Measurement of the *trans* Influence in 1-Platinacyclopent-4-ene-2,3-dione Complexes: A Proton, Carbon-13, and Phosphorus-31 Nuclear Magnetic Resonance Study

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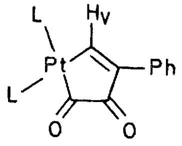
The preparation of a series of 1-platinacyclopent-4-ene-2,3-dione complexes $[\overline{\mathrm{PtL_2\cdot CO\cdot CO\cdot CPh{:}C}}_v\mathrm{H}_v]$ [L = $AsPh_3$, PPh_3, PEt_2Ph, PEt_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, $Ph_2PCH_2CH_2PPh_2$ (dppe), pyridine (py), 2,2′-bipyridine (bipy), or 1,10-phenanthroline (phen)] is described. Measurement of the coupling $^2J(PtH_v)$ between the vinylic proton, H_v, and platinum is expected to provide a measure of the *trans* influence of L. Instead an apparent *trans*-influence order $AsPh_3 \sim PPh_3 > P(OPh)_3 > PMePh_2 > PEt_2Ph > PMe_2Ph > PEt_3 >$ dppe > py is indicated, more or less the reverse of what is expected. Determination of $^1J(Pt^{13}C_v)$ from ^{13}C n.m.r. spectra of a selection of the complexes, however, has indicated the correct order. Phosphorus-31 n.m.r. spectra of the complexes L = PEt_3, $PMePh_2$, and PPh_3 indicate that the COCO half of the chelate has a considerably lower *trans* influence than the vinylic half.

MEASUREMENT of *trans* influence by means of n.m.r. spectroscopy is now a well tried and established technique, so much so that an extensive review has already appeared.[1] In the case of complexes of platinum(II) containing a *trans*-A–Pt–(X or L) system, the coupling constant between ^{195}Pt ($I = \frac{1}{2}$, 33.8% naturally abundant) and a magnetically active nucleus on the indicator ligand A provides a measure of the *trans* influence of X or L. Such couplings, which were shown to be dominated by the Fermi-contact equation [2] and in particular the term defining the *s* character of the hybrid orbital used by platinum ($\alpha^2_{\mathrm{Pt}(6s)}$),[3] were originally limited to direct coupling, for instance $^1J(PtP)$ in *cis*- and *trans*-$[PtXMe(PEt_3)_2]$ complexes [4] and $^1J(PtH)$ in *trans*-$[PtHL(PEt_3)_2]^+$ complexes.[5] In later years this treatment was shown to be applicable to indirect couplings, for example $^2J(PtY)$ in *trans*-$[Pt(CY_3)X(PR_3)_2]$ (Y = H [4] or F [6]), $^3J(PtF)$ in *trans*-$[PtX(PEt_3)_2(SCF_3)]$,[7] or $^3J(PtF)$ and $^3J(PtH_v)$ in *trans*-$[Pt\{C(CF_3){=}CH_v(OMe)\}(X\text{ or }L)(PMe_2Ph)_2]^{n+}$ (n = 0 or 1).[8]

With the advent of commercially available Fourier-transform n.m.r. spectrometers, $^1J(Pt^{13}C)$ in a variety of complexes has been reported [9–13] and used on some occasions [11–13] as a measure of *trans* influence. Consequently, when we obtained complex (1; L = $AsPh_3$) from the reaction of tetrakis(triphenylarsine)platinum(0) and 4-phenylcyclobut-3-ene-1,2-dione (pcbd) in chloroform solution [14,‡] and found that the arsine ligand could be readily displaced by phosphorus and nitrogen donors, we thought it worthwhile to construct a limited *trans*-influence series based on $^1J(PtC_v)$ and $^2J(PtH_v)$, especially since neither two-bond coupling through an sp^2 carbon nor direct coupling to an sp^2 carbon have yet been used as measures of *trans* influence.



(1)

EXPERIMENTAL

The starting materials $[Pt(AsPh_3)_4]$ [15] and pcbd [16] were obtained as previously described.

