BRENČIČ, J. V., ČEH, B. & LEBAN, I. (1987). Z. Anorg. Allg. Chem. 549, 233–239.

BRENČIČ, J. V., ČEH, B. & LEBAN, I. (1988). J. Cryst. Spectrosc. Res. 18, 345–351.

CROMER, D. T. (1965). Acta Cryst. 18, 17–23.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

HUHEEY, J. E. (1983). Inorganic Chemistry: Principles of Structure and Reactivity, p. 258. Cambridge: Harper.

JOHNSON, C. K. (1965). ORTEP. Report ORNL 3794. Oak Ridge National Laboratory, Tennessee, USA.

MALLISON, P. R. & MUIR, K. W. (1985). J. Appl. Cryst. 18, 51–53.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

Structure of *trans*-(Ethanenitrile)(hydrido)bis(tricyclohexylphosphine)platinum Tetraphenylborate Dichloromethane Solvate

By RICHARD H. HEYN, STEVEN D. GRUMBINE AND T. DON TILLEY*

Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093-0506, USA

Abstract. *trans*-[Pt(H){P(C$_6$H$_{11}$)$_3$}$_2$(C$_2$H$_3$N)][B-(C$_6$H$_5$)$_4$].CH$_2$Cl$_2$, $M_r = 1202·1$, triclinic, $P\bar{1}$, $a = 11·462$ (4), $b = 14·274$ (5), $c = 19·715$ (8) Å, $\alpha = 74·89$ (3), $\beta = 78·24$ (3), $\gamma = 85·54$ (3)°, $V = 3048$ (2) Å^3, $Z = 2$, $D_x = 1·31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 25·0$ cm^{-1}, $T = 296$ K, $F(000) = 1248$, $R = 0·0411$ for 6847 observed reflections [$I > 3\sigma(I)$]. The cation has a distorted square-planar geometry, with Pt—P 2·302 (2) and Pt—N 2·079 (6) Å. The P—Pt—P angle is 161·4 (1)°.

Introduction. There is continuing interest in the steric demands of bulky ligands and the distortions they undergo to relieve strain in overcrowded systems. In particular, Pt complexes containing the bulky ligand PCy$_3$ (Cy = cyclohexyl, C$_6$H$_{11}$) have been the subject of a recent review (Clark & Hampden-Smith, 1987). Distortions of complexes *trans*-Pt(PCy$_3$)$_2$HX from an ideal square-planar geometry, which occur to accommodate the bulky phosphine ligands, depend to some degree on the size of the substituent X. In this paper, we report the effects of the ligand NCCH$_3$ on distortions in *trans*-[Pt(H)(PCy$_3$)$_2$(NCCH$_3$)][BPh$_4$].

Experimental. The compound was prepared by reaction of *trans*-Pt(PCy$_3$)$_2$H(SiPh$_2$OSO$_2$CF$_3$) with NaBPh$_4$ and acetonitrile in dichloromethane. Crystals were grown by slow cooling of a concentrated dichloromethane solution layered with pentane. ^{1}H NMR (CD$_2$Cl$_2$): δ – 18·46 (t, $^2J_{H—P} = 12$ Hz, $^1J_{H—Pt} = 1234$ Hz, 1 H), 1·0–2·2 (m, 69 H), 6·87 (t, $^3J_{H—H} = 7$ Hz, 4 H), 7·03 (t, $^3J_{H—H} = 7$ Hz, 8 H), 7·73 (*br s*, 8 H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 40·66 ($^1J_{Pt—P} = $

2677 Hz). (Proton chemical shifts are relative to Me$_4$Si at 0·00 p.p.m.; phosphorus chemical shifts are relative to 85% H$_3$PO$_4$ at 0·00 p.p.m.)

