

°C. Clearly, other complexes with heterocyclic ring systems should be studied to further test this thesis.

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Registry No. Triiron dodecacarbonyl, 12088-65-2; 2-chloro-1,3,2-dioxaphosphorinane, 2428-06-0; [(μ-DMP)Fe(CO)₃]₂, 65150-25-6; 2,2,5,5-tetramethyl-1,3,2-dioxaphosphorinane iodide, 65150-05-2; 2,2,5,5-tetramethyl-2-iodo-1,3,2-dioxaphosphorinane, 65150-06-3; 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane, 873-99-4.

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Preparation and Properties of Hydroxo(methyl)-1,2-bis(diphenylphosphino)ethaneplatinum(II). A Trans-Influence Series Including σ Carbon Donor Ligands Based on Platinum-Phosphorus Coupling Constants

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The monomeric hydroxo(methyl)platinum(II) complex Pt(OH)(CH₃)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂PPh₂) is obtained from PtCl(CH₃)(dppe) by treatment of the derived labile cation [Pt(CH₃OH)(CH₃)(dppe)]⁺ with aqueous methanolic sodium hydroxide. It undergoes anation with a variety of acids, including fairly weak carbon acids such as acetone and acetonitrile, and provides a convenient route to unsymmetrical bis(alkyls) of platinum(II), e.g., Pt(CH₂COCH₃)(CH₃)(dppe) and Pt(CH₂CN)(CH₃)(dppe). The values of J_{PtP} trans to X or L derived from the ³¹P{¹H} NMR spectra of PtXR(dppe) (X = various anionic ligands and R = methyl or 1-cyclohexenyl), [Pt(CH₃)L(dppe)]⁺ (L = various neutral ligands), and sundry other neutral complexes of the type PtXY(dppe) permit the establishment of a trans-influence series which includes OH⁻ and a variety of σ carbon donors. The former has a trans influence comparable with those of typical sulfur donors and higher than those of NO₃⁻ and CH₃CO₂⁻. The generally high trans influence of σ carbon donors is lowered by the presence of conjugated electron-withdrawing groups on the ligating carbon atom. Tricyanomethide, C(CN)₃⁻, binds through nitrogen rather than carbon, and C-bonded triacetylmethyl, C(COCH₃)₃⁻, is only slightly higher than Cl⁻ in the trans-influence series, whereas the trans influence of CF₃⁻ is high and only slightly less than that of CH₃⁻. In contrast, Pt-Cl bond length and stretching frequency data indicate the trans influence of CF₃⁻ to be considerably lower than that of CH₃⁻. The discrepancy is thought to arise because the J_{PtP} values primarily reflect changes in hybridization, whereas the Pt-Cl bond parameters are also sensitive to electrostatic effects induced by the electronegative fluorine atoms.

Introduction

In recent years there has been considerable interest in NMR coupling constants in planar platinum(II) complexes, e.g., ¹J(¹⁹⁵Pt-¹H) in hydrides, ¹J(¹⁹⁵Pt-¹³C) in organo derivatives, and ¹J(¹⁹⁵Pt-³¹P) in tertiary phosphine complexes. These data have been compared¹ with those available from other spectroscopic techniques and from x-ray diffraction studies to develop the trans-influence series, which permits a relative estimate of the tendency of a ligand to weaken the bond trans to itself in the ground state of a complex.²

It is generally assumed that the magnitude of a coupling constant such as ¹J(¹⁹⁵Pt-³¹P) is dominated by the Fermi contact term and that it can be expressed by relation 1, where

$${}^1J_{\text{PtP}} \propto \gamma_{\text{Pt}}\gamma_{\text{P}}\alpha_{\text{Pt}}^2\alpha_{\text{P}}^2|\psi_{\text{Pt}(6s)}(0)|^2|\psi_{\text{P}(3s)}(0)|^2(\Delta E)^{-1} \quad (1)$$

γ_{Pt} and γ_{P} are the gyromagnetic ratios for the respective nuclei having spin $1/2$, α_{Pt}^2 and α_{P}^2 are the s characters of the bonding orbitals used by the respective atoms in the Pt-P bond, $|\psi_{\text{X}(ns)}(0)|^2$ is the electron density of the ns orbital at nucleus X (X = Pt, n = 6; X = P, n = 3), and ΔE is an average singlet-triplet excitation energy. For closely related complexes, variations in $\alpha_{\text{P}}^2|\psi_{\text{P}(3s)}(0)|^2$ are likely to be negligible compared with those in the corresponding term involving platinum, and it is further assumed that variations in α_{Pt}^2 are of most importance. This assumption is supported by a comparison of J_{PtP} for analogous planar platinum(II) and octahedral platinum(IV) complexes and by the observation³ that in complexes such as *cis*-PtCl(CH₃)(PEt₃)₂ J_{PtP} trans to CH₃ (1719 Hz) is very much less than J_{PtP} trans to Cl (4179 Hz). Since ΔE and $|\psi_{\text{Pt}(6s)}(0)|^2$ are common to both couplings, the large

difference in J_{PtP} is reasonably interpreted as indicating that α_{Pt^2} trans to CH₃ is lower than that trans to Cl; i.e., the Pt-P bond trans to CH₃ has less Pt 6s character than the Pt-P bond trans to Cl, a manifestation of the high trans influence of CH₃ relative to Cl. For a limited number of complexes of the type *cis*-PtX(CH₃)(PEt₃)₂, J_{PtP} trans to X varies over a much wider range than J_{PtP} trans to CH₃, so that J_{PtP} can be used to assess the trans influence of ligand X.³ There is a correlation between J_{PtP} and Pt-P bond length, at least for monodentate tertiary phosphine complexes;⁵ the exceptional behavior of bidentate 1,2-bis(diphenylphosphino)methane, Ph₂PCH₂PPh₂, has been noted.⁶ In practice, the tendency of PtX(CH₃)(PEt₃)₂ complexes to undergo spontaneous *cis* → *trans* isomerization severely limits the availability of J_{PtP} data, a difficulty which can obviously be overcome by the use of a bidentate di(tertiary phosphine) such as Ph₂PCH₂CH₂PPh₂(dppe). We have recently isolated a range of planar 1-cyclohexenylplatinum(II) complexes, PtX(C₆H₉)(dppe),^{7,8} by protonation of the cyclohexeneplatinum(0) complex Pt(C₆H₈)(dppe)^{8,9} or by anation of the derived hydroxoplatinum(II) complex Pt(OH)(C₆H₉)(dppe). We report here on the preparation and reactions of the methylhydroxoplatinum(II) complex Pt(OH)(CH₃)(dppe)¹⁰ and on the J_{PtP} values for a wide variety of methyl- and 1-cyclohexenylplatinum(II) complexes. These enable us to derive a trans-influence series which includes substituted carbon σ -donor ligands.

Experimental Section

General Data. IR spectra were measured on a PE-457 spectrometer calibrated with polystyrene. ¹H NMR spectra were obtained on Jeol MH-100 and Varian HA-100 instruments using (CH₃)₄Si as an internal reference. Direct ³¹P{¹H} NMR spectra were measured on a Jeol C60 CW spectrometer at 24.3 MHz, and INDOR spectra were recorded on a modified Varian HA-100 spectrometer as previously described.¹¹ Chemical shifts obtained by INDOR on the Pt-CH₃ resonances were converted into ppm from external 85% H₃PO₄ using the values obtained for Pt(CH₃)(NCO)(dppe), which was measured by both methods. Microanalyses and osmometric molecular weight measurements (Knauer, CHCl₃, 37 °C) were performed in the Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, The Australian National University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates).

Analytical data are in Table I. Pt-CH₃ ¹H and ³¹P NMR data for neutral and cationic methylplatinum(II) complexes are in Tables II and III, respectively, and ³¹P data for 1-cyclohexenyl complexes are in Table IV. Table V contains ³¹P NMR data for other complexes of the general type PtXY(dppe). All complexes showed broad multiplet dppe CH₂ resonances at δ 7.5–8.0. Other spectroscopic data are given below. IR band maxima are in cm⁻¹ and chemical shifts are on the δ scale. Abbreviations (IR): s, strong; vs, very strong; m, medium; sp, sharp; br, broad.

Many dppe complexes tenaciously retain small amounts of solvent of crystallization which cannot be removed even by prolonged evacuation (Table I). In such cases, solvent peaks of the appropriate intensity were generally observed in the ¹H NMR spectra of the complexes. The presence of foreign solvent (<0.5% v/v) will cause small errors in osmometry; hence, the values found for the molecular weights of solvated complexes in Table I must be considered as approximate. However, the values are generally close enough to those calculated for the solvent-free complexes to establish their molecularity. The ¹H NMR data in Table II were recorded on samples obtained by evaporation to dryness under reduced pressure of chloroform solutions, thus eliminating traces of solvents such as *n*-hexane, which have resonances in the Pt-CH₃ region.

Preparations. (1) Neutral Methylplatinum(II) Complexes, PtX(CH₃)(dppe) (X = Various Anionic Ligands). (i) X = Cl. This was prepared by the reaction of dppe with PtCl(CH₃)(COD) as previously described.^{11–13}

(ii) X = I. A solution of PtCl(CH₃)(dppe) (0.06 g, 0.13 mmol) in 100 mL of refluxing acetone was treated with sodium iodide (0.068 g, ca. fourfold excess) dissolved in 10 mL of acetone. The solution, which immediately turned cloudy as sodium chloride precipitated,

was heated under reflux for 30 min and allowed to cool to room temperature. After removal of acetone under reduced pressure, the residue was extracted with dichloromethane (10 mL). The filtered solution was concentrated under reduced pressure, and the colorless product was precipitated by dropwise addition of *n*-hexane, filtered off, washed with *n*-pentane, and dried in vacuo for 24 h; yield of PtI(CH₃)(dppe) 0.045 g (66%).

(iii) X = NO₂. A stirred solution of PtCl(CH₃)(dppe) (0.254 g, 0.394 mmol) in 100 mL of acetone was treated with a solution of silver perchlorate (0.084 g, 0.406 mmol) in 10 mL of acetone. Silver chloride precipitated immediately and was filtered off. To the filtrate, which contained [Pt(CH₃)(acetone)(dppe)]ClO₄, was added a large excess (ca. 0.1 g) of solid sodium nitrite. The mixture was heated briefly and allowed to stand at room temperature for 1 h. Acetone was removed under pressure, and the residue was extracted with dichloromethane (10 mL). This solution was evaporated to dryness under reduced pressure, and the residual white solid was recrystallized from dichloromethane/*n*-hexane and dried in vacuo for 24 h: yield of Pt(NO₂)(CH₃)(dppe) 0.15 g (61%); IR (Nujol) 1363 s, 1331 s [ν (NO₂)].

(iv) X = NCO. This was prepared in 62% yield as above, using sodium cyanate: IR (Nujol) 2215 vs [ν (CN)].

(v) X = SCN/NCS. This was prepared in 66% yield as above, using sodium thiocyanate. It was not necessary to heat the reaction mixture owing to the solubility of sodium thiocyanate in acetone. The product is a mixture of N- and S-linkage isomers with the latter predominating (see text): IR (CH₂Cl₂) 2212 s, sp, 2108 s, br [ν (CN)].

(vi) X = OCOCH₃. To a solution of [Pt(CH₃)(acetone)(dppe)]BF₄ prepared from PtCl(CH₃)(dppe) (0.216 g, 0.32 mmol) and AgBF₄ in acetone (80 mL) was added a large excess (ca. 0.5 g) of solid sodium acetate trihydrate. After heating of the mixture under reflux for 4 h, the acetone was removed under reduced pressure, and the residue was extracted with dichloromethane (10 mL). The solution was passed down a short Florisil column and evaporated to dryness under reduced pressure. The resulting solid was recrystallized from chloroform/*n*-hexane and dried for 24 h in vacuo: yield of Pt(OCOCH₃)(CH₃)(dppe) 0.087 g (37%); IR (Nujol) 1619 s, br [ν (C=O)], 1315 s [ν (C-O)]; NMR (CDCl₃) δ 1.93 (s, C-CH₃).

