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(Triethylphosphine)(diethylethylidene phosphine)-
[2-methyl-1,2-dicarbadodecaboranyl(10)]platinum(II)

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Abstract. $\text{PtP}_2\text{B}_{10}\text{C}_{15}\text{H}_{42}$, $M_r = 587.6$, triclinic, $P\bar{1}$ (from structure determination), $a = 16.39$ (8), $b = 11.20$ (6), $c = 7.98$ (5) Å, $\alpha = 103.2$ (1), $\beta = 107.4$ (1), $\gamma = 90.5$ (1)°, $U = 1357.1$ Å³, $D_c = 1.44$, $Z = 2$, $D_m = 1.46$ g cm⁻³ (by flotation), $\mu(\text{Mo } K\alpha) = 55.6$ cm⁻¹. The structure was solved by Patterson and Fourier methods and refined to $R = 9.5\%$ for 2961 independent reflexions. The 2-methyl-1,2-carboranyl group is σ -bonded to Pt through its 1C atom. One phosphine is coordinated to the metal atom through its P atom, the other through its P atom and the first C atom of one ethyl side group.

Introduction. Single crystals were obtained by slow evaporation of a dichloromethane solution. Intensities were collected on a Siemens diffractometer by the θ - 2θ scan technique with Mo $K\alpha$ radiation for a maximum 2θ angle of 54°. All reflexions with $I < 3\sigma(I)$ were rejected, the remainder being corrected for Lorentz and polarization effects. 2961 independent reflexions were used in the subsequent calculations. No correction for absorption was applied, because of the small size of the crystal used (approximately a cylinder with a diameter of ca 0.2 mm). During data collection a strong decrease of the standard reflexion intensity was observed suggesting a significant disordering of the crystal, due to X-ray exposure, which greatly affects the accuracy of the structure analysis. This was partly avoided by correcting the intensities, which decreased by about 50% during the overall recording time with a nearly linear trend. The structure was determined by conventional Patterson and Fourier methods and refined by

the block-diagonal least-squares method. After isotropic refinement, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ was 0.152. The final anisotropic refinement reduced R to

Table 1. Fractional coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Pt	2363 (1)	1299 (1)	897 (1)
P(1)	3651 (4)	2067 (6)	834 (11)
P(2)	1547 (4)	2811 (6)	1260 (10)
B(1)	1540 (17)	-1520 (29)	4 (49)
B(2)	2329 (21)	-1402 (28)	2077 (53)
B(3)	3337 (20)	-1331 (28)	1644 (60)
B(4)	3129 (17)	-1394 (26)	-736 (59)
B(5)	1585 (23)	-2883 (31)	-1626 (59)
B(6)	1794 (21)	-2826 (27)	771 (62)
B(7)	2915 (25)	-2785 (30)	1803 (73)
B(8)	3405 (22)	-2703 (33)	58 (68)
B(9)	2529 (25)	-2787 (36)	-2095 (70)
B(10)	2399 (25)	-3621 (36)	-692 (60)
C(1)	3816 (16)	3605 (36)	1884 (52)
C(2)	4675 (25)	4402 (33)	2104 (75)
C(3)	4638 (16)	1483 (26)	2005 (50)
C(4)	4754 (23)	1706 (36)	4019 (58)
C(5)	3813 (20)	1844 (37)	-1533 (46)
C(6)	3178 (31)	2554 (51)	-2705 (50)
C(7)	1719 (21)	4041 (33)	3290 (54)
C(8)	937 (24)	4476 (40)	3684 (60)
C(9)	865 (20)	3443 (37)	-618 (49)
C(10)	548 (24)	2510 (38)	-2358 (49)
C(11)	1114 (13)	1421 (21)	1368 (34)
C(12)	999 (16)	1115 (31)	3007 (39)
C(13)	2482 (13)	-593 (19)	498 (32)
C(14)	2036 (17)	-1545 (28)	-1599 (46)
C(15)	1608 (28)	-811 (41)	-3182 (51)

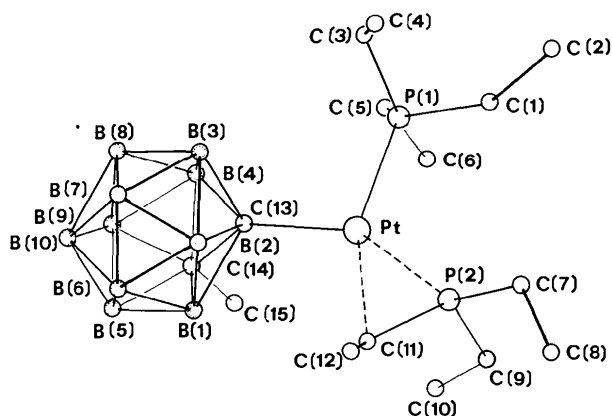


Fig. 1. A view of the molecule together with the numbering scheme for the atoms.

