The overall cage geometry of the complex is seen to be based on a closed dodecahedral structure in which the Co and C atoms occupy adjacent positions on a triangulated face. Such a cage structure is in agreement with that previously proposed (Zimmerman, Hall & Sneddon, 1980) and is consistent with skeletal electron-counting rules (Wade, 1976) which predict a closed polyhedral cage for such a $2n + 2$ electronic system (8 cage atoms, 18 skeletal electrons). Similar cage geometries have been confirmed for isoelectronic cage systems, 1,7-$(CH_3)_2C_2B_6H_6$ (Hart & Lipscomb, 1968), $B_8H_8^{2-}$ (Guggenberger, 1969), and *commo*-[η-$C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (Finster, Sinn & Grimes, 1981) and proposed based on the NMR data for the isomeric complex, 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$ (Miller & Grimes, 1973). In addition, it should be noted that closed dodecahedral cage structures have also been observed for boron clusters with other skeletal electron counts. For example, B_8Cl_8 (Pawley, 1966; Jacobson & Lipscomb, 1958, 1959) and (η-$C_5H_5)_4Co_4B_4H_4$ (Pipal & Grimes, 1979), which are both $2n$ electron cage systems, and (η-$C_5H_5)_4Ni_4B_4H_4$ (Bowser, Bonny, Pipal & Grimes, 1979), which has a $2n + 4$ skeletal electron count, have each been shown to adopt such a cage structure. Thus, as noted previously (Pipal & Grimes, 1979) the dodecahedral cage structure appears to be a favored geometry for eight-vertex boron clusters.

In 1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$, the atoms C(1), C(2), B(7) and B(8) occupy four-coordinate positions, while Co and B(4), B(5) and B(6) are in five-coordinate positions in the cage. In general the distances and angles observed in the cage are normal and within the ranges observed for metallacarborane complexes (Grimes, 1982). The B(7)—B(8) distance, 1·617 (3) Å, is somewhat short; however, it is longer than the comparable distance, 1·56 (3) Å, observed between four-coordinate borons in $B_8H_8^{2-}$. Likewise, the B(4)—B(5) and B(4)—B(6) distances are long, 1·907 (3) and 1·904 (3) Å respectively, but are again similar to the distances reported between the five-coordinate borons in $B_8H_8^{2-}$, 1,7-$(CH_3)_2C_2B_6H_6$ and *commo*-[η-$C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$.

The bonding of the Co atom to the cyclopentadienyl ring appears normal, with an average Co—ring carbon distance of 2·029 (3) Å and an average C—C ring distance of 1·341 (6) Å.

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Carbonatobis(triisopropylphosphine)platinum(II), $C_{19}H_{42}O_3P_2Pt$

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Abstract. M_r = 575·59, monoclinic, space group $P2/c$, a = 11·223 (1), b = 9·901 (1), c = 13·505 (1) Å, β = 128·67 (1)°, U = 1176·0 Å^3, Z = 2, D_x = 1·63 Mg m^{-3}, λ(Mo $K\alpha_1$) = 0·7093 Å, μ = 5·862 mm^{-1}, T = 295 (2) K. Final R = 0·014 for 3158 unique observed reflections. Principal bond lengths and angles are Pt—P 2·263 (1), Pt—O 2·060 (2), —O—C 1·330 (2), C=O 1·212 (4) Å, P—Pt—P 108·04 (4), P—Pt—O 93·98 (5) and O—Pt—O 64·2 (1)°. The molecular geometry is compared with that in the corresponding triphenylphosphine complex.

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Introduction. Following our interest in the effects of steric interactions on transition metal–phosphine bond lengths (Mazid, Russell & Tucker, 1980; Robertson & Tucker, 1982) we have attempted, recently, to grow crystals of *trans*-$PtH_2(P^iPr_3)_2$ (1) suitable for X-ray and neutron diffraction analyses. The desired complex (1) was prepared by the method of Clark, Goel & Wong (1978). Unexpectedly, however, attempted slow recrystallization of (1) from 2-methoxyethanol in air yielded crystals of the title compound (2) whose structure we now report. Attempts to obtain authentic crystals of (1), using inert atmosphere and vacuum sublimation techniques, are continuing.

