preparation of a polymeric simple and complex TCNQ salt is given.

Infrared, electronic absorption, and ^{1}H NMR spectroscopies were used to characterize the TCNQ salts.

Synthesis of $N_3^+P_3(NC_5H_{10})_6 \cdot CH_3(TCNQ)^-$. $N_3^+P_3(NC_5H_{10})_6 \cdot CH_3I^-$ **(20)** (2 g, 0.0026 mol) was dissolved in boiling acetonitrile (75 mL). Li^+TCNQ^- (0.72 g, 0.0034 mol) was dissolved in boiling ethanol (50 mL) and then rapidly added to the phosphazene solution. The boiling reaction mixture was stirred for 1 h, and the solvent was then removed with the use of a rotary evaporator. Lithium iodide and excess Li^+TCNQ^- were extracted from the residue with methanol (2 L). The product was washed with diethyl ether (200 mL) until the washings were colorless. The dark green salt was then vacuum-dried. Yield: 1.3 g (66%).

Synthesis of $N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3(TCNQ)_2^-$. TCNQ (0.82 g, 0.004 mol) was dissolved in boiling acetonitrile (100 mL). $N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3I^-$ **(11)** (5 g, 0.006 mol) was dissolved in boiling acetonitrile (20 mL) and then added rapidly to the TCNQ solution. The boiling mixture was stirred for 0.5 h after which the stirring was stopped and the system cooled to room temperature. After 28 h, the precipitated product was collected and washed with cold acetonitrile (5 mL). The black crystals were then vacuum-dried. Yield: 0.6 g (27%).

Synthesis of $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2(TCNQ)^-)_{0.28}]_n \cdot [NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2I^-)_{0.28}]_n$ **(35)** (1.0 g; 0.0009 mol of I^-) was dissolved in boiling acetonitrile (75 mL). Li^+TCNQ^- (0.39 g, 0.0018 mol) was dissolved in boiling ethanol (50 mL) and added to the polymer solution. The hot reaction mixture was stirred for 0.5 h, and then the solvent was removed with the use of a rotary evaporator. The residue was purified by Soxhlet extraction with methanol and then dried in vacuum. Yield: 0.95 g (89%).

Synthesis of $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2(TCNQ)_2^-)_{0.28}]_n \cdot [NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2(TCNQ)^-)_{0.28}]_n$ (0.3 g; 0.00024 mol of $TCNQ^-$) was dissolved in hot acetonitrile (100 mL). TCNQ (0.05 g, 0.00024 mol) was dissolved in boiling acetonitrile (5 mL) and added to the polymer solution. After the hot reaction mixture was stirred for 0.5 h, the solvent was removed with the use of a rotary evaporator and

the polymer residue was dried under vacuum. Yield: 0.3 g (86%).

Conductivity Measurements. Electrical conductivities of the TCNQ salts in the form of pressed pellets were measured by a standard in-line probe technique with pressure contacts.[33] Samples (70 mg) were compacted under 10 tons of pressure to give pellets of dimensions 0.5 mm × 13 mm diameter. Conductivity measurements also were obtained for some of the polymeric samples in the form of thin films (solution cast) on a glass substrate. Room-temperature measurements were obtained with the use of a commercial probe (Alessi Industries Model ATP test probe fixture fitted with a A4P four point probe) with 0.635-mm probe spacings. Conductivities were corrected for finite sample thickness, and no correction was considered necessary for boundary effects.[34] Currents were imposed with a Keithley Model 225 current source and voltages were measured with a Keithley Model 614 electrometer.

Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557, and University of Warwick, Coventry CV47AL, England

Four- and Five-Coordinate Platinum Complexes of Divinylphenylphosphine

Mark S. Holt,[†] John H. Nelson,*[†] and Nathaniel W. Alcock*[‡]

A series of platinum(II) complexes of the type L_2PtX_2 (L = divinylphenylphosphine; X = Cl, Br, I) have been prepared and characterized by elemental analyses, physical properties, conductance measurements, infrared spectroscopy, and ^{1}H, ^{1}H$\{^{31}$P$\}$, ^{13}C$\{^1$H$\}$, ^{13}C$\{^1$H,^{31}P$\}$, ^{31}P$\{^1$H$\}$ and ^{195}Pt$\{^1$H$\}$ NMR spectroscopy. All complexes are nonelectrolytes, and most possess the cis geometry in solution as well as in the solid state. However, L_2PtI_2 slowly isomerizes from cis to trans in CDCl$_3$ solution. Variable-temperature ^{31}P$\{^1$H$\}$ NMR spectroscopy and conductance studies of the equilibrium $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ have been analyzed in terms of intra- and intermolecular equilibria of the pentacoordinate species L_3PtX_2. The formation of L_3PtX_2 is enthalpy-driven. The crystal structures of dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) (**1**) and dichlorobis(divinylphenylphosphine)platinum(II) (**2**) have been determined from three-dimensional X-ray data collected by counter methods. Compound **1** crystallizes in space group $P2_1/c$ with $a = 11.285$ (2) Å, $b = 11.269$ (2) Å, $c = 19.386$ (3) Å, $\beta = 92.36$ (1)°, and $Z = 4$. Compound **2** crystallizes in space group $P\bar{1}$, with $a = 7.861$ (2) Å, $b = 16.783$ (5) Å, $c = 8.804$ (3) Å, $\alpha = 107.59$ (2)°, $\beta = 94.93$ (2)°, $\gamma = 101.56$ (2)°, and $Z = 2$. Both structures were refined by least-squares methods with $R = 0.028$ for **1** and $R = 0.033$ for **2** for 3327 and 3446 reflections with $I/\sigma(I) > 3.0$ for **1** and **2**, respectively. The molecular structures are remarkably similar to one another and contain cis-four-coordinate platinum(II) with no unusual bond distances or internuclear contacts. Detailed comparisons of these structures together with the solution NMR data for the L_3PtX_2 complexes suggest that steric rather than electronic factors are dominant in determining the thermodynamic stability of the pentacoordinate complexes. These conclusions are strengthened by analysis of the infrared data in the CO stretching region for the complexes $LMo(CO)_5$ (L = divinylphenylphosphine, 1-phenyl-3,4-dimethylphosphole). Cotton–Kraihanzel force field analyses and Graham σ- and π-bonding parameters suggest that the phosphole is both a better σ-donor and π-acceptor than the phosphine toward Mo(0). All the data for the platinum complexes suggest that toward Pt(II) these two ligands have similar donor abilities.

Introduction

Recent studies in this laboratory have shown that pentacoordinate species play significant roles in the geometrical isom-

erizations of square-planar platinum(II) and palladium(II) complexes.[1] Our previous studies concentrated on 1-substituted 3,4-dimethylphospholes as ligands because these ligands have been shown[2] to be reasonably good π-acceptors and sterically small,

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two properties thought to promote pentacoordination.[3]

In this paper we report results from a similar study using divinylphenylphosphine (3) as a ligand. Divinylphenylphosphine was expected to be electronically similar to 1-phenyl-3,4-dimethylphosphole (4) while sterically it could be much larger.

3   **4**
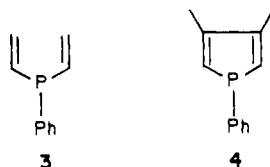
We have prepared and characterized the complexes L_2PtX_2 (L = divinylphenylphosphine; X = Cl, Br, I) and examined their $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra in solution and in solution with added ligand. X-ray structural studies of dichlorobis(divinylphenylphosphine)platinum(II) (2) and dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) (1) were completed in order to compare structural features of these two complexes and to gain further insight into those factors that stabilize pentacoordinate platinum(II) complexes.