A colorless crystal exhibiting an irregular shape and dimensions of 0·34 × 0·42 × 0·50 mm was mounted in a thin-walled glass capillary and flame sealed. Data were measured with a Siemens $R3m/V$ diffractometer equipped with a highly oriented graphite monochromator set for Mo $K\alpha$ radiation. Orientation matrix and unit-cell parameters were obtained from 23 randomly selected reflections with $15 \leq 2\theta \leq 30°$. Intensities were measured using ω–2θ scans ($3 \leq 2\theta \leq 50°$) at a variable scan speed, $5·0$–$29·3°$ min^{-1} in 2θ, hkl ranges $-13 < h < 13$, $-17 < k < 17$, $-1 < l < 23$. A total of 12 496 reflections were measured, of which 10 747 were unique ($R_{int} = 3·3$ %). Three check reflections (161, 517, 1,2,11) revealed a linear decay to 81% of the initial intensity data collection. The data were corrected for this decay, as well as for Lorentz and polarization effects, and for absorption. The absorption correction was made using the ψ-scan method, based on eight reflections with $5 \leq 2\theta \leq 35°$, with χ in the range 260–280°. The min./max. corrections were 0·746/0·991.

The structure was solved by direct methods in $P1$ and refined in $P\bar{1}$ by full-matrix least squares using 6847 observed reflections [$I > 3\sigma(I)$]. The quantity minimized was $\sum w(F_o - F_c)^2$, where $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$; $g = 0·0006$. All non-H atoms were refined anisotropically. The phenyl groups of the anion were refined as rigid hexagons [d(C—C) = 1·40 Å]. All H atoms, except for H(Pt), were placed in calculated, idealized positions [d(C—H) = 0·96 Å], isotropic thermal parameters approximately equal to 1·2 times the

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$) *in trans-*[Pt(H){P(C₆H₁₁)₃}₂(NCCH₃)][BPh₄].CH₂Cl₂

