Platinum–Phosphorus Bond Lengths and Nuclear Magnetic Resonance Coupling Constants in Complexes of Tri(n-alkyl)- and Tricyclohexylphosphines. Crystal and Molecular Structure of *trans*-Di-iodobis(trimethylphosphine)platinum(II) †

By **Peter B. Hitchcock,* Barbara Jacobson,** and **Alan Pidcock,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The crystal and molecular structure of *trans*-$[PtI_2(PMe_3)_2]$ has been determined. Crystals are monoclinic, space group $P2_1/n$, with $a = 8.845(6)$, $b = 10.298(8)$, $c = 7.936(5)$ Å, $\beta = 95.12(4)°$, and $Z = 2$. Intensities have been measured by diffractometer and the structure solved by the heavy-atom method and refined to R 0.041. The crystal comprises discrete centrosymmetric molecules with only small deviations from square-planar co-ordination [Pt–P 2.315(4) and Pt–I 2.599(2) Å]. The intramolecular H · · · I distances are longer than in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$. The configuration of the cyclohexyl groups of the $P(C_6H_{11})_3$ ligands is determined by H · · · H interactions and leads to strong H · · · I interactions between hydrogen atoms on two α-carbon atoms and the iodide ligands, with consequent lengthening of the Pt–P and Pt–I bonds in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$. The coupling constants ^1J(Pt–P) for *trans*-di-iodo(tricyclohexylphosphine) complexes are larger than expected, probably due to large $|\Psi_{Pt,6s}(0)|^2/(^3\Delta E)$ terms for complexes with bonds lengthened by steric repulsions.

A CORRELATION between Pt–P bond lengths and n.m.r. coupling constants ^1J(Pt–P) in trialkylphosphine complexes of platinum(II) [1] led us to expect that the exceptionally long Pt–P bond in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ [2] would be associated with a relatively small value of the coupling constant ^1J(Pt–P) of *ca.* 1 500 Hz. The measured value (2 288 Hz) was, however, of normal magnitude for *trans*-bis(trialkylphosphine) complexes [3] and furthermore was very similar to the values reported for the related complexes *trans*-$[PtI_2(PR_3)_2]$ [R = Me, ^1J(Pt–P) 2 230 Hz; [4] R = Bu, ^1J(Pt–P) 2 200 Hz [5]]. It was evident, therefore, that the correlation failed to accommodate the results for *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ and that it may also fail for other iodoplatinum(II) complexes. We have therefore measured coupling constants for a range of $P(C_6H_{11})_3$ complexes to compare them with values for related PR_3 (R = Me, Et, or Bu) complexes, and have carried out an *X*-ray crystal-structure analysis of *trans*-$[PtI_2(PMe_3)_2]$ for comparison with the $P(C_6H_{11})_3$ analogue.

EXPERIMENTAL

General.—All the reactions were carried out under dry nitrogen. Solvents were dried and degassed before use. The $^{31}P-\{^1H\}$ spectra were obtained at 40.5 MHz with a JEOL PFT spectrometer using dichloromethane solutions in 8-mm tubes with $P(OMe)_3$ in C_6D_6 as external reference. Elemental analyses were by Mrs. G. Olney of this laboratory.

Complexes.—The complexes *trans*-$[PtX_2(PR_3)_2]$ (X = Cl; R = Me, Et, or Bu; X = I, R = Et or Bu), *trans*-$[PtXH(PEt_3)_2]$ (X = Cl or I), and *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ [6] were prepared by established methods and characterised by elemental analyses, m.p., and $^{31}P-\{^1H\}$ n.m.r. spectra.

