amalgam in THF to yield the corresponding cis dihydride complexes. These dihydride species possess unusual thermal stability and are not highly air sensitive. When diphosphines of intermediate steric bulk are involved it is possible to observe a reversible loss of H_2 from these dihydrides. Spectroscopic data are consistent with the presumption that the products of these dehydrogenations are derived from highly reactive bent diphosphine species Pt(diphos). Electron-poor olefins will irreversibly displace H_2 from the cis dihydride complexes to yield coordinated olefin complexes. Electron-rich olefins do not exhibit this behavior, but under forcing condition can be catalytically hydrogenated in the presence of the cis dihydride. A proof by induction of the dimeric nature of the product of the reversible dehydrogenation is presented in the form of a crystal structure determination of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$. The dimeric molecule has crystallographically imposed C_2 symmetry. Each Pt atom is three-coordinate, being bound to two P atoms and the other Pt atom. The Pt-Pt separation is 2.765 (1) Å, and the angle between the two P-Pt-P planes is 82°. The molecule as a whole exhibits very severe crowding. The compound crystallizes as a toluene solvate in the monoclinic space group C_{2h}^6-C2/c in a cell of dimensions $a = 19.101$ (6), $b = 11.723$ (6), $c = 23.202$ (9) Å, with $\beta = 100.07$ (3)°. There are four dimeric molecules and four solvent molecules per unit cell. Based on 5350 unique reflections having $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by full-matrix least-squares techniques to conventional agreement indices (on F) of $R = 0.030$ and $R_w = 0.040$. The nature of the Pt-Pt interaction is discussed and possible explanations for the observed geometry of the dimer are offered.

Four-coordinate, planar d^8 metal complexes with cis hydrido ligands are rare. We are aware of only one example, that of $\text{PtH}_2[1,2(t\text{-Bu})_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}(t\text{-Bu})_2]$, which has recently been reported.² The cis arrangement of hydrido ligands is not unusual in transition metal complexes of coordination number six or higher.³ Hence, the rarity of cis dihydride complexes of d^8 metals cannot be ascribed to the geometrical arrangement which might facilitate cis elimination of H_2 . A number of thermally and kinetically stable trans dihydride complexes, *trans*- MH_2L_2 , have been isolated with a bulky *tert*-phosphine as the auxiliary ligand L.⁴⁻⁷ Since the trans influence of the hydrido ligand is stronger than that of *tert*-phosphines⁸ (including trialkylphosphines), we would expect cis dihydrides to be more stable electronically than trans dihydrides. The existence of stable *trans*- MH_2L_2 species therefore suggests that a series of *cis*- MH_2L_2 (L = phosphine) complexes can be prepared.

In recent years, the predominant role of steric effects in determining the chemistry of low-valent, late transition-metal complexes has become obvious.⁹ Thus, for example, a number of "14" electron complexes, formerly thought to be innately unstable,^{6,11-19} have been prepared utilizing bulky phosphine ligands.⁴⁻¹³ Ligands of high steric demand are thus expected to stabilize kinetically normally labile dihydride species, the small size of the hydrido ligand allowing complexation and the bulk of the ligand matrix prohibiting attack on the coordinated hydride.^{2,5-7,20}

In order to prepare complexes of the type *cis*- MH_2L_2 our tactic as described here was to use chelating diphosphines having bulky substituents at the phosphorus atoms. In this way we would force cis coordination of the P atoms and provide steric protection for the hydrido ligands. We were thus able to prepare a series of dihydrides of general formula $\text{PtH}_2(\text{diphos})[\text{diphos} = \text{R}_1\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_1\text{R}_2$ ($\text{R}_1 = \text{R}_2 = t\text{-Bu}$, Men (*l*-menthyl), Ph; $\text{R}_1 = \text{Ph}$, $\text{R}_2 = t\text{-Bu}$, Men), $(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(t\text{-Bu})_2$]. In this series we found some labile *cis* dihydride complexes in which the hydride coordination is reversible. Although some Ir(I) complexes²¹ are known to coordinate H_2 reversibly, there were apparently no known

examples of reversible hydrogenation among complexes of the nickel triad. A pertinent question here is whether the "14" electron metal (diphos) species exist in solution and are isolable. The existence and reactivity of such species should depend on several factors, such as the bulk and electronic properties of the substituents on the phosphorus atoms and the interligand angle $\angle\text{PMP}$, which in turn is a function of the methylene chain connecting the two phosphorus atoms. In a search for these M(diphos) species we have found several strongly colored complexes of Pt(0), which we have formulated as dimers. These are apparently derived from the reactive mononuclear complexes M(diphos). Since Pt(0) cluster complexes having no bridging ligands are unknown and since these new dimers may involve multiple metal-metal bonds, we undertook the structure determination of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$ in order to obtain metrical details on one of these new dimers.



Experimental Section

All reactions and manipulations were carried out under a pure dinitrogen atmosphere. ¹H and ³¹P NMR spectra were recorded on JEOL JNM-4H-100 or JNM-C-60HL and Varian CFT-20 spectrometers, respectively, and IR spectra on a Hitachi Perkin-Elmer 225 spectrometer. Starting materials, $\text{PtCl}_2[\text{R}_1\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_1\text{R}_2]$ ($\text{R}_1 = \text{R}_2 = t\text{-Bu}$, $n = 2, 3$; $\text{R}_1 = \text{R}_2 = \text{Men}$, $n = 2$; $\text{R}_1 = \text{Ph}$, $\text{R}_2 = t\text{-Bu}$, $n = 2$; $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{Men}$, $n = 2$) were prepared from $\text{PtCl}_2(\text{COD})$ and the corresponding diphosphine; the details will be published separately. The *cis* chelate structure for $\text{PtCl}_2[(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]$ was confirmed by an x-ray analysis²² as well as from ¹H NMR and IR spectra. This contrasts to the report of Moulton and Shaw² that $(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2$ prefers to bridge metal atoms rather than chelate. The physical properties and analytical data for some of the complexes prepared here are summarized in Table I. Table II presents spectral data for some of the *cis* dihydride products.

Preparation of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$ (1). A mixture of $\text{PtCl}_2[(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]$ (0.60 g, 1 mmol) and Na/Hg (1%,

Table I. Physical Properties and Analytical Data

	Color	Mp, °C ^a	Anal. ^b	
			C	H
[Pt(<i>t</i> -Bu) ₂ P(CH ₂) ₃ P(<i>t</i> -Bu) ₂] ₂ · C ₆ H ₅ CH ₃ (1)	Red	234	46.97 (47.07)	8.16 (8.09)
Pt(CO) ₂ [(<i>t</i> -Bu) ₂ P(CH ₂) ₃ P(<i>t</i> -Bu) ₂] (2)	Colorless	210–239	43.73 (43.12)	7.40 (7.25)
PtH ₂ [(<i>t</i> -Bu) ₂ PCH ₂ CH ₂ P(<i>t</i> -Bu) ₂] (3)	Colorless	224–226	41.33 (41.93)	7.99 (8.21)
PtH ₂ (Men ₂ PCH ₂ CH ₂ PMen ₂) ^c (4)	Colorless	202–224	59.02 (59.48)	9.60 (10.22)
PtH ₂ [(<i>t</i> -Bu) ₂ P(CH ₂) ₃ P(<i>t</i> -Bu) ₂] (5)	Colorless	283	43.65 (44.35)	8.35 (8.19)
PtH ₂ [Men(Ph)PCH ₂ CH ₂ P(Ph)Men] ^d (6)	Colorless	202–220	54.94 ^e (56.73)	7.48 (7.56)
PtH ₂ [<i>t</i> -Bu(Ph)PCH ₂ CH ₂ P(Ph) <i>t</i> -Bu] (7)	Colorless	97	47.79 (47.56)	6.42 (6.17)

^a Under N₂, with decomposition. ^b Required value is shown in parentheses. ^c [α]³⁰_D –72.9° (*c* 0.24, benzene). ^d [α]²⁸_D –33.2° (*c* 0.71, toluene). ^e Owing to instability of the compound, an analytically pure sample was not obtained.

Table II. Spectral Data of *cis*-PtH₂(diphos)

(diphos)	Pt–H, ^a ppm	J _{H–P(trans)} , Hz	J _{H–P(cis)} , Hz	J _{H–Pt} , Hz	Other	IR, cm ^{–1b} (Pt–H)
(<i>t</i> -Bu) ₂ PCH ₂ CH ₂ P(<i>t</i> -Bu) ₂ (3)	–0.60 (dd)	183.5	16.4	1101	CH ₃ , 1.19 (d), J _{H–P} = 12.9 Hz CH ₂ , 0.4–2.2 (m)	2008 sh 1980 vs
Men ₂ PCH ₂ CH ₂ PMen ₂ (4)	–1.51 (dd)	183.9	15.5	1138	Men, 0.5–3.6 (m)	1989 vs
(<i>t</i> -Bu) ₂ P(CH ₂) ₃ P(<i>t</i> -Bu) ₂ (5)	–2.14 (dd)	171.2	19.4	1064	CH ₃ , 1.21 (d), J _{H–P} = 12.9 Hz CH ₂ , 0.9–1.7 (m)	1995 vs
Men(Ph)PCH ₂ CH ₂ P(Ph)Men (6)	–0.32 (dd)	184.0	15.0	1149	Men, 0.5–3.0 (m) <i>o</i> -H, 7.6–8.3 (m) <i>m</i> - and <i>p</i> -H, 6.9–7.3 (m)	2004 sh 1977 vs
<i>t</i> -Bu(Ph)PCH ₂ CH ₂ P(Ph) <i>t</i> -Bu (7)	0.07 (dd)	181.5	14.0	1131	CH ₃ , 1.12 (d), J _{H–P} = 14.7 Hz CH ₂ , 0.6–2.2 (m) <i>o</i> -H, 7.75 (m) <i>m</i> - and <i>p</i> -H, 6.7–7.2 (m)	1985 vs
Ph ₂ PCH ₂ CH ₂ PPh ₂ (8)						1930 b

^a Measured in toluene-*d*₈ at 35 °C. ^b Measured in Nujol mull.