(vii) X = NCC(CN)₂. To a solution of [Pt(CH₃)(acetone)(dppe)]BF₄ prepared from PtCl(CH₃)(dppe) (0.20 g, 0.31 mmol) and AgBF₄ in acetone (80 mL) was added an excess (ca. 0.1 g) of solid potassium tricyanomethide.¹⁴ The suspension was stirred for 2 h at room temperature and worked up as under (vi). Recrystallization from dichloromethane/*n*-hexane gave 0.16 g (75%) of pale yellow Pt[NCC(CN)₂](CH₃)(dppe): IR (Nujol) 2215 w [ν (CN) coord], 2175 s, br [ν (CN) uncoord].

(viii) X = CN. To a solution of PtCl(CH₃)(dppe) (0.241 g, 0.374 mmol) in ca. 100 mL of acetone was added 0.42 g (ca. eightfold excess) of freshly prepared silver cyanide. The mixture, shielded from light, was heated under reflux for 2 h and filtered while hot. Workup as under (vi) using chloroform instead of dichloromethane gave colorless, crystalline Pt(CN)(CH₃)(dppe)·CHCl₃ (0.167 g, 59%): IR (Nujol) 2135 s, sp [ν (CN)].

(ix) X = OH. To a solution of PtCl(CH₃)(dppe) (1.084 g, 1.68 mmol) in ca. 100 mL of warm acetone was added AgBF₄ (0.347 g, 1.78 mmol). After being stirred for 30 min at room temperature, the solution was evaporated under reduced pressure to give a colorless oil. It is important not to heat at this stage, otherwise a colorless, crystalline, methanol-insoluble solid of unknown composition is formed, and the yield of hydroxo complex is greatly reduced. The oil was dissolved in ca. 30 mL of methanol, and the solution was evaporated under reduced pressure at ca. 35 °C several times to remove the last traces of acetone. The resulting oil was dissolved in methanol (10 mL) and treated with a solution of sodium hydroxide (0.093 g, 2.3 mmol) in methanol (10 mL). After filtration to remove traces of silver compounds, methanol was removed at 30–35 °C (10⁻³ mm) (again, it is important not to overheat at this stage). The residue was extracted with dichloromethane (20 mL), and the solution was evaporated to give a colorless oil. This was washed with *n*-pentane and dissolved in the minimum volume of dichloromethane. Addition of benzene and concentration of the solution yielded colorless microcrystals of Pt(OH)(CH₃)(dppe)·C₆H₆, which were filtered off, washed with benzene, and air-dried: yield 0.71 g (60%); IR (CH₂Cl₂) 3655, 3602 m ν (OH). No bands assignable to ν (OH) or ν (PtO) were observed in the Nujol mull spectrum.

Table I. Analytical and Melting Point Data for New Complexes^a

Complex	Mp, °C	Calcd					Mol wt	Found					Mol wt
		% C	% H	% P	% other	% C		% H	% P	% other			
PtI(CH ₃)(dppe)	250 eff	44.1	3.7	8.4	17.3 (I)		44.3	3.7	8.2	17.4 (I)			
Pt(NCO)(CH ₃)(dppe)	190–211 dec	51.7	4.2	9.5	2.2 (N)	651	51.5	4.4	9.3	2.5 (N)	709		
Pt(SCN)(CH ₃)(dppe)·0.2CH ₂ Cl ₂ ^b	224	49.5	4.1	9.1	2.1 (Cl)		50.0	4.3	9.3	2.2 (Cl)			
Pt(NO ₂)(CH ₃)(dppe)	232 dec	49.5	4.2	9.5	2.1 (N)		49.2	4.3	9.2	2.0 (N)			
Pt(CN)(CH ₃)(dppe)·CHCl ₃ ^c	233 dec	46.2	3.7	8.2	14.1 (Cl)	634	46.3	3.8	8.2	12.1 (Cl)	760		
Pt(O ₂ CCH ₃)(CH ₃)(dppe)	75 eff	53.1	4.8	8.7			53.3	4.9	9.0				
Pt(OC ₂ H ₄ OCH ₃ -p)(CH ₃)(dppe)·0.1CH ₂ Cl ₂	192–195 eff	55.3	4.7	8.4	1.0 (Cl)		55.3	4.3	8.1	0.7 (Cl)			
Pt(OH)(CH ₃)(dppe)·C ₆ H ₆	160 dec	56.3	4.9	8.8			56.5	5.0	8.5				
Pt(SH)(CH ₃)(dppe)·0.7CHCl ₃	210 eff	46.0	4.0	8.6	4.4 (S)	630	45.6	4.4	7.8	3.8 (S)	721		
Pt(SC ₂ H ₅)(CH ₃)(dppe)·0.1CHCl ₃ ^d	222–227 eff	54.5	4.4	8.5	1.5 (Cl)	717	54.6	4.8	8.1	2.0 (Cl)	713		
Pt(NHCOCH ₃)(CH ₃)(dppe) ^e	175–182 dec	53.0	4.5	9.2	2.1 (N)	676	51.4	4.6	8.9	2.0 (N)	683		
Pt[NCC(CN) ₂](CH ₃)(dppe)	169–173 dec	53.3	3.9	8.9	6.0 (N)	699	53.2	3.9	8.7	6.0 (N)	768		
Pt(CNO)(CH ₃)(dppe)	265 dec	51.7	4.2	9.5	2.1 (N)		52.0	4.1	9.5	3.1 (N)			
Pt(CH ₂ COCH ₃)(CH ₃)(dppe)·0.5CHCl ₃	178 eff	49.8	4.9	8.8			49.9	4.5	8.4				
Pt(CH ₂ NO ₂)(CH ₃)(dppe)·0.1CHCl ₃ ^f	181–188 eff	49.6	4.3	9.1	1.6 (Cl)	668	49.4	4.4	8.6	2.0 (Cl)	695		
Pt(CH ₂ CN)(CH ₃)(dppe)	204–211	53.7	4.5	9.6	2.2 (N)	649	53.3	4.7	9.3	1.9 (N)	645		
Pt[CH(COCH ₃) ₂](CH ₃)(dppe)	170–188 eff	54.3	4.8	8.8			54.4	4.8	8.7				
Pt[CH(CN)] ₂ (CH ₃)(dppe)	200 dec	53.5	4.2	9.2	4.2 (N)		53.7	4.4	9.1	4.6 (N)			
	(darkens >160)												
Pt[C(COCH ₃) ₃](CH ₃)(dppe)	60 eff	54.5	4.8	8.3		750	54.7	5.0	7.9		749		
Pt(C ₂ C ₆ H ₅)(CH ₃)(dppe)·0.25CH ₂ Cl ₂	170–175 dec	57.9	4.5	8.5		709	57.6	4.6	8.4		706		
Pt(C ₂ H ₅)(CH ₃)(dppe)·0.3CHCl ₃	125 dec	54.4	4.6	8.7		673	54.6	4.9	9.0		735		
Pt(NCO)(C ₆ H ₅)(dppe) ^g	<i>h</i>	55.3	4.6	8.6	2.0 (N)		54.6	4.8	8.3	2.2 (N)			
Pt(SH)(C ₆ H ₅)(dppe)	114 dec	54.3	4.8	8.8	4.5 (S)		55.0	5.0	8.8	3.3 (S)			
Pt(CNO)(C ₆ H ₅)(dppe)	210 dec	55.3	4.7	8.6	2.0 (N)	717	55.3	4.8	8.7	2.2 (N)	761		
Pt[CH(COCH ₃) ₂](C ₆ H ₅)(dppe)·0.2CHCl ₃	130 dec	56.0	5.1	7.8	2.7 (Cl)	773	55.8	5.0	8.2	2.0 (Cl)	795		
Pt[CH(CN)] ₂ (C ₆ H ₅)(dppe) ^h	115 dec	56.8	4.6	8.4	3.8 (N)		55.0	4.6	7.8	4.5 (N)			
[Pt(CH ₃)(CH ₂ CN)(dppe)]BF ₄	148–152 dec	47.3	4.1	8.4	1.9 (N)		47.3	4.3	8.1	1.7 (N)			
[Pt(CH ₃)(C ₂ H ₅ N)(dppe)]BF ₄	105 eff	49.6	4.2	8.0	1.8 (N)		50.1	4.6	7.1	1.8 (N)			
[Pt(CH ₃)(PPh ₃)(dppe)]BF ₄ ·0.2CH ₂ Cl ₂	236–237 dec	55.6	4.4	9.5	1.5 (Cl)		55.9	4.4	9.5	1.0 (Cl)			
[Pt(CH ₃)(P(OPh) ₃)(dppe)]BF ₄	185	53.7	4.2	9.2			53.4	4.4	9.3				
[Pt(CH ₃)(AsPh ₃)(dppe)]BF ₄	214 eff	54.0	4.2	6.2			53.8	4.2	6.1				
[Pt(CH ₃)(SbPh ₃)(dppe)]BF ₄	192–194 eff	51.6	4.0	5.9			51.6	4.2	5.8				
[Pt(CH ₃)(CO)(dppe)]BF ₄	95 dec	46.5	3.8	8.6			45.7	4.0	8.5				
[Pt(CH ₃)(H ₂ O)(dppe)]BF ₄ ·0.5C ₆ H ₁₄	130 eff	47.6	4.8	8.2			48.0	4.5	8.4				
PtI(C ₂ H ₅)(COD)	73 dec	26.0	3.7		27.6 (I)	459	26.3	3.9		27.7 (I)	464		
PtI(C ₂ H ₅)(dppe)	100 dec	47.65	4.1	7.8	15.9 (I)	749	48.0	4.2	7.7	15.8 (I)	802		
PtCl(C ₂ H ₅)(dppe)	180 eff	51.1	4.4	9.4	5.4 (I)	658	50.9	4.6	9.0	5.9 (I)	694		
	(darkens >140)												
PtCl(CH ₂ C ₆ H ₅)(dppe)	211–213	55.0	4.3	8.6		720	54.9	4.7	7.8		738		
PtCl(C ₆ H ₅)(dppe)	214–220 dec	54.4	4.1	8.8	4.8 (Cl)	706	56.3	4.5	8.1	4.8 (Cl)	714		
Pt(C ₆ H ₅) ₂ (dppe)	207–212 dec	61.0	4.6	8.3			61.3	4.9	8.0				
Pt(CF ₃) ₂ (dppe)	295 dec	46.0	3.3	8.5	15.6 (F)		46.2	3.6	8.5	15.1 (F)			

^a Abbreviations: dec, decomposes; eff, decomposes with effervescence. ^b % N: calcd, 2.1; found, 2.0. % S: calcd, 4.7; found, 4.0. ^c % N: calcd, 1.9; found, 1.7. ^d % S: calcd, 4.4; found, 3.8. ^e % Cl: calcd, 0.0; found, 0.4. ^f % N: calcd, 2.1; found, 1.9. ^g % Cl: calcd, 0.0; found, 0.7. ^h Not measured.

A general procedure (with minor variations in particular cases) was followed in the preparation of a range of complexes PtX-(CH₃)(dppe) from Pt(OH)(CH₃)(dppe) and acids. The hydroxo compound (ca. 0.15–0.2 mmol) in dichloromethane (5–10 mL) was treated with a slight excess of the acid, and the mixture was set aside for 12 h at room temperature. Solvent was removed under reduced pressure, and the residue was recrystallized from dichloromethane/*n*-hexane or chloroform/*n*-hexane. The yields of recrystallized products were generally 60–80%.

The following compounds of general formula PtX(CH₃)(dppe) were prepared in this way (recrystallization solvent is given first).