$[Pt(AsPh_3)_2(\sigma\text{-pcbd})]$ ‡.—The complex $[Pt(AsPh_3)_4]$ (0.62 g, 0.44 mmol) and pcbd (0.07 g, 0.45 mmol) were stirred together in degassed $CHCl_3$ (20 cm^3) under dry N_2 for *ca.* 12 h. After this time the solution had become dark orange. It was subsequently evaporated *in vacuo* to a small volume and diethyl ether was added until crystallisation just began. Storage overnight at 0 °C gave complex (1; L = $AsPh_3$) as dark orange crystals (0.3 g, 0.31 mmol).

$[Pt(\sigma\text{-pcbd})L_2]$ [L = PPh_3, PEt_2Ph, PEt_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, *Pyridine* (py); L_2 = $Ph_2PCH_2CH_2PPh_2$, (dppe), 2,2′-*Bipyridyl* (bipy), *or* 1,10-*Phenanthroline* (phen)].—

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‡ We use the notation σ to represent the ring-opened platinacyclopentenedione complex (1) obtained under these conditions If the reaction is conducted in a suspension of diethyl ether a η-bonded cyclobutenedione species is obtained.[14]

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TABLE 1

Characterisation data for the complexes (1)

L [a]	M.p. (θ_c/°C)	Analysis (%) [b]			Infrared data (cm^{-1})	
		C	H	N	ν(C=O) region	ν(Pt–C) region
$AsPh_3$	192—193 (decomp.)	56.7 (57.2)	3.9 (3.8)		1 657s, 1 677s	541w
PPh_3	203	63.2 (62.9)	4.4 (4.1)		1 658vs, 1 667(sh)	*c*
PEt_2Ph	120—121	52.1 (52.6)	5.1 (5.3)		1 639vs, 1 666s	542w
PEt_3	88—89	44.8 (44.8)	6.0 (6.2)		1 640vs, 1 668s	541.5w
$PMePh_2$	201—203 (decomp.)	57.0 (57.4)	3.9 (4.3)		1 641vs, 1 670s	545w
PMe_2Ph	108—111 (decomp.)	49.5 (49.6)	4.4 (4.5)		1 633vs, 1 671s	545.5w
$P(OPh)_3$	148—150	56.7 (56.7)	3.6 (3.7)		1 656vs, 1 685s	*c*
dppe	258—261 (decomp.)	57.5 (57.5)	3.7 (4.0)		1 642vs, 1 670s	*c*
py	170—175 (decomp.)	47.9 (47.0)	3.5 (3.2)		1 639vs, 1 667s	*c*
bipy	243—245 (decomp.)	46.6 (47.2)	2.7 (2.8)	5.3 (5.5)	1 633vs, 1 663s	549.5w
phen	*ca.* 330	49.9 (49.5)	2.8 (2.7)	5.2 (5.2)	1 632vs, 1 654s	549w, 554w

[a] All the complexes are orange-red, except L_2 = bipy which is emerald green and L_2 = phen which is deep purple. [b] Calculated values are given in parentheses. [c] Not observed.

These complexes were all obtained by the same general method whereby a suspension of $[Pt(AsPh_3)_2(\sigma\text{-pcbd})]$ (1 mol) was treated with the appropriate ligand L (2 mol) under nitrogen. Conversion was rapid (<1 min) unless otherwise stated. Thus, essentially quantitative yields were obtained in 100% diethyl ether [L = PPh_3, $PMePh_2$, dppe, py (reaction time, 1 week), bipy, or phen], in light petroleum–diethyl ether (1 : 4) (L = PMe_2Ph), in light petroleum–diethyl ether (2 : 3) [L = PEt_2Ph or $P(OPh)_3$], or in light petroleum–diethyl ether (9 : 1) (L = PEt_3). The choice of solvent depended on suppressing the solubility of the product, thus avoiding precipitation of intractable oils.