50 g) in THF was stirred at room temperature for 15 h. After filtration the reddish orange filtrate was concentrated in vacuo to give a dark red, crystalline residue. Extraction with *n*-hexane and subsequent evaporation gave reddish orange crystals which were recrystallized from hot toluene to give an analytically pure sample (0.190 g, 35%).

Reaction of 1 with CO. Into a toluene (10 mL) solution of **1** (53 mg, 0.05 mmol) CO was bubbled at room temperature for 30 min. Concentration of the colorless solution gave colorless microcrystals (42 mg, 77%) of Pt(CO)₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] (**2**).

Reaction of 1 with D₂. A red solution of **1** (58 mg, 0.055 mmol) in *n*-hexane (7 mL) was stirred under D₂ (1 atm) at room temperature for 17 h. From the colorless solution a colorless solid separated whose IR spectrum showed two bands at 1430 and 1995 cm^{–1}, which we attribute to the Pt–D and Pt–H stretching vibrations, respectively. This indicates the presence of such species as PtD₂(diphos), PtHD(diphos), and PtH₂(diphos) [diphos = (*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂].

Reaction of 1 with CHCl₃. A sample of **1** (65 mg, 0.062 mmol) was dissolved in a mixture of toluene and CHCl₃ (volume ratio 10:1, 1 mL) and the solution was heated at 50 °C for 10 min. On cooling to room temperature PtCl₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] (30 mg, 40%) separated as colorless crystals. VPC (Apiezon grease L, 1.4 m) of the solution showed the formation of CH₂Cl₂ (10 mg, 92%).

Preparation of Cis Dihydrides. PtH₂[(*t*-Bu)₂PCH₂CH₂P(*t*-Bu)₂] (**3**). A mixture of PtCl₂[(*t*-Bu)₂PCH₂CH₂P(*t*-Bu)₂] (0.58 g, 1 mmol) and Na/Hg (1%, 50 g) in THF was stirred at room temperature for 17 h. After filtration the solvent was removed in vacuo to give a red oil, which was dissolved in *n*-hexane (10 mL) and allowed to stand in a freezer. Colorless crystals of **3** separated and were subsequently recrystallized from toluene and *n*-hexane (0.18 g, 35%). Compound

3 was also prepared by reduction of the corresponding dichloride with Na/Hg under H₂ (1 atm) in 68% yield.

PtH₂(Men₂PCH₂CH₂PMen₂) (**4**). This complex was prepared similarly by reducing PtCl₂(Men₂PCH₂CH₂PMen₂) (0.39 g, 0.4 mmol) with Na/Hg (1%, 25 g) in the absence or presence of H₂ in 32 and 48% yield, respectively.

PtH₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] (**5**). Into a toluene solution of **1** (53 mg, 0.05 mmol) H₂ was bubbled for 30 min. The red solution became colorless. Concentration in vacuo gave **5** quantitatively as colorless crystals. Compound **5** was also prepared by reducing PtCl₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] with Na/Hg under H₂ in 80% yield.

PtH₂[Men(Ph)PCH₂CH₂P(Ph)Men] (**6**). This compound was prepared by the reduction of PtCl₂[Men(Ph)PCH₂CH₂P(Ph)Men] (0.15 g, 0.19 mmol) by Na/Hg (1%, 20 g) in THF under a H₂ atmosphere. After filtration under H₂ the colorless filtrate was concentrated in vacuo and the resultant reddish, oily residue was dissolved in toluene (5 mL). On addition of MeOH (3 mL) the red solution turned colorless. Concentration to half volume in vacuo gave colorless crystals of **6** (0.10 g, 73%).

PtH₂[*t*-Bu(Ph)PCH₂CH₂P(Ph)*t*-Bu] (**7**). This complex was prepared in 58% yield in a manner similar to **6** by reducing PtCl₂[*t*-Bu(Ph)PCH₂CH₂P(Ph)*t*-Bu] with Na/Hg under H₂.

PtH₂(Ph₂PCH₂CH₂PPh₂) (**8**). A mixture of PtCl₂(Ph₂PCH₂CH₂PPh₂) (0.33 g, 0.5 mmol) and Na/Hg (1%, 25 g) in THF (15 mL) was stirred under a H₂ atmosphere for 3 h. After filtration under H₂ the yellow filtrate was concentrated in vacuo to give a dark reddish brown oil. Attempts to crystallize the oil were fruitless. The IR spectrum of the oil under H₂ shows a broad signal at 1930 cm^{–1}, probably arising from ν (Pt–H).

Reversibility of H₂ Coordination of 6 and 7. A colorless toluene-*d*₈ solution (0.5 mL) of **7** (50 mg) in a ¹H NMR tube was heated grad-

ually from room temperature to 95 °C. At 55 °C the intensity of the hydride signal (δ 0.07) began to decrease and at 95 °C it had almost completely disappeared and the solution was dark red. The ^1H NMR of the red solution showed two *tert*-butyl resonances at δ 1.32 (m, $^3J_{\text{H-P}} + ^6J_{\text{H-P}} = 13.9$ Hz) and 1.15 (d, $^3J_{\text{H-P}} = 14.7$ Hz) with relative intensity of 5:1. On bubbling H_2 into the red solution at room temperature for 30 min, the solution became pale yellow and the ^1H NMR spectrum was completely identical with that of **7**. Alternatively, the red solution was treated with MeOH (0.1 mL) to give a pale brown solution, from which **7** was obtained on concentration in vacuo.

When treated in a similar manner **6** almost quantitatively released its coordinated dihydrogen at 80 °C to give a dark red solution. Introduction of H_2 (1 atm) or MeOH at room temperature regenerated **6**.

Reaction of 3 with Olefins. $\text{Pt}(\text{AN})[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ (**11**, AN = Acrylonitrile). To a toluene solution (10 mL) of **3** (89 mg, 0.17 mmol) was added AN (45 mg, 0.86 mmol) at room temperature. Immediately H_2 gas evolution was observed. The colorless solution was concentrated under reduced pressure. VPC analysis shows the absence of $\text{CH}_3\text{CH}_2\text{CN}$ in the distillate.

Recrystallization of the residue from CH_2Cl_2 -*n*-heptane gave colorless crystals (62 mg, 55%): ^1H NMR (C_6D_6) δ 0.98 (d, 9, $J_{\text{P-H}} = 12.4$ Hz, *t*- C_4H_9), 1.02 (d, 18, $J_{\text{P-H}} = 12.7$ Hz, *t*- C_4H_9), 1.24 (d, 9, $J_{\text{P-H}} = 13.0$ Hz, *t*- C_4H_9), 1.9–2.6 (m, 3, $\text{CH}=\text{C}$); IR (Nujol mull) 2190 cm^{-1} ($\nu(\text{CN})$).

$\text{Pt}(\text{MA})[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ (**12**, MA = Maleic Anhydride). This compound is prepared in 38% yield in a manner similar to **11**, using **3** (84 mg, 0.16 mmol) and MA (80 mg, 0.81 mmol): ^1H NMR (CDCl_3) δ 1.25 (d, 18, $J_{\text{P-H}} = 13.9$ Hz, *t*- C_4H_9), 1.28 (d, 18, $J_{\text{P-H}} = 13.9$ Hz, *t*- C_4H_9), 3.47 (d, 2, $J_{\text{P-H}} = 8.4$, $J_{\text{Pt-H}} = 53.1$ Hz, $\text{CH}=\text{C}$); IR (Nujol mull) 1965 cm^{-1} ($\nu(\text{CO})$).

$\text{Pt}(\text{FN})[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ (**13**, FN = Fumaronitrile). Similarly this complex was prepared in 44% yield by treating **3** (27 mg, 0.05 mmol) with FN (82 mg, 0.10 mmol): ^1H NMR (C_6D_6) δ 0.90 (d, 18, $J_{\text{P-H}} = 13.4$ Hz, *t*- C_4H_9), 1.13 (d, 18, $J_{\text{P-H}} = 13.4$ Hz, *t*- C_4H_9), 2.50 (d, 2, $J_{\text{P-H}} = 7.1$, $J_{\text{Pt-H}} = 58.4$ Hz, $\text{CH}=\text{C}$); IR (Nujol mull) 2200 cm^{-1} ($\nu(\text{CN})$).

Catalytic Hydrogenation of Cyclohexene by 3. To a benzene solution (10 mL) of **3** (0.12 g, 0.23 mmol) was added cyclohexene (1.93 g, 23.5 mmol) at room temperature. No hydrogen evolution was observed and **3** was recovered quantitatively. In a separate run, the above mixture was heated under H_2 (80 kg/cm²) at 100 °C for 3.5 h. The reaction mixture was distilled under reduced pressure. VPC showed the formation of cyclohexane (13.4 mol/mol **3**). Recrystallization of the distillation residue from toluene-*n*-hexane gave **3** almost quantitatively.

Collection and Reduction of the X-Ray Data. Upon standing, a toluene solution of the dimer complex, $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$ (**1**), yielded a crop of red, hexagonal platelets. A suitable crystal was chosen and encapsulated in a glass capillary under an atmosphere of N_2 . Preliminary photographic data revealed Laue symmetry $2/m$. Systematic extinctions (hkl , $h + k = 2n + 1$; $h0l$, $h = 2n + 1$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) characteristic of the space groups $C_2^4 - Cc$ and $C_{2h}^6 - C2/c$ were observed. The latter, centrosymmetric group was chosen initially. This choice was subsequently shown to be correct, as (1) the intensities of 543 Friedel pairs proved to be internally equivalent; (2) a total of 32 of the 36 independent hydrogen atoms of the methyl groups were located by Fourier methods; and (3) reasonable positional and thermal parameters were refined successfully.

Cell constants were obtained, as previously described,²³ by a least-squares refinement of the setting angles of 13 hand-centered reflections, which had been chosen from diverse regions of reciprocal space with $31.0^\circ \leq 2\theta(\text{Mo}) \leq 38.7^\circ$. These cell constants and other pertinent data are shown in Table III. The density calculated for four molecules in the cell is reasonable when compared with those of related compounds.¹¹ With Z of 4 either a center of symmetry or a twofold axis is imposed on the dimer in space group $C2/c$.