(x) X = OC₆H₄OCH₃-p: CH₂Cl₂/*n*-hexane; NMR (CDCl₃) δ 3.63 (s, OCH₃), 6.51, 6.72 (apparent AB, OC₆H₄, *J* = 9 Hz).

(xi) X = SH: CHCl₃/*n*-hexane; IR (Nujol) 2550, 2540 w (CH₂Cl₂) 2545 m [ν(SH)]; NMR (CDCl₃) δ -0.14 (1.4:1 t, SH, ²J_{PtH} = 59.0 Hz).

(xii) X = SPh: CHCl₃/*n*-hexane.

(xiii) X = NHCOCH₃: CHCl₃/*n*-hexane after removal of excess acetamide at 90 °C (1 mm); IR (Nujol) 3375 vw [ν(NH)], 1628, 1603 s, br [ν(C=O)]; NMR (CDCl₃) δ 1.86 (s, C-CH₃), 5.37 (br, s, NH).

(xiv) X = CH₂COCH₃: CHCl₃/*n*-hexane; 10 mL of acetone used as reaction solvent; IR (Nujol) 1630 s [ν(C=O)]; NMR (CDCl₃) δ 2.62 (dd with ¹⁹⁵Pt satellites, ²J_{PtH} = 100, ³J_{PtH} = 12.0, 9.0 Hz),

1.62 (s with ¹⁹⁵Pt satellites, C-CH₃, ⁴J_{PtH} = 12 Hz).

(xv) X = CH₂NO₂: CHCl₃/*n*-hexane; 1 mL of nitromethane and 4 mL of toluene used as reaction solvent; IR (Nujol and HCBDD) 1495, 1351 s [ν(NO₂)]; NMR (CDCl₃) δ 5.17 (dd with ¹⁹⁵Pt satellites, ²J_{PtH} = 94, ³J_{PtH} = 5.8, 9.8 Hz).

(xvi) X = CH₂CN: CH₂Cl₂/*n*-hexane; 10 mL of acetonitrile used as reaction solvent, heated under reflux for 2 h, and then worked up; IR (Nujol) 2195 m, sp [ν(CN)]; NMR (CDCl₃) δ 1.67 (t with ¹⁹⁵Pt satellites, ²J_{PtH} = 91.5, ³J_{PtH} = 8.4, 8.4 Hz).

(xvii) X = CH(COCH₃)₂: CH₂Cl₂/*n*-hexane; IR (Nujol) 1642, 1627 s, br [ν(C=O)]; NMR (CDCl₃) δ 5.10 (t with ¹⁹⁵Pt satellites, ²J_{PtH} = 100, ³J_{PtH} = 11.0, 11.0 Hz), 1.87 (s with ¹⁹⁵Pt satellites, C-CH₃, ⁴J_{PtH} = 7.5 Hz).

(xviii) X = CH(CN)₂: Crystallized from CH₂Cl₂ reaction solvent; IR (Nujol) 2225 m [ν(CN)]; insufficiently soluble in CHCl₃ or CH₂Cl₂ for ¹H NMR measurements.

(xix) X = C(COCH₃)₃: CH₂Cl₂/*n*-hexane; IR (Nujol) 1602 s, br; NMR (CDCl₃) δ 2.29 (s with ¹⁹⁵Pt satellites, C-CH₃, ⁴J_{PtH} = 5 Hz).

(xx) X = C₂Ph: CH₂Cl₂/*n*-hexane; IR (Nujol) 2110 m [ν(C≡C)].

(xxi) X = C₅H₅: CHCl₃/*n*-hexane after treatment with activated charcoal; NMR (CDCl₃) δ 6.08 (dd with ¹⁹⁵Pt satellites, C₅H₅, ²J_{PtH} = 34.5, ³J_{PtH} = 1.3, 3.8 Hz).

(2) Neutral 1-Cyclohexenylplatinum(II) Complexes, PtX-(C₆H₉)(dppe) (X = Various Anionic Ligands). These were prepared

as described above, starting from Pt(OH)(C₆H₅)(dppe)^{7,8} dissolved in dichloromethane, benzene, or methanol and the appropriate acid or salt thereof. In the following, the reactant, solvent, and recrystallizing medium are given first. Yields were 50–80%.

(i) X = NCO: NaNCO; CH₃OH; CH₂Cl₂/*n*-hexane; IR (Nujol) 2225 vs [ν(CN)].

(ii) X = SH: H₂S; C₆H₆; precipitated from reaction mixture by addition of *n*-heptane; IR (Nujol or CH₂Cl₂) 2545 w [ν(SH)].

(iii) X = CH₂COCH₃: CH₃COCH₃; C₆H₆/C₂H₅OH; identical with the product obtained from Pt(C₆H₅)(dppe) and aqueous acetone.^{7,8}

(iv) X = CH₂NO₂: 10 mL of benzene, 0.5 mL of nitromethane; C₆H₆/*n*-heptane; identical with the product obtained from Pt(C₆H₅)(dppe) and nitromethane in toluene.^{7,8}

(v) X = CH(COCH₃)₂: 5 mL of dichloromethane, 1 mL of acetylacetone; CHCl₃/*n*-hexane; IR (Nujol) 1625 s [ν(C=O)]; NMR (CDCl₃) δ 5.4 (m, =CH of acac and C₆H₅), 1.84 (s, C-CH₃, overlaps with C₆H₅ methylene resonances).

(vi) X = CH(CN)₂: CH₂Cl₂, malononitrile; CH₂Cl₂/*n*-hexane; the product appeared to be contaminated with malononitrile even after passage down a short Florisil column. IR (Nujol) 2220 m [ν(CN)].

(3) Fulminate Complexes, Pt(CNO)R(dppe). (i) R = CH₃. A solution of Pt(OH)(CH₃)(dppe) (0.152 g, 0.24 mmol) in nitromethane (5 mL) was set aside for 12 h and then evaporated to dryness by warming under reduced pressure. The IR spectrum of the crude product showed peaks due to coordinated fulminate as well as to Pt(CH₂NO₂)(CH₃)(dppe). There was no change on heating in acetone for 2 h, but after heating in nitromethane for 2 h the σ -nitromethyl compound disappeared. The solid remaining after removal of nitromethane was recrystallized from dichloromethane/*n*-hexane to give Pt(CNO)(CH₃)(dppe) in ca. 50% yield: IR (Nujol) 2135 m, sp [ν(CN)]. The compound was insufficiently soluble in CH₂Cl₂ or CHCl₃ for ¹H NMR measurement.

(ii) R = C₆H₅. A solution of Pt(OH)(C₆H₅)(dppe) (0.112 g, 0.16 mmol) in nitromethane (15 mL) was heated under reflux for 15 min and then set aside for 2 h. Nitromethane was removed under reduced pressure, and the residual solid, after being washed with *n*-pentane, was recrystallized from chloroform/*n*-hexane to give 0.075 g (66%) of pale yellow Pt(CNO)(C₆H₅)(dppe): IR (Nujol) 2140 m, sp [ν(CN)]; NMR (CDCl₃) δ 1.28, 2.61 (m, CH₂ of C₆H₅), 5.17 (d with ¹⁹⁵Pt satellites, =CH of C₆H₅, ³J_{PH} = 61, ⁴J_{PH} = 11 Hz).

(4) Cationic Methylplatinum(II) Complexes, [Pt(CH₃)L(dppe)]BF₄. (i) L = H₂O. To a solution of Pt(OH)(CH₃)(dppe) (0.107 g, 0.152 mmol) in dichloromethane (3 mL) was added with stirring 0.5 mL of 0.32 M aqueous tetrafluoroboric acid. Solvent was removed under reduced pressure to give a colorless oil. This was extracted with dichloromethane (5 mL), and the solution was filtered from the insoluble material. A drop of water was added, and the product was precipitated with *n*-hexane, filtered, and air-dried. Vacuum drying or addition of ether appeared to cause loss of water: yield of hexane solvate 0.036 g (31%); IR (Nujol) 3600–3300 w, br [ν(OH)], 1550 m, br [δ(H₂O)]; NMR (CD₂Cl₂) δ 0.60 (d with ¹⁹⁵Pt satellites, PtCH₃, ²J_{PH} = 50.5, ³J_{PH} = 7.5 Hz). Integration indicates that the H₂O protons are obscured beneath P-CH₂ signals at δ ca. 2.5.

(ii) L = CH₃CN. A solution of PtCl(CH₃)(dppe) (0.83 g, 1.29 mmol) in ca. 100 mL of acetonitrile was treated with a solution of AgBF₄ (0.28 g, 1.44 mmol) in 15 mL of acetonitrile. The mixture was stirred for 30 min, the precipitated silver chloride was filtered off, and the filtrate was evaporated under reduced pressure to give a colorless oil. This was dissolved in dichloromethane (5 mL), and the solution was passed down a short Florisil column. Evaporation and addition of ether gave colorless [Pt(CH₃)(NCCH₃)(dppe)]BF₄ (0.65 g, 67%), which was dried in vacuo for 24 h: IR (Nujol) 2300 w [ν(CN)]; NMR (CDCl₃) δ 2.21 (s, C-CH₃).

A solution of KOH (0.093 g, 1.65 mmol) in 3 mL of water was added to [Pt(CH₃)(NCCH₃)(dppe)]BF₄ (0.48 g, 0.65 mmol) in 10 mL of acetonitrile and set aside for 1 h. Removal of solvents, sublimation at 100 °C (1 mm) to remove any acetamide, and recrystallization of the residue from dichloromethane/*n*-hexane gave Pt(NHCOCH₃)(CH₃)(dppe) (0.371 g, 76%) identical with the compound obtained above (1, xiii).

(iii) L = CO. Carbon monoxide was bubbled into a solution of [Pt(CH₃)(acetone)(dppe)]BF₄ prepared from PtCl(CH₃)(dppe) (0.199 g, 0.309 mmol) and AgBF₄ (0.062 g, 0.318 mmol) in 75 mL of acetone. The solution was evaporated under reduced pressure at room temperature to give a colorless oil. Workup as under (ii) and recrystallization from dichloromethane/ether gave [Pt(CH₃)(CO)(dppe)]BF₄

(0.14 g, 63%); IR (Nujol) 2117 m, sp [ν(CO)].

(iv) L = PPh₃, AsPh₃, SbPh₃, P(OPh)₃, and C₅H₅N. These were prepared similarly by addition of the ligand to [Pt(CH₃)(acetone)(dppe)]BF₄ and were recrystallized from dichloromethane/ether or dichloromethane/*n*-hexane. Yields were generally 50–70%.

(5) Ethylplatinum(II) Complexes. (i) PtI(C₂H₅)(COD). A Grignard reagent (freshly prepared from magnesium turnings) (0.73 g, 30 mmol) and ethyl iodide (2.5 mL, 30.7 mmol) in 20 mL of ether (freshly distilled from LiAlH₄) was filtered through glass wool and added to a suspension of PtI₂(COD) (2.51 g, 4.8 mmol) in 20 mL of dry ether. The dark brown solution was stirred for 18 h, and then the excess of Grignard reagent was decomposed by addition of a saturated aqueous solution of ammonium chloride. The brown ether layer was separated, and the aqueous layer was extracted several times with ether. The combined ether extracts were washed with water, dried (Na₂SO₄), shaken with activated charcoal, filtered, and evaporated to dryness under reduced pressure. The resulting pale yellow solid was recrystallized from a large volume of *n*-pentane to give the pure product: dec pt 73 °C; 1.04 g, 48%; ¹H NMR (CDCl₃) δ 5.55 (br, s with ¹⁹⁵Pt satellites, =CH trans to C₂H₅, J_{PH} = 37 Hz), 4.57 (br, s with ¹⁹⁵Pt satellites, =CH trans to I, J_{PH} = 76 Hz), 2.28 (m, CH₂ of C₆H₅), 1.89 (q, PtCH₂CH₃), 1.16 (t with ¹⁹⁵Pt satellites, PtCH₂CH₃, ³J_{HH} = 7.5, ³J_{PH} = 32 Hz).