The mono(phosphine)pentacarbonylmolybdenum complexes have also been prepared and characterized. Their infrared carbonyl stretching frequencies have been analyzed to yield force constants by the method[4] of Cotton and Kraihanzel and Graham σ and π parameters.[5] This independent comparison of the bonding properties of divinylphenylphosphine and 1-phenyl-3,4-dimethylphosphole was made in order to further address those factors that contribute to the stability of L_3PtX_2 complexes.

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. All solvents were dried, when necessary, by standard procedures and stored over Linde 4-Å molecular sieves. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer as Nujol mulls between CsBr plates or as hexane solutions in 0.1-mm NaCl cells. Far-infrared spectra were recorded on a Polytec FIR 30 FT interferometer as polyethylene pellets. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 40.26 and 21.30 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded respectively at 300.00 and 75.00 MHz on a General Electric QE-300 spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si, while the phosphorus chemical shifts are relative to external 85% H_3PO_4 with a positive value being downfield of the respective reference. Platinum-195 chemical shifts are referenced to the standard frequency 21.4 MHz relative to the proton resonance of Me_4Si at 100 MHz.[5] Spin simulations were performed on the JEOL JEC 980B computer using the program FASN03-760812 supplied by JEOL Co. Equilibrium constants for the equilibria $L_2PTX_2 + L \rightleftharpoons L_3PTX_2$ were obtained by integrating the areas under the appropriate $^{31}P\{^1H\}$ signals for $CDCl_3$ solutions containing a 1:1 mole ratio of L and L_2PtX_2. Conductivity studies were performed as previously described.[7] The complexes are nonelectrolytes in CH_3NO_2 in the presence and absence of excess ligand. Divinylphenylphosphine was obtained from Strem Chemicals and used as received.

(B) Synthesis. The syntheses of 1-phenyl-3,4-dimethylphosphole and its platinum chloride complex L_2PtCl_2 have been previously described.[1]

Dichlorobis(divinylphenylphosphine)platinum(II). To 3.63 g (7.7 mmol) of dichlorobis(benzonitrile)platinum(II) in 50 mL of CH_2Cl_2 under N_2 was added 2.75 mL (16.9 mmol) of divinylphenylphosphine via syringe. The resulting solution was stirred magnetically overnight at ambient temperature, and the solvent was then removed via rotary evaporation. The colorless crystals that resulted were washed with anhydrous diethyl ether and vacuum-dried overnight; yield 3.46 g (70%). The crystals used for X-ray structure determination were obtained by slow crystallization from methanol/acetone/water.

The bromide and iodide complexes were prepared by metathesis of the chloride complex in $CH_2Cl_2/CH_3OH/H_2O$ for 7 days with a 4:1 molar ratio of NaX to chloride complex. As has been previously noted,[1] sufficient time must be allowed for these reactions to go to completion, or mixed-halide species will result (vide infra). Satisfactory carbon and hydrogen analyses were obtained for all compounds (Galbraith Laboratories, Knoxville, TN 37921).

(Divinylphenylphosphine)pentacarbonylmolybdenum(0). To 2.94 g (11 mmol) of molybdenum hexacarbonyl (Strem) in 100 mL of methylcyclohexane under N_2 was added 1.60 mL (10 mmol) of divinylphenylphosphine via syringe. The mixture was refluxed for 1.5 h and filtered hot. The solvent was removed via rotary evaporation at 50 °C, which also removed most of the excess molybdenum hexacarbonyl. An IR spectrum of the resulting viscous oil revealed the presence of both $LMo(CO)_5$ and cis-$L_2Mo(CO)_4$. Chromatography of this oil on silica gel (30–270 mesh, Aldrich) with hexane affected separation of these two products with $LMo(CO)_5$ eluting first. Both (divinylphenylphosphine)-pentacarbonylmolybdenum(0) and cis-bis(divinylphenylphosphine)tetracarbonylmolybdenum(0) are low-melting solids that are difficult to crystalize; yield of $LMo(CO)_5$ 0.157 g (37%). Anal. Calcd for $C_{15}H_{11}MoO_5P$: C, 45.26; H, 2.76. Found: C, 45.10; H, 2.52.

(1-Phenyl-3,4-dimethylphosphole)pentacarbonylmolybdenum(0) was prepared in a similar manner[8] in 45% yield.

(C) Crystal Structure Analyses. Blocklike pale yellow crystals of cis-dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II)[1] (1) were isolated from a dichloromethane/methanol solution, and thin colorless plates of cis-dichlorobis(divinylphenylphosphine)platinum(II) (2) were isolated from an acetone/methanol/water solution. Crystal data and additional details of data collection and refinement are given in Table I. Intensity data were taken with a Syntex P2$_1$ diffractometer and corrected for Lorentz, polarization, and absorption effects, the last with ABSCOR.[9] Systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) indicated space group $P2_1/C$ for 1, and no systematic absences were found for 2. The heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses using the data collected at 173 and 193 K for 1 and 2, respectively. The crystals were held at low temperature with the Syntex LT-1 attachment with temperature regulation good to ±1 K. Hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors and were not refined except for the methyl groups of 1, which were treated as rigid bodies. Final refinement was by least-squares methods (minimizing $\sum w(F_o - F_c)^2$) in cascaded large blocks. The largest peak on a final difference Fourier synthesis was of height 0.5 e/Å^3 for 1, and the only peak greater than 0.3 e/Å^3 for 2 was located near the platinum atom. Weighting schemes of the form $1/\sigma^2(F) + gF^2$), with $g = 5 \times 10^{-5}$ for 1 and $g = 8 \times 10^{-4}$ for 2, were shown to be satisfactory by weight analyses. Three standard reflections were monitored every 200 reflections and showed slight changes during data collection for 2. The data were rescaled to correct for this. Computing was with the SHELXTL system[10] on a Data General NOVA 3, following initial processing on a Burroughs B6800. Scattering factors, including anomalous scattering, were taken from ref 11. Final atom coordinates for 1 and 2 are given in Tables II and III and selected bond lengths and angles in Tables IV and V, respectively.

Results and Discussion

Four-Coordinate Complexes. The geometries of the complexes L_2PtX_2 (L = divinylphenylphosphine; X = Cl, Br, I) were determined by a combination of ^{31}P NMR (Table VI) and infrared spectroscopy.[12–16] Infrared assignments were made by comparison of the spectra of the free ligands and their complexes in the 700–50-cm^{-1} region. The infrared spectra suggest that all three complexes are cis in the solid state as two ν_{PtX} ($\nu_{PtCl} = 293, 309$ cm^{-1}; $\nu_{PtBr} = 189, 202$ cm^{-1}; $\nu_{PtI} = 191, 215$ cm^{-1}) and two ν_{PtP}

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Table I. Crystal and Refinement Data for **1** and **2**[a]