Intensity data were collected on a computer-controlled Picker four-circle diffractometer. Background counts were measured at both ends of the scan range with the counter and crystal held stationary. Six of every 100 reflections measured were standards. No significant deviation in the intensities of these standards was observed. A total of 8456 intensities (including some Friedel pairs) were recorded out to $2\theta \leq 59.5^\circ$; past this point few intensities appeared to be significantly above background. The data were processed as described previously,²⁴ using a value of p of 0.04. After processing, only those 5350

Table III. Summary of Crystal Data and Intensity Collection

Compd	$[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2 \cdot \text{C}_6\text{H}_5\text{CH}_3$
Formula	$\text{C}_{45}\text{H}_{96}\text{P}_4\text{Pt}_2$
Formula weight	1151.34 amu
<i>a</i>	19.101 (6) Å
<i>b</i>	11.723 (6) Å
<i>c</i>	23.202 (9) Å
β	100.07 (3)°
<i>V</i>	5115 Å ³
<i>Z</i>	4
Density (calcd)	1.494 g cm ⁻³
Space group	$C_{2h}^6 - C2/c$
Crystal dimensions	0.82 × 0.64 × 0.16 mm
Crystal shape	Hexagonal plate with well-developed faces of the forms {100}, {001}, and {110}
Crystal volume	0.0632 mm ³
Temp	22 °C
Radiation	MoK α (0.7093 Å) from monochromator
Linear absorption coefficient	56.7 cm ⁻¹
Transmission factors	0.075–0.431
Receiving aperture	3.0 × 5.4 mm; 30 cm from crystal
Takeoff angle	2.5°
Scan speed	2° in 2θ /min
Scan range	0.8° below K α_1 to 0.8° above K α_2
Background counts	10 s for $2\theta \leq 53^\circ$ 20 s for $2\theta > 53^\circ$
2θ limits	3.0–59.5°
Final number of variables	204
Unique data used, $F_o^2 > 3\sigma(F_o^2)$	5350
<i>R</i>	0.030
<i>R_w</i>	0.040
Error in observation of unit weight	1.38 electrons

unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. An absorption correction was applied to the data.²⁵

Solution and Refinement of the Structure. The platinum atom was easily located in an origin-removed, sharpened Patterson synthesis. Its position near 0, y , $1/4$ implies that the dimer molecule must have a crystallographically imposed twofold axis. The positions of the remaining nonhydrogen atoms were obtained through the usual combination of full-matrix least-squares refinements and difference Fourier syntheses. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$ and $|F_o|$ and $|F_c|$ are respectively the observed and calculated structure amplitudes. The agreement indices for the refinement on F_o are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors for the nonhydrogen atoms were taken from the usual tabulation,²⁶ whereas the hydrogen scattering factors used were those of Stewart et al.²⁷ Anomalous dispersion terms were included in F_c .²⁸

A total of 32 of the 36 methyl hydrogen atoms in the dimer half were located in difference maps. These positions, those of the remaining four methyl hydrogen atoms, and the six methylene hydrogen atoms of the propane chain were idealized assuming tetrahedral coordination at each C atom and a C–H bond distance of 0.95 Å. The isotropic thermal parameter of each hydrogen atom was assigned a value 1.0 Å² greater than that of the C atom to which it is attached. The contribution of these hydrogen atoms to the total scattering was held constant in later refinements. All nonhydrogen atoms were refined anisotropically after inclusion of the hydrogen contribution.

At the stage where the agreement indices of 0.042 and 0.072 were obtained, a difference Fourier synthesis revealed significant electron density disposed about the inversion center at $1/4, 1/4, 0$, well removed from the dimer. The density was resolved into discrete peaks upon which a disordered phenyl ring could be superimposed. Although chemically the ring must be part of a toluene solvate molecule, the methyl carbon atom could not be located. The methyl group of the toluene molecule seems to be disordered among the possible positions. The ring was included in the subsequent refinement as an idealized rigid body, having uniform C–C distances of 1.392 Å and a group thermal parameter.

Table IV. Positional and Thermal Parameters for the Nongroup Atoms of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$

ATOM	X ^A	Y	Z	B ₁₁ ^B	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Pt	0.023762(9)	0.14731(2)	0.197042(8)	2.03(1)	5.10(1)	1.17(1)	0.05(1)	0.46(1)	-0.06(1)
P(1)	0.10910(6)	0.0356(1)	0.16912(6)	2.14(3)	6.0(1)	1.55(3)	0.39(4)	0.41(2)	-0.39(4)
P(2)	-0.00698(7)	0.2640(1)	0.11879(6)	2.71(4)	5.77(10)	1.20(2)	0.25(5)	0.46(2)	0.01(4)
C(1)	0.1300(3)	0.0757(5)	0.0974(3)	3.0(2)	9.7(6)	1.9(1)	0.4(2)	1.1(1)	-0.5(2)
C(2)	0.0685(3)	0.1153(6)	0.0514(3)	3.7(2)	10.5(6)	1.8(1)	0.2(3)	1.0(1)	-0.8(2)
C(3)	0.0439(3)	0.2379(5)	0.0593(2)	3.0(1)	8.7(5)	1.4(1)	0.5(2)	0.62(10)	0.2(2)
C(4)	0.1993(3)	0.0563(5)	0.2172(3)	2.3(1)	8.8(5)	2.4(1)	0.5(2)	0.1(1)	-0.8(2)
C(8)	0.0887(3)	-0.1217(5)	0.1600(3)	3.0(2)	6.9(5)	2.5(2)	0.4(2)	0.4(1)	-0.5(2)
C(12)	0.0129(3)	0.4211(5)	0.1333(3)	4.1(2)	6.5(5)	1.5(1)	-0.1(2)	0.3(1)	-0.1(2)
C(16)	-0.1032(3)	0.2477(5)	0.0799(3)	2.8(2)	8.3(5)	1.7(1)	0.7(2)	0.3(1)	-0.1(2)
C(5)	0.2625(4)	0.0829(9)	0.1930(4)	2.8(2)	20.1(1)	4.5(3)	2.3(4)	0.3(2)	-2.9(5)
C(6)	0.1993(4)	0.0111(7)	0.2794(4)	3.9(3)	10.4(7)	3.1(2)	1.1(3)	-0.7(2)	0.0(3)
C(7)	0.2085(3)	0.1865(7)	0.2242(4)	3.1(2)	11.8(7)	3.4(2)	-0.8(3)	-0.5(2)	-1.9(3)
C(9)	0.0849(4)	-0.1748(6)	0.2205(4)	5.3(3)	7.7(6)	3.8(2)	-0.3(3)	1.7(2)	0.5(3)
C(10)	0.0137(5)	-0.1302(6)	0.1237(6)	6.1(3)	6.1(7)	6.7(5)	-0.4(3)	-2.7(3)	-1.6(4)
C(11)	0.1407(5)	-0.1934(7)	0.1334(4)	6.8(4)	8.4(6)	4.0(3)	1.4(4)	2.2(3)	-1.3(3)
C(13)	-0.0408(4)	0.4712(5)	0.1687(3)	5.9(3)	6.4(5)	2.3(2)	1.3(3)	1.1(2)	-0.6(2)
C(14)	0.0135(4)	0.4963(6)	0.0792(3)	6.1(3)	7.9(6)	2.2(2)	-1.0(3)	1.0(2)	0.9(2)
C(15)	0.0868(3)	0.4251(6)	0.1715(3)	4.1(2)	7.5(5)	2.6(2)	-1.2(3)	0.2(1)	-0.7(2)
C(17)	-0.1526(3)	0.2561(8)	0.1250(4)	2.9(2)	14.4(9)	3.5(2)	1.5(3)	0.9(2)	0.0(4)
C(18)	-0.1093(4)	0.1276(7)	0.0553(4)	2.8(2)	10.3(7)	3.7(2)	-0.1(3)	0.0(2)	-1.1(3)
C(19)	-0.1283(5)	0.3296(7)	0.0302(4)	4.3(3)	13.0(9)	2.7(2)	0.5(4)	-0.4(2)	1.8(3)

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^B THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $\text{EXP}(-\text{B}_{11}\text{H}^2 + \text{B}_{22}\text{K}^2 + \text{B}_{33}\text{L}^2 + 2\text{B}_{12}\text{HK} + 2\text{B}_{13}\text{HL} + 2\text{B}_{23}\text{KL})$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^{-4}$.

Table V. Derived Parameters for the Rigid Group Atoms of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$

ATOM	X	Y	Z	B ₁₁ ^{A2}	ATOM	X	Y	Z	B ₁₁ ^{A2}
TOLC1	0.2671(3)	0.2743(5)	0.0260(1)	9.0(2)	TOLC4	0.1988(8)	0.177(1)	-0.0780(4)	9.0(2)
TOLC2	0.2121(4)	0.3324(5)	-0.0091(5)	9.0(2)	TOLC5	0.2538(8)	0.1190(7)	-0.0429(6)	9.0(2)
TOLC3	0.1780(5)	0.284(1)	-0.0611(4)	9.0(2)	TOLC6	0.2879(4)	0.1676(5)	0.0091(5)	9.0(2)

RIGID GROUP PARAMETERS

GROUP	X _C ^A	Y _C	Z _C	DELTA ^B	EPSILON	ETA
TOL	1/4	1/4	0	-2.506(8)	-3.071(9)	-0.909(7)

^A X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^B THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIAN) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

Agreement indices of $R = 0.030$ and $R_w = 0.040$ were obtained from the final cycle of refinement, which included an isotropic extinction correction. The standard deviation of an observation of unit weight is 1.38 electrons. The highest residual found in a final difference synthesis ($1.1 \text{ e}/\text{\AA}^3$) is located near the symmetry position between the platinum atoms. Residuals between 0.8 and $0.9 \text{ e}/\text{\AA}^3$ are observed for three poorly resolved peaks which are shoulders on this larger peak. The peaks decrease in intensity as the distance from the symmetry position increases. The third of these shoulders ($0.81 \text{ e}/\text{\AA}^3$) is approximately 1.6 and 2.4 \AA from the two platinum atoms and forms an angle of 84° with those two atoms. Although these peaks are poorly resolved, their positions do not conform to those expected for hydride ligands if the present compound were a dihydride. A number of smaller residuals associated with the partially refined toluene ring are also present. An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices reveals no unexpected trends.

