Molecular and Crystal Structure of *trans*-Cyanomethylhydridobis(triphenylphosphine)platinum(II), [PtH(CH$_2$CN)(PPh$_3$)$_2$]

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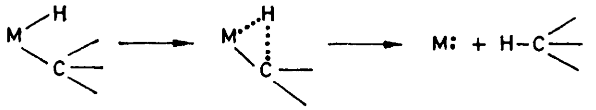
The structure of the title complex has been determined from three-dimensional X-ray data. The complex crystallises in the monoclinic system, space group C^5_{2h}-$P2_1/n$ with four molecules in a unit cell of dimensions a = 14.610(6), b = 18.809(7), c = 12.083(5) Å, and β = 93.0(1)°. Least-squares refinement has led to a value of the conventional R index (on F) of 0.039 for the 2 544 independent reflections having $I > 3\sigma(I)$. The complex has typical square-planar co-ordination. Structural parameters: Pt–P 2.272(4) and 2.276(4), Pt–H 1.5, Pt–C(37) 2.16(1), C(37)–C(38) 1.43(2), C(38)–N(1) 1.12(3) Å; Pt–C(37)–C(38) 106(1) and C(37)–C(38)–N(1) 175(2)°. The crystal packing is determined only by van der Waals interactions and all intermolecular contacts agree with those predicted from radii-sum rules.

HYDRIDO-σ-ALKYL complexes of transition metals have been generally regarded as thermally unstable. For example, they have been suggested as intermediates in catalytic processes mostly involving hydrogenation of olefins [1,2] and activation of the C–H bond of saturated hydrocarbons.[3,4] This instability was interpreted on the basis of a three-centred interaction (Scheme) which is allowed when d orbitals participate in the bonding.[4] The *cis* reductive elimination of alkane can be rationalised if homolytic metal–carbon(sp^3) and metal–hydrogen bond dissociation is the dominant decomposition mechanism; nevertheless, other pathways are possible for the destruction of one or both M–H and M–C bonds.[2,3,5]



SCHEME

Particularly interesting among hydrido-σ-alkyl complexes are those of Pt^{II} of type [PtH(R)L$_2$], because they should have an enhanced thermal stability as compared to the analogous complex of Ni^{II} and Pd^{II}, and hence they can be regarded as models of more reactive intermediates. Hitherto, no complexes with both Pt–H and Pt–R$_H$ bonds were known, although a large number of dialkyl-[6,7] and some dihydrido-platinum(II) compounds with bulky phosphines [1,8] have been isolated. However, the synthesis and characterisation at −80 °C of some *cis*-[PtH(R)(PR'$_3$)$_2$] (R' = aryl) have recently been reported [9] together with preliminary kinetics of the ready intramolecular reductive elimination of HR at −25 °C.

Some evidence indicates that the Pt–C(sp^3) bond increases in strength with increasing electronegativity of the alkyl chain R$_X$, as dictated by alkyl substituents such as X = CN, F, NO$_2$, CO$_2$R, *etc.*[6,10–12] This enhanced Pt–R$_X$ bond strength may be invoked to explain the unusual stability of complexes containing both Pt–H and Pt–C bonds. Only a limited number of hydrido-σ-(substituted) alkyl complexes of Pt^{II} have been isolated to date: *trans*-[PtH(R$_X$)(PPh$_3$)$_2$] [R$_X$ = CF$_3$;[12] (CH$_2$)$_n$CN, n = 1, 2, or 3;[10] CH(CN)$_2$;[13] or C(CN)$_3$ [14]]; *cis*-[PtH(R$_X$)(PPh$_3$)(CNR)] (R$_X$ = CF$_3$ [12] or CH$_2$CN [11]); and [PtH(R$_X$)(L–L)] [R$_X$ = CF$_3$, (L–L) = 1,2-bis(diphenylphosphino)ethylene;[12] R$_X$ = (CH$_2$)$_n$CN (n = 1, 2, or 3) or CH$_2$C$_6$H$_4$CN-*o*, (L–L) = a diphosphine or diarsine [10]].