Experimental. Laue symmetry $2/m$, systematic absences $h0l$ for $l = 2n + 1$, space group $P2/c$ (confirmed by structure solution); specimen crystal bounding faces, with perpendicular distances (cm) from one vertex, 100 (0·0020), $\bar{1}00$ (0·0128), $10\bar{2}$ (0·0088), $\bar{1}02$ (0·0105), 011 (0·0325), $01\bar{1}$ (0·0345), $0\bar{1}1$ (0), $0\bar{1}\bar{1}$ (0), $11\bar{1}$ (0·0300), $11\bar{1}$ (0), $\bar{1}11$ (0·0373) and $\bar{1}\bar{1}1$ (0·0020); Picker FACS-1 diffractometer, Mo $K\alpha$ radiation, $2\theta_{max} = 60°$, forms recorded $h, \pm k, \pm l$, 7964 reflections including standards (three every 97 data, indices 080, 700 and 008), 3158 unique data $[I \geq 3\sigma(I)]$, corrected for absorption (de Meulenaer & Tompa, 1965; transmission factor range 0·1467–0·4264) and for crystal degradation [0·169 (19) × 10^{-4} per measured reflection]; $R_s = 0·009$ (Robertson & Whimp, 1975) and $R_{int}(= \sum|F^2 - <F^2>|/\sum F^2) = 0·023$; cell dimensions from 12 reflections each with $2\theta > 40°$; structure solved from Patterson and Fourier syntheses; refined by full-matrix least squares minimizing $\sum w(|F_o|-|F_c|)^2$ with $w = [\sigma_s^2(F_o) + 0·0005|F_o|^2]^{-1}$ (Robertson & Whimp, 1975), anisotropic thermal parameters for Pt, P, C, O; H atoms located from difference synthesis; H-atom coordinates and two average isotropic thermal parameters refined (one for methyl, one for methine H atoms); final $R = 0·014$, $R_w = 0·021$; maximum shift-to-error = 0·2, average shift-to-error = 0·05; $(\rho_o - \rho_c)$ max. = 0·75, $(\rho_o - \rho_c)$min. = –0·54 e Å^{-3}; X = 0·002 [in $F_c^{corr.} = F_c\ (1–0·0001XF_c^2/\sin\theta)$]; atomic scattering amplitudes, with dispersion corrections for Pt, from *International Tables for X-ray Crystallography* (1974); computer programs *ANUCRYS* (McLaughlin, Taylor & Whimp, 1977), *SHELX*76 (Sheldrick, 1976), *PLUTO* (Motherwell, 1978).

Discussion. Final atomic coordinates for non-H atoms are listed in Table 1 and principal bond lengths and bond angles are listed in Table 2.* The atom-numbering scheme is defined in Fig. 1.

Table 1. *Atomic coordinates (with e.s.d.'s in parentheses) and equivalent isotropic thermal parameters*

	x	y	z	U_{eq}*(Å^2)
Pt(1)	0·5	0·11248 (1)	0·25	0·0189
P(1)	0·31863 (5)	0·24672 (5)	0·22286 (5)	0·0215
C(11)	0·1349 (2)	0·1699 (2)	0·0901 (2)	0·0297
C(12)	0·1126 (3)	0·1631 (3)	–0·0337 (2)	0·0412
C(13)	–0·0067 (3)	0·2273 (3)	0·0674 (3)	0·0433
C(21)	0·3147 (2)	0·4321 (2)	0·2018 (2)	0·0259
C(22)	0·2713 (3)	0·4702 (2)	0·0748 (2)	0·0312
C(23)	0·2211 (3)	0·5153 (3)	0·2280 (3)	0·0345
C(31)	0·3231 (3)	0·2278 (2)	0·3616 (2)	0·0302
C(32)	0·4729 (3)	0·2807 (2)	0·4795 (2)	0·0411
C(33)	0·2951 (4)	0·0832 (3)	0·3820 (3)	0·0417
C(1)	0·5	–0·1399 (3)	0·25	0·0266
O(1)	0·3863 (2)	–0·0637 (2)	0·2244 (2)	0·0289
O(2)	0·5	–0·2624 (2)	0·25	0·0356

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma)$.

Table 2. *Bond lengths* (Å) *and angles* (°) (*with e.s.d.'s in parentheses*)

Pt(1)–P(1)	2·2626 (7)	C(11)–C(12)	1·532 (4)
Pt(1)–O(1)	2·060 (2)	C(11)–C(13)	1·529 (3)
O(1)–C(1)	1·330 (2)	C(21)–C(22)	1·513 (3)
C(1)–O(2)	1·212 (4)	C(21)–C(23)	1·540 (3)
P(1)–C(11)	1·855 (2)	C(31)–C(32)	1·517 (4)
P(1)–C(21)	1·854 (2)	C(31)–C(33)	1·528 (4)
P(1)–C(31)	1·855 (2)		
Pt(1)–P(1)–C(11)	105·2 (1)	C(11)–P(1)–C(21)	110·6 (1)
Pt(1)–P(1)–C(21)	122·6 (1)	C(11)–P(1)–C(31)	104·5 (1)
Pt(1)–P(1)–C(31)	108·9 (1)	C(21)–P(1)–C(31)	103·8 (1)
P(1)–Pt(1)–O(1)	93·98 (5)	P(1)–C(11)–C(12)	113·6 (2)
P(1)–Pt(1)–P(1)′	108·04 (4)	P(1)–C(11)–C(13)	115·6 (2)
O(1)–Pt(1)–O(1)′	64·2 (1)	P(1)–C(21)–C(22)	112·4 (2)
C(1)–O(1)–Pt(1)	92·5 (1)	P(1)–C(21)–C(23)	116·6 (2)
O(1)–C(1)–O(1)′	110·8 (3)	P(1)–C(31)–C(32)	110·0 (2)
O(1)–C(1)–O(2)	124·6 (1)	P(1)–C(31)–C(33)	113·5 (2)
		C(12)–C(11)–C(13)	110·9 (2)
		C(22)–C(21)–C(23)	110·2 (2)
		C(32)–C(31)–C(33)	110·6 (2)