The final positional and thermal parameters of the nonhydrogen atoms appear in Tables IV and V. Idealized hydrogen atom positions are compiled in Table VI. Table VII contains the root mean square amplitudes of vibration.²⁹ A listing of the observed and calculated structure amplitudes is available.²⁹

Results

Syntheses and Reactions. When sodium amalgam was added to a suspension of $\text{PtCl}_2[(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]$ in THF at room temperature an orange-red color developed. From this

solution a diamagnetic binuclear compound $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$ (**1**) was obtained as red crystals. A similar reduction of the dichloride with Na/K alloy in benzene at room temperature resulted in a complete reduction of Pt(II) to metallic platinum with liberation of free phosphine, $(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2$. Compound **1** is stable in the solid state in air for a few days but is extremely unstable in solution. It is more readily soluble in *n*-hexane than in toluene. The mass spectrum shows both the parent (m/e 1054) and the fragment ion (m/e 527) with the expected isotope pattern of platinum of 1:10 relative intensity. The fragment ion is assignable to the mononuclear cis chelate two-coordinate complex, Pt(diphos).

The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of **1** shows complex resonances centered at $\delta + 70.1$ (ppm downfield from H_3PO_4). The complex pattern arises from three possible combinations of two platinum atoms with different nuclear spins (^{195}Pt , $I = 1/2$; other Pt isotopes, $I = 0$), i.e., $\text{P}_2\text{Pt}-\text{PtP}_2$, $\text{P}_2\text{Pt}-^{195}\text{PtP}_2$, and $\text{P}_2^{195}\text{Pt}-^{195}\text{PtP}_2$. Their relative ratios calculated from the natural abundance are 4:4:1. A singlet signal is expected for $\text{P}_2\text{Pt}-\text{PtP}_2$. In $\text{P}_2\text{Pt}-^{195}\text{PtP}_2$, however, the P atoms on one PtP_2 moiety are no longer equivalent to those on the other. On the basis of the present molecular structure or a rapid rotation around the Pt-Pt bond, two triplet signals are expected with

Table VI. Idealized Positional Coordinates for Hydrogen Atoms^a

Atom	x	y	z	Atom	x	y	z
H1C(1)	0.161	0.143	0.104	H1C(11)	0.142	-0.280	0.151
H2C(1)	0.152	0.019	0.082	H2C(11)	0.124	-0.196	0.086
H1C(2)	0.079	0.112	0.012	H3C(11)	0.194	-0.156	0.144
H2C(2)	0.026	0.070	0.051	H1C(13)	-0.023	0.555	0.185
H1C(3)	0.015	0.263	0.023	H2C(13)	-0.093	0.478	0.141
H2C(3)	0.086	0.283	0.065	H3C(13)	-0.045	0.415	0.205
H1C(5)	0.272	-0.083	0.210	H1C(14)	0.030	0.582	0.093
H2C(5)	0.250	0.000	0.145	H2C(14)	0.051	0.461	0.053
H3C(5)	0.310	0.055	0.206	H3C(14)	-0.040	0.499	0.053
H1C(6)	0.149	0.034	0.293	H1C(15)	0.085	0.383	0.213
H2C(6)	0.205	-0.081	0.280	H2C(15)	0.125	0.382	0.149
H3C(6)	0.244	0.049	0.309	H3C(15)	0.103	0.514	0.180
H1C(7)	0.261	0.205	0.249	H1C(17)	-0.144	0.337	0.148
H2C(7)	0.203	0.226	0.181	H2C(17)	-0.208	0.252	0.103
H3C(7)	0.168	0.220	0.247	H3C(17)	-0.142	0.186	0.156
H1C(9)	0.063	-0.113	0.247	H1C(18)	-0.165	0.109	0.037
H2C(9)	0.051	-0.250	0.215	H2C(18)	-0.077	0.120	0.021
H3C(9)	0.138	-0.199	0.242	H3C(18)	-0.090	0.067	0.090
H1C(10)	-0.023	-0.080	0.144	H1C(19)	-0.138	0.413	0.048
H2C(10)	0.014	-0.097	0.080	H2C(19)	-0.088	0.337	0.003
H3C(10)	-0.003	-0.219	0.121	H3C(19)	-0.177	0.298	0.004

^a These values are those used in all metrical calculations involving hydrogen atoms and have been idealized with an aliphatic C-H distance of 1.09 Å.

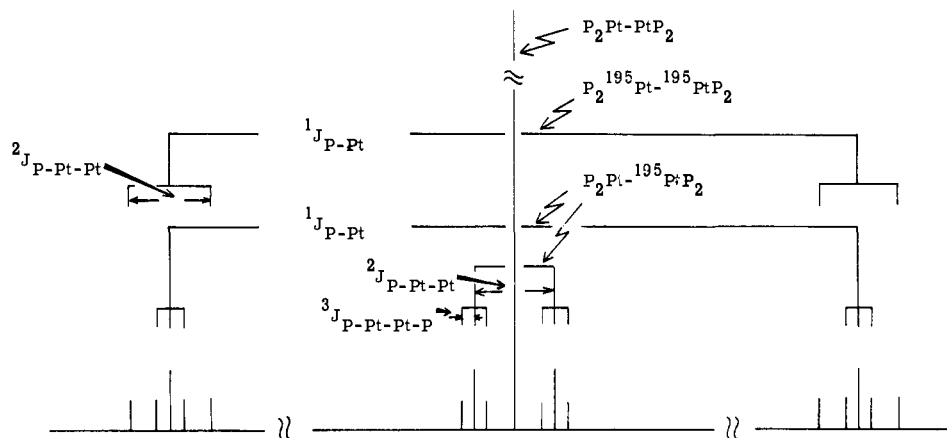


Figure 1. The proposed ³¹P coupling scheme for **1**, [Pt(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂]₂.

a long range coupling ³J_{P-Pt-Pt-P}. These triplet signals from PtP₂ and ¹⁹⁵PtP₂ would be further split by ²J_{P-Pt-Pt} and ¹J_{P-Pt}, respectively. Since the P atoms of both dimer halves under identical chemical environments should show only one chemical shift, we expect two pairs (²J_{P-Pt-Pt}, ¹J_{P-Pt}) of triplets (³J_{P-Pt-Pt-P}). Finally, the four equivalent phosphorus atoms in P₂¹⁹⁵Pt-¹⁹⁵PtP₂ should show two pairs of singlets from the different coupling schemes, ¹J_{P-Pt} and ²J_{P-Pt-Pt}. The observed spectrum is explicable in terms of this coupling scheme (Figure 1). The values of ¹J_{P-Pt}, ²J_{P-Pt-Pt}, and ³J_{P-Pt-Pt-P} assessed from the observed spectrum are 3945, 178.3, and 32.6 Hz, respectively.

The *tert*-butyl protons exhibit a complex ¹H NMR signal centered at δ 1.35 comprised of two sharp signals (12 Hz) and a broad complex triplet lying at the midpoint between the sharp peaks. The complex second-order signal of the *tert*-butyl protons may be described as a (AA'X₁₈X'₁₈)₂ or (ABX₁₈X'₁₈)₂ spin system. Consistently a *tert*-butyl singlet is observed in the ¹H{P} NMR spectrum.

The Pt-Pt bond cleavage of **1** occurs readily in the presence of CO (1 atm), producing Pt(CO)₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] (**2**) as colorless crystals. A *tert*-butyl proton signal was observed in the ¹H NMR spectrum as a doublet at δ 1.13 (*J*_{H-P} = 12.4 Hz); stretching vibrations ν(CO) are found at 1912 and

1660 cm⁻¹ in the IR spectrum. Compound **1** absorbs H₂ at atmospheric pressure and room temperature to give the *cis* dihydride PtH₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] (**5**). The hydride complex obtained using D₂ (99% purity) unexpectedly shows a fairly intense band at 1995 cm⁻¹ (ν(Pt-H)). Upon treatment of **1** with CHCl₃ in toluene at 50 °C the solid product PtCl₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂] was obtained. An analytical GLC of the liquid product indicated formation of CH₂Cl₂ in a quantity expected for the reaction of the possible compound Pt₂H₂[(*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂]₂ with CHCl₃. This compound would then be analogous to Ni₂(μ-H)₂[(*c*-C₆H₁₁)₂-P(CH₂)₃P(*c*-C₆H₁₁)₂]₂ (*c*-C₆H₁₁ = cyclohexyl), which has a hydride-bridged structure.³⁰ Thus, on the basis of these chemical reactions compound **1** could be formulated as a bridging dihydride complex. However, no physical evidence for the presence of hydrido ligands was obtained. The IR spectrum shows no band in the expected region (1500–2300 cm⁻¹) for metal hydrides. Note that Pt₂(μ-H)₂(H)₂[P(*c*-C₆H₁₁)₃]₂³¹ shows a broad band at 1550 cm⁻¹ which has been assigned to ν_{Pt-H-Pt}. Careful search for a hydride signal in the ¹H NMR spectrum failed to reveal any resonance in the high-field region up to δ -25. Recent results by Stone³² and Haymore³³ have demonstrated that, contrary to earlier belief, hydride resonances may occur in the low-field region, δ 0–4.

Stone has shown that $\text{Pt}_2(\mu\text{-H})_2[\text{Si}(\text{C}_2\text{H}_5)_3]_2[\text{P}(\text{C-C}_6\text{H}_{11})_3]_2$, a dimer similar to **1**, exhibits a bridging hydride resonance at δ 3.35, which is only observed at temperatures below -50°C . Thus our inability to observe a hydride signal does not rule out the possibility that **1** contains bridging hydride ligands. Note, however, that in the analogous nickel dimers, $[\text{Ni}(\mu\text{-H})(\text{C-C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_n\text{P}(\text{C-C}_6\text{H}_{11})_2)]_2$, $n = 2, 4$, hydride resonances are observed at high field, $\delta -11.4$ and -10.4 , respectively.³⁰ The results of the x-ray determination of the structure of **1** (see below) also do not suggest a bridging hydride formulation.