trans-*Di-iodobis(trimethylphosphine)platinum*(II). This complex was obtained by treatment of aqueous $K_2[PtI_4]$ with $Ag[NO_3]\cdot PMe_3$.[7] The yellow-green precipitate was extracted with dichloromethane. The resulting solution was evaporated to dryness and the residue was further purified by Soxhlet extraction with chloroform, evaporation of solvent, and recrystallisation from dichloromethane–methyl iodide to give the product as yellow crystals, m.p. 190—191 °C (lit.,[7] 194—195 °C), yield 67% (Found: C, 12.0; H, 3.0. Calc. for $C_6H_{18}I_2P_2Pt$: C, 12.2; H, 3.1%).

trans-*Dichlorobis(tricyclohexylphosphine)platinum*(II). A solution of $[PtCl_2(SEt_2)_2]$ (1.9 g) and $P(C_6H_{11})_3$ (2.4 g) in benzene (50 cm^3) was put aside for 15 min. Addition of hexane (10 cm^3) gave the product as a cream solid, m.p. >300 °C (lit.,[8] 322—325 °C), yield 83% (Found: C, 51.7; H, 7.8. Calc. for $C_{36}H_{66}Cl_2P_2Pt$: C, 52.3; H, 8.0%). Obtained in a similar manner from $[PtI_2(SEt_2)_2]$ was *trans*-di-iodobis(tricyclohexylphosphine)platinum(II) as an orange-yellow powder, m.p. 285—289 °C (lit.,[8] 289—292 °C), yield 59% (Found: C, 43.0; H, 6.9. Calc. for $C_{36}H_{66}I_2P_2Pt$: C, 42.8; H, 6.6%).

trans-*Chlorohydridobis(tricyclohexylphosphine)platinum*(II). A benzene solution of *trans*-$[PtClH(PEt_3)_2]$ (1.0 g) was treated with $P(C_6H_{11})_3$ (1.2 g). Evaporation of solvent gave a white powder which was recrystallised from dichloromethane–methanol to give the product, m.p. 230—235 °C (lit.,[8] 235—237 °C), yield 50% (Found: C, 53.3; H, 8.8. Calc. for $C_{36}H_{67}ClP_2Pt$: C, 54.6; H, 8.5%). Obtained similarly from *trans*-$[PtHI(PEt_3)_2]$ was *trans*-hydridoiodobis(tricyclohexylphosphine)platinum(II), m.p. 255—256 °C (lit.,[8] 257—258 °C), yield 50% (Found: C, 49.0; H, 7.8. Calc. for $C_{36}H_{67}IP_2Pt$: C, 48.9; H, 7.6%).

cis-*Dichloro(diethyl sulphide)(tricyclohexylphosphine)platinum*(II). A solution of $P(C_6H_{11})_3$ (0.9 g) in benzene (100 cm^3) was added dropwise to a vigorously stirred solution of $[PtCl_2(SEt_2)_2]$ (1.5 g) in benzene (20 cm^3). The volume of solution was reduced to 10 cm^3 by evaporation of

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† No reprints available.

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solvent under reduced pressure. Addition of diethyl ether gave the product as a pale yellow powder, m.p. 159—165 °C, yield 88% (Found: C, 45.8; H, 7.8. $C_{24}H_{48}Cl_2PPtS$ requires C, 45.3; H, 7.6%).

cis-*(Diethyl sulphide)di-iodo(tricyclohexylphosphine)-platinum*(II). A solution of $P(C_6H_{11})_3$ (0.29 g) in benzene (100 cm^3) was added dropwise to a vigorously stirred solution of $[PtI_2(SEt_2)_2]$ (0.66 g) in benzene (20 cm^3). The volume of solution was reduced to 10 cm^3 by evaporation of solvent under reduced pressure. Addition of hexane gave the product as a yellow-orange solid, m.p. 173—174 °C, yield 62% (Found: C, 33.0; H, 5.1. $C_{24}H_{48}I_2PPt_2$ requires C, 32.2; H, 5.3%).