	PtC$_{24}$H$_{26}$Cl$_2$P$_2$ (**1**)	PtC$_{20}$H$_{22}$Cl$_2$P$_2$ (**2**)
fw	641.2	590.2
a, Å	11.285 (2) [11.335 (3)]	7.861 (2) [7.894 (1)]
b, Å	11.269 (2) [11.272 (2)]	16.783 (5) [16.968 (3)]
c, Å	19.386 (3) [19.440 (4)]	8.804 (3) [8.788 (2)]
α, deg		107.59 (2) [108.09 (1)]
β, deg	92.36 (1) [92.51 (1)]	94.93 (2) [94.46 (1)]
γ, deg		101.56 (2) [100.93 (1)]
space group	$P2_1/C$	$P\bar{1}$
Z	4	2
no. of reflcns used to determine cell consts	15	15
d(calcd), g/cm^3	1.73	1.82
linear abs coeff, cm^{-1}	61.1	70.2
cryst dimens, mm	0.25 × 0.25 × 0.12	0.023 × 0.38 × 0.51
abs factor range	1.44–1.53	1.15–1.80
data collcn method	–2	–2
2θ range, deg	3–50	3–50
temp, K	173 [298]	193 [298]
scan rate, deg/min	2.5–29[a]	3–29[a]
scan range, deg below 2θ (Kα$_2$ (–)) to deg above 2θ (Kα$_2$ (+))	–0.9 to +1.1	–1.0 to +1.05
no. of unique data collcd	4855	3794
no. of data used in refinement ($I/\sigma(I) > 3.0$)	3327	3446
no. of params in final cycles	275	227
g	0.00005	0.0008
final R_F	0.028	0.033
final R_{wF}	0.025	0.036

[a] Stationary background counts were taken before and after the scan for 0.25 of the scan time; room-temperature cell constants are in brackets; Mo Kα radiation; graphite monochromator; λ = 0.71069 Å.

Table II. Atom Coordinates (×10^4) for C$_{24}$H$_{26}$Cl$_2$P$_2$Pt (**1**)

atom	x	y	z
Pt	2305 (1)	1135 (1)	1212 (1)
Cl(1)	3713 (2)	1370 (1)	372 (1)
Cl(2)	1515 (2)	3022 (1)	931 (1)
P(1)	950 (1)	1076 (1)	2023 (1)
P(2)	3041 (1)	–649 (1)	1475 (1)
C(111)	–574 (5)	962 (5)	1675 (3)
C(112)	–812 (6)	957 (6)	973 (4)
C(113)	–1964 (8)	837 (7)	713 (5)
C(114)	–2883 (8)	760 (8)	1146 (5)
C(115)	–2643 (7)	717 (8)	1852 (5)
C(116)	–1485 (6)	841 (8)	2126 (4)
C(121)	1081 (5)	21 (5)	2723 (3)
C(122)	1312 (5)	558 (6)	3313 (3)
C(123)	1372 (5)	1893 (6)	3255 (3)
C(124)	1127 (5)	2299 (5)	2612 (3)
C(125)	1544 (8)	–68 (7)	3989 (4)
C(126)	1675 (8)	2658 (7)	3873 (4)
C(211)	3924 (5)	–681 (5)	2284 (3)
C(212)	4375 (8)	–1733 (7)	2529 (4)
C(213)	5035 (9)	–1791 (7)	3142 (4)
C(214)	5313 (6)	–770 (7)	3499 (4)
C(215)	4839 (7)	293 (7)	3266 (4)
C(216)	4120 (6)	324 (6)	2658 (4)
C(221)	3929 (5)	–1405 (5)	856 (3)
C(222)	3422 (5)	–2410 (5)	656 (3)
C(223)	2280 (5)	–2649 (5)	991 (3)
C(224)	1988 (5)	–1836 (5)	1452 (3)
C(225)	3889 (6)	–3250 (6)	128 (3)
C(226)	1546 (7)	–3719 (5)	790 (4)

Table III. Atom Coordinates (×10^4) for C$_{20}$H$_{22}$P$_2$Cl$_2$Pt (**2**)

atom	x	y	z
Pt	4860 (1)	2548 (1)	5432 (1)
Cl(1)	6980 (2)	3541 (1)	7565 (2)
Cl(2)	6907 (2)	1680 (1)	4844 (2)
P(1)	3028 (2)	1498 (1)	3380 (2)
P(2)	2932 (2)	3370 (1)	6061 (2)
C(11)	3133 (10)	572 (5)	170 (8)
C(12)	3718 (11)	504 (5)	–1308 (8)
C(13)	4938 (11)	1171 (6)	–1517 (8)
C(14)	5622 (10)	1913 (6)	–250 (9)
C(15)	5090 (9)	2003 (5)	1258 (8)
C(16)	3856 (8)	1354 (4)	1442 (7)
C(17)	2815 (9)	481 (4)	3751 (8)
C(18)	1312 (11)	–89 (5)	3536 (11)
C(19)	772 (8)	1556 (4)	2971 (8)
C(110)	–38 (9)	1547 (5)	1615 (9)
C(21)	114 (10)	3699 (5)	4321 (10)
C(22)	–634 (11)	3882 (7)	3031 (12)
C(23)	282 (13)	3943 (6)	1782 (12)
C(24)	1966 (12)	3830 (6)	1835 (10)
C(25)	2736 (10)	3665 (5)	3110 (9)
C(26)	1803 (8)	3586 (4)	4360 (8)
C(27)	3881 (10)	4455 (5)	7404 (10)
C(28)	3214 (14)	4881 (7)	8551 (10)
C(29)	1237 (9)	2925 (5)	7043 (8)
C(210)	1400 (11)	2365 (6)	7728 (10)

vibrations are observed for each complex. For L$_2$PtCl$_2$ this conclusion is confirmed by X-ray crystallography (vide infra).

All three complexes display typical 1:4:1 "pseudotriplets" in their ^{31}P NMR spectra with $^1J_{PtP}$ determined by the separation of the outer lines. The L$_2$PtCl$_2$ and L$_2$PtBr$_2$ complexes are wholly cis in CDCl$_3$ solution while L$_2$PtI$_2$, which is initially cis, spontaneously isomerizes to an equilibrium mixture (63% cis, 37% trans) in a few hours at 25 °C. As is typical for (R$_3$P)$_2$PtX$_2$ complexes,[17,18] the magnitude of the platinum–phosphorus coupling constants are indicative of geometry. Cis complexes generally

have $^1J_{PtP} > 3000$ Hz while trans complexes have $^1J_{PtP} < 2400$ Hz. The ^{195}Pt{^{1}H} NMR spectrum (Table VI) shows a first-order 1:2:1 triplet for each complex. It might be anticipated that both the coordination chemical shift, $\Delta\delta(^{31}P)$, and the platinum–phosphorus coupling constant, $^1J_{PtP}$, would be reasonable measures of the platinum–phosphorus bond strength and both parameters would be expected to increase with increasing bond strength. We note for both series of complexes that both these parameters decrease in the sequence Cl > Br > I as a result of the increasing trans influence[19] of the halides (Cl < Br < I). For the cis-divinylphenylphosphine complexes, there is a linear relationship between $\Delta\delta(^{31}P)$ and $^1J_{PtP}$ of the form $\Delta\delta(^{31}P) = 0.166(^1J_{PtP}) - 46.56$ ($r^2 = 0.99$). For the cis-phosphole complexes the relationship

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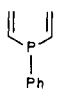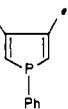
Table IV. Selected Bond Distances and Angles for
Dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) (1)[a]

	Bond Lengths (Å)		
Pt–P(1)	2.239 (2)	Pt–P(2)	2.227 (1)
Pt–Cl(1)	2.336 (2)	Pt–Cl(2)	2.360 (2)
P(1)–C(124)	1.796 (6)	P(1)–C(121)	1.805 (6)
P(1)–C(111)	1.826 (6)	P(2)–C(211)	1.823 (6)
P(2)–C(221)	1.808 (6)	P(2)–C(224)	1.789 (6)
C(121)–C(122)	1.312 (9)	C(122)–C(123)	1.510 (9)
C(222)–C(223)	1.491 (8)	C(123)–C(124)	1.346 (8)
C(223)–C(224)	1.330 (8)	C(221)–C(222)	1.320 (8)