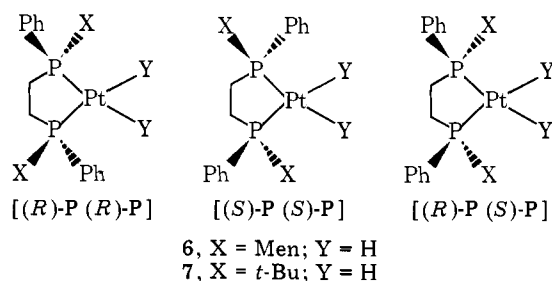
An attempt to prepare a $(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2$ analogue of **1** by reduction of $\text{PtCl}_2[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ with Na/Hg in THF was unsuccessful; rather a cis dihydride, $\text{PtH}_2[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ (**3**), was isolated in 35% yield. Formation of $\text{Pt}[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ was not detected. A similar reduction of $\text{PtCl}_2[(\text{Men})_2\text{PCH}_2\text{CH}_2\text{P}(\text{Men})_2]$ ($\text{Men} = l\text{-menthyl}$) gave the corresponding cis dihydride $\text{PtH}_2[(\text{Men})_2\text{PCH}_2\text{CH}_2\text{P}(\text{Men})_2]$ (**4**).

The binuclear complex **1** does not react with THF, and the corresponding cis dihydride compound is not formed simply by heating a THF solution of **1**. Hence, the formation of **3** and **4** must arise from highly reactive species initially formed upon reduction of the $\text{Pt}(\text{II})$ compounds. The species could be highly coordinatively unsaturated, mononuclear, cis chelate intermediates, $\text{Pt}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)$, which promptly abstract hydrogen atoms, possibly from the solvent.

The cis dihydrides $\text{PtH}_2[\text{R}_1\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_1\text{R}_2]$ (**3**; **4**; **5**; **6**, $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \text{Men}$, $n = 2$; **7**, $\text{R}_1 = \text{Ph}$, $\text{R}_2 = t\text{-Bu}$, $n = 2$; **8**, $\text{R}_1 = \text{R}_2 = \text{Ph}$, $n = 2$) are prepared more conveniently in higher yield by reducing the corresponding dichlorides with Na/Hg in a hydrogen atmosphere. Interestingly, the cis dihydrides **3-7** are stable toward air in the solid state as well as in solution, perhaps because of the presence of bulky substituents on the two phosphorus atoms. An analogous cis dihydride compound $\text{PtH}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (**8**) may be prepared from $\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ as an unstable species which exists only under a dihydrogen atmosphere. We are able to deduce its transient existence from the IR spectrum (Table II) of the reaction mixture ($\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2) + \text{Na}/\text{Hg}$ in THF) and by the fact that the red color of the mixture does not fade in a reducing atmosphere. The hydride coordination must be very weak.

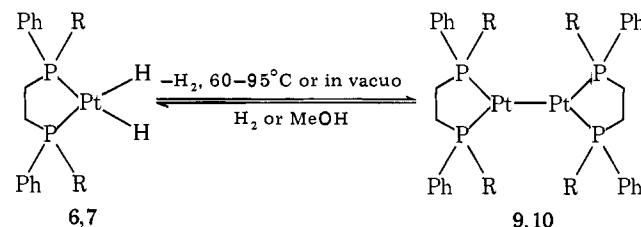
The IR spectra of **3** and **6** contain two Pt-H stretching absorptions in the region of $1977\text{-}2008\text{ cm}^{-1}$, while **4**, **5**, and **7** show only a single $\nu(\text{Pt-H})$ vibration. The cis alignment of the hydride ligands was confirmed by ^1H NMR spectra, which show the hydride signal in a region of δ 0.07 to -2.14 as a doublet of doublets with Pt satellites. The chemical shift of the hydride resonance of **7** (δ 0.07) is amazingly low, the lowest one among those of square-planar $\text{Pt}(\text{II})$ hydrides hitherto reported, e.g., *trans*- $\text{PtH}_2[\text{P}(i\text{-Pr})_3]_2$ ($\delta -3.22$).⁴ The large values of $J_{\text{H-Pt}}$ and the high Pt-H frequencies of cis dihydrides compared with those found in *trans*- PtH_2L_2 ⁴ (e.g., $J_{\text{H-Pt}} = 690.4\text{ Hz}$, $\nu(\text{Pt-H}) 1735\text{ cm}^{-1}$ for $\text{L} = \text{P}(i\text{-Pr})_3$) suggest stronger Pt-H bonding in the cis dihydrides. This is consistent with the stronger trans influence of the hydride with respect to the phosphine ligand.⁸

There are three possible stereoisomers for **6** and **7**, con-



taining two chiral phosphorus atoms, two enantiomers $[(R)\text{-P}(R)\text{-P}]$ and $[(S)\text{-P}(S)\text{-P}]$, and one meso form $[(R)\text{-P}(S)\text{-P}]$. The two chemically different *tert*-butyl or *l*-menthyl groups are expected for the racemate. However, a single *tert*-butyl proton signal was observed for **7** and for the precursor $\text{PtCl}_2[(t\text{-Bu})\text{PhPCH}_2\text{CH}_2\text{PPh}(t\text{-Bu})]$. The latter sample had been purified by recrystallization. This may cause a selective crystallization either of the racemate or the meso form. Therefore, **7** derived from the dichloride could also be either the racemate or the meso form.

Cis dihydrides **3**, **4**, and **5** are thermally stable even in solution at 100°C and show no tendency to dissociate the coordinated dihydrogen, whereas **8** is too unstable to isolate and is detected only under an H_2 atmosphere from its IR spectrum ($\nu(\text{Pt-H}) 1930\text{ cm}^{-1}$). Compounds **6** and **7** are moderately stable crystalline complexes but the dihydrogen coordination is reversible in solution. Thus on heating a colorless solution of **6** the intensity of the hydride signals and the $\nu(\text{Pt-H})$ band begin to decrease at 60°C and disappear completely at 80°C , affording a reddish brown solution. Compound **6** also dissociates dihydrogen in toluene solution under reduced pressure. The resulting reddish brown solution readily reacts with H_2 (1 atm) or MeOH at room temperature to regenerate **6**. Similarly **7** in toluene dissociates the coordinated dihydrogen completely at 95°C to give a reddish solution, suggesting a slightly higher stability for **7**. Attempts to isolate a pure compound from the reddish, amorphous solid obtained upon concentration of the reddish brown solution failed. The deep red compound is tentatively formulated as a binuclear complex $[\text{Pt}(\text{R}_1\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_1\text{R}_2)]_2$ (**9**, $\text{R}_1 = \text{Men}$, $\text{R}_2 = \text{Ph}$; **10**, R_1



$= t\text{-Bu}$, $\text{R}_2 = \text{Ph}$) on the basis of the spectroscopic data. Thus the ^1H NMR spectrum of **10** formed in situ from **7** at 95°C shows, in addition to the signal of **7**, a *tert*-butyl resonance centered at δ 1.32 which resembles the complex multiplet observed for **1**. A dimer structure analogous to that of **1**, containing a Pt-Pt bond, is thus inferred.

As is evident from the above results, the stability of a cis dihydride depends on the nature of the diphosphine ligand. Qualitatively the stability of the hydride coordination increases in the order $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (**8**) < $\text{Men}(\text{Ph})\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{Men}$ (**6**) < $t\text{-Bu}(\text{Ph})\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})t\text{-Bu}$ (**7**) < $\text{Men}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Men})_2$ (**4**) $\approx (t\text{-Bu})_2\text{P}(\text{CH}_2)_n\text{P}(t\text{-Bu})_2$ ($n = 2, 3$) (**3**, **5**). The relative stability order for **6** and **7** was obtained from the temperature-dependent ^1H NMR study. The order for the rest was assessed from the observations made during preparative studies.

Although **3** shows no tendency to dissociate coordinated dihydrogen even in solution at 100°C , dissociation of H_2 takes place readily at room temperature in the presence of olefins with strong π -accepting properties. Thus, on addition of acrylonitrile (AN), maleic anhydride (MA), or fumaronitrile (FN) to **3** in toluene, H_2 was immediately evolved with formation of the corresponding olefin complex $\text{PtL}[(t\text{-Bu})_2\text{PCH}_2\text{CH}_2\text{P}(t\text{-Bu})_2]$ (**11**, $\text{L} = \text{AN}$; **12**, $\text{L} = \text{MA}$; **13**, $\text{L} = \text{FN}$) as colorless crystals. No hydrogenated product of the olefin was detected. In sharp contrast, **3** does not react with alkenes with σ -donating properties under similar conditions. The results seem to suggest that the cis dihydride **3** is a fairly strong nucleophile inert to an attack by electron-rich olefins. Thus the

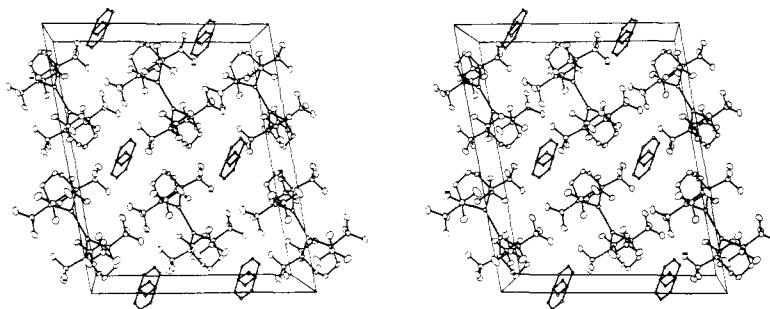


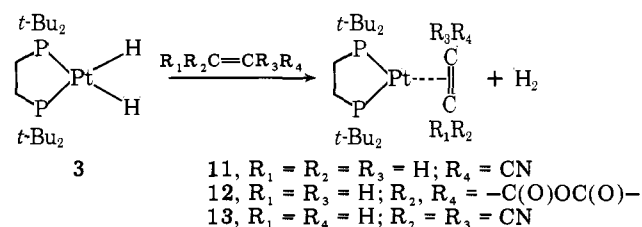
Figure 2. A stereoview of the unit cell of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$. Hydrogen atoms have been omitted as has the methyl group of the toluene of solvation. The disorder of the solvent is shown. The x axis is horizontal to the right, the y axis is perpendicular to the paper going away from the reader, and the z axis is vertical from bottom to top. The vibrational ellipsoids are drawn at the 20% level.