trans-*Dichloro(pyridine)(tricyclohexylphosphine)platinum*-(II). A solution of *cis*-$[PtCl_2\{P(C_6H_{11})_3\}(SEt_2)]$ (0.2 g) in benzene (10 cm^3) was treated with pyridine (1 cm^3) and the mixture put aside for 3 h. Addition of hexane gave the product as yellow crystals, m.p. 120—122 °C, yield 58% (Found: C, 44.4; H, 6.7; N, 2.1. $C_{23}H_{38}Cl_2NPPt$ requires C, 44.4; H, 6.1; N, 2.2%). Similarly prepared were trans-*di-iodo(pyridine)(tricyclohexylphosphine)-platinum*(II) as orange-yellow needles, m.p. 157—158 °C, yield 49% (Found: C, 34.1; H, 4.8; N, 2.0. $C_{23}H_{38}I_2NPPt$ requires C, 34.2; H, 4.7; N, 1.7%), and trans-*(diethylamine)di-iodo(tricyclohexylphosphine)platinum*(II) as pale yellow needles, m.p. 210—215 °C, yield 56% (Found: C, 34.3; H, 4.9; N, 2.0. $C_{22}H_{34}I_2NPPt$ requires C, 33.3; H, 4.3; N, 1.8%).

Complexes trans-$[PtCl_2L\{P(C_6H_{11})_3\}]$ [L = $P(OPh)_3$, $PPh(OMe)_2$, or $P(NMe_2)_3$]. Solutions of these complexes were prepared *in situ* by treatment of a solution of *trans*-$[PtCl_2\{P(C_6H_{11})_3\}(SEt_2)]$ in dichloromethane with an equimolar proportion of L. The $^{31}P-\{^1H\}$ n.m.r. spectra recorded within 1 h comprised AB spectra with large (>500 Hz) values of $^2J(PPtP)$, establishing the constitution and *trans* configuration of the complexes.[9] When left to stand the solutions gave white insoluble products which were not characterised.

Crystal Data for trans-$[PtI_2(PMe_3)_2]$.—$C_6H_{18}I_2P_2Pt$, M = 601.07, Monoclinic, $a = 8.845(6)$, $b = 10.298(8)$, $c = 7.936(5)$ Å, $\beta = 95.12(4)°$, $U = 720.0$ Å^3, $Z = 2$, $D_m = 2.84$ (by flotation), $D_c = 2.77$ g cm^{-3}, $F(000) = 536$, Mo-K_α radiation, μ(Mo-K_α) = 53 cm^{-1}, space group $P2_1/n$ from systematic absences; $0k0$ for k odd and $h0l$ for $h + l$ odd.

Crystallographic Measurements.—The crystal was bounded by faces of the form {100}, {010}, and {101} with distances between parallel faces of 0.100, 0.098, and 0.143 mm. It was accurately centred on a Y290 Hilger and Watts four-circle diffractometer (graphite crystal monochromator) and unit-cell parameters were determined by least-squares treatment of the accurate setting angles of 12 strong reflections [λ(Mo-$K_{\alpha1}$) 0.709 26 Å]. Data were collected by an ω—2θ scan in 60 steps of 0.5 s to $2\theta_{max.}$ 60°; backgrounds at either side of each peak were counted for 15 s. The integrated intensities of three standard reflections, remeasured after every 100 reflections, varied by only ±2%, so correlations for crystal decay were unnecessary. Lorentz and polarisation corrections were applied and the data were corrected for absorption with the program ABSCOR.[10] Symmetry-equivalent reflections were averaged to give 2 362 independent reflections of which 2 026 with $I > 3\sigma(I)$ were used in the structure analysis.