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pt	4314 (1)	2179 (1)	−2200 (1)	41 (1)
P(1)	3317 (2)	2273 (1)	−1082 (1)	45 (1)
P(2)	5411 (2)	2605 (1)	−3347 (1)	43 (1)
Cl(1)	3333 (4)	4272 (6)	2783 (2)	144 (2)
Cl(2)	3889 (4)	2709 (3)	3931 (2)	173 (2)
N(1)	4007 (6)	749 (4)	−2164 (3)	56 (2)
B(1)	9833 (7)	1842 (6)	2708 (4)	46 (3)
C(1)	3781 (7)	5 (5)	−2179 (4)	62 (3)
C(2)	3481 (8)	−957 (6)	−2220 (6)	98 (5)
C(3)	3087 (10)	3066 (7)	3258 (5)	104 (5)
C(11)	4252 (7)	2860 (5)	−658 (3)	52 (3)
C(12)	5432 (7)	2302 (6)	−597 (4)	70 (4)
C(13)	6246 (8)	2784 (7)	−271 (5)	87 (5)
C(14)	6401 (10)	3849 (8)	−656 (5)	100 (5)
C(15)	5237 (10)	4379 (7)	−688 (5)	92 (5)
C(16)	4469 (8)	3927 (5)	−1055 (5)	72 (4)
C(21)	2948 (7)	1080 (5)	−447 (3)	60 (3)
C(22)	2696 (9)	998 (5)	352 (4)	78 (4)
C(23)	2579 (12)	−70 (6)	765 (4)	117 (5)
C(24)	1645 (13)	−566 (7)	573 (5)	138 (7)
C(25)	1827 (11)	−458 (6)	−220 (5)	122 (6)
C(26)	1912 (8)	625 (6)	−633 (4)	82 (4)
C(31)	1929 (8)	3024 (6)	−1112 (4)	77 (4)
C(32)	1629 (12)	3492 (11)	−1744 (6)	187 (9)
C(33)	553 (8)	4108 (7)	−1791 (5)	85 (4)
C(34)	−64 (10)	4357 (9)	−1114 (6)	129 (6)
C(35)	182 (12)	3830 (11)	−491 (7)	179 (9)
C(36)	1318 (8)	3288 (6)	−426 (4)	73 (4)
C(41)	6821 (6)	3095 (5)	−3327 (3)	47 (3)
C(42)	7508 (7)	2456 (5)	−2766 (4)	64 (3)
C(43)	8516 (7)	3009 (7)	−2666 (4)	78 (4)
C(44)	9352 (8)	3392 (7)	−3368 (5)	88 (5)
C(45)	8703 (7)	4003 (6)	−3943 (4)	78 (4)
C(46)	7675 (7)	3470 (6)	−4046 (4)	63 (3)
C(51)	5665 (7)	1663 (4)	−3860 (3)	48 (3)
C(52)	6484 (7)	836 (5)	−3566 (4)	58 (3)
C(53)	6488 (8)	0 (5)	−3903 (4)	65 (3)
C(54)	6822 (8)	323 (6)	−4702 (4)	75 (4)
C(55)	6040 (8)	1146 (5)	−5008 (4)	68 (3)
C(56)	6022 (8)	1993 (5)	−4670 (3)	60 (3)
C(61)	4620 (6)	3605 (5)	−3889 (3)	50 (3)
C(62)	4478 (8)	4532 (5)	−3611 (4)	66 (3)
C(63)	3759 (9)	5310 (6)	−4040 (4)	81 (4)
C(64)	2550 (9)	4959 (7)	−4053 (5)	89 (4)
C(65)	2699 (8)	4083 (7)	−4359 (5)	82 (4)
C(66)	3411 (7)	3274 (5)	−3930 (4)	64 (3)
C(111)	8780	2529	2308	56 (3)
C(112)	8861 (5)	2678 (4)	1572 (3)	69 (4)
C(113)	7938	3166	1245	98 (5)
C(114)	6935	3505	1655	100 (6)
C(115)	6854	3355	2391	98 (6)
C(116)	7777	2867	2717	75 (4)
C(121)	11200	2058	2210	47 (3)
C(122)	11484 (4)	2979 (3)	1768 (3)	63 (3)
C(123)	12658	3180	1420	80 (4)
C(124)	13549	2460	1513	79 (4)
C(125)	13265	1539	1955	68 (4)
C(126)	12091	1338	2303	56 (3)
C(131)	9936	2082	3486	53 (3)
C(132)	10272 (5)	1333 (3)	4030 (3)	65 (3)
C(133)	10481	1533	4650	85 (4)
C(134)	10355	2482	4726	98 (5)
C(135)	10019	3231	4183	82 (4)
C(136)	9810	3031	3562	74 (4)
C(141)	9425	708	2813	48 (3)
C(142)	9817 (4)	239 (3)	2266 (2)	57 (3)
C(143)	9403	−678	2328	69 (3)
C(144)	8596	−1127	2938	76 (4)
C(145)	8204	−658	3485	76 (4)
C(146)	8619	260	3422	64 (3)

isotropic thermal parameter of the parent C atom]. H(Pt) was not included in the final refinement. Coordinates for an electron-density peak of 0.44 e $Å^{-3}$ near that expected for a hydride ligand did not refine
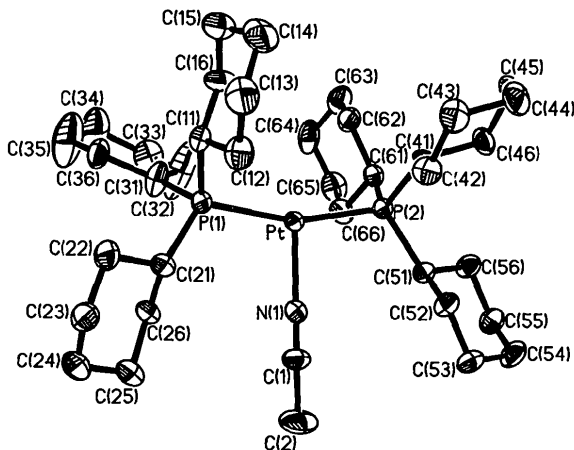
Table 2. *Selected bond distances* (Å) *and bond angles* (°) *in trans-*[Pt(H){P(C₆H₁₁)₃}₂(NCCH₃)][BPh₄].-CH₂Cl₂