Table VIII. Selected Distances (Å) in $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$

Bond Distances			
Pt-Pt' ^a	2.765 (1)	C(4)-C(5)	1.549 (9)
Pt-P(1)	2.272 (1)	C(4)-C(6)	1.536 (10)
Pt-P(2)	2.268 (2)	C(4)-C(7)	1.543 (10)
P(1)-C(1)	1.840 (6)	C(8)-C(9)	1.547 (11)
P(1)-C(4)	1.898 (5)	C(8)-C(10)	1.533 (10)
P(1)-C(8)	1.890 (6)	C(8)-C(11)	1.513 (9)
P(2)-C(3)	1.847 (5)	C(12)-C(13)	1.539 (9)
P(2)-C(12)	1.899 (6)	C(12)-C(14)	1.535 (9)
P(2)-C(16)	1.910 (6)	C(12)-C(15)	1.531 (8)
C(1)-C(2)	1.516 (9)	C(16)-C(17)	1.529 (9)
C(2)-C(3)	1.533 (8)	C(16)-C(18)	1.517 (9)
		C(16)-C(19)	1.513 (9)
Nonbonded Distances			
Interdimer		Intradimer	
H1C(7)-H3C(9)	2.21	H1C(6)-H3C(17)'	2.16
		H3C(13)-H1C(15)'	2.20
Intramonomer			
H2C(13)-H1C(17)	1.95	H3C(14)-H2C(19)	2.12
H2C(6)-H3C(9)	1.97	H2C(9)-H3C(10)	2.27
H2C(5)-H3C(11)	2.11	H3C(13)-H1C(17)	2.30
H1C(5)-H3C(11)	2.13		

^a Primed atoms are related to corresponding unprimed atoms by the twofold axis.

hydrogen liberation upon attack by a π -accepting olefin may be ascribed to the thermodynamic stability of the η^2 -olefinic complexes **11**–**13** relative to the dihydride **3**. Under drastic conditions (100 °C, H₂ 80 kg/cm²), however, **3** catalyzes hydrogenation of cyclohexene to give cyclohexane with a complete recovery of **3**.



Description of the Crystal and Molecular Structure of $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$ (1**).** The crystal structure of **1** consists of the packing of four dimeric molecules and four disordered toluene molecules. A stereoscopic packing diagram of the unit cell is shown in Figure 2. The disorder of a solvent molecule (without the methyl group) is depicted in this representation. Bond distances are given in Table VIII and bond angles in Table IX. Calculations show that there is a short contact, 2.21 Å, between H1C(7) and H1C(9) on adjacent dimers (see Table VIII). The hydrogen positions used in this

Table IX. Selected Angles (deg) in $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$

Pt'-Pt-P(1)	128.1 (1)	C(4)-P(1)-C(8)	109.8 (3)
Pt'-Pt-P(2)	129.2 (1)	C(12)-P(2)-C(16)	109.1 (3)
P(1)-Pt-P(2)	102.6 (1)	P(1)-C(4)-C(5)	114.8 (5)
Pt-P(1)-C(1)	113.0 (2)	P(1)-C(4)-C(6)	111.1 (4)
Pt-P(1)-C(4)	112.4 (2)	P(1)-C(4)-C(7)	105.2 (4)
Pt-P(1)-C(8)	116.8 (2)	P(1)-C(8)-C(9)	109.5 (5)
P(1)-C(3)-C(2)	113.7 (2)	P(1)-C(8)-C(10)	106.2 (4)
Pt-P(2)-C(12)	115.3 (2)	P(1)-C(8)-C(11)	116.8 (5)
Pt-P(2)-C(16)	114.3 (2)	P(2)-C(12)-C(13)	109.5 (4)
P(1)-C(1)-C(2)	116.8 (4)	P(2)-C(12)-C(14)	116.3 (4)
P(2)-C(3)-C(2)	117.2 (4)	P(2)-C(12)-C(15)	105.6 (4)
C(1)-C(2)-C(3)	114.7 (5)	P(2)-C(12)-C(17)	109.1 (5)
C(1)-P(1)-C(4)	100.5 (3)	P(2)-C(16)-C(18)	105.9 (4)
C(1)-P(1)-C(5)	102.8 (3)	P(2)-C(16)-C(19)	116.5 (5)
C(3)-P(2)-C(12)	100.3 (3)		
C(3)-P(2)-C(16)	102.7 (3)		

and subsequent distance calculations are derived from a post-refinement least-squares fitting of the observed hydrogen positions in which an aliphatic C-H bond distance of 1.09 Å was used. This relatively short contact is indicative of the crowding present in **1**, vide infra. Figure 3 contains a representation of the unique dimer half and the numbering scheme used throughout this discussion. Selected bond distances and angles are shown in Figure 4, which also includes the coordination spheres of both metal centers.

The coordination sphere of each metal center consists of a second platinum and two phosphorus atoms. These four atoms form a distorted trigonal array which is planar. The central atom is displaced only 0.04 Å out of the plane defined by the three ligating atoms (see Table X). There are no short (<3.0 Å) Pt-H or Pt-C contacts. Thus, the Pt is truly three coordinate. Note in particular the nonexistence of distortions which could be attributed to bridging hydride ligands. An examination of the final electron difference map in the vicinity of the platinum atoms yielded no evidence for bridging hydride atoms. Also indicative is the approximate 82° dihedral angle between coordination planes of the platinum atoms. This value is markedly different from those observed in two analogous hydride-bridged dimers, $[\text{Ni}(\mu\text{-H})((\text{c-C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{c-C}_6\text{H}_{11})_2)]_2$ ³⁰ and $[\text{Pt}(\mu\text{-H})(\text{Si}(\text{C}_2\text{H}_5)_3)(\text{P}(\text{c-C}_6\text{H}_{11})_3)]_2$,³¹ 26 and 21°, respectively. These results, which are in accord with all available spectroscopic data, suggest the absence of bridging hydride ligands in **1**.

The Pt-P bonding parameters are in no way unusual. The distances, 2.268 (2) and 2.272 (1) Å, are equivalent and well within the range of known Pt(0)-P bonding distances (2.24–2.33 Å).¹¹ The structural details of the monomer unit are compared with those of the parent, $\text{PtCl}_2[(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]$,²² in Table XI. Considering the covalent radii of Pt(II) (1.31 Å)³⁴ and Pt(0) (1.38 Å),¹¹ it is of interest

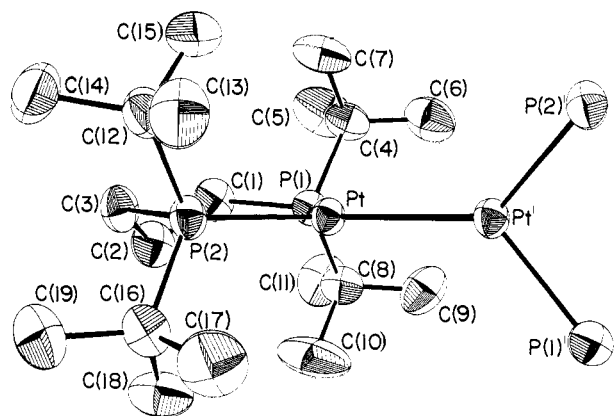


Figure 3. A perspective view of the monomer unit with the twofold related Pt and P atoms included. Again hydrogen atoms have been omitted for clarity. The numbering scheme is also shown. Vibrational ellipsoids are drawn at the 50% level here and in subsequent figures.

Table X. Weighted Least-Squares Planes

Plane Equation: $Ax + By + Cz - D = 0$ with x, y, z in crystal coordinates

Plane no.	A, Å	B, Å	C, Å	D, Å
1	-12.498	-7.674	-6.003	-2.652
2	12.171	7.673	6.720	2.743
3	12.171	-7.673	6.720	6.167

Deviations from Planes, Å ^a				
Atom	Plane no. ^b			
	1	2	3	
Pt	0.042	0.001 (2)		
P(1)	0	-0.006 (2)		
P(2)	0	-0.004 (1)		
C(1)		0.075 (6)		
C(2)		[-0.68]		
C(3)		0.015 (6)		
Pt'	0		-0.001 (2)	
P(1)'			0.006 (2)	
P(2)'			0.004 (1)	
C(1)'			-0.075 (6)	
C(2)'			[0.68]	
C(3)'			-0.015 (6)	

^a Values shown in brackets are for atoms not used in the calculation of the plane. ^b The dihedral angle between planes 2 and 3 is 81.7°.

to observe very slightly shorter Pt-P distances (0.01 Å) in the dimer. That the Pt-P distances are essentially equal may stem either from the enhanced π -bonding character of Pt(0) with respect to Pt(II) and/or from the change in hybridization of the metal center (i.e., change in coordination number). The increase in the P-Pt-P angle, 99.1° in the Pt(II) dichloride complex, to 102.4° in **1** may also result from increased metal to phosphorus electron flow. Recently, a number of studies have demonstrated that the angle subtended by a pair of ligand atoms increases with the relative degree of π interaction.³⁵ Again an alternative explanation based on steric grounds is possible. Repulsive interactions within the diphosphine are relieved by the angular increase. The intraring distances and angles show no unusual trends. There are no significant differences between corresponding distances in **1** and the dichloride complex. However, there are a number of noteworthy differences between analogous angles. These result from the enlargement of the P-Pt-P angle, which requires compensatory changes in the other intraring angles. Thus the Pt-P(1,2)-C(1,3) angles decrease while the P(1,2)-C(1,3)-C(2) angles increase.