The analytical and ¹H NMR spectroscopic data show the compound to be PtI(C₂H₅)(COD) rather than Pt(C₂H₅)₂(COD), which is the reported¹⁵ product from this reaction.

(ii) PtI(C₂H₅)(dppe). A stirred solution of PtI(C₂H₅)(COD) (0.555 g, 1.21 mmol) in benzene (15 mL) was treated dropwise with a solution of dppe (0.482 g, 1.21 mmol) in benzene (20 mL). An initial precipitate dissolved to give a colorless solution. Addition of *n*-heptane gave a colorless crystalline solid which was filtered off, washed successively with *n*-heptane and *n*-pentane, and dried in vacuo for 24 h; yield of PtI(C₂H₅)(dppe)·0.7C₆H₆ 0.76 g (79%).

(iii) PtCl(C₂H₅)(dppe). An acetone solution of PtI(C₂H₅)(dppe)·0.7C₆H₆ (0.223 g, 0.30 mmol) was treated with AgBF₄ (0.068 g, 0.35 mmol). The precipitated silver iodide was filtered off, and the filtrate was treated with an excess of lithium chloride (ca. 0.1 g). Evaporation and recrystallization from dichloromethane/*n*-hexane gave PtCl(C₂H₅)(dppe) (0.164 g, 84%); IR (Nujol) 290 [ν(PtCl)].

(6) Benzylplatinum(II) Complexes, PtCl(CH₂Ph)(dppe). A sample of Pt(CH₂Ph)₂(COD) was prepared from PtI₂(COD) and benzylmagnesium bromide¹⁵ and was converted into PtCl(CH₂Ph)(COD) by the addition of an equimolar amount of hydrogen chloride in ether. However, analytical and ¹H NMR data revealed that both benzyl complexes contained PtI(CH₂Ph)(COD) as an impurity. Hence, addition of dppe to the impure PtCl(CH₂Ph)(COD) gave PtCl(CH₂Ph)(dppe) contaminated with PtI(CH₂Ph)(dppe).¹⁶ The impurity was removed by treatment with a small excess of AgBF₄ in acetone and addition of lithium chloride to the filtered solution as described in (5, iii). After the usual workup, the product was recrystallized from dichloromethane/*n*-hexane: IR (Nujol) 300 [ν(PtCl)]; ¹H NMR (CDCl₃) δ 2.78 (dd with ¹⁹⁵Pt satellites, PtCH₂, ³J_{PH} = 9.5, 4.5, ²J_{PH} = 78 Hz).

(7) Phenylplatinum(II) Complexes. (i) Pt(C₆H₅)₂(COD) and PtCl(C₆H₅)(COD). The former was prepared from PtCl₂(COD) and excess phenyllithium following literature procedures for related compounds.^{15,17} After recrystallization of the crude oily product from 60–80 °C petroleum ether, the yield of colorless Pt(C₆H₅)₂(COD) was 26%. ¹H NMR (CDCl₃) δ 2.67 (br, s with ¹⁹⁵Pt satellites, CH₂, J_{PH} = 16 Hz), 5.0 (br, s with ¹⁹⁵Pt satellites, =CH, J_{PH} = 40 Hz).

Treatment of Pt(C₆H₅)₂(COD) (1 mol) in methanol with acetyl chloride (1 mol) gave PtCl(C₆H₅)(COD).¹⁵

(ii) PtCl(C₆H₅)(dppe). A stirred solution of PtCl(C₆H₅)(COD) (0.54 g, 1.30 mmol) in benzene (25 mL) was treated dropwise with a solution of dppe (0.53 g, 1.33 mmol) in benzene (25 mL). The colorless product which precipitated immediately was washed with benzene and dried in vacuo (0.78 g, 85%).

(iii) Pt(C₆H₅)₂(dppe). This was prepared in 94% yield from Pt(C₆H₅)₂(COD) and dppe as described above.

(8) The Trifluoromethylplatinum(II) Complex, Pt(CF₃)₂(dppe). To a solution of Pt(CF₃)₂(COD) (0.099 g, 0.24 mmol) in 10 mL of benzene was added dropwise dppe (0.095 g, 0.24 mmol). Concentration under reduced pressure gave colorless crystals of the product, which were filtered off, washed with benzene, and dried in vacuo; yield 0.145 g (83%). The complex is only slightly soluble in benzene, chloroform, nitrobenzene, or acetone.

Table II. ^1H (PtCH_3) and ^{31}P NMR Data for Neutral Methylplatinum(II) Complexes, $\text{PtX}(\text{CH}_3)(\text{dppe})^a$

X	^1H NMR			^{31}P NMR			
	δ_{PtCH_3}	$^2J_{\text{PtCH}_3}$	$^3J_{\text{PPtCH}_3}$	$\delta_{\text{P}(1)}$ (trans to CH_3)	$\delta_{\text{P}(2)}$ (trans to X)	$J_{\text{PtP}(1)}$ (trans to CH_3)	$J_{\text{PtP}(2)}$ (trans to X)
ONO_2^b	0.48	48.5	2.0, 7.5	46.2	30.4	1820	4510 ^c
Cl^d	0.51	53.5	3.5, 8.0	43.4 (39.0)	42.0 (38.1)	1737 (1765)	4224 (4236)
$\text{NCC}(\text{CN})_2^e$	0.53	55.3	3.0, 7.0	51.7	43.0	1748	4222
OCOCH_3	0.57	54.0	2.0, 8.0	46.9	34.0	1786	4122
$\text{C}(\text{COCH}_3)_3$	0.44	53.0	2.0, 7.5	47.3	34.5	1808	4124
I	1.29	59.0	4.0, 7.0	44.8	45.6	1726	4050
NCO^f	0.60	56.5	3.6, 7.8	43.1	39.5	1706 (1727)	<i>g</i> (4057)
$\text{OC}_6\text{H}_4\text{OCH}_3^p$	0.59	56.3	2.9, 7.9	42.3	34.4	1782	3840
SCN	0.54	56.5	4.0, 6.5	45.0	45.0	1791	3719
OH^h	0.43	60.5	3.0, 7.1	40.5	34.9	1804	3546
SPh	0.35	63.0	6.0, 6.0	45.1	45.1	1814	3380
NO_2	0.53	60.8	3.8, 6.9	45.9	33.1	1775	3345
NHCOCH_3	0.41	59.0	4.0, 7.3	45.9	43.0	1883	3322
SH	0.62	63.0	6.5, 6.5	46.2	45.6	1779	3201
$\text{CH}(\text{COCH}_3)_2$	0.54	60.0	5.5, 7.0	48.9	46.3	1770	2948
CN	0.83	64.0	6.8, 6.8	44.7	46.7	1633	2870
$\eta^1\text{-C}_5\text{H}_5$	0.12	62.0	5.3, 7.1	49.3	45.8	1852	2764
CH_2NO_2	0.56	61.3	5.5, 6.8	47.2	45.6	1785	2580
C_6Ph	0.90	66.0	7.0, 7.0	41.6	46.5	1624	2538
CH_2CN	0.67	65.0	6.0, 6.0	46.6	45.9	1770	2422
CH_2COCH_3	0.55	66.0	7.0, 7.0	48.0	48.0	1756	2346
CH_3^i	1.08	71.0	<i>j</i>	45.4		1794	

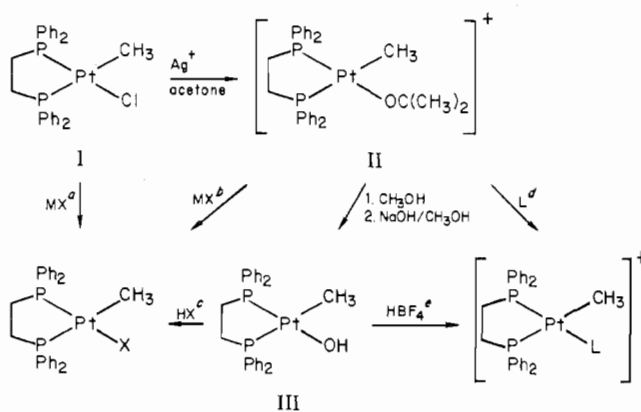
^a ^1H NMR spectra run at 34 °C in CDCl_3 , unless stated otherwise. Chemical shifts δ in ppm downfield of internal Me_4Si (± 0.01 ppm); coupling constants J in Hz (± 0.5). ^{31}P NMR spectra run at 32 °C in CH_2Cl_2 or CD_2Cl_2 , unless stated otherwise. Chemical shifts δ_{P} in ppm downfield of external 85% H_3PO_4 (± 0.5 ppm); coupling constants J_{P} in Hz (± 20 , except as indicated). ^b ^1H NMR and ^{31}P NMR data (by INDOR) in CD_2Cl_2 from ref 11. ^c ± 40 Hz. ^d ^1H NMR data in CD_2Cl_2 ; ^e ^{31}P NMR data in parentheses obtained by INDOR in $\text{C}_6\text{D}_5\text{NO}_2$. ^f ^{31}P NMR data in $(\text{CH}_3)_2\text{CO}$. ^g Data in parentheses obtained by INDOR. ^h Satellites not observed owing to broadening of central peak (see text). ⁱ ^1H NMR data in CD_2Cl_2 . ^j $^1\text{H}^{13}$ and ^{31}P NMR data in C_6D_6 . ^k Cannot be determined (see ref 13).

Results

Chemistry and ^1H NMR Spectra. A range of neutral and cationic methylplatinum(II) complexes of dppe can be prepared from $\text{PtCl}(\text{CH}_3)(\text{dppe})$, I, as shown in Scheme I. The preparation of the labile cation $[\text{Pt}(\text{CH}_3)(\text{acetone})(\text{dppe})]^+$, II, follows the procedure used to generate synthetically useful cationic methylplatinum(II) complexes containing monodentate tertiary phosphines and arsines.¹⁸ In order to prepare the hydroxo complex $\text{Pt}(\text{OH})(\text{CH}_3)(\text{dppe})$, III, it is first necessary to displace the acetone in II by methanol and then to react the resulting methanol complex with NaOH. If this is not done, the product is the acetonil complex $\text{Pt}(\text{CH}_2\text{COCH}_3)(\text{CH}_3)(\text{dppe})$, identical with that obtained from III and acetone (see below). Treatment of I with AgBF_4 in acetonitrile affords the cationic acetonitrile complex $[\text{Pt}(\text{CH}_3)(\text{NCCCH}_3)(\text{dppe})]\text{BF}_4$, which on reaction with aqueous KOH gives the amido-*N* complex $\text{Pt}(\text{NHCOCH}_3)(\text{CH}_3)(\text{dppe})$. Attempts to generate $[\text{Pt}(\text{CH}_3)(\text{CH}_3\text{OH})(\text{dppe})]^+$ directly from I and AgBF_4 in methanol are hindered by the sparing solubility of I in that solvent.

