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Structure of a Nine-Membered Palladacycloalkane, Bis[*dimethyl(phenyl)phosphine*]-3,3,6,6,9,9,13,13-octamethyl-*anti, syn, anti, syn*-11-palladapentacyclo[10.1.0.0^{2,4}.0^{5,7}.0^{8,10}]tridecane, C₃₆H₅₄P₂Pd

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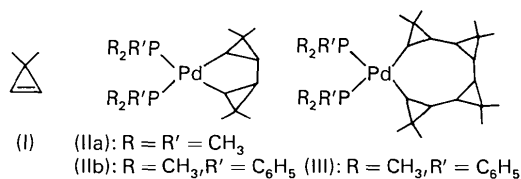
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Abstract. $M_r = 654.8$, triclinic, $P\bar{1}$, $a = 11.236$ (2), $b = 11.774$ (2), $c = 14.682$ (2) Å, $\alpha = 74.01$ (2), $\beta = 86.92$ (2), $\gamma = 75.59$ (2)°, $V = 1808$ Å³, $Z = 2$, $D_x = 1.203$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.611$ mm⁻¹, $F(000) = 692$, $T = 293$ K. Final $R = 0.031$ for 6282 unique observed X-ray diffractometer data. The nine-membered metallacycle contains a slightly distorted square-planar Pd atom coordinated by two phosphine ligands. The four cyclopropane rings impose steric rigidity on the ring, whose conformation resembles the all-*cis* boat conformation of 1,3,5,7-cyclononatetraene rather than the twisted-boat–chair and twisted-chair–boat forms calculated for cyclononane. There are no short intermolecular distances.

Introduction. Transition-metal-catalysed cyclo-oligomerizations of alkenes are known to proceed *via* metallacyclic intermediates and in some cases such complexes have been isolated (Stockis & Hoffmann, 1980). By subsequent thermolysis or substitution reactions of these species catalytic cycles have been simulated (Doyle, McMeeking & Binger, 1976; Binger & Doyle, 1978; Bezman, Bird, Frazer & Osborn, 1980). Oxidative couplings of alkenes with low-valent transition-metal complexes normally give five-membered metallacycles. Only for rhodium(I) and iridium(I) complexes (Cetinkaya, Binger & Krüger, 1982; Bezman *et al.*, 1980) has the isolation of seven- and eight-membered metallacycloalkanes been achieved. Unfortunately the use of rhodium(I) and iridium(I) complexes as catalysts for the cyclo-

oligomerization of alkenes is very limited. While iridium(I) complexes show no activity at all (Bezman *et al.*, 1980), rhodium(I) complexes only catalyse the oligomerization of 8,9,10-trinorbornadiene (Katz, Acton & Paul, 1969). In contrast, a number of activated alkenes are cyclo-oligomerized smoothly and selectively in the presence of palladium(0) complexes (Binger, Cetinkaya, Doyle, Germer & Schuchardt, 1979). In this context we were able to isolate five- and nine-membered palladacycloalkanes (II, III) by oxidative coupling of 3,3-dimethylcyclopropene (I) with latent palladium(0) complexes (Binger, Büch, Benn & Mynott, 1982). Compounds (II) and (III) underwent reductive elimination upon thermolysis to give the expected cyclodi- and cyclotetramers of (I).



To our knowledge, (III) is the first example of an isolable nine-membered metallacycloalkane. We performed a three-dimensional X-ray structure analysis in order to confirm the structure, which has been primarily derived from spectroscopic data. In addition, we wished to obtain information on the exact geometry of the molecule and to establish whether it is monomeric or dimeric in the crystalline state (magnesia- and zincacycloalkanes are known to be dimeric: Spek, Schat, Holtkamp, Blomberg & Bickelhaupt, 1977; Freijee, Seetz, Akkerman & Bickelhaupt, 1982).

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Experimental. Cell dimensions obtained by least-squares fit to 2θ angles of 75 reflections. Intensities of 8180 reflections (index range: $-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $0 \leq l \leq 20$), from which 1898 considered unobserved [$I_o < 2\sigma(I_o)$], measured on a Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan technique, $2\theta_{\max} = 55^\circ$ (largest $\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$). Three standard reflections (014, 410, 040) measured after every 90 reflections, max. intensity variation 5.4%. Intensities corrected for Lorentz and polarization, not for absorption. Structure solved by heavy-atom technique and refined initially using *SHELX76* (Sheldrick, 1976). A difference density synthesis confirmed structure and yielded reasonable positions for all H atoms. Structure then refined by blocked full-matrix least squares on F (Brauer & Krüger, 1976) allowing all atoms except H anisotropic thermal motion (352 parameters refined). Scattering factors from Cromer & Waber (1965), from Stewart, Davidson & Simpson (1965) for H; real and imaginary components of anomalous-scattering factors of Pd and P included (Cromer & Liberman, 1970). Refinement converged at $R = 0.031$, $R_w = 0.036$; $w = 1/\sigma^2(F_o)$. $\Delta/\sigma < 1$. Final difference Fourier synthesis essentially flat with largest peaks ($< 0.42 \text{ e \AA}^{-3}$) in vicinity of heavy atoms.