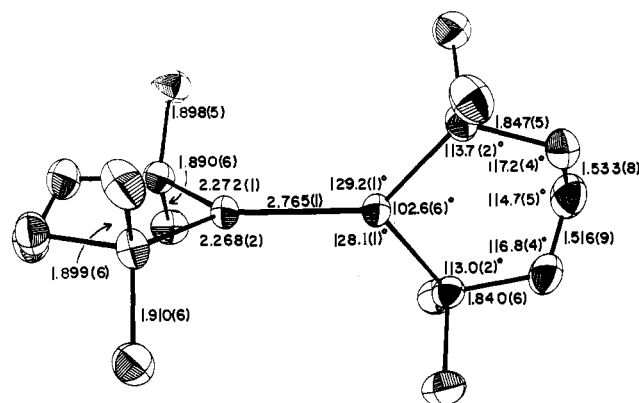


Figure 4. The coordination spheres of the two Pt atoms including the entire chelate ring. Relevant bond lengths and angles are also shown.

Table XI. Comparison of Selected Distances and Angles in $\text{PtCl}_2[(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]^a$ and $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$

	$\text{PtCl}_2[(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]^a$	$[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$
Distances, Å		
Pt-P	2.281 (3)	2.268 (2)
P(1,2)-C(1,3)	2.282 (3)	2.272 (1)
P(1,2)-C(4,8,17,18)	1.847 (12)	1.840 (6)
C(1,3)-C(2)	1.850 (13)	1.847 (5)
	1.899 (13)	1.890 (6)
	1.907 (12)	1.898 (5)
	1.917 (14)	1.899 (6)
	1.923 (13)	1.910 (6)
	1.50 (2)	1.516 (9)
	1.52 (2)	1.533 (8)
Angles, deg		
P-Pt-P	99.1 (1)	102.6 (1)
Pt-P(1,2)-C(1,3)	115.3 (4)	113.0 (2)
P(1,2)-C(1,3)-C(2)	115.7 (4)	113.7 (2)
	113.7 (9)	116.8 (4)
	117.3 (9)	117.2 (4)
C(1)-C(2)-C(3)	113.8 (11)	114.7 (5)

^a Reference 22.

The six-membered metallocyclic ring adopts the half-chair conformation. Thus atoms Pt, P(1), P(2), C(1), and C(3) lie very nearly within the same plane (Table X). Atom C(2) is displaced approximately 0.7 Å out of this plane. This configuration undoubtedly arises so as to minimize repulsive contacts between the bulky substituents of the diphosphine ligand. In the full chair form common to hydrocarbon hexacycles, considerable repulsion is observed between 1,3 diaxial substituents. *tert*-Butyl groups on each of the geminally disubstituted P atoms would be forced into these positions and the resulting interactions would be severe.

The bonding parameters of the *tert*-butyl groups are especially indicative of the crowding present in the diphosphine portion of **1**. General trends, rather than unusual individual details, are particularly illustrative. The *tert*-butyl groups on atoms C(8) and C(16) lie adjacent to the C(2) methylene fragment. As such there is a substantial increase in the local steric demand which is especially evident in the shortened C-C bond lengths of the butyl groups. Similar bond lengths associated with the C(4) and C(12) groups, which lie in a less congested area, do not show this trend. More pronounced is the consistent deformation of P-C-C bond angles present in all four *tert*-butyl groups. In each group there is an ordering of the three angles present in which one angle is compressed below

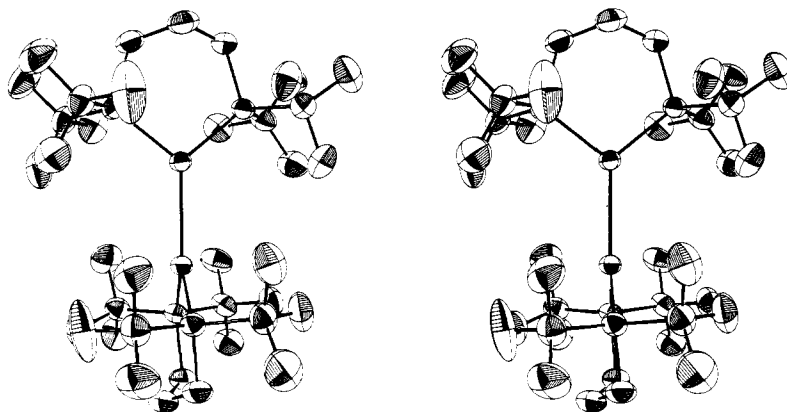


Figure 5. A stereoview of the entire dimer, omitting hydrogen atoms.

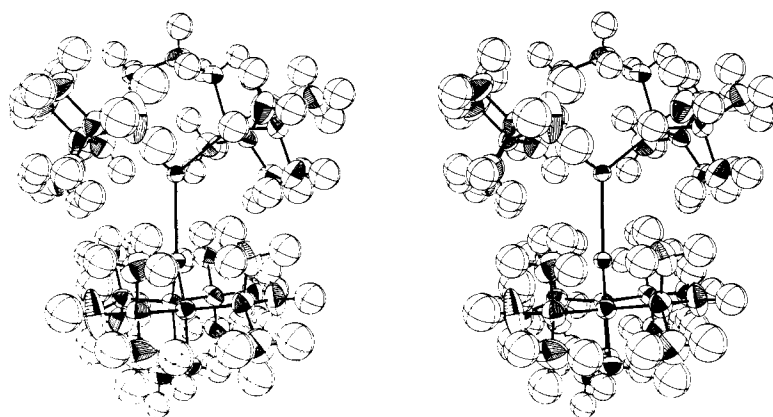


Figure 6. A stereoview of the dimer. The hydrogen atoms appear as the nonshaded ellipsoids. The isotropic thermal parameter of a given hydrogen atom is set at 1 \AA^2 greater than the equivalent isotropic thermal parameter of the carbon atom to which it is attached.

the tetrahedral value, another is normal, and the third is significantly larger than 109.5° . Those methyl carbon atoms involved in the smaller angles, C(7,10,15,18), lie closest to the center of the metallocycle. Methyl carbon atoms C(5,11,14,19), which lie about the periphery of the diphosphine, are associated with the enlarged angles. This increase in P-C-C angles arises from the eclipsing of these methyl groups resulting from the half-chair conformation adopted by the metallocycle. Figure 5 contains a stereoscopic representation of the dimer which illustrates this phenomenon.

Much of the above discussion has dealt with the extreme crowding in the monomer unit. The best demonstration of this steric compression involves the construction of space-filling molecular models. One is then confronted with a hemisphere of highly congested hydrocarbon. An attempt to represent this severe crowding is shown in Figure 6. The arguments above have related distortions to a minimization of repulsive interactions. Such minimization becomes very obvious during inspection of the model. Calculations to determine H...H contact distances within the monomer are helpful (Table VIII). For example, despite the distortion of the P(1)-C(4)-C(5) and P(1)-C(8)-C(11) angles to large values, which results in an increased separation between atoms C(5) and C(11), there remains a short contact between hydrogen atoms bound to each.

The Pt-Pt interaction will be discussed below.

Discussion

Recently some linear two-coordinate complexes PtL_2 and PdL_2 have been isolated.¹¹ The compounds PtL_2 (L = electron-donating phosphine) show very high reactivity⁴ and unprecedented molecular hydrogen absorption to yield *trans*-

PtH_2L_2 . It should be possible to prepare two-coordinate complexes $\text{M}(\text{diphos})$, providing that there is a sufficient chain length connecting the two phosphorus atoms. Indeed compounds $\text{M}(\text{diphos})$, with *trans* P atoms, have been prepared.³⁶ Our original intention here was to prepare Pt(0) complexes having one diphosphine ligand whose geometry allows only *cis* chelation. Despite numerous attempts, the preparation of discrete two-coordinate Pt(0) complexes has so far been successful only with $(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2$ and the isolated complex is dimeric as shown by the crystal structure above. One obvious reason for the preparative difficulty is the propensity for polynucleation. Moulton and Shaw,² in fact, were unable to prepare mononuclear Pt(II) compounds containing the trimethylene diphosphine ligand. Their starting material, $\text{PtCl}_2(\text{PhCN})_2$, differs from ours. With careful purification of solvent (THF) we were able to prepare the compound **1** with a substantial yield (>30%) from $\text{PtCl}_2(\text{diphos})$. We expected that the similar reduction of $\text{PtCl}_2(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)$ (Na/Hg, THF) would produce the Pt(0) species $\text{Pt}(\text{diphos})$. The bulk of the R group (*t*-Bu, *l*-menthyl) is certainly effective in preventing the formation of a tetracoordinate species $\text{Pt}(\text{diphos})_2$. The product, however, is *cis*- $\text{PtH}_2(\text{diphos})$. This strong propensity to abstract hydrogen atoms, even from solvents such as THF, constitutes an unavoidable obstacle for the preparation of $\text{Pt}(\text{diphos})$.

Isolation of the dimeric compound $[\text{Pt}(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2]_2$ (**1**) from a hydrogen-containing solvent suggests a diminished tendency for hydrogen abstraction. However, the reaction of **1** with D_2 or CHCl_3 is always accompanied by formation of a Pt-H containing species, suggesting facile hydrogen abstraction upon Pt-Pt bond cleavage.