III resembles the 1-cyclohexenyl complex $\text{Pt}(\text{OH})(\text{C}_6\text{H}_9)(\text{dppe})$, IV, which has been made by the addition of water to the cyclohexyne complex $\text{Pt}(\text{C}_6\text{H}_8)(\text{dppe})$.^{8,9} Like IV, III reacts with weak organic acids, e.g., acetone, nitromethane, acetonitrile, acetylacetone, malonitrile, triacetylmethane, phenylacetylene, and cyclopentadiene, to give C-bonded platinum(II) complexes (Scheme I). Similar reactions occur with diethyl malonate and with acetaldehyde, but the complexes could not be purified; ethyl acetate was unreactive. III also reacts with *p*-methoxyphenol, hydrogen sulfide, and benzenethiol to give monomeric phenoxy, thiolato, and benzenethiolato complexes, respectively, with acetamide to give the amido-*N* complex mentioned above, and with tetrafluoroboric acid to give the cationic aquo species $[\text{Pt}(\text{CH}_3)(\text{H}_2\text{O})(\text{dppe})]\text{BF}_4$. III is readily soluble in dichloromethane but reacts with it over a 3-day period at room temperature to give I. A similar reaction occurs much more rapidly with chloroform. The fact that III can be isolated in

Scheme I. Preparation of Methylplatinum(II) dppe Complexes



^a $\text{MX} = \text{NaI}$ or AgCN . ^b $\text{MX} = \text{NaNO}_2$, NaNCO , NaNCS , NaO_2CCH_3 , or $\text{K}[\text{C}(\text{CN})_3]$. ^c $\text{HX} = p\text{-CH}_3\text{OC}_6\text{H}_4\text{OH}$, H_2S , CH_3CONH_2 , CH_3COCH_3 , CH_3CN , $\text{CH}_2(\text{COCH}_3)_2$, $\text{CH}_2(\text{CN})_2$, $\text{CH}(\text{COCH}_3)_3$, PhC_2H_5 , or C_5H_6 . ^d $\text{L} = \text{CH}_3\text{CN}$, $\text{C}_5\text{H}_5\text{N}$, CO , PPh_3 , AsPh_3 , SbPh_3 , or $\text{P}(\text{O}i\text{Pr})_3$. ^e $\text{L} = \text{H}_2\text{O}$.

a reasonably pure state is probably due to its insolubility in benzene, with which it forms a 1:1 solvate. In contrast, IV is soluble in benzene and is unaffected by refluxing dichloromethane. We have been unable to locate the hydroxyl resonance in the ^1H NMR spectrum of III, and the solid-state IR spectrum shows no discernible $\nu(\text{OH})$ bands. However, in dichloromethane there are two $\nu(\text{OH})$ bands at 3655 and 3602 cm^{-1} which are very similar to those observed in the IR spectrum of IV. Otsuka et al.¹⁹ have reported the preparation of *trans*- $\text{Pt}(\text{OH})\text{R}(\text{PPh}_3)_2$ ($\text{R} = \text{CH}_3$ or C_6H_5) and the reaction with acetophenone and nitromethane to give σ -phenacyl- and σ -nitromethylplatinum(II) complexes, respectively.

The neutral and cationic methylplatinum(II) dppe complexes generally exhibit a doublet of doublets in their ^1H NMR spectra due to $\text{Pt}-\text{CH}_3$; this pattern arises from three-bond coupling with the cis and trans phosphorus atoms and is

Table III. ¹H (PtCH₃) and ³¹P NMR Data for Cationic Methylplatinum(II) Complexes, [Pt(CH₃)L(dppe)]BF₄^a

L	¹ H NMR			³¹ P NMR			
	δ_{PtCH_3}	$^2J_{\text{PtCH}_3}$	$^3J_{\text{PPtCH}_3}$	$\delta_{\text{P}(1)}$ (trans to CH ₃)	$\delta_{\text{P}(2)}$ (trans to L)	$J_{\text{PtP}(1)}$ (trans to CH ₃)	$J_{\text{PtP}(2)}$ (trans to L)
CH ₃ CN ^b	0.54	52.9	3.0, 7.0	49.1	38.9	1809	4370
C ₅ H ₅ N	0.57	55.0	2.8, 7.3	50.5	37.3	1708	3738
SbPh ₃	0.79	<i>c</i>	5.7, 5.7	49.9	54.2	1802	3472
AsPh ₃	0.51	56.5	5.6, 5.6	49.8	51.6	1825	3300
CO ^d	1.01	61.0	6.0, 6.0	52.4	49.1	1606	3212
PPh ₃ ^e	0.42	58.5	7.0, 7.0, 7.0 ^f	49.6	53.2	1818	2743
P(OPh) ₃ ^g	0.48	58.8	6.5, 6.5, 6.5 ^f	51.6	52.5	1714	2718

^a Experimental conditions and units as given in Table II, footnote a. ^b ³¹P NMR data by INDOR. ^c Satellites broadened by interaction with Sb (see text). ^d $J_{\text{PP}} = 9$ Hz. ^e $\delta_{\text{P}(3)}(\text{PPh}_3) = 26.3$ ppm, $J_{\text{PtP}_3} = 2777$ Hz; $^2J_{\text{P}(1)\text{P}(2)} = 6$, $^2J_{\text{P}(2)\text{P}(3)} = 380$, $^2J_{\text{P}(1)\text{P}(3)} = 18$ Hz. ^f Near equality of the three values of $^3J_{\text{PPtCH}_3}$ causes the PtCH₃ signal to be a 1:3:3:1 quartet. ^g $\delta_{\text{P}(3)}[\text{P(OPh)}_3] = 105.8$ ppm, $J_{\text{PtP}(3)} = 4834$ Hz; $^2J_{\text{P}(1)\text{P}(2)} = 8$, $^2J_{\text{P}(2)\text{P}(3)} = 585$, $^2J_{\text{P}(1)\text{P}(3)} = 26$ Hz.

flanked by satellites arising from coupling (ca. 50 Hz) with ¹⁹⁵Pt ($I = 1/2$; 33.6% abundance) (Table II). The methylene resonances of the complexes Pt(CH₂COCH₃)(CH₃)(dppe), Pt(CH₂NO₂)(CH₃)(dppe), and Pt(CH₂CN)(CH₃)(dppe) also show ¹⁹⁵Pt satellites, and the magnitude of J_{PtH} (ca. 100 Hz) indicates that the methylene carbon atoms in these complexes are attached to the metal.^{7,8,20,21} Similarly, the methine proton of Pt[CH(COCH₃)₂](CH₃)(dppe) exhibits a large Pt-H coupling, indicative of a γ -bonded acetylacetonate group,²² and this is confirmed by the appearance of $\nu(\text{C}=\text{O})$ bands above 1600 cm⁻¹ in the IR spectrum. Although the complexes obtained from reaction of III or IV with malononitrile are not sufficiently soluble for the ¹⁹⁵Pt satellites of their CH₂ resonances to be observed, the IR spectra show just one $\nu(\text{CN})$ band, indicative of C-bound dicyanomethyl groups, Pt-C-H(CN)₂, rather than N-bound monocyano ketenimino groups, Pt-N=C=CHCN.²³ In contrast, the IR spectrum of the complex Pt(C₄N₃)(CH₃)(dppe) obtained from [Pt(CH₃)(acetone)(dppe)]⁺ and potassium tricyanomethide shows two $\nu(\text{CN})$ bands due to coordinated and free CN groups. Hence, this complex contains the N-bound dicyano ketenimino group, Pt-N=C=C(CN)₂.²⁴

The σ -nitromethyl complexes Pt(CH₂NO₂)R(dppe) (R = CH₃, C₆H₅) are unchanged on heating in toluene or acetone, but in refluxing nitromethane they lose water and form fulminato complexes Pt(CNO)R(dppe) which decompose without violence above 200 °C and which show a typical $\nu(\text{CN})$ band at 2140 cm⁻¹ in their IR spectra. This reaction provides support for the suggestion²⁵ that σ nitromethyls are intermediates in the formation of fulminato complexes, e.g., Pt(CNO)₂(PPh₃)₂ from Pt(PPh₃)₄ and nitromethane.

The Pt-CH₃ resonance pattern of the thiocyanate complex Pt(CNS)(CH₃)(dppe)²⁶ is the usual doublet of doublets with ¹⁹⁵Pt satellites, but a second doublet of doublets of ca. one-fifth the intensity superimposed on this indicates the presence of a second isomer in solution. This conclusion is confirmed by the IR spectrum of a dichloromethane solution, which shows a sharp band at 2112 cm⁻¹ overlapping a broader absorption at 2108 cm⁻¹. By analogy with published data on planar bis(thiocyanato) complexes,²⁷ we assign the higher frequency $\nu(\text{CN})$ absorption to the more abundant S-bonded isomer Pt(SCN)(CH₃)(dppe) and the lower frequency absorption to the N-bonded isomer Pt(NCS)(CH₃)(dppe). Although the ³¹P resonance of the minor isomer could not be located, the J_{PP} values for the phosphorus trans to thiocyanate in the major isomer are consistent with its assignment as an S-bonded thiocyanate complex (see below).

The pale yellow complex Pt(C₅H₅)(CH₃)(dppe) obtained from III and cyclopentadiene also exhibits the usual Pt-CH₃ resonance pattern in addition to a doublet of doublets C₅H₅ signal with ¹⁹⁵Pt satellites ($^3J_{\text{PtH}} = 1.3$, 3.8 , $^2J_{\text{PtH}} = 34$ Hz).

Thus, the phosphorus atoms are inequivalent, and the C₅H₅ protons are apparently equivalent on the NMR time scale. The first feature, which is confirmed by the ³¹P NMR spectrum, indicates that the complex has an η^1 -cyclopentadienyl structure rather than a half-sandwich structure containing an η^5 -cyclopentadienyl group since the latter would have equivalent phosphorus atoms. The ¹H NMR spectrum in CD₂Cl₂ is unchanged down to -50 °C; below this temperature crystallization occurs. The process which averages the C₅H₅ proton environments must be intramolecular since coupling to ³¹P and ¹⁹⁵Pt is maintained, and an η^5 intermediate can be ruled out since this would equivalence the phosphorus atoms. Probably the Pt-C bond is undergoing a series of 1,2 shifts, as occurs in Fe(η^5 -C₅H₅)(η^1 -C₅H₅)(CO)₂ and related compounds.²⁸ Other η^1 -cyclopentadienyls of platinum(II) have been described recently.^{29,30}

In the ¹H NMR spectrum of [Pt(CH₃)(SbPh₃)(dppe)]BF₄, the central part of the Pt-CH₃ resonance consists of a sharp triplet owing to the accidental equality of $^3J_{\text{HP(cis)}}$ and $^3J_{\text{HP(trans)}}$, but the ¹⁹⁵Pt satellites are very broad. ³¹P coupling in the satellites cannot be resolved, and $^2J_{\text{PtCH}_3}$ cannot be obtained. This behavior can be accounted for in terms of scalar coupling between ¹⁹⁵Pt and two quadrupolar antimony nuclei (¹²¹Sb, $I = 5/2$, 57% abundance; ¹²³Sb, $I = 7/2$, 43% abundance). If this interaction causes relaxation of ¹⁹⁵Pt at a rate comparable with that corresponding to the value of $|^2J_{\text{PtCH}_3}|$, the platinum nucleus will be partially decoupled from the methyl protons, thus causing partial collapse and broadening of the satellites. Unless the antimony nuclei are in a very symmetrical environment, e.g., SbF₆⁻, nuclear quadrupole relaxation is usually very fast and there is no significant interaction with other nuclei. Presumably in [Pt(CH₃)(SbPh₃)(dppe)]⁺ the field gradient at the antimony nucleus happens to be close to zero. Hence, the quadrupole relaxation rate is slow enough to allow interaction with ¹⁹⁵Pt. Similar effects involving ⁷⁵As ($I = 3/2$) have been observed in tertiary arsine complexes of platinum(II) and mercury(II),^{31,32} though they are not present in [Pt(CH₃)(AsPh₃)(dppe)]⁺.