Initial characterisation data are summarised in Table 1. Microanalyses were by Beller Mikroanalylishes Laboratorium, West Germany, F. Pascher Mikroanalylishes Laboratorium, West Germany, or C. H. N. Analysis Ltd., Wigston, Leicester. Infrared spectra were recorded on Nujol mulls between caesium iodide plates on a Perkin-Elmer 225 spectrometer. Frequencies were calibrated against polystyrene film (band at 1 601 cm^{-1}) or atmospheric CO_2 (band at 671 cm^{-1}) and are considered accurate to ±1 cm^{-1}. Hydrogen-1 n.m.r. spectra were obtained at 100 MHz on a Jeol JNMPS 100 spectrometer, ^{13}C spectra at 22.63 MHz on a Bruker WH-90, and ^{31}P spectra at 36.4 MHz on a Bruker WH-90 and at 24.3 MHz on a Bruker WP-60DS. Complexes were examined as saturated solutions in [^2H]chloroform (^1H and ^{13}C spectra) with $SiMe_4$ as internal standard or [$^2H_6$]benzene (^{31}P spectra) with $P(OMe)_3$ as external standard. Carbon-13 and ^{31}P spectra were obtained using the Fourier-transform method with (except where stated in the Results section) broad-band decoupling of protons. Phosphorus-31 spectra were straightforward, typically involving 12 or 7.5 kHz sweep widths with a pulse angle of *ca.* 30°. Each transient consisted of 16 k data points and normally between 100 and 500 were stored. Carbon-13 spectra required careful optimisation of field and radiofrequency (r.f.) pulse conditions in order to extract the required amount of information from single carbon-atom resonances in complexes of molecular weight 500—1 000. In the case of the phosphine complexes the carbon resonances were split into four lines, 34% of which were further split by the ^{195}Pt isotope. Pulse lengths chosen corresponded to small dip angles (17—22°) and 50—100 k 8 k interferograms, depending on the solubility of the complex, were accumulated overnight. The sweep width was always 6 kHz. Difficulties were nevertheless encountered in the case of the carbonyl carbons. In these cases even shorter pulses were reverted to (13°) in order to observe phosphorus spitting (see Results section).

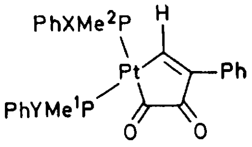
RESULTS

Data relating to the characterisation of the new complexes are summarised in Table 1. The green colour of $[Pt(\sigma\text{-pcbd})(bipy)]$ was unexpected. However, the extreme insolubility of the complex, whilst possibly indicating a polymeric nature, precluded further investigation. The i.r. spectrum of $[Pt(\sigma\text{-pcbd})(bipy)]$ showed no anomalies in the positions of the ν(CO) or ν(PtC) bands.

Infrared Spectra.—Carbonyl-stretching frequencies for our complexes provide a reliable guide to the identity of the complex, whether a ring-opened platinum(II) or an olefinic platinum(0) species (see footnote on p. 261). The former species have ν(CO) at between 1 650 and 1 680 cm^{-1} whilst the latter have the appropriate vibration in the range 1 690—1 730 cm^{-1}.[14] The new ring-opened complexes provided no exception to this rule. Platinum–carbon stretching frequencies in *trans*-$[PtMeX(PEt_3)_2]$ complexes correlate well [4] with ν(Pt–H) in analogous hydride complexes. Since the latter correlation has been used as an indication of *trans* influence,[5] we might expect ν(Pt–C) to behave similarly. Although we observed a single band in the correct region of the spectrum, this did not behave in either a consistent or sensitive manner with the changing nature of the *trans* ligand. Since, in addition, this band could be attributed to the CH=CPh or COCO halves of the chelate, or to both, we did not explore this aspect further.

^1H *N.M.R. Spectra.*—Proton n.m.r. data are summarised in Table 2. Those complexes containing methylphosphines showed well separated doublet resonances for the methyl group(s) on each phosphorus. Platinum satellites were also observed and from the magnitudes of the coupling and knowledge of the relative *trans* influence of the CH=CPh and COCO fragments (see below) these were assigned according to structure (2). In the case of the ethylphosphines the situation is complicated by proton–proton coupling between the CH_2 and Me groups. Separate resonances were again observed, however, and consisted of overlapping 1 : 2 : 2 : 2 : 1 quintets, ^3J(PH) ~ 2|^3J(HH)| (Me groups) or 1 : 4 : 6 : 4 : 1 quintets ^2J(PH) ~ ^3J(HH) (CH_2 groups). No platinum satellites were observed but, since chemical shifts probably follow the same order as the methylphosphines, the resonances were assigned in an analogous manner, *i.e.* with Et^1 *trans* to the CH=CPh group.