In square-planar platinum(II) complexes [PtH(R$_X$)L$_2$] the co-existence of the two ligands R$_X$ and H, both in *cis* and in *trans* positions, was thought to provide an ideal basis for a study of the structural features of these complexes, and of the possible implications for the more general subject of *cis* and *trans* influence. We present here the crystal and molecular structure of *trans*-[PtH(CH$_2$CN)(PPh$_3$)$_2$] (2). A preliminary communication on this complex and its parent *trans*-[PtCl(CH$_2$CN)(PPh$_3$)$_2$] (1) has been published.[15]

EXPERIMENTAL

Crystal-structure Analysis of trans-[PtH(CH$_2$CN)(PPh$_3$)$_2$].—Single crystals, suitable for X-ray analysis, were obtained by evaporation of the solvent from a solution of CH$_2$Cl$_2$–CH$_3$OH. The crystal used was a pale yellow transparent prism of dimensions *ca.* 0.050 × 0.10 × 0.20 mm. All X-ray experiments were performed on a single-crystal PW 1100 Philips diffractometer using graphite-monochromatised Mo-K_α radiation (λ = 0.710 7 Å). The unit-cell dimensions were determined on the basis of 25 strong reflections found by mounting the crystal at random, varying the orientation angles ϕ and ψ over ranges of 90 and 45° respectively, with detector positions varying between θ = 6 and 12°. For the determination of precise lattice parameters 20 strong reflections with $15 < \theta < 20°$ were considered and precise diffraction angles were evaluated as centres of gravity of their profiles $I = f(\theta)$ averaging over positive and negative θ values.

Integrated intensities for hkl reflections with $k, l \geqslant 0$ and $3 < \theta < 21°$ were measured using the θ—2θ scan mode with a scan speed of 3° min^{-1}, a scan width of 0.9°, and two background counts of 10 s at each end of the scan. The intensities of two standard reflections, which were measured every 2 h, decreased nearly linearly by *ca.* 10% during the course of data collection, presumably as a result of crystal decomposition. (The limitation of $\theta_{max.}$ at 21° and the speed of data collection were chosen by taking into account the crystal decay.) Of the 3 904 reflections thus considered, 2 544 having a net intensity greater than 3σ (σ = standard error based on counting statistics) were used in the structure determination and refinement; $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$ where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$. A value of 0.04 was assigned to the factor p to allow for other error sources. Intensities were corrected for Lorentz and polarisation effects and were converted into an absolute scale by Wilson's method. An absorption correction was applied following the method proposed by North *et al.*[16]

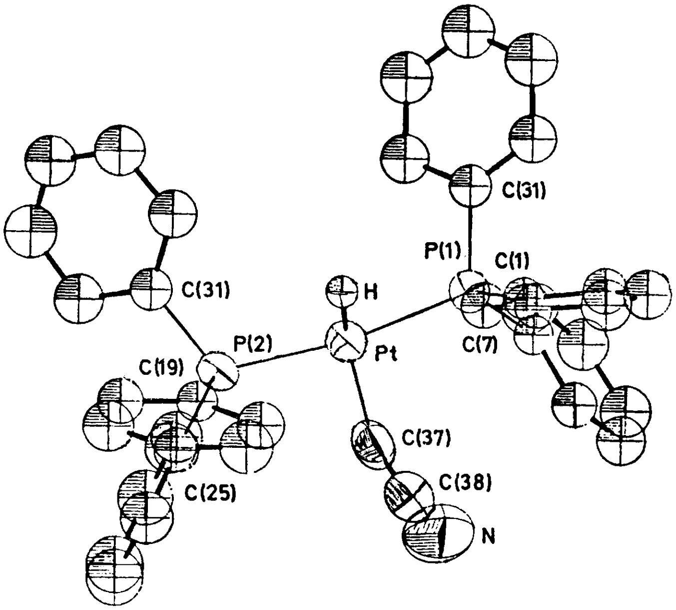


FIGURE 1 Molecular structure of *trans*-[PtH(CH$_2$CN)(PPh$_3$)$_2$] viewed down *a*

Crystal data. $C_{38}H_{33}NP_2Pt$, M 760.7, Monoclinic, a = 14.610(6), b = 18.809(7), c = 12.083(5) Å, β = 93.0(1)°, U = 3 316 Å^3, Z = 4, D_c = 1.52 g cm^{-3}, space group $P2_1/n$, μ(Mo-K_α) = 89.9 cm^{-1}.