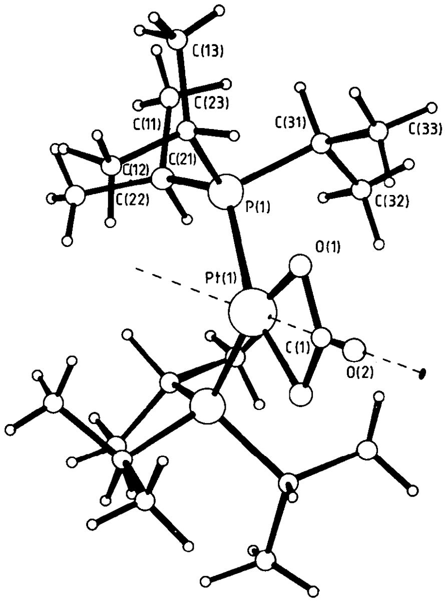

Fig. 1. The molecular geometry and atom numbering in the title compound.

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* Lists of observed and calculated structure amplitudes, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, and inter- and intramolecular non-bonding contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38475 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

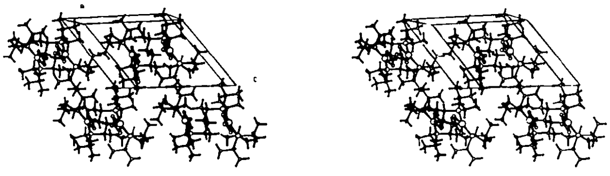

Fig. 2. The molecular packing viewed approximately along the *b* axis.

Molecules of (2) have exact *C*2 symmetry, with a crystallographic diad axis passing through Pt, C(1) and O(2) (Fig. 1), and are separated by normal van der Waals interactions. The crystal-packing arrangement and the molecular stereochemistry are each illustrated in the stereopair of Fig. 2.

The Pt—P distance in (2) [2·263 (1) Å] agrees well with the longer of the two inequivalent values [2·266 (5) and 2·223 (4) Å] observed in the triphenylphosphine analogue, carbonatobis(triphenylphosphine)platinum(II), (3) (Cariati, Mason, Robertson & Ugo, 1967; Robertson, 1968, unpublished data). Pt—O distances [2·060 (2), (2); 2·049 (12) and 2·072 (11) Å, (3)] and O—Pt—O angles [64·2 (1), (2); 63·4 (4)°, (3)] for (2) and (3) are also in excellent agreement. In contrast, and reflecting the increased steric requirement of triisopropyl *vis à vis* triphenylphosphine, the P—Pt—P angle in (2) [108·04 (4)°] is some 9° greater than that in (3) [98·6 (2)°]. In a more crowded system the increased steric requirement of the triisopropylphosphine ligand might be expected to generate both angle and (bond) length changes. That the substantial angular strain in (2) is not accompanied by bond-length compression is, we suggest, simply a fortuitous consequence of the rather small steric requirement of the carbonato ligand.

Bond lengths in the phosphine ligand in (2) are unexceptional [av. P—C 1·855 (1), av. C—C 1·527 (9), av. C—H 1·00 (6) Å]* and bond angles follow expectations based on the detailed molecular geometry. Thus the largest Pt—P—C angle [Pt(1)—P(1)—C(21) 122·6 (1)°] is associated with the (equivalent) closely contacting isopropyl groups C(2*n*) and C(2*n*)′ [directly below the P atoms in Fig. 2; H···H 2·18 (6), 2·29 (6) Å]. Similarly, the largest P—C—C angle [P(1)—C(21)—C(23) 116·6 (2)°] involves that methyl group [C(23)] making the shortest inter-isopropyl group contact [C(23)H(3)···C(31)H 2·01 (6) Å]. The C—C—H angles average 111 (5)° and the H—C—H angles average 108 (8)°. The geometry of the carbonato ligand is similar to that reported for other (bidentate) carbonato–transition-metal complexes [*e.g.* Cariati *et al.* (1967) and Woon, Mackay & O'Connor (1980) and references therein].

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* Errors quoted in association with average bond lengths and bond angles are r.m.s. deviations from the mean value.

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