	Bond Angles (deg)		
P(1)–Pt–P(2)	94.1 (1)	P(1)–Pt–Cl(1)	175.2 (1)
P(2)–Pt–Cl(1)	90.2 (1)	P(1)–Pt–Cl(2)	85.8 (1)
P(2)–Pt–Cl(2)	179.7 (1)	Cl(1)–Pt–Cl(2)	89.9 (1)
Pt–P(1)–C(111)	113.7 (2)	Pt–P(1)–C(121)	120.7 (2)
C(111)–P(1)–C(121)	106.2 (3)	Pt–P(1)–C(124)	111.2 (2)
C(111)–P(1)–C(124)	111.6 (3)	C(121)–P(1)–C(124)	91.4 (3)
Pt–P(2)–C(211)	113.6 (2)	Pt–P(2)–C(221)	119.0 (2)
C(211)–P(2)–C(221)	105.3 (3)	Pt–P(2)–C(224)	115.3 (2)
C(211)–P(2)–C(224)	110.2 (3)	C(221)–P(2)–C(224)	91.0 (3)
P(1)–C(124)–C(123)	109.9 (4)	P(1)–C(121)–C(122)	111.0 (5)
C(122)–C(123)–C(134)	113.6 (5)	P(2)–C(224)–C(223)	110.4 (4)
P(2)–C(221)–C(222)	110.7 (4)	C(221)–C(222)–C(223)	113.5 (5)
C(222)–C(223)–C(224)	114.2 (5)	C(121)–C(122)–C(123)	113.8 (5)

[a] Numbers in parentheses are estimated standard deviations.

Table V. Selected Bond Distances and Angles for
Dichlorobis(divinylphenylphosphine)platinum(II) (2)[a]

	Bond Lengths (Å)		
Pt–P(1)	2.248 (1)	Pt–P(2)	2.243 (2)
Pt–Cl(1)	2.354 (1)	Pt–Cl(2)	2.368 (2)
P(1)–C(17)	1.811 (8)	P(1)–C(16)	1.844 (7)
P(1)–C(19)	1.806 (7)	P(2)–C(26)	1.841 (8)
P(2)–C(29)	1.809 (8)	P(2)–C(27)	1.809 (7)
C(17)–C(18)	1.322 (10)	C(19)–C(110)	1.299 (11)
C(27)–C(28)	1.269 (13)	C(29)–C(210)	1.281 (14)

	Bond Angles (deg)		
P(1)–Pt–P(2)	95.7 (1)	P(1)–Pt–Cl(1)	173.7 (1)
P(2)–Pt–Cl(1)	90.4 (1)	P(1)–Pt–Cl(2)	85.2 (1)
P(2)–Pt–Cl(2)	178.4 (1)	Cl(1)–Pt–Cl(2)	88.6 (1)
Pt–P(1)–C(16)	112.4 (2)	Pt–P(1)–C(17)	109.5 (2)
C(17)–P(1)–C(16)	106.3 (3)	Pt–P(1)–C(19)	119.1 (2)
C(16)–P(1)–C(19)	105.3 (3)	C(17)–P(1)–C(19)	103.1 (3)
Pt–P(2)–C(26)	115.6 (2)	Pt–P(2)–C(27)	114.8 (3)
C(26)–P(2)–C(27)	100.8 (4)	Pt–P(2)–C(29)	112.4 (3)
C(26)–P(2)–C(29)	106.7 (3)	C(27)–P(2)–C(29)	105.3 (4)
P(1)–C(19)–C(110)	126.5 (6)	P(1)–C(17)–C(18)	124.6 (7)
P(2)–C(27)–C(28)	126.5 (7)	P(2)–C(29)–C(210)	123.0 (7)

[a] Numbers in parentheses are estimated standard deviations.

Table VI. ^{31}P{^{1}H} and ^{195}Pt NMR Spectral Data for L$_2$PtX$_2$

L	X	$\delta(^{31}P)^a$	$\Delta\delta(^{31}P)^b$	$\delta(^{195}Pt)^c$	$^1J_{PtP}^d$	geom
	Cl	-4.37	12.58	-4412	3574	cis
	Br	-4.91	12.04	-4699	3520	cis
	I	-7.69	9.26	-5280	3368	cis
	I	-7.09	9.86	-5629	2412	trans
	Cl	8.1	10.6	-4483	3345	cis
	Br	7.9	10.4	-4805	3268	cis
	I	5.6	8.1	-4876	3125	cis

[a] Vs. 85% H$_3$PO$_4$. [b] $\Delta\delta(^{31}P)$ = $\delta(^{31}P$ complex) – $\delta(^{31}P$ ligand). [c] Vs. H$_2$PtCl$_6$ at 21.4 MHz. [d] In hertz. [e] Reference 1.

is $\Delta\delta(^{31}P)$ = 0.0120($^1J_{PtP}$) – 29.12 (r^2 = 0.92), and for all six complexes the relationship is $\Delta\delta(^{31}P)$ = 0.0093($^1J_{PtP}$) – 20.74 (r^2 = 0.83). Thus, both $\Delta\delta(^{31}P)$ and $^1J_{PtP}$ increase in the order anticipated. The coordination chemical shifts are slightly larger and the platinum–phosphorus coupling constants considerably larger for the divinylphenylphosphine complexes than for the phosphole complexes. This suggests that divinylphenylphosphine is a slightly better donor toward platinum(II) than is 1-phenyl-
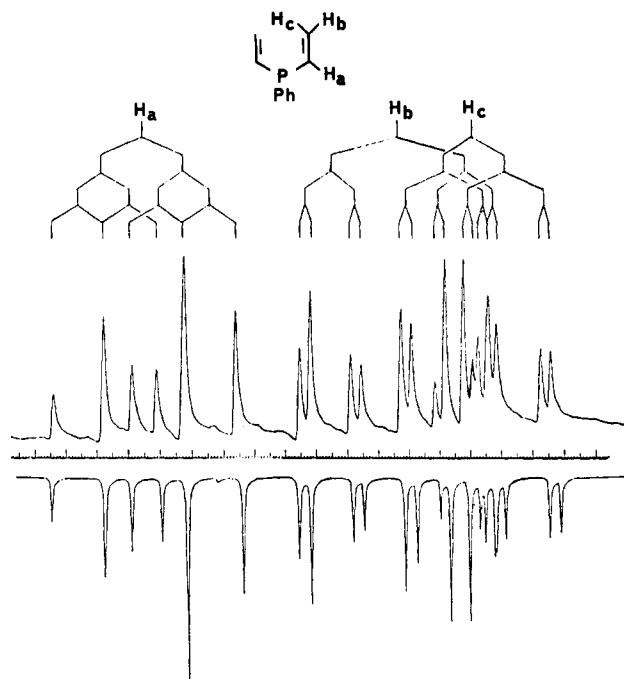

100 MHz ^{1}H NMR, VINYL PROTONS

Figure 1. 100-MHz ^{1}H NMR spectrum of divinylphenylphosphine in the vinyl region (upper) and spin simulation using the parameters derived from the stick diagram (lower). See Table XIII.