The structure was determined by the heavy-atom technique. A sharpened-Patterson synthesis with the origin removed revealed the position of the platinum and phosphorus atoms. The positions of the remaining non-hydrogen atoms were derived from subsequent difference-Fourier maps. The structure was refined by full-matrix least-squares techniques, the quantity minimised being $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$. Atomic scattering factors for the platinum were taken from ref. 17, for the remaining non-hydrogen atoms from ref. 18, and for hydrogens from ref. 19. A correction for the real and imaginary parts of the anomalous dispersion was applied to Pt.[20]

The refinement was carried out by allowing the Pt atom to vibrate anisotropically and with isotropic thermal parameters for all non-hydrogen atoms. The conventional R value fell to 0.045. At this stage the co-ordinates of the phenyl-ring hydrogen atoms as well as those of the CH_2 hydrogen atoms were calculated assuming the C–H distance to be 0.95 Å and the C–C–H angles 120 and 109° respectively. The thermal parameters of the hydrogen atoms were assumed to be equal to those of the carbon atoms to which they are bonded. The refinement was carried on allowing Pt, P(1), and P(2) to vibrate anisotropically and the remaining non-hydrogen atoms isotropically; the structural parameters of the H atoms were included, as a fixed contribution, to the calculation of F_c. An electron-density difference map was calculated at this stage in an attempt to locate the hydrogen atom attached to the platinum atom. It was encouraging that the highest peak in the electron-density difference map (0.8 e Å^{-3}) was located in the approximate position for the hydrogen atom bound to platinum (Pt–H 1.5 Å). Fourier syntheses for different values of $[(\sin\theta)/\lambda]_{max.}$ for this peak never varied significantly and, therefore, the peak could represent the hydrogen atom. A final structure-factor calculation including the contribution of the hydrido-ligand, the position of which was not refined, gave a value of R 0.039, which was considered as final.

All data processing and computations were carried out using the '*X*-Ray '73' System of crystallographic programs.[21] Observed and calculated structure factors and thermal parameters are contained in Supplementary Publication No. SUP 22574 (16 pp.).*

RESULTS AND DISCUSSION

Structure of the Compound.—A view of the molecule down the *a* axis showing its conformation and the numbering system is presented in Figure 1. The final structural parameters, with their estimated standard deviations (e.s.d.s), of the non-hydrogen and H atoms are reported in Tables 1 and 2 respectively; Table 3 gives bond lengths and angles for all non-hydrogen atoms, not corrected for changes due to thermal vibrations, and some least-squares planes and dihedral angles are shown in Table 4.

The structure described by the cell constants, the symmetry operations of the space group, and the atomic parameters consists of discrete molecules of [PtH(CH$_2$CN)(PPh$_3$)$_2$] separated by van der Waals contacts (Figure 2). The closest Pt $\cdots$ Pt approach is 7.379(1) Å and all remaining intermolecular contacts agree with those predicted from radii-sum rules. The complex exhibits the typical square-planar co-ordination of Pt^{II}, but it is somewhat distorted owing to the reduced steric requirements of the hydrido-ligand.

The two P atoms of the phosphine ligands are approximately *trans* to one another; the P(1)–Pt–P(2) angle of 169.6(1)° deviates significantly from the ideal value of 180° as in [PtH(PPh$_3$)$_2$(*p*-CH$_3$C$_6$H$_4$NNNC$_6$H$_4$CH$_3$-*p*)] [169.6(2)°].[22] The two remaining co-ordination sites are occupied by the carbon atom of the cyanomethyl ligand and by the hydrido-ligand. The best mean plane through Pt, C(37), P(1), and P(2) shows good coplanarity between platinum and co-ordinated atoms. Although it is very difficult to detect the position of a hydrido-ligand, when it is near to a heavy-metal atom, such as platinum, in our case its presence has been verified, by the usual crystallographic techniques [inspection of the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

largest peak of residual electron density, which has been found to lie approximately in the co-ordination plane and in the position expected for the hydrido-ligand (see Experimental section)], by i.r. [ν(Pt–H) at 2 027 cm^{-1}], and ^{1}H n.m.r. spectroscopy (triplet of triplets centred at −7.32 p.p.m.).