The vinylic proton H_v occurred at *ca.* −9 p.p.m. and consisted invariably of a 1 : 1 : 1 : 1 doublet of doublets further complicated by closely spaced coupling to ^{195}Pt (Figure 1). Following normal procedure we assign the larger coupling in the main pattern to the *trans* phosphorus.



(2) X = Me^2 or Ph
Y = Me^1 or Ph

It is worth noting the considerable degree of deshielding observed on passing from the d^{10} [Pt(η-pcbd)L_2] complexes [δ −4.75 (L = PPh_3) or −5.0 p.p.m. ($AsPh_3$)] [14] to the d^8 [Pt(σ-pcbd)L_2] complexes.

The coupling constants ^2J(PtH_v) indicate an apparent *trans*-influence order for different L in complex (1) of: $AsPh_3$ ~ PPh_3 > $P(OPh)_3$ > $PMePh_2$ > PEt_2Ph > PMe_2Ph > PEt_3 > dppe > py. With the exception of py and dppe, the indicated order is exactly the opposite of that expected. Triphenylphosphine and PEt_3 occupy reverse positions at either end of the scale, whilst the replacement of aryl by alkyl groups should progressively increase rather than decrease the *trans* influence of L. It appears, therefore, that we have a case in which the Fermi-contact term and, in particular $\alpha^2_{\mathrm{Pt}(6s)}$, does not dominate the coupling between platinum and the indicator nucleus. We reasoned that the effects most likely to contribute to such a spurious result would be steric, particularly since the order followed relates to the size of L. Such effects, however, would be considerably less likely to affect the direct coupling between ^{195}Pt and the donor carbon atom, C_v, of the vinylic fragment. Our intended ^{13}C studies, therefore, became of paramount importance.

TABLE 2

100 MHz ^{1}H N.m.r. data for complexes (1)

L	$\delta(H_v)$ [a]	^2J(PtH_v) [b]	^3J(H_vP) *trans*	^3J(H_vP) *cis*	Other data
$AsPh_3$	9.40	21.5			
PPh_3	9.20	21.5	17.0	8.5	
PEt_2Ph	9.54	30.0	14.9	8.9	Me^1: δ 0.88. Me^2: δ 0.98, ^3J(PCH_3) ~13, ^3J(HH) ~6.5. CH_2^1: δ ~1.8. CH_2^2: δ ~2.07
PEt_3	9.54	32.0	14.6	9.2	Me^1: δ 1.03. Me^2: δ 1.10. ^3J(PCH_3) ~16, ^3J(HH) 7—8. CH_2^1: δ 1.89. CH_2^2: δ 1.96, ^2J(PCH_2) 7—8
$PMePh_2$	8.94	24.8	16.7	8.4	Me^1: δ 1.28, ^2J(PH) 7.5, ^3J(PtH) 15.7. Me^2: δ 2.13, ^2J(PH) 9.0, ^3J(PtH) 24.6
PMe_2Ph	9.57	31.2	16.5	9.2	Me^1: δ 1.44, ^2J(PH) 8.2, ^3J(PtH) 16.0. Me^2: δ 1.73, ^2J(PH) 8.8, ^3J(PtH) 24.0
$P(OPh)_3$	9.16	22.0	20.5	16.5	
dppe	9.90	32.2	14.3	8.5	$\delta(C_2H_4)$ *ca.* 2.4
py	8.56	40.7			

[a] In p.p.m. downfield of internal $SiMe_4$. [b] In Hz.