³¹P NMR Spectra. The ³¹P{¹H} NMR spectra of all complexes of the general type PtXY(dppe) consist of two sharp central peaks at ca. 40 ppm downfield from external 85% H₃PO₄, each with ¹⁹⁵Pt satellites, though in a few cases the two central peaks are accidentally degenerate, and in some of the cationic complexes small additional splitting due to P-P coupling is observed. The spectrum of PtCl(CH₃)(dppe) has been described previously.¹³

Within the series PtX(CH₃)(dppe) and [Pt(CH₃)L(dppe)]⁺, one value of J_{PP} is always in the range 1606–1883 Hz while the other ranges from 2400 to 4500 Hz (Tables II and III). In Pt(CH₃)₂(dppe), J_{PtP} is 1794 Hz. Thus, the coupling in the range 1606–1883 Hz is assigned to J_{PP} trans to CH₃ and

Table IV. ^{31}P NMR Data for 1-Cyclohexenylplatinum(II) Complexes, $\text{PtX}(\text{C}_6\text{H}_9)(\text{dppe})^a$

X	$\delta_{\text{P}(1)}$ (trans to C_6H_9)	$\delta_{\text{P}(2)}$ (trans to X)	$J_{\text{PtP}(1)}$ (trans to C_6H_9)	$J_{\text{PtP}(2)}$ (trans to X)
Cl	39.0	38.4	1558	4418
NCO	37.9	35.0	1535	<i>b</i>
OH	35.4	30.4	1652	3401
$\text{CH}(\text{CN})_2$	43.9	41.3	1582	3104
CNO	39.6	42.4	1474	2820
CH_2NO_2	43.9	41.4	1570	2624
CH_2CN	41.4	41.4	1544	2484
CH_2COCH_3	41.7	41.7	1567	2460

^a In CH_2Cl_2 . Symbols and units as in Table II. ^b Satellites not observed owing to partial decoupling with ^{14}N .

Table V. ^{31}P NMR Data for Miscellaneous Complexes, $\text{PtXY}(\text{dppe})^a$

X	Y	$\delta_{\text{P}(1)}$ (trans to X)	$\delta_{\text{P}(2)}$ (trans to Y)	$J_{\text{PtP}(1)}$ (trans to X)	$J_{\text{PtP}(2)}$ (trans to Y)
Cl	Cl	41.4		3618	
$\text{CH}_2\text{C}_6\text{H}_5$	Cl	40.4	40.4	1714	4332
C_6H_5	Cl	39.5	37.0	1613	4165
C_2H_5	Cl	42.4	41.9	1561	4386
I	I	45.9		3388	
CF_3 ^b	CF_3 ^b	41.2		1984	
C_6H_5	C_6H_5	40.4		1690	

^a In CH_2Cl_2 unless indicated otherwise. Symbols and units as in Table II. ^b In $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$.

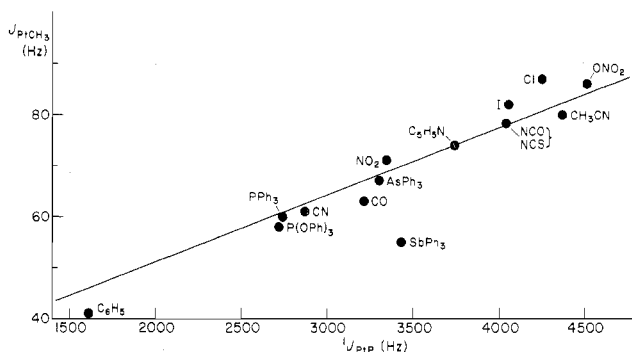


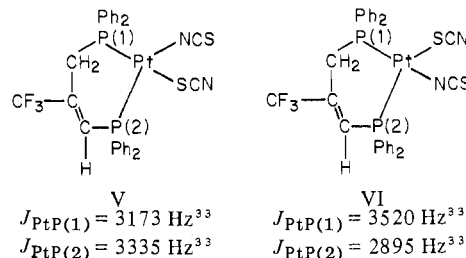
Figure 1. Plot of $^2J_{\text{PtCH}_3}$ in *trans*- $\text{PtX}(\text{CH}_3)(\text{PMe}_2\text{Ph})_2$ or *trans*- $[\text{Pt}(\text{CH}_3)\text{L}(\text{PMe}_2\text{Ph})_2]^+$ vs. $^1J_{\text{PtP}}$ in $\text{PtX}(\text{CH}_3)(\text{dppe})$ or $[\text{Pt}(\text{CH}_3)\text{L}(\text{dppe})]^+$. Values of $^2J_{\text{PtCH}_3}$ are from ref 1. The value of J_{PtP} for $\text{X} = \text{C}_6\text{H}_5$ refers to that trans to C_6H_5 in $\text{PtCl}(\text{C}_6\text{H}_5)(\text{dppe})$, and the value of J_{PtCH_3} for $\text{X} = \text{C}_6\text{H}_5$ actually refers to *m*- FC_6H_4 [G. W. Parshall, *J. Am. Chem. Soc.*, **88**, 704 (1966)]. The point for $\text{X} = \text{SbPh}_3$ has not been included in the least-squares fit because the $^2J_{\text{PtCH}_3}$ value of 55 Hz quoted in ref 1 for $[\text{Pt}(\text{CH}_3)(\text{SbPh}_3)(\text{PMe}_2\text{Ph})_2]^+$ is almost certainly too low. The ^{195}Pt satellites of the Pt- CH_3 resonances are broadened (i.e., partially collapsed toward the central peak) owing to interaction with the antimony quadrupoles ^{121}Sb and ^{123}Sb (T. G. Appleton, unpublished work).

the other coupling is J_{PtP} trans to X or L. Similarly, in the series $\text{PtX}(\text{C}_6\text{H}_9)(\text{dppe})$, J_{PtP} trans to C_6H_9 is in the range 1470–1660 Hz, whereas J_{PtP} trans to X again varies between 2400 and 4500 Hz (Table IV). There is no corresponding regularity in the variation of the ^{31}P chemical shifts. In the series $\text{PtClY}(\text{dppe})$ ($\text{Y} = \text{Cl}, \text{CH}_3, \text{C}_6\text{H}_5$) (Tables II, IV, and V), J_{PtP} trans to Cl varies over a somewhat greater range (3618–4418 Hz), although the relative variation (22%) is comparable with those in J_{PtP} trans to CH_3 (17%) and to C_6H_9 (12%). The variation in J_{PtP} trans to I in the complexes $\text{PtI}_2(\text{dppe})$ and $\text{PtI}(\text{CH}_3)(\text{dppe})$ is slightly more than in the corresponding chloro complexes.

In direct ^{31}P NMR spectra of $\text{Pt}(\text{NCO})\text{R}(\text{dppe})$ ($\text{R} = \text{CH}_3$ or C_6H_9) the signal for P trans to NCO is very broad and shows no satellites, whereas the signal for P trans to R in both cases is sharp and satellites are observed. This is probably due to partial decoupling of the trans ^{31}P nucleus from the ^{14}N nucleus ($I = 1$) whose relaxation rate (determined by the interaction of the ^{14}N quadrupole with the asymmetric electric field at the ^{14}N nucleus) must be comparable with $|J_{\text{PN}(trans)}|$. Since only the one ^{31}P signal is broad, $|J_{\text{PN}(trans)}| \gg |J_{\text{PN}(cis)}|$,

in agreement with recent findings.³³ No broadening is observed in the INDOOR spectrum of $\text{Pt}(\text{NCO})(\text{CH}_3)(\text{dppe})$, whence J_{PtP} for P trans to NCO is obtained.

Owing to identical chemical shifts for the two inequivalent ^{31}P nuclei, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Pt}(\text{CNS})(\text{CH}_3)(\text{dppe})$ shows only a single central peak together with two sets of satellites corresponding to $J_{\text{PtP}} = 1791$ (trans to CH_3) and 3719 Hz (trans to CNS). The second value is significantly smaller than that for J_{PtP} trans to NCO in $\text{Pt}(\text{NCO})(\text{CH}_3)(\text{dppe})$, 4057 Hz, whereas coupling constants to nuclei trans to N-bound cyanate and thiocyanate are usually very similar (e.g., $^2J_{\text{PtCH}_3}$, $^3J_{\text{PtCF}_3}$, $^{34}J_{\text{PtH}}$,³⁵ and $^1J_{\text{PtP}}$ ³⁶). Further, the value of 3719 Hz is significantly smaller than that observed for triethylphosphine trans to N-bonded thiocyanate in *cis*- $\text{Pt}(\text{NCS})(\text{CH}_3)(\text{PET}_3)_2$ (3994 Hz), whereas the values for J_{PP} trans to Cl in $\text{PtCl}(\text{CH}_3)(\text{dppe})$ and *cis*- $\text{PtCl}(\text{CH}_3)(\text{PET}_3)_2$ are very similar (4224 and 4179 Hz, respectively). These arguments suggest but do not unequivocally prove that the predominant isomer in $\text{Pt}(\text{CNS})(\text{CH}_3)(\text{dppe})$ is S bound, in agreement with the IR results (see above). It must be noted that, in the isomeric complexes V and VI studied by Carty,³³



J_{PtP} for P trans to SCN is ca. 300 Hz less than that for P trans to NCS, as expected, but the highest value observed, for $J_{\text{PtP}(1)}$ trans to NCS in VI, is only 3520 Hz, i.e., 200 Hz less than the value we observe in $\text{Pt}(\text{SCN})(\text{CH}_3)(\text{dppe})$. Unfortunately we could not observe ^{31}P resonances due to the minor isomer of $\text{Pt}(\text{CNS})(\text{CH}_3)(\text{dppe})$.

The spectra of $[\text{Pt}(\text{CH}_3)(\text{PPh}_3)(\text{dppe})]\text{BF}_4$ and $[\text{Pt}(\text{CH}_3)\{\text{P}(\text{OPh})_3\}(\text{dppe})]\text{BF}_4$ are complex, but because the cis couplings are small compared with the trans couplings, the spectra can be readily analyzed to give the values in Table III.

Our spectrum of $\text{Pt}(\text{CF}_3)_2(\text{dppe})$ (Table V) was of poor quality, owing to poor solubility and coupling to six ^{19}F nuclei. The central resonance was an ill-defined multiplet, and ^{195}Pt satellites were just discernible ($J_{\text{PtP}} = 1984$ Hz). Sparing

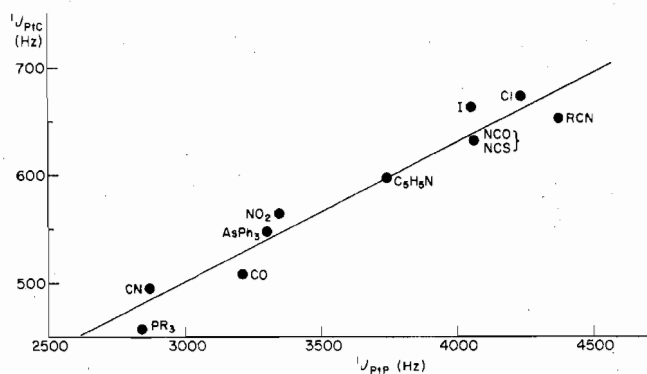


Figure 2. Plot of $^1J_{PtC}$ in *trans*-PtX(CH₃)(PMe₂Ph)₂ or *trans*-[PtL(CH₃)(PMe₂Ph)₂]⁺ vs. $^1J_{PtP}$ in PtX(CH₃)(dppe) or [Pt(CH₃)L(dppe)]⁺. Values of $^1J_{PtC}$ are from ref 32. The J_{PtP} value for Pt(CH₃)(NCS)(dppe) has been assumed to be equal to that for Pt(CH₃)(NCO)(dppe). The point for RCN refers to CH₃CN in the case of J_{PtP} and to *p*-CH₃OC₆H₄CN in the case of J_{PtC} . The point for PR₃ refers to PPh₃ in the case of J_{PtP} and to PMe₂Ph in the case of J_{PtC} .

solubility also resulted in a poor spectrum for Pt(C₆H₅)₂(dppe).