Structure Determination.—The positions of all the non-hydrogen atoms were obtained by the usual Patterson and Fourier methods. Scattering-factor curves for non-hydrogen atoms were taken from ref. 11 and that for hydrogen from ref. 12. The anomalous-dispersion factors for carbon, iodine, phosphorus, and platinum were taken from ref. 13. Atoms other than hydrogen were refined by full-matrix least squares with anisotropic Debye–Waller factors to R 0.046. Six prominent electron-density regions on a subsequent difference map could be assigned to hydrogen atoms. All the nine hydrogen atoms were placed at idealised positions [d(C–H) 1.08 Å, HCH 109.5°] with $U_{iso} = 0.047$ Å^2, and their contributions to F_c were included in further cycles of refinement as fixed contributions, to give R 0.041 and R' 0.046. The final weighting scheme was determined from $w = 1/\{1 + [(F_o - 60.0)/38.8]^2\}$ which gave approximately constant averages of $w(|F_o| - |F_c|)^2$ against $|F_o|$. The final maximum shift-to-error was 0.11 and the final difference-Fourier map was everywhere less than 0.35 eA^{-3}. Structure solution and refinement were carried out using the 'X-RAY' program system.[14]

Visible–U.v. Spectra.—Spectra were recorded for dichloromethane solutions of *trans*-$[PtI_2(PR_3)_2]$ (R = Me or C_6H_{11}) on a Unicam SP 800 spectrophotometer. The complex with R = C_6H_{11} absorbs at longer wavelengths than for R = Me: R = Me, $\lambda_{max.}$ 2 830 (ε 1.3 × 10^5), 3 280 (ε 3 × 10^4); R = C_6H_{11}, $\lambda_{max.}$ 2 950 (ε 9 × 10^4), 4 060 Å (ε 1 × 10^4 mol^{-1} dm^{-4}).

RESULTS AND DISCUSSION

Crystal Structure of trans-$[PtI_2(PMe_3)_2]$.—Final atomic co-ordinates are given in Table 1 and a diagram of the molecular structure with the numbering scheme for the atoms is given in Figure 1. Observed and calculated

TABLE 1

Fractional atomic co-ordinates (× 10^4) with standard deviations in parentheses

Atom	x	y	z
Pt	0	0	0
I	−2 360(1)	501(1)	1 619(1)
P	1 297(4)	1 582(4)	1 620(5)
C(1)	3 248(16)	1 958(17)	1 320(21)
C(2)	475(19)	3 142(15)	1 426(25)
C(3)	1 424(19)	1 212(17)	3 852(18)
H(1)	3 735	2 606	2 279
H(2)	3 836	1 025	1 404
H(3)	3 326	2 306	29
H(4)	974	3 773	2 409
H(5)	596	3 601	210
H(6)	−747	3 071	1 560
H(7)	2 057	307	4 070
H(8)	1 987	1 958	4 617
H(9)	293	1 071	4 244

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structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22110 (10 pp.).*

The crystals are composed of discrete centrosymmetric units separated by normal van der Waals contacts. The deviation of the bond angles at platinum from 90° is small (Table 2) and arises from an imbalance about the Pt–I bonds in the I · · · H and I · · · C steric repulsions (Table 2, van der Waals contact distances: I · · · H 3.15, I · · · C 3.60 Å). Carbon atom C(1) is close to the co-ordination plane [torsion angle I′–Pt–P–C(1) 0.6°] and H(2) and H(3) adopt positions in which contact with I′ is minimised. The orientation of the hydrogen atoms of the other two methyl groups is approximately that given by C_3 rotation of the C(1) methyl group about the Pt–P axis. The distances I · · · H(6 and 9) and H(4) · · · H(8) [Table 2(*c*)] do not imply strong repulsions.

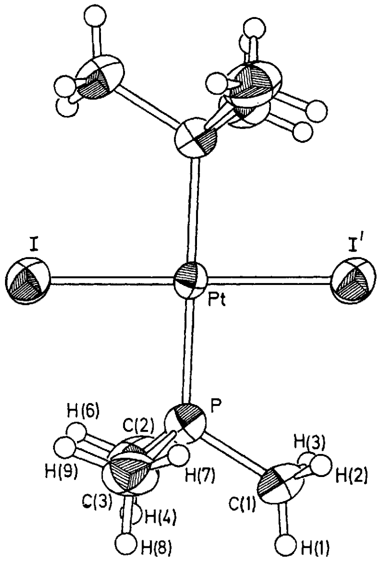

FIGURE 1 View of the molecular structure. Thermal-vibration ellipsoids enclose 50% of probability