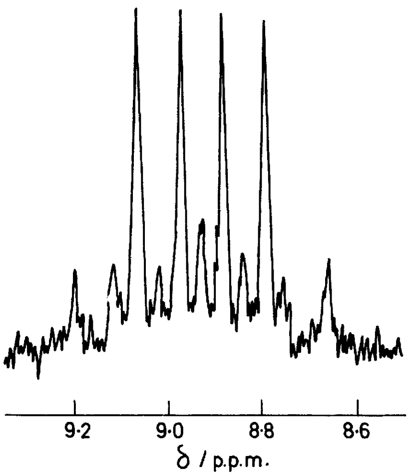


FIGURE 1 100 MHz ^{1}H N.m.r. spectrum of H_v in [Pt(σ-pcbd)($PMePh_2$)$_2$]

^{13}C *N.M.R. Spectra.*—Carbon-13 n.m.r. data were accumulated for a representative selection of the complexes and are summarised in Table 3. The ^{13}C n.m.r. spectrum of (1; L = $AsPh_3$) (80 k scans) from *ca.* 130 to 230 p.p.m. is shown in Figure 2. The atoms C^5(C_v) and C^4 were readily identified both from their expected relative chemical shifts and the magnitude of their coupling to platinum. The identity of C^5 was further established by an off-resonance spectrum, it being the only carbon in the range 130—230 p.p.m. to show a doublet. The peak at 145 p.p.m. could be assigned, on the basis of calculated chemical shifts [17] and the observation of a singlet in the off-resonance spectrum, to the substituted phenyl carbon $C^{1'}$. The signals at 204 and 218 p.p.m. clearly derive from the carbonyl carbons C^2 and C^3. We were able to distinguish between these by virtue of the magnitude of their coupling to ^{31}P. Figure 3 shows the ^{13}C spectrum (50 k scans) of (1; L = PEt_3). Using a routine pulse width we were able to derive no information from the CO signals. Carbonyl carbons have very long relaxation times, consequently with successive pulses even of short duration (corresponding to dip angles of, say, 25°) steady state is not reattained before the succeeding pulse and the signal becomes attenuated. We resorted therefore to extremely short pulses (dip angle, 13°), rather more scans

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[17] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York and London, 1972, p. 197.

(*ca.* 80 k), and maintained a pulse repetition rate equal to the acquisition time for each transient. Using such conditions we were able to positively identify C^2 by its phosphorus-splitting pattern (insert Figure 3). Unfortunately we were never able to improve signal-to-noise ratios sufficiently to 'see' the platinum satellites for either C^2 or C^3.

TABLE 3

22.63 MHz ^{13}C Chemical shifts [a] and coupling constants [b] for complexes (1)

	$C^{5\,c}$				C^4			C^3	
			^2J(CP)				^3J(CP)		^3J(CP)
L	δ	^1J(PtC)	*cis*	*trans*	δ	^2J(PtC)	(*trans*)	δ	(*trans*) [d]
$AsPh_3$	183.3	1 056			136.3	48		203.9	
PPh_3	191.1	920	91	8	136.6	42	9	206.3	22
PEt_2Ph	185.7	882	90	9	135.9	42	9	204.5	22
PEt_3	188.8	871	93	10	137.8	40	9	207.0	22
$PMePh_2$	190.9	892	93	8	136.9	40	9	206.4	21
py	165.1	1 158			*g*			*g*	

	C^2			$C^{1'}$	
		^2J(CP)			
L	δ	*trans*	*cis*	δ	Other data
$AsPh_3$	218.1			145.4	
PPh_3	228.4	90	6	145.3	
PEt_2Ph	231.6	108	3	144.9	
PEt_3	235.9	107	7	146.7	$\delta(C^{4'})$ 127.1,[e] $\delta(C^{2',6'})$ 127.3, $\delta(C^{3',5'})$ 128.0
$PMePh_2$	231.5	107	9	146.5	Phosphine methyls:[f] C^1 δ 12.0, ^1J(PC) 26, ^2J(PtC) 13, C^2 δ 13.8, ^1J(PC) 32, ^2J(PtC) 27
py	*g*			151.5	

[a] In p.p.m. downfield of internal $SiMe_4$. [b] In Hz. [c] See Figure 2 or 3. Referred to as 'C_v' in the text. [d] The shortest coupling route is referred to by the 'number of bonds' notation (see also C^2). [e] Phenyl carbons, see Figure 3. [f] Assigned according to the magnitude of ^2J(PtC) and the known *trans* influence of the adjacent ligand (see ^{31}P *N.M.R.* section). [g] Not observed.