3,4-dimethylphosphole. The X-ray data for the two complexes (vide infra) suggest, however, that the difference in donor ability is quite small and in the opposite sense. The coordination chemical shift is related to the free ligand chemical shift for phosphorus donor ligands by the relationship $\Delta\delta(^{31}P)$ = $A\delta(^{31}P(ligand))$ + B. For phospholes,[1] A = -0.110 and B = 14.06 when X = Cl, A = -0.411 and B = 11.37 when X = Br, and A = -0.283 and B = 9.35 when X = I. For phosphines,[20] A = -0.326 and B = 18.83 when X = Cl. All these values are for cis complexes. Using these relations, one can predict the $\Delta\delta(^{31}P)$ values for the divinylphenylphosphine complexes from $\delta(^{31}P)$ = -16.95 for the free ligand as follows: L$_2$PtCl$_2$ (15.92), L$_2$PtBr$_2$ (18.34), and L$_2$PtI$_2$ (14.15) using the phosphole equations; L$_2$PtCl$_2$ (24.36) using the phosphine equation. Clearly, the $\Delta\delta(^{31}P)$ values for the divinylphenylphosphine complexes are closer to those of the phosphole complexes than to those of phosphine complexes. Overall, then, we conclude that the donor abilities of the two ligands toward platinum(II) must be quite similar.

Additional information regarding the structure and bonding within these complexes may be obtained from their ^{13}C{^{1}H} and ^{1}H NMR spectra. At 300 MHz it was possible to assign all proton resonances for the chloride and bromide complexes. However, for the iodide complex, it was also necessary to decouple phosphorus in order to distinguish and assign the resonances due to the cis and trans isomers. The 300-MHz ^{1}H NMR spectrum of PhP(CH=CH$_2$)$_2$ is shown along with a spin simulation in Figure 1. The spectra of the L$_2$PtX$_2$ (X = Cl, Br) complexes are shown in Figure 2, and the ^{1}H and ^{1}H{^{31}P} spectra of the iodide complex are shown in Figure 3. The data obtained together with assignments are given in Table VII.

Assignments were made by comparing chemical shifts and coupling constants of the complexes with those of the free ligand and similar unsaturated phosphines.[21–24] The vinyl group reso-

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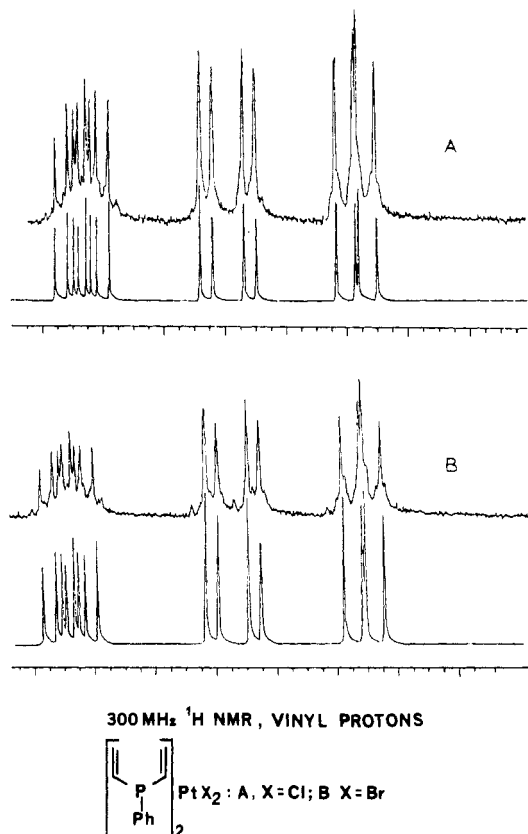(23) Anderson, W. A.; Freeman, R.; Reilly, C. A. *J. Chem. Phys.* **1963**, *39*, 1518.

300 MHz ^{1}H NMR, VINYL PROTONS

Figure 2. 300-MHz ^{1}H NMR spectrum (vinyl region) in $CDCl_3$ at 30 °C of (A) *cis*-dichlorobis(divinylphenylphosphine)platinum(II) and (B) *cis*-dibromobis(divinylphenylphosphine)platinum(II). In each case, the experimental spectrum is at the top and the simulated spectrum (ABCX spin system) is at the bottom. Assignments are as in Figure 1 and Table VII.

Table VII. Proton NMR Data for Phenyldivinylphosphine and Its Platinum Halide Complexes L_2PtX_2

X	position	δ	$^3J_{ab}$	$^3J_{ac}$	$^2J_{bc}$	$^nJ_{PH}$
free ligand	H_a	6.47	11.7	17.9		11.7
	H_b	5.88	11.7		2.3	31.3
	H_c	5.71		17.9	2.3	14.7
	$H_{o,m,p}$	7.42				
Cl	H_a	6.44	12.1	18.2		22.3
	H_b	5.96	12.1		0.7	42.1
	H_c	5.55		18.2	0.7	21.3
	H_m	7.73				
	$H_{o,p}$	7.42				
Br	H_a	6.48	12.1	18.2		22.3
	H_b	5.94	12.1		0.0	41.6
	H_c	5.51		18.2	0.0	20.7
	H_m	7.73				
	$H_{o,p}$	7.42				
cis I	H_a	6.53	11.8	18.3		34.9
	H_b	5.89	11.8		0.0	41.9
	H_c	5.47		18.3	0.0	20.9
	H_m	7.71				
	$H_{o,p}$	7.42				
trans I	H_a	6.98	12.2	18.3		36.6
	H_b	6.05	12.2		0.0	39.2
	H_c	5.48		18.3	0.0	19.2
	H_m	7.71				
	$H_{o,p}$	7.42				

nances were analyzed as ABCX subspectra of the complete $[ABCX]_2$ spin system: A, B, C = ^{1}H; X = ^{31}P. This approximation was proven correct by computer simulations of the spectra[25]

(24) For the free ligand it was assumed that the relative signs of $^nJ_{PH}$ and $^nJ_{HH}$ are consistent with those determined[23] by double-quantum techniques for trivinylphosphine. The relative signs of the coupling constants for the complexes were not determined and should not be assumed to be the same as for the free ligand.
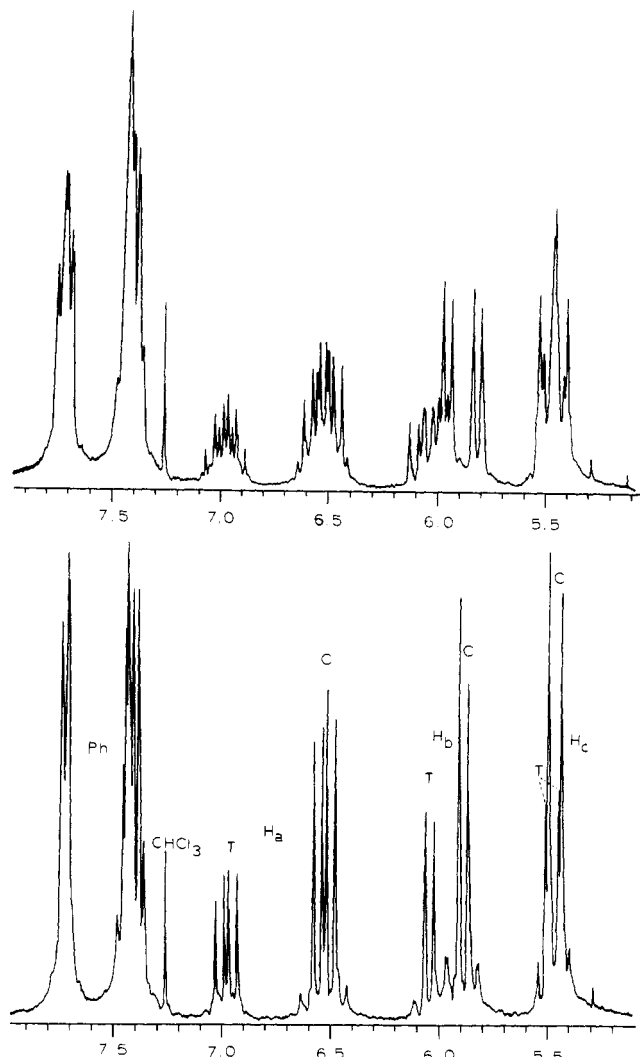

Figure 3. 300-MHz ^{1}H NMR spectrum (top) and ^{1}H$\{^{31}$P$\}$ NMR spectrum (bottom) of (C) *cis*- and (T) *trans*-diiodobis(divinylphenylphosphine)platinum(II) in $CDCl_3$ at 30 °C. See Table VII for data.

for the *cis*-L_2PtX_2 complexes and indicates that $^2J_{pp}$ is essentially zero for these cis complexes.