Discussion. The structure of the title compound (III) is shown in Fig. 1. Final atomic coordinates* of the anisotropically refined atoms and equivalent isotropic temperature factors are collected together in Table 1. Selected bond lengths and angles are given in Table 2.

The molecule is monomeric and comprises a nine-membered metallacycle which contains a slightly distorted square-planar Pd atom, which is coordinatively saturated (16 electrons) by two phosphine ligands. The degree of distortion, which can be expressed quantitatively by the angle between normals to the planes through the atoms [Pd, C(1), C(20)] and [Pd, P(1), P(2)] is 16° .

As expected, the conformation of the metallacyclononane ring differs considerably from the twisted-boat-chair and twisted-chair-boat forms calculated for cyclononane (Casanova & Waegell, 1975). This is due to steric rigidity originating from the four cyclopropane rings. The conformation is best compared with the all-*cis* boat conformation calculated for 1,3,5,7-cyclononatetraene (Buemi, Nicolosi, Zuccarello & Grasso, 1979). The *anti,syn,anti,syn* arrangement of the cyclopropane rings is best illustrated by looking at the torsion angles H(5)–C(5)–C(6)–H(6) (-161.3°),

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and C–H distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38830 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

H(10)–C(10)–C(11)–H(11) (161.7°) and H(15)–C(15)–C(16)–H(16) (-163.4°).

The two Pd–C bond lengths [2.085 (3) and 2.083 (3) Å] are equal within experimental error and slightly shorter than normal Pd–C(sp^3) bonds. The metallacyclononane ring shows alternating C–C bond lengths. The C–C distances in the cyclopropyl rings are *ca* 0.3 Å longer than the remaining C–C bonds. This feature has been observed in related compounds (Binger, Doyle, McMeeking, Krüger & Tsay, 1977) and

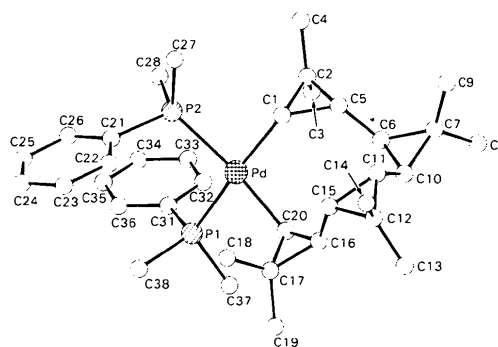


Fig. 1. General view of the molecule with the atom-numbering scheme.

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses and U_{eq} values

$U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_i are the eigenvalues of the U_{ij} matrix.