The configuration of the molecule is very similar to that of *trans*-[$PtBr_2(PEt_3)_2$] [15] in which the methyl groups occupy positions closely related to the positions of H(1), H(5), and H(7) in Figure 1; these positions minimise steric hindrance between the methyl groups and between the methyl groups and the *cis* ligands. The Br–Pt–P angle corresponding to I′–Pt–P is 92.8(1)°, the deviation from 90° resulting from Br · · · H and Br · · · C steric interactions similar to those present in the iodo-complex. The Pt–P distance in the bromo-complex [2.314(8) Å] is identical to that in the iodo-complex (Table 2) and is significantly longer than in *trans*-[$PtH_2\{P(C_6H_{11})_3\}_2$] [2.26(1) Å].[16] This difference (*ca.* 0.05 Å) does not appear to be due to steric repulsion between *cis* ligands in the bromo- and iodo-complexes because the non-bonded distances are only slightly shorter than normal van der Waals contacts. The relative weakness of steric interactions between *cis* bromo and PEt_3 ligands is also indicated by the fact that the Br–Pt–P angle opens only to 94° in *trans*-[$PtBrH(PEt_3)_2$].[17] Since the PMe_3, PEt_3, and $P(C_6H_{11})_3$ ligands have similar Pt–P–C angles in platinum(II) complexes, electronic differences between them are presumably small, so the difference in Pt–P lengths in *trans*-[$PtX_2(PR_3)_2$] (X = H, R = C_6H_{11}; X = Br, R = Et; X = I, R = Me) must be mainly due to different effects of H and Br or I on the platinum orbitals. That is, that the electronic *cis* influence (tendency to weaken bonds in the *cis* position) is in the order H < Br, I.

TABLE 2

Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Bond lengths			
Pt–I	2.599(2)	P–C(2)	1.764(16)
Pt–P	2.315(4)	P–C(3)	1.805(15)
P–C(1)	1.805(15)		
(*b*) Bond angles			
I–Pt–P	88.0(1)	Pt–P–C(3)	112.4(6)
I′–Pt–P	92.0(1)	C(1)–P–C(2)	100.6(8)
Pt–P–C(1)	120.6(6)	C(1)–P–C(3)	101.4(8)
Pt–P–C(2)	114.3(6)	C(2)–P–C(3)	105.5(9)
(*c*) Intramolecular non-bonded distances			
I′ · · · H(2)	3.06	I′ · · · C(1)	3.485(17)
I′ · · · H(3)	3.24	I · · · C(2)	3.712(16)
I · · · H(6)	3.01	I · · · C(3)	3.718(16)
I · · · H(9)	3.05	H(4) · · · H(8)	2.66

The Pt–I bond length [2.599(2) Å] in *trans*-[$PtI_2(PMe_3)_2$] is much shorter than that in *trans*-[$PtMe(I)(PPh_3)_2$]·SO_2 [2.707(1) Å],[18] showing that the *trans* influence of iodide (on the Pt–I length) is much less than that of methyl. Since both iodine and carbon have electronegativity 2.5,[19] this suggests that the correlation between the *trans* influence and electronegativity of the donor atom applies only to a rather limited set of ligands having light donor atoms (H, C, O, Si, P, and Cl).[20]

Comparison of the Structures of trans-[$PtI_2(PR_3)_2$] (R = Me *or* C_6H_{11}).—The ready elimination of $P(C_6H_{11})_3$ from *trans*-[$PtI_2\{P(C_6H_{11})_3\}_2$] has been attributed to steric crowding, and this has been supported by an *X*-ray crystal-structure determination [2] which shows that the molecules are centrosymmetric with exceptionally long Pt–P bonds [2.371(2) Å], have Pt–I bonds [2.612(1) Å] slightly longer than in the PMe_3 complex, and have