TABLE 1

Atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms

	X	*Y*	*Z*
Pt	2 241.7(3)	5 702.0(3)	4 247.4(4)
P(1)	2 240(2)	5 230(2)	5 982(3)
P(2)	2 383(2)	5 990(2)	2 438(3)
N(1)	2 689(17)	7 442(9)	5 601(18)
C(1)	3 338(10)	5 286(8)	6 756(12)
C(2)	3 376(10)	5 213(8)	7 915(13)
C(3)	4 234(12)	5 240(9)	8 517(14)
C(4)	5 022(12)	5 340(9)	7 932(15)
C(5)	5 006(12)	5 387(9)	6 800(15)
C(6)	4 133(10)	5 356(8)	6 186(13)
C(7)	1 441(9)	5 618(8)	6 904(11)
C(8)	554(10)	5 352(8)	6 942(12)
C(9)	−78(11)	5 699(10)	7 613(14)
C(10)	181(12)	6 307(11)	8 232(15)
C(11)	1 054(11)	6 574(9)	8 175(14)
C(12)	1 699(10)	6 253(8)	7 502(13)
C(13)	1 947(9)	4 273(8)	5 972(11)
C(14)	2 208(11)	3 839(9)	6 848(14)
C(15)	1 943(12)	3 121(10)	6 810(16)
C(16)	1 398(12)	2 866(10)	5 908(15)
C(17)	1 133(12)	3 297(10)	5 034(15)
C(18)	1 424(11)	4 035(9)	5 031(14)
C(19)	3 548(9)	6 268(7)	2 155(12)
C(20)	4 129(11)	6 481(9)	3 059(14)
C(21)	5 047(13)	6 680(10)	2 859(16)
C(22)	5 328(12)	6 696(9)	1 792(15)
C(23)	4 760(12)	6 504(9)	911(15)
C(24)	3 841(10)	6 274(8)	1 076(13)
C(25)	1 640(10)	6 718(8)	1 875(13)
C(26)	701(12)	6 597(9)	1 873(15)
C(27)	107(13)	7 155(11)	1 448(16)
C(28)	487(13)	7 768(11)	1 030(16)
C(29)	1 410(13)	7 884(11)	1 033(16)
C(30)	2 022(12)	7 339(10)	1 470(15)
C(31)	2 159(9)	5 252(8)	1 480(12)
C(32)	1 638(11)	5 348(9)	464(14)
C(33)	1 476(12)	4 742(10)	−230(15)
C(34)	1 866(12)	4 099(9)	36(15)
C(35)	2 375(11)	3 996(9)	1 011(15)
C(36)	2 513(11)	4 566(9)	1 770(14)
C(37)	1 483(10)	6 642(8)	4 649(11)
C(38)	2 137(15)	7 112(10)	5 176(15)

TABLE 2

Atomic co-ordinates ($\times 10^3$) of the calculated positions for hydrogen atoms

	X	*Y*	*Z*		*X*	*Y*	*Z*
H *	307	525	417	H(21)	546	680	346
H(2)	283	515	829	H(22)	594	684	167
H(3)	427	519	930	H(23)	497	652	18
H(4)	560	538	834	H(24)	345	613	47
H(5)	556	544	643	H(26)	46	616	214
H(6)	410	538	540	H(27)	−54	710	145
H(8)	37	494	652	H(28)	9	812	73
H(9)	−68	552	765	H(29)	164	832	75
H(10)	−24	653	869	H(30)	267	740	140
H(11)	123	698	860	H(32)	140	580	25
H(12)	229	645	745	H(33)	109	479	−89
H(14)	256	402	747	H(34)	178	371	−47
H(15)	213	281	740	H(35)	263	354	118
H(16)	121	238	590	H(36)	284	449	246
H(17)	76	311	443	H(371)	122	686	399
H(18)	127	434	442	H(372)	102	653	514
H(20)	392	649	379				

* Positional parameters as derived from difference-Fourier map. (A fictitious value of $B = 7.0$ was attributed to this atom.)

TABLE 3

Interatomic distances (Å) and angles (°) with their e.s.d.s in parentheses

Pt–P(1)	2.276(4)	C(14)–C(15)	1.40(2)
Pt–P(2)	2.272(4)	C(15)–C(16)	1.40(2)
Pt–C(37)	2.16(1)	C(16)–C(17)	1.37(2)
P(1)–C(1)	1.82(1)	C(17)–C(18)	1.45(2)
P(1)–C(7)	1.81(1)	C(18)–C(13)	1.41(2)
P(1)–C(13)	1.85(1)	C(19)–C(20)	1.41(2)
P(2)–C(19)	1.83(1)	C(20)–C(21)	1.42(2)
P(2)–C(25)	1.85(1)	C(21)–C(22)	1.37(3)
P(2)–C(31)	1.83(1)	C(22)–C(23)	1.36(2)
C(37)–C(38)	1.43(2)	C(23)–C(24)	1.43(2)
C(38)–N	1.12(3)	C(24)–C(19)	1.39(2)
C(1)–C(2)	1.41(2)	C(25)–C(26)	1.39(2)
C(2)–C(3)	1.42(2)	C(26)–C(27)	1.44(3)
C(3)–C(4)	1.40(2)	C(27)–C(28)	1.39(2)
C(4)–C(5)	1.37(2)	C(28)–C(29)	1.37(3)
C(5)–C(6)	1.44(2)	C(29)–C(30)	1.44(3)
C(6)–C(1)	1.39(2)	C(30)–C(25)	1.39(2)
C(7)–C(8)	1.39(2)	C(31)–C(32)	1.42(2)
C(8)–C(9)	1.42(2)	C(32)–C(33)	1.43(2)
C(9)–C(10)	1.41(3)	C(33)–C(34)	1.37(2)
C(10)–C(11)	1.38(2)	C(34)–C(35)	1.37(2)
C(11)–C(12)	1.41(2)	C(35)–C(36)	1.42(2)
C(12)–C(7)	1.44(2)	C(36)–C(31)	1.43(2)
C(13)–C(14)	1.37(2)		