The ^{1}H NMR spectrum of the *trans*-L_2PtI_2 complex could not be analyzed in this way because it was obviously second order. The proton–proton couplings for the L_2PtI_2 complexes were determined from 300-MHz ^{1}H$\{^{31}$P$\}$ spectra and $|^nJ_{PH} + {}^{n+2}J_{PH}|$ for *trans*-L_2PtI_2 were determined by comparing the phosphorus coupled and decoupled spectra. Comparison of the data for *cis*- and *trans*-L_2PtI_2 leads to the conclusion that $^nJ_{PH}$ and $^{n+2}J_{PH}$ have the same signs for coupling to H_a but opposite signs for coupling to H_b and H_c in *trans*-L_2PtI_2. In each case the magnitude of $^nJ_{PH}$ is roughly 19 times $^{n+2}J_{PH}$.

There is little change in the proton spectrum of the ligand upon coordination. Only a slight upfield shift in $\delta(H_c)$, slight downfield shifts in $\delta(H_a)$ and $\delta(H_b)$, and the usual increases in J_{PH} were noted. These chemical shift changes probably result from the magnetic anisotropy of the vinyl groups such that the resultant shielding of H_c overwhelms the deshielding anticipated upon coordination.

The 75-MHz ^{13}C$\{^1$H$\}$ NMR data are presented in Table VIII. Assignments were made consistent with earlier data of Bundesgaard and Jakobsen,[26] with the aid of ^{31}P-decoupling experiments (Figure 4) and with field-dependence studies (25 and 75 MHz). Several trends in the data are notable. Upon coordination, the phenyl ortho, meta, and para carbons all shift downfield slightly.

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Table VIII. Carbon-13 NMR Data for Dihalobis(phenyldivinylphosphine)platinum(II) ($\delta(^{13}C)$, "J_{PC}", $^nJ_{PtC}$, Multiplicity)[a]

position	free ligand[b]	Cl	Br	cis	trans
				I	
α	136.95, −13.91	133.5, 0, 33.4, s	133.2, 0, 30.5, s	132.8, 0, 32.8, s	132.3, 3.5, 24.9, t
β	128.10, 23.16	127.6, 62.2, 0, m	128.7, 61.9, 0, d	130.7, 61.1, 31.6, m	132.3, 55.8, 23.9, m
C_1	137.31, 9.17	130.3, 0, 0, s	129.7, 0, 0, s	129.1, 32, NO, t	129.76, NO, NO, s
ortho	132.32, 18.70	133.9, 11.7, 0, t	133.9, 11.1, 0, m	133.8, 11.1, 26.1, t	134.2, 12.9, 17.5, t
meta	128.48, 6.74	128.5, 11.3, 0, t	128.4, 11.0, 0, t	128.3, 11.5, 14.7, m	128.0, 11.5, 0, t
para	128.56, 0.48	131.7, 0, 0, s	131.6, 0, 0, s	131.4, 0, 0, s	130.7, 0, 0, s

[a] J values in hertz, "J_{PC}" = $^nJ_{PC}$ + $^{n+2}J_{PC}$, s = singlet, d = doublet, t = triplet, m = multiplet, NO = not observable. [b] Reference 27.
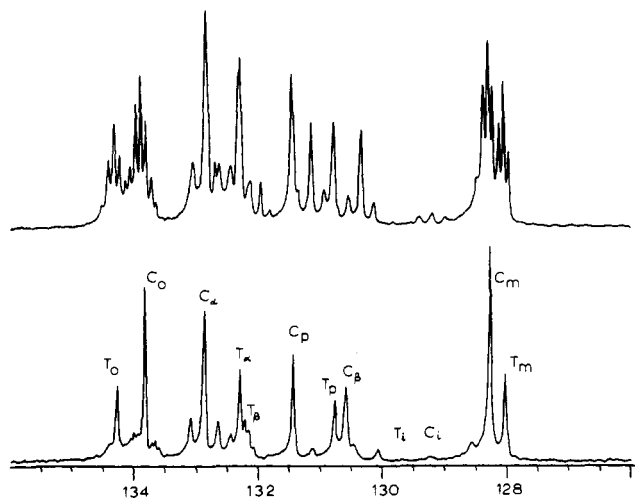

Figure 4. 75-MHz $^{13}C\{^1H\}$ (top) and $^{13}C\{^1H,^{31}P\}$ (bottom) NMR spectra of (C) cis- and (T) trans-diiodobis(divinylphenylphosphine)platinum(II) in CDCl₃ at 30 °C (o = ortho, p = para, m = meta, i = ipso phenyl carbons; α, β = vinyl carbons). See Table VIII.

The α-carbons of the vinyl group shift upfield, while the β-carbons shift increasingly downfield as the metal–ligand bond weakens in the sequence Cl < Br < I. For the analogous cis-dichlorobis(phenyldiethylphosphine)platinum(II) complex,[27] as for other alkylphosphine complexes,[28] coordination induces an upfield shift in both the alkyl α-, and β-carbon resonances, while for cis-dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II), the phosphole α-carbons shift upfield and the β-carbons shift downfield upon coordination.[1] This anomalous downfield shift for the resonance of the β-carbons of the phosphole complexes has been attributed[1] to a (2p–3d) interaction between the phosphole ring butadiene moiety and phosphorous. This explanation has been extended to explain the small coordination chemical shifts for phosphines having unsaturated groups that may conjugate with phosphorus in similar ways.[29–31] Comparing the data in Table VIII with those previously reported[1] for the phosphole complexes shows that the chemical shifts on coordination for the phosphine carbons are lesser in magnitude than those observed for the phosphole carbons.

Five-Coordinate Complexes. One of the goals of the present research was to determine whether divinylphenylphosphine would also stabilize pentacoordinate platinum complexes, as found for 1-substituted 3,4-dimethylphospholes, and thus to gain further insight into the factors responsible for the stability of such species. Accordingly, solutions containing equimolar ratios of L and L₂PtX₂ in CDCl₃ were prepared and investigated by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ variable-temperature NMR spectroscopy and by conductance measurements.
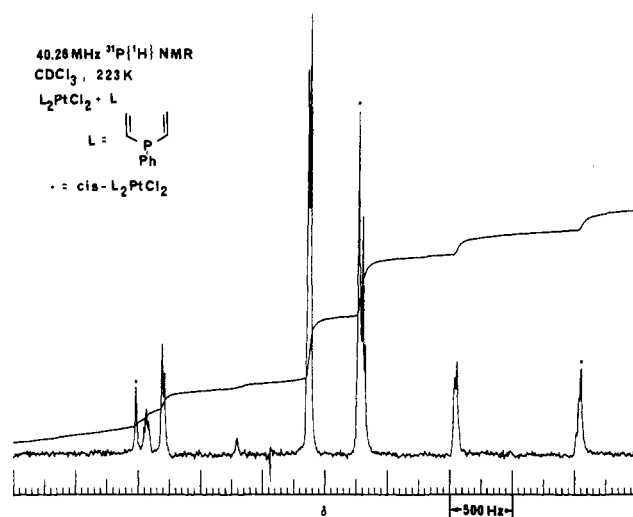

Figure 5. 40.26-MHz ^{31}P NMR spectrum of a solution containing an equimolar mixture of divinylphenylphosphine and cis-dichlorobis(divinylphenylphosphine)platinum(II) in CDCl₃ at −50 °C.