Inspection of $^1J(PtC_v)$ values from Table 3 shows that the direct coupling constant reflects *trans* influence correctly, *i.e.* $PEt_3 > PEt_2Ph > PMePh_2 > PPh_3 > AsPh_3 >$ py. As postulated, changes in $^1J(PtC_v)$ are dominated by changes in $\alpha^2_{Pt(6s)}$. It is interesting to note that the indirect coupling to C^4, ^2J(PtC), also follows the correct order, although compared to the direct coupling this parameter is less sensitive to change.

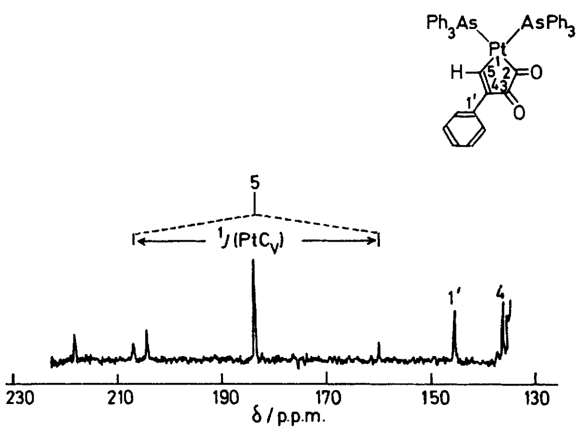

FIGURE 2 22.63 MHz ^{13}C N.m.r. spectrum (80 k scans) of carbons 2—5 and 1′ in $[Pt(AsPh_3)_2(\sigma\text{-pcbd})]$

^{31}P *N.M.R. Spectra.*—During the course of our preliminary investigation of cyclobutenedionemetal complexes we noted that the proton-decoupled ^{31}P n.m.r. spectrum of $[Pt(\eta\text{-pcbd})(PPh_3)_2]$ consisted of an AB quartet (with platinum satellites) and that this resulted in a deceptively simple ABX proton spectrum.[14] In order to verify that this was not the case with the ring-opened complexes and that the platinum–proton coupling constants were justifiably obtained by simple first-order analysis, we undertook to record the phosphorus spectra of (1; L = PPh_3, $PMePh_2$, or PEt_3). The spectra, as expected, each consisted of two well separated doublets with the appropriate platinum satellites. We were able to distinguish between phosphorus atoms by irradiating the phosphine ethyl protons in $[Pt(\sigma\text{-pcbd})(PEt_3)_2]$ selectively using a narrow modulation range (*ca.* 200 Hz). This enabled us to observe the coupling $^3J(PH_v)$ between the vinylic proton and the *trans*-phosphorus atom to higher field. We designate this P^1 in accordance with the nomenclature used earlier for the phosphine methyl