P(1)–Pt–C(37)	95.0(4)	P(1)–C(13)–C(14)	121(1)
P(2)–Pt–C(37)	95.5(4)	P(1)–C(13)–C(18)	115(1)
Pt–P(1)–C(1)	114.0(5)	C(14)–C(13)–C(18)	123(1)
Pt–P(1)–C(7)	116.2(4)	C(13)–C(14)–C(15)	119(2)
Pt–P(1)–C(13)	112.6(4)	C(14)–C(15)–C(16)	120(2)
C(1)–P(1)–C(7)	103.9(6)	C(15)–C(16)–C(17)	122(2)
C(1)–P(1)–C(13)	104.9(6)	C(16)–C(17)–C(18)	120(2)
C(7)–P(1)–C(13)	103.9(6)	C(17)–C(18)–C(13)	117(1)
Pt–P(2)–C(19)	112.4(5)	P(2)–C(19)–C(20)	118(1)
Pt–P(2)–C(25)	116.6(5)	P(2)–C(19)–C(24)	121(1)
Pt–P(2)–C(31)	114.0(5)	C(20)–C(19)–C(24)	121(1)
C(19)–P(2)–C(25)	104.7(6)	C(19)–C(20)–C(21)	119(2)
C(25)–P(2)–C(31)	104.3(7)	C(20)–C(21)–C(22)	120(2)
C(19)–P(2)–C(31)	103.6(6)	C(21)–C(22)–C(23)	122(2)
Pt–C(37)–C(38)	106(1)	C(22)–C(23)–C(24)	120(2)
C(37)–C(38)–N	175(2)	C(23)–C(24)–C(19)	118(1)
P(1)–C(1)–C(2)	120(1)	P(2)–C(25)–C(26)	116(1)
P(1)–C(1)–C(6)	119(1)	P(2)–C(25)–C(30)	121(1)
C(2)–C(1)–C(6)	121(1)	C(26)–C(25)–C(30)	123(1)
C(1)–C(2)–C(3)	120(1)	C(25)–C(26)–C(27)	117(2)
C(2)–C(3)–C(4)	118(2)	C(26)–C(27)–C(28)	119(2)
C(3)–C(4)–C(5)	123(2)	C(27)–C(28)–C(29)	123(2)
C(4)–C(5)–C(6)	119(2)	C(28)–C(29)–C(30)	119(2)
C(5)–C(6)–C(1)	119(1)	C(29)–C(30)–C(25)	118(2)
P(1)–C(7)–C(8)	120(1)	P(2)–C(31)–C(32)	121(1)
P(1)–C(7)–C(12)	119(1)	P(2)–C(31)–C(36)	119(1)
C(8)–C(7)–C(12)	120(1)	C(32)–C(31)–C(36)	120(1)
C(7)–C(8)–C(9)	119(1)	C(31)–C(32)–C(33)	118(1)
C(8)–C(9)–C(10)	121(1)	C(32)–C(33)–C(34)	121(2)
C(9)–C(10)–C(11)	120(2)	C(33)–C(34)–C(35)	122(2)
C(10)–C(11)–C(12)	121(2)	C(34)–C(35)–C(36)	120(2)
C(11)–C(12)–C(7)	119(1)	C(35)–C(36)–C(31)	119(1)