0.095. The H atoms were neglected. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 11.0$, $B = 1.0$ and $C = 0.0045$ were chosen to maintain $w(|F_o| - |F_c|)^2$ nearly constant over all range of $|F_o|$ and $(\sin \theta/\lambda)$. Scattering factors were calculated according to Moore (1963). Table 1 gives the final atomic parameters; the numbering scheme of the atoms is shown in Fig. 1.*

Discussion. The Pt^{II} atom is coordinated by the carboranyl group and two phosphine ligands, the four-coordination being achieved by internal metallation involving the ethyl C atom bonded to P (as shown in Fig. 1). The Pt and the four-coordinated atoms are coplanar within 0.1 Å. The carboranyl group is σ -bonded to the metal atom through its 1C atom [C(13)] with a Pt—C bond length of 2.09 (2) Å. The carboranyl atoms adjacent to the coordinated C atom are nearly equidistant from the Pt [from 3.26 (3) to 3.45 (3) Å]. These values are consistent with a 'pure' σ bond between the carboranyl group and the metal atom, as found in the analogous complex 1-[(ⁿPr₃P)Pt^{II}(ⁿPr₂PCHCH₂CH₃)]-2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀) (I) (Bresciani, Calligaris, Delise, Nardin & Randaccio, 1974). On the other hand, this mode of bonding differs from that found in [(C₆H₅)₃Pl₂Rh(CB₁₀H₁₀C₂H₁₀)] (Allegra, Calligaris, Furlanetto, Nardin & Randaccio, 1974), where the metal-carboranyl coordination is provided by a Rh—C σ bond and by a Rh—H—B bridge bond. The geometry of the three-membered Pt—P(2)—C(11) ring is very close to that of the analogous ring in (I) and may be well described on the assumption of a π olefin-like

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32760 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) and angles (°) of interest, with estimated standard deviations in parentheses

	Present compound	Compound I
Pt—P(1)	2.291 (8)	2.286 (5)
Pt—P(2)	2.189 (7)	2.202 (5)
Pt—C(11)	2.19 (2)	2.17 (2)
Pt—C(13)	2.09 (2)	2.13 (1)
P(2)—C(11)	1.73 (3)	1.76 (2)
P(2)—C(7)	1.82 (4)	1.81 (2)
P(2)—C(9)	1.87 (4)	1.82 (3)
P(1)—C(1)	1.72 (4)	1.83 (2)
P(1)—C(3)	1.82 (3)	1.89 (2)
P(1)—C(5)	1.95 (4)	1.86 (2)
P(1)—Pt—P(2)	109.2 (2)	107.3 (2)
P(1)—Pt—C(11)	155.1 (6)	154.7 (5)
P(1)—Pt—C(13)	103.4 (7)	102.8 (4)
P(2)—Pt—C(11)	46.7 (7)	47.5 (5)
P(2)—Pt—C(13)	147.4 (7)	149.9 (4)
C(11)—Pt—C(13)	101.0 (9)	102.4 (6)
Pt—P(2)—C(11)	66.7 (8)	65.3 (6)
Pt—C(11)—P(2)	66.6 (9)	67.3 (6)

bond between Pt and a P(2)=C(11) double bond, rather than two σ bonds [Pt—C(11) and Pt—P(2)]. In fact, although the structural data are largely affected by errors, it may be assumed that the P(2)—C(11) distance of 1.73(3) Å is shorter than the other P—C distances, whose mean value is 1.84(4) Å [ranging from 1.72(4) to 1.95(4) Å]. Furthermore, the sum of the C—P—C angles around P(2) (332°) is greater than that around P(1) (310°), supporting the case that P(2) is closer to the sp^2 -hybridization state than is P(1). That these figures may be of value is confirmed by the similar trend already found in the analogous compound (I). A comparison of bond lengths and angles for the present complex and (I), reported in Table 2, shows that the two compounds have very similar geometry around the metal atom. The C atoms of the [—(CH₂)₂P=CHCH₃] group are coplanar within ± 0.32 Å, the P atom being displaced 0.49 Å. Their mean plane is normal to the coordination plane, with a dihedral angle of 88°.

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