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* For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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several I · · · C distances [I · · · C(13) 3.396(8), I · · · C(14) 3.725(9), I · · · C(1) 3.483, I · · · C(6) 3.719(9), I · · · C(8) 3.716 Å] shorter than or close to the van der Waals contact distance (3.60 Å). We examined the steric interactions in more detail by calculating the idealised positions of the hydrogen atoms (C–H 1.08 Å, C–C–H 109.5°) (Figure 2); intramolecular I · · · H distances less than 3.3 Å are given in Table 3 together with distances (less than 2.3 Å) between hydrogen atoms of different cyclohexyl groups.

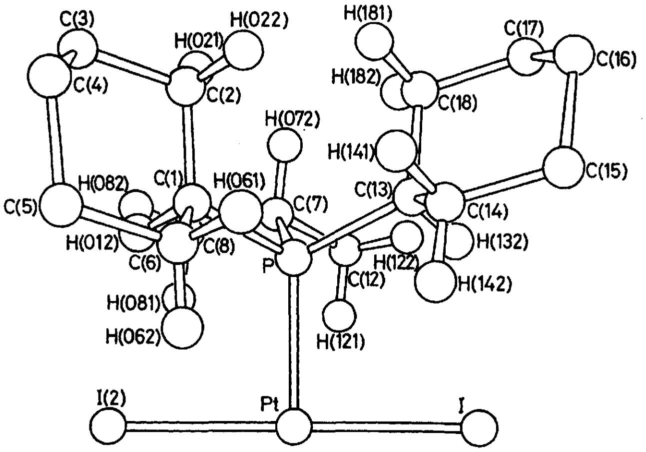

FIGURE 2 View of part of the molecular structure of *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$.[2] Hydrogen atom positions are idealised, and some hydrogen atoms and atoms C(9)—C(11) have been omitted for clarity

The configuration of the cyclohexyl groups of the $P(C_6H_{11})_3$ ligands appears to be determined by interactions between α- and β-hydrogen atoms on different cyclohexyl groups (Table 3 and Figure 2). The ligand is roughly symmetrical about the plane containing atoms Pt, P, and C(7). There are short contact distances H(022) · · · H(181) and H(061) · · · H(141) between axial hydrogen atoms on β-carbon atoms of the two rings related by the symmetry plane, and the configuration of the third ring is determined by contacts H(012) · · · H(082), H(021) · · · H(072), and H(122) · · · H(132) (van der Waals contact distance 2.4 Å) between itself and the other two rings. We have also shown that the configuration of the $P(C_6H_{11})_3$ ligand in $[NiMe(MeCOCHCOMe)\{P(C_6H_{11})_3\}]$ and in other $P(C_6H_{11})_3$ complexes[21] is almost identical to that for *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$, providing further support for the view that the configuration is mainly determined by interactions within the ligand and not by interactions with the *cis* ligands of the complex.

With this configuration of the $P(C_6H_{11})_3$ ligand, the orientation of the PC_3 moiety adopted in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ minimises the H · · · I interactions (Table 3, van der Waals contact distance 3.15 Å), but H · · · H interactions between the cyclohexyl groups prevent further relief of the very short contacts I(1) · · · H(132) and I(2) · · · H(012) by rotation of the cyclohexyl groups about the P–C bonds. Since the remaining short I · · · H contacts (Table 3) are comparable with those in *trans*-$[PtI_2(PMe_3)_2]$ (Table 2), for which the steric effects appear to be too small too affect the Pt–P length significantly, the lengthening of the Pt–P bond (and to a smaller extent the Pt–I bond) in the $P(C_6H_{11})_3$ complex can be attributed to the repulsions I(1) · · · H(132) and I(2) · · · H(012). These hydrogen atoms on the α-carbon atoms of $P(C_6H_{11})_3$ are much closer to the iodine atoms than any in the PMe_3 complex, even though the Pt–P bond is substantially longer in the $P(C_6H_{11})_3$ complex, and such short I · · · H contacts are not expected to occur in complexes of tri(n-alkyl)phosphines because they derive from the unusual positions of H(132) and H(012) in the rather rigid $P(C_6H_{11})_3$ ligand.