In the parent compound *trans*-[PtCl(CH$_2$CN)(PPh$_3$)$_2$] (1)[15] the Pt–P distances are equal [2.308(3) and 2.310(3) Å], and agree well with the weighted average [2.302(1) Å][23] for Pt^{II}–P bond lengths in several complexes containing two tertiary phosphines PR$_n$Ph$_{3-n}$ (R = alkyl, n = 0—3) in *trans* positions. Better agreement is observed with triphenylphosphine derivatives with similar steric and electronic properties: *trans*-[PtCl(σ-C$_3$H$_5$)(PPh$_3$)$_2$], 2.304(2) and 2.302(2) Å;[24] and *trans*-[Pt(I·SO$_2$)Me(PPh$_3$)$_2$], 2.310(2) and 2.300(2) Å.[25] These data indicate that the cyano-group is ineffective in modifying the structural *cis* influence of the alkyl ligands. However, ^1J(Pt–PPh_3) of some *trans*-[PtCl(σ-alkyl)$(PPh_3)_2$] complexes show that the (n.m.r.) *cis*-influence increases with increasing electronegativity of the alkyl chain: alkyl = σ-C_3H_5, 3 218 Hz;[26] CH_3, 3 147 Hz;[27] $CH_2CH_2CH_2CN$, 3 160 Hz;[28] CH_2CH_2CN, 3124 Hz,[28] and CH_2CN, 2 850 Hz.[10] These ^{195}Pt–^{31}P coupling constants, which are thought to measure the *s* component of the Pt–P bond,[29] display a range of *ca.* 350 Hz. The data show no correlation with the Pt–P bond lengths, which reflect the overall Pt–P bond order. On the contrary, in the present complex (2) the Pt–P distances [2.272(4) and 2.276(4) Å] are significantly shorter, by *ca.* 0.03 Å, than corresponding values in (1), despite a difference in the coupling constant of only 184 Hz [(2) ^1J(PtP) 3 034 Hz [10]]. This indicates that structural and (n.m.r.) *cis* influences of ligand L *cis* to PPh_3 are sensitive to the different electronic mechanisms in the molecular framework.

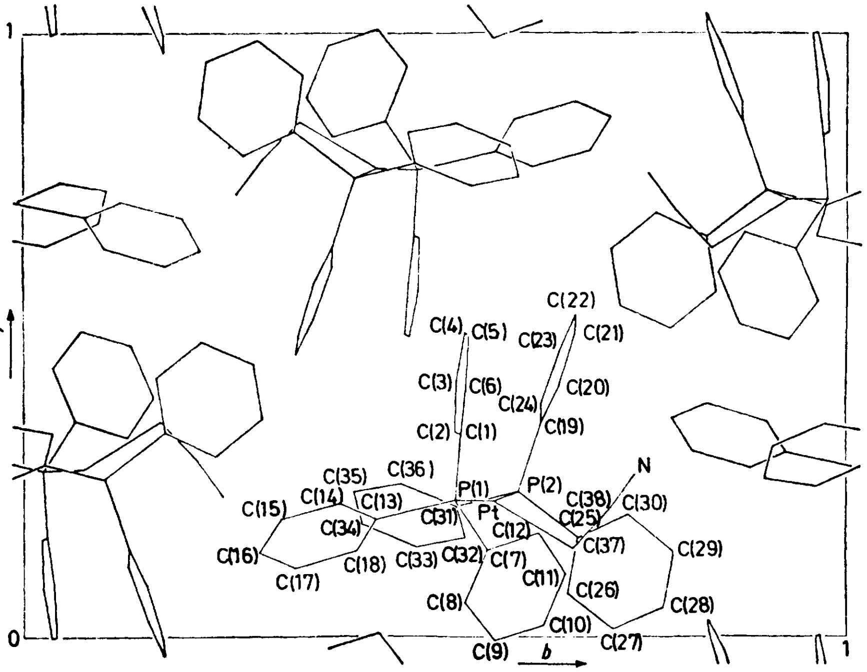

FIGURE 2 The crystal packing of *trans*-[PtH(CH_2CN)$(PPh_3)_2$] down *c*

Several workers [30,31] have suggested that the Pt–P bond length may be affected by the *cis* L ligand *via* competition for the d_π electrons of platinum. Thus in the *cis*-influence series of L, ligands with strong π-acceptor properties (such as CO and PF_3) occur at the upper end of the series, while ligands with weak π-acceptor properties (such as Cl and carbenoid) occur at the lower end of the series. If competition for d_π electrons is the cause of *cis* interaction, we suggest that the hydrido-ligand (which has no π-accepting properties) has the lowest structural *cis* influence. Also, the Pt–P distances in some hydridobis(phosphine)platinum(II) complexes {*e.g.* 2.268(5) and 2.267(5) Å in *trans*-[PtH(*p*-$CH_3C_6H_4NNNC_6H_4CH_3$-*p*)$(PPh_3)_2$],[22] 2.267(8) and 2.269(8) Å in *trans*-[PtH(Cl)$(PEtPh_2)_2$] [32]} are comparable to the value found in this investigation. It appears to us that the length of the Pt–P bond can be reasonably explained in terms of π interactions, even if the electronic mechanism which determines the metal–phosphorus equilibrium distance is still a subject of debate.[29,33]