Pt—P(1)	2·299 (2)	Pt—P(2)	2·304 (2)
Pt—N(1)	2·079 (6)	P(1)—C(11)	1·848 (8)
P(1)—C(21)	1·852 (6)	P(1)—C(31)	1·851 (9)
P(2)—C(41)	1·822 (8)	P(2)—C(51)	1·856 (7)
P(2)—C(61)	1·843 (7)	N(1)—C(1)	1·121 (10)
B(1)—C(111)	1·686 (10)	B(1)—C(121)	1·675 (9)
B(1)—C(131)	1·684 (11)	B(1)—C(141)	1·668 (9)
C(1)—C(2)	1·468 (12)		

P(1)—Pt—P(2)	161·4 (1)	P(1)—Pt—N(1)	100·6 (2)
P(2)—Pt—N(1)	98·0 (2)	Pt—P(1)—C(11)	110·2 (2)
Pt—P(1)—C(21)	114·2 (2)	C(11)—P(1)—C(21)	105·2 (3)
Pt—P(1)—C(31)	112·5 (3)	C(11)—P(1)—C(31)	105·9 (4)
C(21)—P(1)—C(31)	108·3 (4)	Pt—P(2)—C(41)	109·1 (2)
Pt—P(2)—C(51)	117·2 (2)	C(41)—P(2)—C(51)	110·6 (3)
Pt—P(2)—C(61)	108·9 (2)	C(41)—P(2)—C(61)	105·9 (3)
C(51)—P(2)—C(61)	104·5 (3)	Pt—N(1)—C(1)	174·6 (6)
C(111)—B(1)—C(121)	111·8 (4)	C(111)—B(1)—C(131)	113·2 (5)
C(121)—B(1)—C(131)	103·7 (6)	C(111)—B(1)—C(141)	103·6 (6)
C(121)—B(1)—C(141)	112·1 (5)	C(131)—B(1)—C(141)	112·8 (4)
N(1)—C(1)—C(2)	178·3 (9)	P(1)—C(31)—C(32)	120·7 (7)
P(1)—C(31)—C(36)	117·0 (6)		

to chemically reasonable values. Final indices included $R = 0.0411$, $wR = 0.044$, and S (goodness of fit) $= 1.08$. The structure converged with the largest $\Delta/\sigma = 0.002$. The largest difference peak was 0.60 e $Å^{-3}$, located 0.97 Å from Pt. All operations were performed on a MicroVAX II computer utilizing *SHELXTL-Plus* computer programs (Sheldrick, 1987) with atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic coordinates are given in Table 1, bond distances and angles in Table 2.* The structure of the cation and the atomic numbering scheme are shown in Fig. 1. The Pt center has a distorted square-planar coordination geometry. Pt, P(1), P(2) and N(1) are nearly coplanar, with a mean deviation of 0.004 (1) Å. The Pt—P distances [average 2.302 (2) Å] are slightly longer than Pt—P in *trans*-Pt(PCy₃)₂H₂, 2.26 (1) Å (Immurzi, Musco, Carturan & Belluco, 1975). The P(1)—Pt—P(2) angle of 161.4 (1)° is highly distorted from the idealized value of 180°. The bending is toward the H ligand. Similar distortions have been observed in related complexes such as H(S₂CH)Pt(PCy₃)₂, in which the P—Pt—P angle is 161.1 (4)° (Albinati, Musco, Carturan & Strukul, 1977). The P—Pt—P angles in compounds of the type *trans*-(PCy₃)₂PtHX range from 180.0 (for $X = $ H) to $142.7°$ (for $X = $ PPhCy₂) (Clark & Hampden-Smith, 1987). The magnitude of

Fig. 1. Thermal ellipsoid drawing of *trans*-[Pt(H){P(C₆H₁₁)₃}₂-(NCCH₃)]⁺ with the atom-labeling scheme and 30 % probability thermal ellipsoids.

this distortion depends on both the size of the ligand X and the Pt—X bond distance.