TABLE 3

Intramolecular non-bonded distances (Å) in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ *

I(1) · · · H(132)	2.63	H(012) · · · H(082)	2.17
I(2) · · · H(012)	2.77	H(021) · · · H(072)	2.23
I(1) · · · H(142)	3.20	H(022) · · · H(181)	2.03
I(2) · · · H(081)	3.06	H(061) · · · H(141)	2.11
I(2) · · · H(062)	3.11	H(122) · · · H(132)	2.27

* From calculations based on fractional atomic co-ordinates given in ref. 2. The unit-cell parameters of ref. 2 require transposition; correct parameters are $a = 10.269$, $b = 11.139$, $c = 10.235$ Å, $\alpha = 90.85$, $\beta = 113.84$, and $\gamma = 110.91°$.

Coupling Constants ^1J(Pt–P).—Coupling constants ^1J(Pt–P) for some platinum(II) complexes of $P(C_6H_{11})_3$ and PR_3 (R = Me, Et, or Bu^n) are given in Table 4. The correlation between ^1J(Pt–P) and the Pt–P length for tri(n-alkyl)phosphine complexes[1] satisfactorily accommodates the results for *trans*-$[PtI_2(PMe_3)_2]$, the coupling constant and bond length being similar to those for *trans*-$[PtBr_2(PEt_3)_2]$ [^1J(Pt–P) 2 327 Hz, l(Pt–P) 2.314(8) Å [15]]. On the basis of the correlation, the long Pt–P bond in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ would be expected to be associated with a coupling constant ^1J(Pt–P) *ca.* 1 500 Hz; the experimental result is 2 288 Hz.

The molecular-orbital expression for the Fermi-contact contribution to ^1J(Pt–P) [equation (1)] contains terms $|\psi_s(0)|^2$, the square of the magnitude of the valence-state s orbital for Pt and P, and $P'_{s_{Pt}s_P}$ is the

$$^1J(\text{Pt–P}) = (64\pi^2/9)\gamma_{Pt}\gamma_P\beta^2(^3\Delta E)^{-1}|\psi_{Pt,6s}(0)|^2|\psi_{P,3s}(0)|^2(P'_{s_{Pt}s_P})^2 \quad (1)$$

s-orbital bond order. Both terms can be affected by changes in the groups attached to phosphorus, $|\psi_{P,3s}(0)|^2$ through changes in orbital contraction and $P'_{s_{Pt}s_P}$ through changes in the s character of the phosphorus orbital used in the Pt–P bond. Since the electronic effects of n-alkyl and C_6H_{11} groups are similar and the mean Pt–P–C angles in *trans*-$[PtI_2(PR_3)_2]$ [115.8(6)°, R = Me; 114.4°, R = C_6H_{11}] and *trans*-$[PtBr_2(PEt_3)_2]$ (115.1°)[15] are also very similar, the terms in equation (1)

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[21] B. L. Barnett and C. Krüger, *J. Organometallic Chem.*, 1972, **42**, 169.

associated with the phosphorus orbitals are not expected to differ significantly for R = n-alkyl and C_6H_{11}. This conclusion is supported by the similarity of coupling constants ^1J(H–P) in $[P(C_6H_{11})_3H]^+$ (457 Hz) and $[PBu_3H]^+$ (460 Hz).[22] Also, for the dichloro- and especially the chlorohydrido-complexes in Table 4 it is presumed that both the coupling constants and Pt–P lengths are similar for R = C_6H_{11} or n-alkyl, because the steric interactions responsible for the long Pt–P bond in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ are expected to be insignificant when the ligands *cis* to $P(C_6H_{11})_3$ are small. Consistently, the results for *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ [Pt–P 2.26(1) Å, ^1J(Pt–P) 2 800 Hz],[23] where the steric interactions between *cis* ligands are negligible, fit well in the correlation between Pt–P lengths and coupling constants for complexes with tri(n-alkyl)phosphine ligands.[23]