Table IX. $^{31}P\{^1H\}$ and ^{195}Pt NMR Data for the Dihalotris(divinylphenylphosphine)platinum(II) Complexes

X	T, K	$\delta(^{31}P)^a$	$^2J_{PP}{}^b$	$^1J_{PtP}{}^b$	$\delta(^{31}P)^a$	$^1J_{PtP}{}^b$	$\delta(^{195}Pt)^c$
Cl	203	5.51 d	19.6	2334	−5.58 t	3454	−4710
Br	223	−3.69 d	NO	2329	−11.40 t	3479	−4907
I	203	−2.48 d	19.8	2315	−8.47 t	3457	−5148

[a] Relative to 85% H₃PO₄, d = doublet, t = triplet, NO = not observed. [b] In hertz. [c] Data obtained at 50-kHz sweep width with 8K data points resulting in 12.2-Hz data point resolution.

Upon addition of ligand to a solution of L₂PtX₂, the solutions darken from pale yellow to orange or red and the resulting solutions show nonelectrolyte behavior in either CDCl₃ or CH₃NO₂. The ^{31}P NMR spectra are temperature-dependent. At 298 K they consist of broad unresolved resonances due to both intra- and intermolecular exchange.[1] When these solutions are cooled to 203 K, the ^{31}P NMR reveals the presence of two species, L₂PtX₂ and L₃PtX₂. No resonance due to free phosphine was observed.[32–35] The pentacoordinate species are characterized by A₂X ^{31}P NMR multiplets with associated platinum satellites (Figure 5). In the cases L₂PtX₂ (X = Cl, I), both platinum–phosphorus and phosphorus–phosphorus spin coupling was observed, but for L₂PtBr₂, limited solubility prevents lowering the temperature below 223 K and only platinum–phosphorus coupling was observed at this temperature.

The platinum-195 NMR spectra of these pentacoordinate complexes display first-order doublets of triplets. The chemical

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
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Table X. Equilibrium Constants for the Formation of L_3PtX_2

$$L_2PtX_2 + L \rightleftharpoons L_3PtX_2$$

L	X	K_{eq}
	Cl	2.13
	Br	2.18
	I	1.85
	Cl	1.61^a
	Br	0.28^a

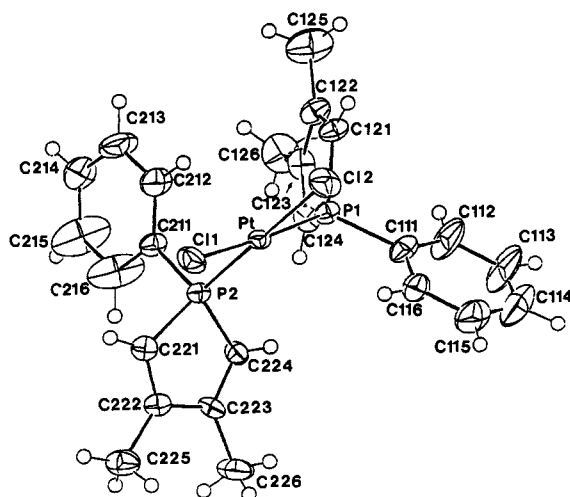^{a} MacDougall, J. J. Ph.D. Thesis, University of Nevada, Reno NV, 1979.

Figure 6. ORTEP plot of the structure of dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) (1) showing the atom-labeling scheme (50% probability ellipsoids).

shifts of the five-coordinate complexes occur upfield of those of the corresponding cis four-coordinate complexes, and the shieldings follow the same order as found for the L_2PtX_2 complexes: Cl < Br < I.

The one-bond platinum–phosphorus coupling constants for both phosphines are typical[1] and follow the same trends as those found for the L_2PtX_2 complexes. See Table IX for the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR data.

The equilibrium constants for the reactions $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ were calculated from the integrations of the respective resonances in the $^{31}P\{^1H\}$ NMR spectra at 223 K in $CDCl_3$ solutions prepared to contain a 1:1 mole ratio of L to L_2PtX_2 and are listed in Table X. Comparison of the present data with previous data suggests similar thermodynamic stabilities for the pentacoordinate complexes of divinylphenylphosphine and 1-phenyl-3,4-dimethylphosphole. It was noted that the amount of L_3PtX_2 increased at the expense of L_2PtX_2 with decreasing temperature. As with the phosphole complexes it is clear that the formation of L_3PtX_2 as expected is enthalpy-driven. The phosphole complexes appear to undergo stereochemical permutations at temperatures slightly higher than those found for the divinylphenylphosphine complexes and are consequently stereochemically more rigid. The thermodynamic stabilities of the phosphine complexes are on the other hand slightly greater than those of the phosphole complexes and in both cases largely determined by steric effects.

Crystal Structures of the Complexes. Figures 6 and 7 show perspective views of molecules 1 and 2, respectively. Although both 1 and 2 would be expected to have either a mirror plane or a C_2 axis relating the two phosphorus ligands, the X-ray data show that the "halves" of the molecule have significantly different dimensions. An examination of the data reported for other cis-bis(phosphine) complexes of platinum(II) and palladium(II) reveals similar anomalies (Table XI). In one study, cis-dichlorobis(methyldiphenylphosphine)platinum(II) was shown[36] to crys-
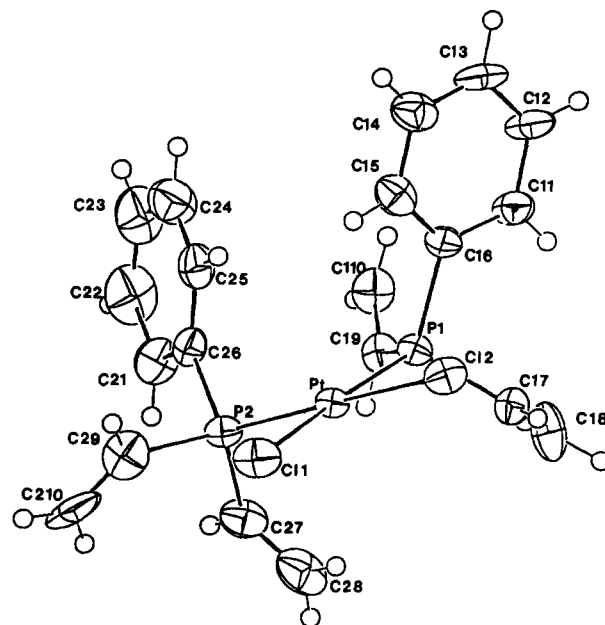

Figure 7. ORTEP plot of the structure of dichlorobis(divinylphenylphosphine)platinum(II) (2) showing the atom-labeling scheme (50% probability ellipsoids).

tallize in two allotropic forms, one symmetric and one asymmetric. The asymmetric case was explained as due to "minimization of interligand repulsion by asymmetric relaxation of the interligand metal–ligand bond angle".[36] However, the mean bond lengths and angles of the two allotropes are identical within experimental error. In the other cases, the differences between the halves are reasonably small and conclusions based upon mean bond lengths and angles are likely to be valid. Interestingly, in all *trans*-dichlorobis(phosphine)platinum(II) or -palladium(II) crystal structures found, the molecules lie on special positions in the unit cell and so both "halves" of the molecule are necessarily symmetry-related.[37-40] These observations remain to be explained. Neither 1 nor 2 shows any unusual intermolecular contacts.