The Pt–C(sp^3) bond length [2.16(1) Å], which is significantly longer than is predicted from radii rules (2.08 Å), seems to be the largest value so far reported for alkyl platinum(II) complexes, *e.g.* 2.08(1) Å in (1),[15] 2.081(6) Å in *trans*-[PtCl(Me)$(PMePh_2)_2$],[34] 2.090(4) Å in *trans*-[PtCl(σ-C_3H_5)$(PPh_3)_2$],[24] 2.120(7) Å in *trans*-[Pt(I·SO_2)(Me)$(PPh_3)_2$],[25] and 2.14(2) Å in [PtCl(σ-C_3H_5)($NCCH_3$)(PPh_3)] (having PPh_3 *trans* to σ-allyl).[35] It is interesting to note that the electronegative CN group in the present complex, as well as in the parent chloride derivative (1), is ineffective in shortening the Pt–C bond, in contrast to the fluorine group in the derivatives *trans*-[PtCl(CF_2CF_3)$(PMePh_2)_2$] [Pt–C 2.014(11) Å].[34] The significantly longer Pt–C distance in (2) confirms the high *trans* influence of the hydrido-ligand.

The cyanoalkyl moiety undergoes a large thermal motion, which affects the accuracy of the determination of its geometry. Its configuration is approximately linear and the C(37)–C(38)–N(1) mean line is tilted by 106.0° with respect the Pt–C(37) bond. The value of 1.12(3) Å found for the C(37)–N(1) distance is slightly shorter than that found in methyl cyanide and other similar molecules.[36] This value is that expected for a triple bond with a very small amount of double-bond character. The C(37)–C(38) distance [1.43(2) Å] is slightly shorter than the corresponding value in methyl

TABLE 4

Least-squares planes with deviations (Å) of the relevant atoms in square brackets. The equation of a plane in direct space is given by $PX + QY + RZ = S$

Plane	P	Q	R	S
Plane (1): Pt, P(1), P(2), C(37) [Pt 0.003, P(1) −0.002, P(2) −0.002, C(37) −0.000]	12.3581	8.9160	2.4107	8.8748
Plane (2): Pt, C(37), C(38), N [Pt 0.000, C(37) 0.005, C(38) −0.010, N 0.006]	−3.5736	−7.4670	10.8303	−0.4585
Plane (3): C(1), C(2), C(3), C(4), C(5), C(6) [C(1) 0.018, C(2) −0.008, C(3) −0.009, C(4) 0.017, C(5) −0.006, C(6) −0.011]	−1.3028	18.6770	0.9944	10.0914
Plane (4): C(7), C(8), C(9), C(10), C(11), C(12) [C(7) −0.017, C(8) 0.005, C(9) 0.007, C(10) −0.007, C(11) −0.005, C(12) 0.017]	−3.8760	10.7723	−9.1894	−0.8338
Plane (5): C(13), C(14), C(15), C(16), C(17), C(18) [C(13) −0.011, C(14) −0.008, C(15) 0.017, C(16) −0.006, C(17) −0.013, C(18) 0.021]	12.5206	−4.6494	−6.0034	−3.1234
Plane (6): C(19), C(20), C(21), C(22), C(23), C(24) [C(19) −0.005, C(20) 0.017, C(21) −0.016, C(22) 0.003, C(23) 0.009, C(24) −0.008]	−4.4570	17.8012	−1.0837	9.3480
Plane (7): C(25), C(26), C(27), C(28), C(29), C(30) [C(25) 0.001, C(26) −0.008, C(27) 0.012, C(28) −0.008, C(29) 0.001, C(30) 0.002]	−0.9190	7.7586	11.0057	7.1230
Plane (8): C(31), C(32), C(33), C(34), C(35), C(36) [C(31) 0.010, C(32) 0.017, C(33) 0.030, C(34) 0.014, C(35) 0.014, C(36) −0.025]	12.5252	4.3934	−6.0831	4.1018

Angles (°) between the planes

(1)–(2)	79.7	(2)–(3)	72.3	(2)–(4)	31.9	(2)–(5)	59.2
(2)–(6)	66.7	(2)–(7)	49.0	(2)–(8)	44.9	(3)–(4)	57.8
(3)–(5)	69.1	(4)–(5)	89.0	(6)–(7)	71.7	(6)–(8)	89.5
(7)–(8)	68.0	(3)–(6)	16.5	(5)–(8)	27.8		

cyanide and other related compounds and corresponds to *ca.* 25% double-bond character.[36]

The triphenylphosphine geometry in this compound, as judged by P–C distances and C–P–C and P–C–C angles, is nearly identical with the geometry of the free ligand and of its derivatives in other transition-metal complexes.[15,32,37] In particular, the P–C distances range from 1.81 to 1.85 Å (average 1.83 Å), the C–P–C angles from 103.6 to 104.9° (average 104.2°), and the P–C–C angles from 115 to 121° (average 119°).