TABLE 4

Phosphorus-31 n.m.r. parameters of some platinum(II) complexes [a,b]

	L			
Complex	$P(C_6H_{11})_3$	PMe_3	PEt_3	PBu_3
trans-$[PtCl_2L_2]$	2 397 (123.6)	2 379 [c]	2 400 (127.8)	2 384 [d]
trans-$[PtI_2L_2]$	2 288 (129.9)	2 230 [c]	2 266 (139.8)	2 200 [d]
trans-$[PtClHL_2]$	2 803 (101.5)		2 708 (117.2)	
trans-$[PtH(I)L_2]$	2 737 (103.7)		2 647 (121.2)	
trans-$[PtCl_2(py)L]$	3 394 (128.8)		3 362 (140.4)	3 360 [d]
trans-$[PtI_2(py)L]$	3 279 (129.3)		3 169 (146.5)	3 140 [d]
trans-$[PtI_2(NHEt_2)L]$	3 259 (126.3)		3 152 (143.7)	
trans-$[PtCl_2L\{P(OPh)_3\}]$	2 554 [e] (106.6)		2 236 [f] (137.7)	2 512 [g] (135.2)
trans-$[PtCl_2L\{P(NMe_2)_3\}]$	2 490 [h] (123.8)			
trans-$[PtCl_2L\{PPh(OMe)_2\}]$	2 368 [i] (99.3)		2 345 [j] (128.7)	

[a] Complexes used in this work were dissolved in dichloromethane. [b] J(Pt–P) in Hz; values of δ (in p.p.m.) from $P(OMe)_3$ in C_6D_6 are given in parentheses. A positive shift is to high field of the reference. [c] Ref. 4. [d] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707. [e] ^2J(PP) 664 Hz. [f] ^2J(PP) 601 Hz. [g] ^2J(PP) 708 Hz. [h] ^2J(PP) 640 Hz. [i] ^2J(PP) 564 Hz. [j] ^2J(PP) 598 Hz.

Since the *s*-orbital bond order $P'_{s_{Pt}s_P}$ presumably decreases with increasing bond length, the term $|\psi_{Pt,6s}(0)|^2/(^3\Delta E)$ thus appears to be larger for R = C_6H_{11} than Me. Previous studies [1,3] have suggested that this term varies only to a small extent in platinum(II) complexes, but these studies have been exclusively concerned with complexes in which steric interactions between ligands are relatively small, and in which the bond lengths are therefore determined by electronic factors alone. In *trans*-$[PtI_2(PR_3)_2]$ steric effects result in both the Pt–P and Pt–I bonds being longer for R = C_6H_{11} than for Me. This bond lengthening is expected to increase the positive charge on Pt and to increase $|\psi_{Pt,6s}(0)|^2$ by contraction of the 6*s* orbital and it is also expected to decrease the separation of the bonding and antibonding molecular orbitals and cause a reduction in $^3\Delta E$. Consistent with this latter effect, the complex with R = C_6H_{11} absorbs at longer wavelengths than that with R = Me (see Experimental section).

This suggests that the correlation between the lengths and coupling constants of Pt–P bonds should fail in complexes where the platinum–ligand bond lengths are substantially affected by steric interactions; an abnormally large value of $|\psi_{Pt,6s}(0)|^2/(^3\Delta E)$ appears to be associated with such complexes. For example, this conclusion should apply to all the *trans*-di-iodo(tricyclohexylphosphine) complexes in Table 4, in which steric effects can be presumed to lead to long Pt–P bonds.

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[22] W. McFarlane and R. F. M. White, *Chem. Comm.*, 1969, 744.
[23] B. Jacobson and A. Pidcock, unpublished work.