The Trans-Influence Series. As noted above, in the series PtX(CH₃)(dppe), [Pt(CH₃)L(dppe)]⁺, and PtX(C₆H₅)(dppe) the coupling constant J_{PtP} trans to X or L varies much more than that trans to CH₃ or C₆H₅. The same feature was noted by Allen and Pidcock³ in their study of a more limited range of J_{PtP} values in complexes of the type *cis*-PtX(CH₃)(PEt₃)₂ and has also been observed for other coupling constants, e.g., $^2J_{PtCH_3}$ in the platinum(IV) complexes PtX(CH₃)₃(bpy) and [Pt(CH₃)₃L(bpy)]⁺.³⁷ The similarity of J_{PtP} trans to CH₃ for both neutral and cationic complexes PtX(CH₃)(dppe) and [Pt(CH₃)L(dppe)]⁺ indicates that these two series may be considered together. Following the treatment outlined in the Introduction, we regard the variation in J_{PtP} for P trans to X or L as representing primarily the change in 6s character of the hybrid orbital of platinum used in bonding to that phosphorus atom. Thus ligands L or X of high trans influence increase the Pt 6s character of their bond at the expense of the trans Pt-P bond which uses the same *s* ± *d* hybrid orbital, while bonds *cis* to L or X which use a different *s* ± *d* hybrid orbital are much less affected.¹ Larger values of J_{PtP} correspond to smaller trans influences and vice versa, so that Tables II and III, in which complexes are listed in decreasing order of J_{PtP} trans to X or L in PtX(CH₃)(dppe) and [Pt(CH₃)L(dppe)]⁺, respectively, give the inverse order of trans influence of X or L. For relatively well-studied ligands, the derived series is CH₃⁻ > P(OPh)₃ ~ PPh₃ > CN⁻ > CO > AsPh₃ ≥ NO₂⁻ ~ SPh⁻ > SbPh₃ > SCN⁻ > C₅H₅N > NCO⁻ ~ I⁻ > O₂CCH₃⁻ > Cl⁻ > CH₃CN > ONO₂⁻, which is similar to the series obtained by other techniques.¹ There is a remarkably good linear correlation between our values of J_{PtP} and the values of $^2J_{PtCH_3}$ and $^1J_{PtC}$ for a series of neutral and cationic complexes of the type PtX(CH₃)(PMe₂Ph)₂ or [PtL(CH₃)(PMe₂Ph)₂]⁺.³² These relationships are summarized in eq 2 and 3 and shown graphically in Figures 1 and 2.

$$^2J_{PtCH_3} = 0.013(^1J_{PtP}) + 24 \quad r = 0.978 \quad (2)$$

$$^1J_{PtC} = 0.13(^1J_{PtP}) + 115 \quad r = 0.975 \quad (3)$$

A similar though poorer correlation also exists between our J_{PtP} values and the $^1J_{PtH}$ values of the hydrido complexes *trans*-PtHX(PR₃)₂ (X = various anionic or neutral ligands and PR₃ = PMe₂Ph or PEt₃). Pidcock et al.³⁶ have previously shown that $^1J_{PtP}$ for the phosphonato group in *trans*-PtX-[(PhO)₂PO](Bu₃P)₂ is linearly related to $^2J_{PtCH_3}$ in *trans*-PtX(CH₃)(PEt₃)₂. The degree of variation in J_{PtP} *cis* to X or

L in our complexes (ca. 20%) indicates that undue emphasis should not be placed on small differences in J_{PtP} for ligands which are close together in the series.

Unexpectedly, the value of J_{PtP} for OH⁻, 3546 Hz, indicates the trans influence of OH⁻ to be comparable with that of typical S donors such as SCN⁻ (3719 Hz) and SPh⁻ (3380 Hz) and greater than that of other anionic O donors such as CH₃CO₂⁻ (4122 Hz) and ONO₂⁻ (4510 Hz). In the past, OH⁻ has usually been assumed to have a low trans influence,³⁸ but the present result, taken together with the value of 3401 Hz for J_{PtP} trans to OH in Pt(OH)(C₆H₅)(dppe), implies that the Pt-OH bond in these complexes has considerable covalent character. A related trend is observed for $^2J_{PtCH_3}$ in the series CH₃HgX, where the value for X = OH (204 Hz in benzene and 214 Hz in pyridine) is the lowest of all the O donors studied and comparable with that for X = SCN (208 Hz in pyridine).³⁹ The value of $^2J_{PtCH_3}$ in [(CH₃)₃Pt(OH)]₄ (80.1 Hz)⁴⁰ is comparable with the values for [(CH₃)₃PtCl]₄ (81.7 Hz) and [(CH₃)₃PtBr]₄ (80.1 Hz) and much larger than that for [(CH₃)₃Pt(SH)]₄ (73.4 Hz),⁴¹ which indicates that a triply bridging hydroxyl has a low trans influence; there is, however, no reason why the same should be true of a monodentate hydroxyl.

The value of J_{PtP} trans to the phenoxy group in Pt-(OC₆H₄OCH₃-*p*)(CH₃)(dppe), 3840 Hz, indicates that this ligand has a lower trans influence than OH, though it is still higher than CH₃CO₂⁻ or ONO₂⁻ in the series.

The trans influence of SH is slightly greater than that of other typical S donors (J_{PtP} = 3201, 3380, and 3719 Hz for SH, SPh, and SCN, respectively), but the difference is less marked than for the O donors discussed above. Its position in the series appears to be comparable with that of triply bridging SH in [(CH₃)₃Pt(SH)]₄.⁴¹

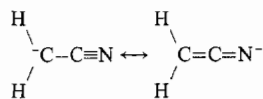
The value of J_{PtP} for P trans to NHCOCH₃ in the amido complex Pt(NHCOCH₃)(CH₃)(dppe), 3322 Hz, is very close to that for the nitro complex Pt(NO₂)(CH₃)(dppe) and is lower than the values for O-donor and other N-donor ligands. This supports the contention that the amido group is N bound, not O bound.

The carbon-donor ligands which we have studied span a wide range of trans influence, the order being C₆H₅⁻ ~ C₂H₅⁻ > C₆H₅⁻ > CH₂Ph⁻ ~ CH₃⁻ > CF₃⁻ > CH₂COCH₃⁻ > CH₂CN⁻ > C₂Ph⁻ ~ CH₂NO₂⁻ > η¹-C₅H₅⁻ > CN⁻ ~ CNO⁻ > CH(COCH₃)₂⁻ > CH(CN)₂⁻ > CO > C(COCH₃)₃⁻ > NCC(CN)₂⁻ (N bound). This series shows the effect on the trans influence of a methyl group as its hydrogen atoms are replaced by other groups. For example, the Pt-P coupling constants indicate that the trans influence of CF₃ is only slightly less than that of CH₃, in agreement with conclusions drawn from $^2J_{PtCH_3}$ and $^2J_{PtCF_3}$ data for platinum(II) and platinum(IV) complexes.^{34,42} In apparent contradiction, the Pt-Cl distance in *trans*-PtCl(C₂F₅)(PMePh₂)₂ (2.363 (5) Å) is significantly shorter than that in *trans*-PtCl(CH₃)(PMePh₂)₂ (2.412(2) Å), a trend which is also reflected in the PtCl stretching frequencies (302 and 272 cm⁻¹, respectively);^{43a} the latter are almost identical for *trans*-PtCl(CF₃)(PMePh₂)₂ and *trans*-PtCl(C₂F₅)(PMePh₂)₂, indicating that CF₃ and C₂F₅ do not differ significantly in trans influence. The discrepancy may arise in part from the sensitivity of Pt-Cl bond lengths to both electrostatic and hybridization effects, whereas NMR coupling constants are sensitive only to the latter.^{1,43b}

The Pt-P coupling constants show that the introduction of even one unsaturated electron-withdrawing substituent such as COCH₃, CN, or CH₂NO₂ lowers the trans influence of σ-bonded carbon far more than the presence of three fluorine atoms; e.g., for the series Pt[CH_{3-n}(COCH₃)_n](CH₃)(dppe) the values of J_{PtP} trans to the acetyl-substituted methyl group are 1794 (*n* = 0), 2346 (*n* = 1), 2948 (*n* = 2) and 4124 Hz

($n = 3$), while J_{PtP} trans to CH_3 remains essentially constant (1770–1808 Hz). In the trans-influence series, C-bonded acetylacetonate lies between CN^- and NO_2^- , an ordering which can also be derived from the $^2J_{\text{PtCH}_3}$ values for CH_3 trans to X in octahedral platinum(IV) complexes $\text{PtX}(\text{CH}_3)_3(\text{bpy})$ (X = CN, NO_2 or $\text{CH}(\text{COCH}_3)_2$).³⁷ X-ray data support this assignment of trans influence based on NMR: in the structure of $\text{K}[\text{PtCl}(\text{O-acac})(\text{C-acac})]$, the Pt–O distance of bidentate O-bonded acac trans to the carbon-bonded acac ligand, 2.072 (14) Å, is significantly longer than that trans to chloride, 1.968 (14) Å, showing that C-bonded acac has a larger trans influence than chloride.⁴⁴ In the structure of $\text{Pt}(\text{CH}_2\text{COPh})(\text{C}_6\text{H}_9)(\text{dppe})$, the Pt–P distance trans to C_6H_9 , 2.289 (3) Å, is significantly longer than that trans to CH_2COPh , 2.254 (3) Å, showing that 1-cyclohexenyl has a larger trans influence than CH_2COPh^- (and by implication $\text{CH}_2\text{COCH}_3^-$).⁷ The trans influence of $\text{CH}_2\text{COCH}_3^-$ ($J_{\text{PtP}} = 2346$ Hz) is remarkably close to the average of those for CH_3^- and $\text{CH}(\text{COCH}_3)_2^-$ (average 2371 Hz), but this additivity is lost in going to $\text{C}(\text{COCH}_3)_3^-$, which is only slightly higher than Cl^- in the trans-influence series. Comparisons within the series of carbanionic ligands $[\text{CH}_3\text{-}n(\text{CN})_n]^-$ cannot be made so readily since, as noted above, $\text{C}(\text{CN})_3^-$ is N bound in $\text{Pt}[\text{NCC}(\text{CN})_2](\text{CH}_3)(\text{dppe})$. Not surprisingly, its trans influence as measured by J_{PtP} is low and close to that of acetonitrile; the same conclusion follows from the hydride chemical shift of *trans*- $\text{PtH}[\text{NCC}(\text{CN})_2](\text{PEt}_3)_2$.²⁴ Owing to the poor solubility of $\text{Pt}[\text{CH}(\text{CN})_2](\text{CH}_3)(\text{dppe})$, the analogous 1-cyclohexenyl complex $\text{Pt}[\text{CH}(\text{CN})_2](\text{C}_6\text{H}_9)(\text{dppe})$ had to be used to obtain a value of J_{PtP} trans to dicyanomethyl; comparison of Tables II and IV suggests that the change of cis ligand from CH_3 to C_6H_9 will not greatly affect the value. The trans influence of $\text{CH}(\text{CN})_2^-$ is very similar to that of $\text{CH}(\text{COCH}_3)_2^-$, and its position in the trans-influence series agrees with that based on $\nu(\text{PtH})$ data in complexes of the type *trans*- $\text{PtHX}(\text{PPh}_3)_2$ (X = Cl, NO_2 , CN, or $\text{CH}(\text{CN})_2$).²³ The trans influences of CH_2CN^- and CH_2NO_2^- appear to be very similar to that of $\text{CH}_2\text{COCH}_3^-$. The position of CH_2CN^- relative to CH_3^- in the series is supported by the observation²¹ that $\nu(\text{PtCl})$ in *trans*- $\text{PtCl}(\text{CH}_2\text{CN})(\text{PPh}_3)_2$, 293 cm^{-1} , is ca. 20 cm^{-1} higher than that in *trans*- $\text{PtCl}(\text{CH}_3)(\text{PPh}_3)_2$ and by the J_{PtP} value for CH_2CN trans to triphenylphosphine in the complex $[\text{Pt}(\text{CH}_2\text{CN})(\text{PPh}_3)_3]\text{BF}_4$.^{20,45}