This facile dihydride formation contrasts with the successful

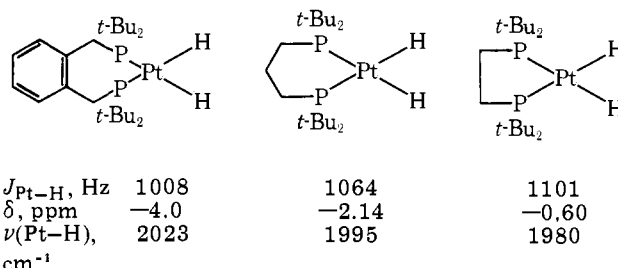
Table XII. Selected Pt-Pt Bond Distances^a

Complex	Pt-Pt, Å	Bridging group
Pt ₃ (C ₈ H ₁₂) ₃ (SnCl ₃) ₂ ^b	2.58 (1)	SnCl ₃
Pt ₂ (η ⁵ -C ₅ H ₅) ₂ (η ⁴ -C ₁₀ H ₁₀) ^c	2.581 (4)	(η ⁴ -C ₁₀ H ₁₀)
[NPr ₄] ₂ [Pt ₂ Cl ₄ (CO) ₂] ^d	2.584 (2)	
[Pt ₂ (C ₈ H ₁₂) ₂ (C ₃ F ₆ O)] ^e	2.585 (1)	(C ₃ F ₆ O)
[Pt ₂ (PPh ₃) ₂ (PPh ₂) ₂] ^f	2.604 (1)	PPh ₂
[Pt{SP(Et) ₂ }(OPh) ₃] ₂ ^g	2.628 (1)	SP(Et) ₂
FePt ₂ (CO) ₅ P(OPh) ₃ ₃ ^h	2.633 (1)	Cluster
(Ph ₃ P) ₂ Pt · S · Pt(CO)- (PPh ₃) ⁱ	2.647 (2)	S
RuPt ₂ (CO) ₅ (PPh ₂ Me) ₃ ^j	2.647 (2)	CO
Pt ₂ (μ-H) ₂ (SiEt ₃) ₂ [P(C- C ₆ H ₁₁) ₃] ₂ ^k	2.692 (3)	H
Pt ₄ (PPhMe ₂) ₄ (CO) ₅ ^l	2.752 (7), 2.790 (7)	CO, CO
(PtS ₄ C ₄ H ₄) ₂ ^m	2.77	
Pt ₃ (PPh ₃) ₂ (PPh ₂) ₃ Ph ⁿ	2.785 (1)	PPh ₂
Mg _{0.82} [Pt(C ₂ O ₄) ₂] ^o	2.85	
Pt ₂ (S ₂ CC ₆ H ₄ C ₃ H ₇) ₄ ^p	2.870 (3)	(S ₂ C ₁₀ H ₁₁)
[Pt ₂ (PMe ₃) ₂ (PhC ₂ Ph) ₂] ^q	2.890 (2)	PhC ₂ Ph
Co ₂ Pt ₂ (PPh ₃) ₂ (CO) ₈ ^r	2.987 (9)	Cluster
[Pt(NH ₃) ₄][PtCl ₄] ^s	3.25	
Pt metal	2.77	
2(Covalent radius) ^{t,u}	2.62, 2.76	
[Pt(<i>t</i> -Bu) ₂ P(CH ₂) ₃ P- (<i>t</i> -Bu) ₂] ₂ ^v	2.765 (1)	

^a Absence of standard deviations occurs only when those values are omitted in the original reference. Abbreviations: Ph, C₆H₅; Me, CH₃; Et, C₂H₅; Pr, C₃H₇. ^b Reference 44. ^c Reference 45. ^d Reference 46. ^e Reference 47. ^f Reference 43. ^g Reference 48. ^h Reference 49. ⁱ Reference 50. ^j Reference 51. ^k Reference 31. ^l Reference 52. ^m Reference 53. ⁿ Reference 43. ^o Reference 54. ^p Reference 55. ^q Reference 56. ^r Reference 57. ^s Reference 58. ^t Reference 59. ^u Reference 11. ^v This work.

isolation of the linear two-coordinate complexes PtL₂ (L = monodentate phosphine).¹¹ The bent two-coordinate diphos complex (C_{2v} for the local symmetry) is undoubtedly much more reactive than the linear PtL₂ one (D_{∞h}). In particular, a strong π basicity must be postulated for the bent structure to account for the facile hydrogen abstraction. This can be understood in terms of the highest nonbonding d orbital (b₁), whose energy level depends on the interligand angle θ. For PtCl₂(diphos) complexes θ values are available: 89.42 (12)° for (*t*-Bu)₂PCH₂CH₂P(*t*-Bu)₂³⁷ and 99.12 (10)° for (*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂²². Thus the θ angle is only slightly greater in **1** (102.6 (1)°) than in the corresponding PtCl₂ compound. There is a distinct difference in the π basicities of the Pt(diphos) species depending on θ. The Pt[(*t*-Bu)₂-PCH₂CH₂P(*t*-Bu)₂] species is apparently much more reactive than the trimethylene analogue and may exist only as a transient species. The correlation of θ with π basicity (π nucleophilicity) may be qualitatively explained in terms of a Walsh-type level diagram plotted against θ.

Physicochemical properties of strained organic molecules have been extensively examined. It is known, for example, that the s character of the ring bonds, as assessed from J_{13C-H} of methylene protons of alicyclic compounds, gradually increases as the ring size decreases from six to three.^{38,39} So far no such data have been reported for transition metal compounds. We have observed an interesting parallel with the carbocyclic compounds; namely, the J_{H-Pt} values increase (1008,² 1064, and 1101 Hz) in going from a seven- to a five-membered chelate ring. The Pt-H stretching frequency decreases (2023,² 1995, and 1980 cm⁻¹) as we go from the seven- to the five-membered ring. This decrease in Pt-H bond strength presumably results from an increased trans influence as a result of a decrease in P-Pt-P angle to ≈ 90°. The increase in J_{Pt-H} values, which would not be expected on the basis of increasing



trans influence implies increasing s character at the Pt atom. This is the first observation of the effect of metallocyclic ring size on the hybridization of a metal in the ring. The reversed order (Ph₂PCH₂CH₂PPh₂ < R(Ph)PCH₂CH₂P(Ph)R < R₂PCH₂CH₂PR₂; R = *t*-Bu, *l*-menthyl) for dehydrogenation would have been expected on the basis of the trans influence of the phosphines. Although the magnitude of J_{Pt-H} increases on substituting phenyl groups for *tert*-butyl and *l*-menthyl groups in R₂PCH₂CH₂PR₂ (R = *t*-Bu, Men) (Table II), no consistent trend can be found for ν_{Pt-H} (cf. 1980 (3) and 1985 cm⁻¹ (7), 1989 (4) and 1977 cm⁻¹ (6)). Thus, it would seem that the steric effect of the phosphine bulk is of paramount importance.

Hence, reversible hydrogen coordination in the five-membered chelate compounds **6** and **7** is reasonable. We believe that compound **8** also adds H₂ reversibly, although only partial hydride formation could be observed. Note the irreversible cis dihydride formation (compounds **4** and **5**) presumably because of the stabilizing effect of the bulky phosphines. The cone angle about each P atom, estimated using the method of Tolman et al.,⁴⁰ is ca. 150° for (*t*-Bu)₂PCH₂CH₂P(*t*-Bu)₂ and ca. 120° for Ph₂PCH₂CH₂PPh₂. Consecutive substitution of *l*-menthyl and phenyl for *tert*-butyl groups yields ligands having intermediate angles.

Of considerable interest is that in some instances H₂ can be displaced from the cis dihydride complexes. The facility of the formal reduction of Pt(II) to Pt(0), which occurs when an olefin is substituted for H₂, is surprising.³ The observation of reversible dehydrogenation of **6** and **7** amplifies this point. These data strongly suggest that relatively stable, bent, two-coordinate, 14-electron species Pt(diphos) are involved in these reactions. These bent 14-electron complexes are analogous to carbenes. Unlike carbenes, which are usually electrophilic, these platinum species exhibit nucleophilic behavior. Thus, while reacting in patterns similar to those seen for carbenes, i.e., hydride abstraction and dimer formation, they also readily react with electron-accepting but not electron-donating olefins.

The dimeric structure of **1**, in which there are no bridging ligands, deserves comment. Triphenylphosphine platinum clusters [Pt(PPh₃)₂]_n (n = 2,⁴¹ 3,⁴² 4⁴²) have been reported but the exact nature of the bonding in these complexes is not known. The phosphide bridged compounds Pt₂(μ-PPh₂)₂(PPh₃)₂ and Pt₃(μ-PPh₂)₂(Ph)(PPh₃)₂,⁴³ which were obtained from a mixture of compounds formed after prolonged heating of Pt(PPh₃)₃, have been structurally characterized. However, the relationship between these complexes and the previously reported oligomers is unclear. Table XII contains a number of complexes⁴³⁻⁵⁸ which involve Pt-Pt bonds. Included in this table is the covalent radius of Pt(0). Pauling's value,⁵⁹ 1.31 Å, has been used to define a Pt-Pt single bond distance of ca. 2.62 Å.^{43,47} A number of shorter bond lengths are known and these are believed to involve some degree of multiple bonding.⁴⁴⁻⁴⁶ However, recent structural studies have shown that a large number of complexes exist in which there is a longer Pt-Pt bond.⁴⁸⁻⁵⁷ This and large values of a series of Pt(0)-P bond distances have led to the suggestion that a more accurate value for the covalent radius of Pt(0) would be 1.38 Å.¹¹ This would

give rise to a single bond distance of ca. 2.76 Å, which is exactly that seen in **1**.

It is conceivable that there is an overlap of a vacant p orbital on one Pt atom with a filled d orbital on the other Pt atom. Then two π -type interactions would be involved,⁶⁰ but essentially no σ -type interaction should be present. The simplest description for the Pt–Pt linkage would then be a rather unusual four electron, two- π bond. Consistent with this valence bond scheme is the observation of long-range coupling, $J_{P-Pt-Pt-P}$. This bonding scheme should lead to a decrease in metal–metal separation, but presumably steric interactions preclude this. As seen in Table VIII, short H···H contacts between dimer halves are already present at the observed Pt–Pt distance. Inspection of the H···H contacts and Figure 6 reveals that hydrogen atoms from one dimer half fit into a pocket in the hydrocarbon structure of the other dimer half. The dihedral angle between the coordination planes, approximately 82°, also lends credence to the synergic d–p overlap argument, since the best overlap of filled and unoccupied orbitals would occur at 90°.

Acknowledgments. This work was supported by the National Science Foundation and the Japanese Society for the Promotion of Science under the Japan–U.S. Cooperative Science Program (GR021/OIP75-09438). The authors wish to thank Professor Roald Hoffmann for helpful discussions.

Supplementary Material Available: A table of the root mean square amplitudes of vibration and a listing of the observed and calculated structure amplitudes (38 pages). Ordering information is given on any current masthead page.

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