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REFERENCES

[1] D. M. Roundhill, *Adv. Organometallic Chem.*, 1975, **13**, 273.
[2] B. R. James, ' Homogeneous Hydrogenation,' Wiley, New York, 1973.
[3] R. F. Heck, ' Organotransition Metal Chemistry,' Academic Press, New York, 1973.
[4] A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1973, **95**, 7262.
[5] P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem Rev.*, 1976, **76**, 219.
[6] M. L. Green, ' Organometallic Compounds,' vol. II, 3rd edn., eds. G. E. Coates, M. L. H. Green, and K. Wade, Methuen, London, 1968.
[7] U. Belluco, ' Organometallic and Coordination Chemistry of Platinum,' Academic Press, London, 1974.
[8] P. G. Leviston and M. G. H. Wallbridge, *J. Organometallic Chem.*, 1976, **110**, 271.
[9] L. Abis, A. Sen, and J. Halpern, *J. Amer. Chem. Soc.*, 1978, **100**, 2915.
[10] R. Ros, R. A. Michelin, R. Bataillard, and R. Roulet, *J. Organometallic Chem.*, 1977, **139**, 355; 1979, **165**, 107.
[11] R. Ros, R. A. Michelin, G. Carturan, and U. Belluco, *J. Organometallic Chem.*, 1977, **133**, 213.
[12] R. A. Michelin, U. Belluco, and R. Ros, *Inorg. Chim. Acta*, 1977, **24**, L33.
[13] W. H. Baddley and P. Choudhury, *J. Organometallic Chem.*, 1973, **60**, C74.
[14] W. Beck, K. Schropp, C. Oetker, R. Schlodder, and H. S. Smedal, *Chem. Ber.*, 1973, **106**, 2144.
[15] R. Ros, R. A. Michelin, U. Belluco, G. Zanotti, A. Del Pra, and G. Bombieri, *Inorg. Chim. Acta*, 1978, **29**, L187.
[16] A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Cryst.*, 1968, **A24**, 351.
[17] D. T. Cromer and G. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
[18] D. T. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[19] ' International Tables for *X*-Ray Crystallography,' Birmingham, Kynoch Press, 1962, vol. 3, p. 202.
[20] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
[21] The *X*-Ray System, version of April 1973, Report TR-192, University of Maryland.
[22] A. Immirzi, G. Bombieri, and L. Toniolo, *J. Organometallic Chem.*, 1976, **118**, 355.
[23] C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J.C.S. Dalton*, 1978, 46.
[24] J. A. Kaduk and J. A. Ibers, *J. Organometallic Chem.*, 1977, **139**, 199.
[25] M. R. Snow and J. A. Ibers, *Inorg. Chem.*, 1973, **12**, 224.
[26] N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Organometallic Chem.*, 1977, **127**, C51.
[27] P. E. Garrou and R. F. Heck, *J. Amer. Chem. Soc.*, 1976, **98**, 4115.
[28] R. Ros, R. Bataillard, and R. Roulet, *J. Organometallic Chem.*, 1976, **118**, C53; R. Ros, R. A. Michelin, R. Bataillard, and R. Roulet, unpublished work.
[29] R. Mason and D. W. Meek, *Angew. Chem. Internat. Edn.*, 1978, **17**, 183 and refs. therein.
[30] J. S. Field and P. J. Wheatley, *J.C.S. Dalton*, 1974, 702.
[31] L. Manojlovic-Muir, K. W. Muir, and T. Solomon, *J. Organometallic Chem.*, 1977, **142**, 265.
[32] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773.
[33] P. B. Hitchock, B. Jacobson, and A. Pidcock, *J.C.S. Dalton*, 1977, 2043.
[34] M. A. Bennett, K. C. Ho, G. B. Robertson, and P. O. Whimp, unpublished work quoted in G. B. Robertson and P. O. Whimp, *Inorg. Chem.*, 1974, **13**, 2082.
[35] A. Scrivanti, G. Carturan, U. Belluco, N. Bresciani Pahor, M. Calligaris, and L. Randaccio, *Inorg. Chim. Acta*, 1976, **20**, L3.
[36] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 269.
[37] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.