These results, taken together with those for the η^1 -cyclopentadienyl and σ -phenylacetylide complexes $\text{PtX}(\text{CH}_3)(\text{dppe})$ (X = C_5H_5 , C_2Ph) (Table II), show that there is a general tendency for J_{PtP} to increase, i.e., for the trans influence to decrease as the carbanionic ligand becomes more stable. In the case of X = C_2Ph , the ligating carbon atom is sp hybridized and presumably makes slightly less demand than the sp³-hybridized carbon atom of methyl on Pt 6s electron density in forming the metal–carbon bond. The result derived from ³¹P NMR is consistent with the observation⁴⁶ that the PtCl distance in *trans*- $\text{PtCl}(\text{C}_2\text{Ph})(\text{PEt}_2\text{Ph})_2$, 2.407 (6) Å, is slightly shorter than those in *trans*- $\text{PtCl}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_2\text{Ph})_2$, 2.415 (5) Å,⁴⁷ and *trans*- $\text{PtCl}(\text{CH}_3)(\text{PMePh}_2)_2$, 2.412 (2) Å,^{43a} this causes $\nu(\text{PtCl})$ to be slightly higher for the phenylacetylide than for the two σ alkyls. The stabilizing influence of substituents such as COCH_3 , CN, and NO_2 on carbanions is generally ascribed to their ability to delocalize the electron pair on the carbon atom into π^* -antibonding orbitals on the substituent;⁴⁸ e.g., for CH_2CN^- in valence-bond terms two hybrids contribute:



The efficiency of delocalization and hence the stability of the

carbanion increase with the number of such substituents. The combined effect of delocalization and of increased p character in the orbital containing the lone pair of electrons is to reduce overlap with the platinum hybrid orbital and hence to reduce the demand for Pt 6s electron density in the bond to carbon. This may account for the remarkably long Pt– CH_2COPh bond length, 2.175 (10) Å, in $\text{Pt}(\text{CH}_2\text{COPh})(\text{C}_6\text{H}_9)(\text{dppe})$.⁷ A similar explanation can be advanced to account for the position of C_5H_5^- in the trans-influence series. In the extreme case of the tricyanomethide anion, delocalization of negative charge to the cyanide nitrogen atom is so effective that the anion adopts a planar configuration and the nitrogen bonds to platinum. In contrast, CF_3^- ($\text{p}K_a = 28\text{--}31$) is a less stable carbanion than C_5H_5^- , $\text{CH}_2\text{COCH}_3^-$, C_2Ph^- , or CH_2CN^- , which have $\text{p}K_a$ values in the range 15–25.⁴⁹ Hence, the position of CF_3^- in the trans-influence series is not so surprising. Recent MO calculations on $\text{MnX}(\text{CO})_5$ (X = CH_3 , CF_3)⁵⁰ indicate that these two groups transfer comparable charge to the metal but that the electronegative fluorine atoms cause the carbon atom in CF_3 to be more positively charged than that in CH_3 , which stabilizes the metal d orbitals in $\text{CF}_3\text{Mn}(\text{CO})_5$ relative to those in $\text{CH}_3\text{Mn}(\text{CO})_5$.

In agreement with previous ³¹P NMR data on the complexes *cis*- $\text{PtX}_2(\text{PMe}_2\text{Ph})_2$ (X = various anionic ligands),⁵¹ we find the trans influence of benzyl, CH_2Ph , to be comparable with that of methyl. However, both phenyl and ethyl have significantly larger trans influences than methyl. The result for phenyl confirms that of Allen and Pidcock³ based on values of J_{PtP} for *cis*- $\text{PtClR}(\text{PEt}_3)_2$ (R = CH_3 , C_6H_5) and is also consistent with ¹H and ¹⁹F NMR data on various platinum(II) complexes.^{42,52,53} Comparison of Tables II and IV shows that J_{PtP} trans to cyclohexenyl is consistently lower than that trans to methyl, indicating that cyclohexenyl has the larger trans influence. Data for J_{PtP} trans to vinyl ($\text{CH}=\text{CH}_2$) are not available, but the PtCl bond length and the value of $\nu(\text{PtCl})$ for *trans*- $\text{PtCl}(\text{CH}=\text{CH}_2)(\text{PEt}_2\text{Ph})_2$ ⁴⁷ indicate that vinyl should have a slightly lower trans influence than methyl. The presence of two aliphatic substituents on the vinylic double bond of σ -cyclohexenyl may be the cause of the reversal (cf. the trans influences of methyl and ethyl).

In agreement with earlier work,¹ the trans influence of the cyanide ion derived from J_{PtP} data is comparable with that of a tertiary phosphine, and not surprisingly the trans influence of fulminate (obtained from the ³¹P NMR spectrum of $\text{Pt}(\text{CNO})(\text{C}_6\text{H}_9)(\text{dppe})$ owing to the poor solubility of the methyl compound) is similar to that of cyanide.

The value of J_{PtP} trans to CO in $[\text{Pt}(\text{CH}_3)(\text{CO})(\text{dppe})]^+$ places CO between triphenylphosphine and triphenylarsine in the trans-influence series, in agreement with orderings based on values of ¹ J_{PtH} and ² J_{PtCH_3} in hydrido- and methylplatinum(II) complexes, respectively.¹ This indication of a moderate trans influence for CO differs from the conclusion based on Pt–Cl bond parameters, e.g., bond length and stretching frequency, that CO has a low trans influence.⁵⁴ The difference probably arises because of the sensitivity of the relatively polar Pt–Cl bond to the electrostatic effect of Pt→CO π bonding; the effect (though not the cause) is similar to that discussed above for Pt– CF_3 bonding.

Cis Effects. For those complexes which contain ligands of the type $\text{C}\equiv\text{Z}$, we find that J_{PtP} cis to the unsaturated ligand is significantly lower than in the other complexes. Thus, J_{PtP} trans to CH_3 in the complexes $[\text{PtX}(\text{CH}_3)(\text{dppe})]$ (X = CN, C_2Ph) and $[\text{Pt}(\text{CH}_3)(\text{CO})(\text{dppe})]^+$ range between 1606 and 1633 Hz, and the next lowest value is 1706 Hz for Pt– $(\text{NCO})(\text{CH}_3)(\text{dppe})$. The low value of J_{PtP} trans to C_6H_9 in the fulminate complex $\text{Pt}(\text{CNO})(\text{C}_6\text{H}_9)(\text{dppe})$, 1474 Hz, compared with the values for the other cyclohexenyl complexes (1535–1652 Hz) suggests that a similar effect operates in this

series too. We can offer no explanation and do not know whether J_{PtP} trans to C≡Z is similarly affected and should be corrected in discussing the trans influences of these ligands. However, a correction of ca. 100 Hz would cause only minor changes in the order we have given.

In general, within the series PtXY(dppe) there is no correlation between J_{PtP} trans to X and J_{PtP} cis to X if X is changed and Y is kept constant. There is also no correlation between J_{PtP} trans to CH₃ and $^2J_{\text{PtCH}_3}$ in the series PtX-(CH₃)(dppe). However, there is a rough inverse correlation in this series between J_{PtP} trans to X and $^2J_{\text{PtCH}_3}$, which varies between 48 and 71 Hz; the ligands with the highest J_{PtP} values (lowest trans influences) tend to give the lowest $^2J_{\text{PtCH}_3}$ values. A separate correlation exists between J_{PtP} trans to L and $^2J_{\text{PtCH}_3}$ in the cations [Pt(CH₃)L(dppe)]⁺, although the value of $^2J_{\text{PtCH}_3}$ for L = CO is much larger than expected on the basis of the correlation. The trend is generally in agreement with the prediction of Syrkin⁵⁵ that ligands of high trans influence would slightly strengthen the cis bonds while weakening the trans bond, but as noted elsewhere,⁵⁶ it is not clear why the trend is not manifest in one-bond couplings or in couplings over more than two bonds; it may well be that ligand size plays a significant role.⁵⁷ At present one can only say that cis influences on NMR coupling constants are less well-understood than trans influences.

Registry No. Pt(CH₃)(dppe), 27711-52-0; Pt(NCO)(CH₃)(dppe), 65310-89-6; Pt(SCN)(CH₃)(dppe), 65310-88-5; Pt(NO₂)(CH₃)(dppe), 65310-87-4; Pt(CN)(CH₃)(dppe), 65310-86-3; Pt(O₂CCH₃)(CH₃)(dppe), 65310-85-2; Pt(OC₂H₄OCH₂Ph)(CH₃)(dppe), 65378-52-1; Pt(OH)(CH₃)(dppe), 43210-95-3; Pt(SH)(CH₃)(dppe), 65310-84-1; Pt(SC₆H₅)(CH₃)(dppe), 65310-83-0; Pt(NHCOCH₃)(CH₃)(dppe), 65310-82-9; Pt[NCC(CN)₂](CH₃)(dppe), 65378-50-9; Pt(CNO)(CH₃)(dppe), 43211-01-4; Pt(CH₂COCH₃)(CH₃)(dppe), 43210-96-4; Pt(CH₂N₂O)(CH₃)(dppe), 43210-99-7; Pt(CH₂CN)(CH₃)(dppe), 43210-97-5; Pt[CH(COCH₃)₂](CH₃)(dppe), 43210-98-6; Pt[CH(CN)₂](CH₃)(dppe), 65378-53-2; Pt[C(COCH₃)₃](CH₃)(dppe), 65310-62-5; Pt(C₂C₆H₅)(CH₃)(dppe), 65310-61-4; Pt(C₂H₅)(CH₃)(dppe), 65310-60-3; Pt(NCO)(C₆H₅)(dppe), 65310-59-0; Pt(SH)(C₆H₅)(dppe), 65310-58-9; Pt(CNO)(C₆H₅)(dppe), 43211-02-5; Pt[CH(COCH₃)₂](C₆H₅)(dppe), 65310-57-8; Pt[CH(CN)₂](C₆H₅)(dppe), 65310-56-7; [Pt(CH₃)(CH₃CN)(dppe)]BF₄, 65310-55-6; [Pt(CH₃)(C₅H₅N)(dppe)]BF₄, 65310-78-3; [Pt(CH₃)(PPh₃)(dppe)]BF₄, 65310-76-1; [Pt(CH₃)(P(OPh)₃)(dppe)]BF₄, 65310-74-9; [Pt(CH₃)(AsPh₃)(dppe)]BF₄, 65310-72-7; [Pt(CH₃)(SbPh₃)(dppe)]BF₄, 65310-70-5; [Pt(CH₃)(CO)(dppe)]BF₄, 65310-68-1; [Pt(CH₃)(H₂O)(dppe)]BF₄, 65310-66-9; Pt(C₂H₅)(COD), 65310-64-7; Pt(C₂H₅)(dppe), 65310-63-6; PtCl(C₂H₅)(dppe), 65098-10-4; PtCl(CH₂C₆H₅)(dppe), 65310-81-8; PtCl(C₆H₅)(dppe), 27711-51-9; Pt(C₆H₅)₂(dppe), 52595-92-3; Pt(CF₃)₂(dppe), 65392-11-2; Pt(ONO₂)(CH₃)(dppe), 39584-15-1; PtCl(CH₃)(dppe), 27711-50-8; Pt(CH₃)₂(dppe), 15630-18-9; PtCl(C₆H₅)(dppe), 65310-80-7; Pt(OH)(C₆H₅)(dppe), 41650-12-8; Pt(CH₂N₂O)(C₆H₅)(dppe), 41729-29-7; Pt(CH₂CN)(C₆H₅)(dppe), 65310-79-4; Pt(CH₂COCH₃)(C₆H₅)(dppe), 41659-99-8; PtCl₂(dppe), 19998-23-3; PtI₂(dppe), 19998-25-5; PtI₂(COD), 12275-67-1; Pt(C₆H₅)₂(COD), 12277-88-2; PtCl(C₆H₅)(COD), 51177-65-2; Pt(CF₃)₂(COD), 37035-32-8.

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