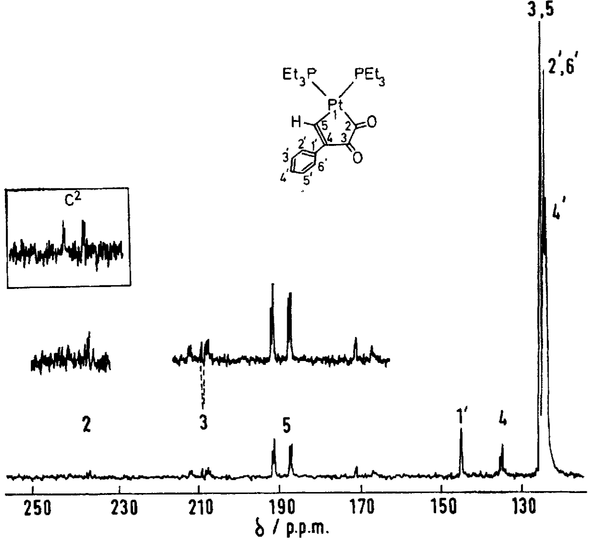

FIGURE 3 22.63 MHz ^{13}C N.m.r. spectrum (50 000 scans) of carbons 2—5 and 1′—6′ in $[Pt(\sigma\text{-pcbd})(PEt_3)_2]$. Insert shows phosphorus-splitting pattern for C^2 obtained as described in the text protons. The magnitudes of $^1J(PtP^1)$ and $^1J(PtP^2)$ indicate that the vinylic half of pcbd has itself a considerably larger *trans* influence than the COCO fragment. If the CH=CPh group is considered to have a *trans* influence similar to CF=CF_2,[7] the COCO group could be compared in terms of *trans* influence to a ligand such as pyridine.

TABLE 4

24.29-MHz ^{31}P N.m.r. data [a] for complexes (1)

	P^1 [b]		P^2			
L	δ [c]	$^1J(PtP)$ [d]	δ	$^1J(PtP)$	$^2J(PP)$	Other data
PEt_3	139.5	1 495	123.1	2 310	14	$^3J(P^1H_v)$ 2.6 [e]
$PMePh_2$	136.9	1 510	129.9	2 320	11.5	
PPh_3	117.3	1 486	113.2	2 448	10	

[a] Under conditions of broad-band decoupling of protons. [b] For nomenclature see text. [c] In p.p.m. upfield of external $P(OMe)_3$. [d] In Hz. [e] Ethyl protons selectively decoupled (see text).

DISCUSSION

Our results demonstrate clearly that in the case of direct coupling to platinum, even in the presence of constraints which can cause problems with two-bond coupling, variation in the *s* character of the Pt–C bond dominates the coupling constant. Deviation from behaviour of this type in the case of $^2J(PtH_v)$ may derive from two sources: (*i*) steric factors such that there is a contribution to the coupling from a non-Fermi-contact term; and (*ii*) perturbation specifically of this coupling as a result of differing *cis* influence in each complex. In the latter respect it is unfortunate that synthetic difficulties prevented us from examining *cis* and *trans* influences separately. Both theories have supporting arguments. Case (*i*) is supported by the position of pyridine. As a result of its small size, steric effects are less likely to play a part, and as we see $^1J(PtC_v)$ and $^2J(PtH_v)$ are the largest coupling constants in their respective series. That is, both ' behave ' from the point of view of the Fermi-contact equation and the expected weak *trans* influence of pyridine. We note also that the two-bond coupling to C^4 behaves reasonably normally. Molecular models do indicate that C^4 is less likely to experience steric constraints than H_v (in particular from the *cis* ligand) and that any angular dependence of the coupling constant in the former case would be therefore reduced. In support of case (*ii*) we note Mössbauer [18] and n.m.r.[19] results which show that *cis* and *trans* influences have an inverse relation. It may indeed be the case that variation in *cis* influence dominates $^2J(PtH_v)$ and that this is a result of the proximity of the *cis* ligand to H_v.

The differing sensitivity of indicator ligands to *trans* influence has been proposed [7] as the factor responsible for intercepts obtained when correlating coupling constants from two series of *trans*-influence measurements, for example $^1J(PtH)$ and $^2J(PtH)$ in $[PtHX(PEt_3)_2]$ and $[PtMeX(PEt_3)_2]$. It has been further proposed that such differing sensitivities arise as a result of differing degrees of polarisation of the platinum–indicator bond towards platinum with increased sensitivity arising from an increased coefficient of the Pt(6*s*) orbital in the bond. This certainly seems a satisfactory answer when applied to the very sensitive Pt–SCF_3 and Pt–H indicators.[7] We note, however, that $^1J(PtC_v)$ in our $[Pt(\sigma\text{-pcbd})L_2]$ complexes (L = $PMePh_2$, $AsPh_3$, or py) has roughly equal sensitivity to the changing nature of L as $^1J(PtC)$ in *trans*-$[PtMeL(PMe_2Ph)_2]^+$ (L = PMe_2Ph, $AsPh_3$, or py).[11] Given the differing degrees of polarisability of an sp^2 compared to an sp^3 carbon this was not expected, although the differing complex geometry as well as charge makes a more definitive statement impossible.

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