The phosphorus-bound carbons of the PCy₃ ligands [C(11), C(21), C(31) and C(41), C(51), C(61)] are nearly eclipsed with one another when viewed along the P—P vector. This feature of the structure is common to *trans*-(PCy₃)₂PtHX compounds containing a planar X ligand that is perpendicular to the PtP₂H plane (Clark & Hampden-Smith, 1987). The Pt—N distance of 2·079 (6) Å is longer than that of

trans-PtCl₂(NCC₆H₅)₂, 1·95 (2) Å (Lauher & Ibers, 1975), probably because of the large steric demands of the bulky PCy₃ ligands. The NCCH₃ ligand is essentially linear [Pt—N(1)—C(1) = 174·6 (6)°].

The BPh₄ anion shows some distortion from regular tetrahedral symmetry, with C—B—C angles ranging from 102·8 (7) to 113·2 (7)°. The CH₂Cl₂ molecule is entirely regular. The cation, anion and solvent of crystallization are all discrete. Considerable thermal motion gives rise to significant apparent distortions in PCy₃.

References

Albinati, A., Musco, A., Carturan, G. & Strukul, G. (1977). *Inorg. Chim. Acta*, **18**, 219–223.

Clark, H. C. & Hampden-Smith, M. J. (1987). *Coord. Chem. Rev.* **79**, 229–255.

Immurzi, A., Musco, A., Carturan, G. & Belluco, U. (1975). *Inorg. Chim. Acta*, **12**, L23–L24.

Lauher, J. W. & Ibers, J. A. (1975). *Inorg. Chem.* **14**, 640–645.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Structure of [Na₂(CH₃OH)₉][Ta₆Cl₁₂(OCH₃)₆].3CH₃OH

By N. Brničević, R. E. McCarley, S. Hilsenbeck and B. Kojić-Prodić

Rudjer Bošković Institute, 41000 Zagreb, Croatia, Yugoslavia and Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

Abstract. Tri-μ-methanol-bis(trimethanolsodium) dodeca-μ-chloro-hexamethoxy-1κO,2κO,3κO,4κO,-5κO,6κO-*octahedro*-hexatantalate methanol solvate (1/3), [Na₂(CH₃OH)₉][Ta₆Cl₁₂(OCH₃)₆].3CH₃OH, M_r = 2127·82, hexagonal, $P6_3/m$, a = 11·696 (1), c = 23·110 (3) Å, V = 2738 (1) Å³, Z = 2, D_x = 2·581 g cm⁻³, λ(Mo $K\alpha$) = 0·71073 Å, μ = 124·65 cm⁻¹, $F(000)$ = 1964, T = 143 K, final R = 0·045, wR = 0·053 for 735 observed reflections with $I > 3\sigma(I)$. The crystal structure reveals a dimeric cation, [Na₂(μ-CH₃OH)₃(CH₃OH)₆]²⁺ with octahedral environment about sodium (Na—O bridging, 2·45 Å; Na—O terminal, 2·37 Å). The octahedral cluster unit, [Ta₆Cl₁₂(OCH₃)₆]²⁻ exhibits Ta—Ta distances of 2·994 (2) and 2·975 (2) Å with Ta—Cl from 2·434 (6) to 2·456 (5) Å (all bridging). Six methoxo groups are in terminal positions with a Ta—O distance of 2·04 (2) Å. The structure is held together by a network of hydrogen bonds between the cations, cluster anions and solvent (methanol) molecules.

Introduction. The research work presented here is part of a project on the investigations of the hexa-