A comparison of the data for 1 and 2 shows that the two complexes are structurally very similar. The coordination geometry of both metal atoms is square planar with very little tetrahedral distortion, as shown by the very small dihedral angles between the planes formed by Cl(1)–Pt–Cl(2) and P(1)–Pt–P(2): 2.14° for 1 and 1.93° for 2. Comparison with a sterically crowded complex, dichlorobis(phenyldibenzylphosphine)platinum(II), shows that although this complex is more tetrahedrally distorted, the Cl–Pt–Cl/P–Pt–P dihedral angle is 5.2°;[41] the two benzyl groups adopt a conformation very similar to that of the vinyl groups in the divinylphenylphosphine complex in order to minimize steric interactions. In contrast, the complex dichlorobis(1-phenyl-3,4-dimethylphosphole)palladium(II) has a Cl–Pd–Cl/P–Pd–P dihedral angle of 7.2°,[7] showing that palladium complexes exhibit tetrahedral distortions more readily than do platinum complexes.

The phosphole complex, 1 has a slightly smaller P–Pt–P bond angle and a shorter Pt–P bond length than the phosphine complex, 2, although both complexes have short Pt–P bond lengths in comparison to the other examples listed in Table XI.[42] The Pt–Cl bonds are also shorter in the phosphole complex, in contradiction to expectations based upon the trans influence.[19] The bond lengths

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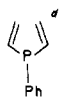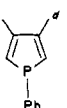
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Table XI. Comparison of Bond Lengths in *cis*-(phosphine)$_2$MCl$_2$ (M = Pt, Pd)

compd	M–P, Å		M–Cl, Å		ref
cis-(Ph$_3$P)$_2$PtCl$_2$	2.265 (2)	2.251 (2)	2.356 (2)	2.333 (2)	a
cis-(Me$_3$P)$_2$PtCl$_2$	2.256 (8)	2.239 (6)	2.388 (4)	2.364 (8)	40
cis-(Bz$_2$PPh)$_2$PtCl$_2$	2.246 (4)	2.246 (4)	2.355 (4)	2.3555 (4)	41
cis-(MePPh$_2$)$_2$PtCl$_2$	2.295 (16)	2.2480 (17)	2.350 (16)	2.3491 (18)	36
cis-(MePPh$_2$)$_2$PtCl$_2$	2.246 (1)	2.2446 (6)	2.3589 (9)	2.3447 (10)	36
cis-(Me$_2$PC$_6$F$_5$)$_2$PtCl$_2$	2.240 (1)	2.231 (1)	2.355 (1)	2.332 (1)	b
cis-(Me$_2$PPh)$_2$PtCl$_2$HgCl$_2$	2.256 (7)	2.253 (7)	2.356 (7)	2.253 (1)	c
cis-(C$_{20}$H$_{22}$P$_2$)$_2$PtCl$_2$	2.248 (1)	2.243 (2)	2.368 (2)	2.354 (1)	d
cis-(C$_{24}$H$_{26}$P$_2$)$_2$PtCl$_2$	2.239 (2)	2.227 (1)	2.360 (2)	2.336 (2)	d
cis-(DPPM)PdCl$_2$	2.250 (1)	2.234 (1)	2.362 (1)	2.352 (1)	e
cis-(DPPE)PdCl$_2$	2.233 (2)	2.226 (2)	2.361 (2)	2.357 (2)	e
cis-(DPPP)PdCl$_2$	2.249 (2)	2.244 (1)	2.358 (2)	2.351 (1)	e
cis-(P-*n*-Pr$_3$)$_2$PdCl$_2$	2.339 (2)	2.227 (2)	2.417 (2)	2.398 (2)	f
cis-(Me$_2$PPh)$_2$PdCl$_2$	2.260 (2)	2.260 (2)	2.362 (3)	2.362 (3)	g
cis-(C$_{24}$H$_{26}$P$_2$)$_2$PdCl$_2$	2.243 (3)	2.238 (2)	2.38 (2)	2.350 (3)	f

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Table XII. Selected IR (Hexane) and NMR (CDCl$_3$) Data for LMo(CO)$_5$

L	ν(CO), cm^{-1}	$K_1{}^a$	K_2	K_i	Δσ^b	Δπ^b	Δδ-(^{13}C$_{CO}$(cis))(J_{PC})	Δδ-(^{13}C$_{CO}$(trans))(J_{PC})^c
PPh$_3{}^c$		15.49	15.96	0.30	0.27	−0.15	4.89 (9)	9.44 (23)
AsPh$_3{}^c$		15.51	15.98	0.30	0.27	−0.13	4.52	9.49
(phosphine structure)^d	2070 A$_1{}^{(1)}$ 1992 B$_1$ 1954 A$_1{}^{(2)}$ 1954 E	15.44	16.02	0.30	0.16	0.02	4.41 (8.8)	8.88 (22)
(phosphole structure)^d	2072 A$_1{}^{(1)}$ 1991 B$_1$ 1954 A$_1{}^{(2)}$ 1954 E	15.62	16.01	0.29	0.35	−0.18	4.05 (8.8)	8.47 (19.1)
P(OEt)$_3{}^c$		15.82	16.01	0.31	0.55	−0.33	3.92 (13.1)	7.85 (39.9)
P(OPh)$_3{}^c$		15.93	16.19	0.29	0.48	−0.13	2.32 (13)	6.51 (46)

^{a}All force constants are in mdyn Å^{-1}. ^{b}Reference 5. ^{c}Reference 47. Δδ(^{13}C$_{CO}$) = δ(^{13}C$_{CO}$(Mo(CO)$_6$)) − δ(^{13}C$_{CO}$(LMo(CO)$_5$)). ^{d}This work.

can be rationalized in the following manner. If the phosphole has a similar σ-donor ability to the phosphine but is a better π-acceptor, then for it the Pt–P bonds will be shorter and stronger than for the phosphine complex. A chloride trans to a π-acceptor can π-donate to the platinum center and thereby shorten and strengthen its bond to platinum.[5,43] This type of bonding should be reflected in the magnitude of $^1J_{PtP}$ since one-bond coupling constants are primarily a function of s electron density.[44] Thus, $^1J_{PtP}$ for the phosphole complexes could be expected to be less than for the phosphine complexes, consistent with the experimental observations.

Molybdenum Complexes. Phosphine molybdenum pentacarbonyl complexes have frequently been used to evaluate the donor and acceptor properties of phosphines.[45] Several spectroscopic techniques have been used for these studies, including

^{13}C and ^{31}P NMR and infrared spectroscopy.[46–50] Evaluation of the carbonyl stretching force constants by the method of Cotton and Kraihanzel[4] allows one to calculate Graham σ- and π-parameters.[5] Although this method has several assumptions that have been criticized, it appears to be qualitatively correct for a series of similar ligands.[51,52]

Table XII compares the force constants and Graham parameters for the two complexes herein synthesized with those of a few representative ligands. These data lead to the conclusion that 1-phenyl-3,4-dimethylphosphole is both a better σ-donor and a better π-acceptor than divinylphenylphosphine toward molybdenum(0).

The coordination chemical shifts of the carbonyl carbons in the LMo(CO)$_5$ complexes (Table XI) suggest[47] this same trend although less clearly.

Supplementary Material Available: Listings of bond distances and angles, hydrogen coordinates, and thermal parameters for anisotropically refined atoms (8 pages). Ordering information is given on any current masthead page.

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