	x	y	z	$U_{eq}(\text{\AA}^2)$
Pd	0.4708 (1)	0.0423 (1)	0.2400 (1)	0.031
P(1)	0.2954 (1)	0.1134 (1)	0.1396 (1)	0.041
P(2)	0.4252 (1)	0.2151 (1)	0.2992 (1)	0.042
C(1)	0.6437 (2)	-0.0050 (2)	0.3044 (1)	0.038
C(2)	0.7442 (2)	0.0575 (2)	0.2564 (2)	0.047
C(3)	0.7307 (3)	0.1195 (2)	0.1520 (2)	0.064
C(4)	0.8104 (3)	0.1181 (3)	0.3098 (3)	0.063
C(5)	0.7708 (2)	-0.0798 (2)	0.2879 (1)	0.040
C(6)	0.8074 (2)	-0.1591 (2)	0.2223 (1)	0.041
C(7)	0.9287 (2)	-0.2549 (2)	0.2373 (2)	0.045
C(8)	0.9933 (2)	-0.2793 (3)	0.1486 (2)	0.065
C(9)	1.0184 (2)	-0.2676 (3)	0.3145 (2)	0.056
C(10)	0.8095 (2)	-0.2936 (2)	0.2595 (1)	0.041
C(11)	0.7582 (2)	-0.3295 (2)	0.3559 (1)	0.040
C(12)	0.6940 (2)	-0.4321 (2)	0.3924 (2)	0.046
C(13)	0.6899 (3)	-0.5220 (2)	0.3386 (2)	0.060
C(14)	0.7027 (3)	-0.4888 (2)	0.4986 (2)	0.063
C(15)	0.6185 (2)	-0.3003 (2)	0.3605 (1)	0.041
C(16)	0.5477 (2)	-0.2564 (2)	0.2694 (1)	0.039
C(17)	0.4089 (2)	-0.2088 (2)	0.2618 (2)	0.042
C(18)	0.3408 (2)	-0.1850 (2)	0.3497 (2)	0.052
C(19)	0.3403 (2)	-0.2627 (2)	0.2059 (2)	0.057
C(20)	0.4922 (2)	-0.1260 (2)	0.2129 (1)	0.035
C(21)	0.2660 (2)	0.2458 (2)	0.3406 (2)	0.047
C(22)	0.2301 (3)	0.1496 (3)	0.4037 (2)	0.061
C(23)	0.1104 (3)	0.1645 (3)	0.4391 (2)	0.074
C(24)	0.0280 (3)	0.2742 (4)	0.4098 (3)	0.076
C(25)	0.0617 (3)	0.3698 (3)	0.3471 (3)	0.074
C(26)	0.1809 (3)	0.3573 (2)	0.3115 (2)	0.062
C(27)	0.5056 (2)	0.2003 (2)	0.4087 (2)	0.055
C(28)	0.4443 (3)	0.3625 (2)	0.2291 (2)	0.061
C(31)	0.2821 (2)	0.2703 (2)	0.0684 (1)	0.047
C(32)	0.3826 (3)	0.2943 (3)	0.0130 (2)	0.064
C(33)	0.3809 (4)	0.4116 (3)	-0.0422 (2)	0.082
C(34)	0.2786 (5)	0.5055 (3)	-0.0434 (3)	0.086
C(35)	0.1803 (4)	0.4841 (3)	0.0110 (3)	0.078
C(36)	0.1806 (3)	0.3658 (3)	0.0661 (2)	0.063
C(37)	0.2981 (3)	0.0402 (2)	0.0446 (2)	0.057
C(38)	0.1413 (2)	0.1130 (3)	0.1835 (2)	0.062

Table 2. Bond lengths (Å) and angles (°)

Pd-P(1)	2.360 (1)	C(11)-C(15)	1.524 (4)
Pd-P(2)	2.359 (1)	C(12)-C(13)	1.495 (5)
Pd-C(1)	2.085 (3)	C(12)-C(14)	1.516 (5)
Pd-C(20)	2.083 (3)	C(12)-C(15)	1.528 (4)
P(1)-C(31)	1.829 (3)	C(15)-C(16)	1.491 (4)
P(1)-C(37)	1.828 (3)	C(16)-C(17)	1.519 (4)
P(1)-C(38)	1.816 (3)	C(16)-C(20)	1.520 (4)
P(2)-C(21)	1.839 (3)	C(17)-C(18)	1.524 (4)
P(2)-C(27)	1.832 (3)	C(17)-C(19)	1.508 (4)
P(2)-C(28)	1.816 (4)	C(17)-C(20)	1.529 (4)
C(1)-C(2)	1.537 (4)	C(21)-C(22)	1.385 (5)
C(1)-C(5)	1.527 (4)	C(21)-C(26)	1.390 (5)
C(2)-C(3)	1.503 (5)	C(22)-C(23)	1.404 (5)
C(2)-C(4)	1.520 (5)	C(23)-C(24)	1.361 (7)
C(2)-C(5)	1.511 (4)	C(24)-C(25)	1.365 (6)
C(5)-C(6)	1.494 (4)	C(25)-C(26)	1.400 (5)
C(6)-C(7)	1.520 (4)	C(31)-C(32)	1.397 (5)
C(6)-C(10)	1.522 (4)	C(31)-C(36)	1.383 (5)
C(7)-C(8)	1.520 (5)	C(32)-C(33)	1.393 (6)
C(7)-C(9)	1.510 (4)	C(33)-C(34)	1.380 (7)
C(7)-C(10)	1.512 (4)	C(34)-C(35)	1.363 (7)
C(10)-C(11)	1.490 (4)	C(35)-C(36)	1.404 (6)
C(11)-C(12)	1.518 (4)		
P(1)-Pd-P(2)	93.6 (1)	C(6)-C(10)-C(7)	60.1 (2)
P(1)-Pd-C(1)	168.5 (1)	C(6)-C(10)-C(11)	115.0 (2)
P(1)-Pd-C(20)	87.5 (1)	C(7)-C(10)-C(11)	125.4 (2)
P(2)-Pd-C(1)	87.6 (1)	C(10)-C(11)-C(12)	126.0 (2)
P(2)-Pd-C(20)	168.0 (1)	C(10)-C(11)-C(15)	115.5 (2)
C(1)-Pd-C(20)	93.7 (1)	C(12)-C(11)-C(15)	60.3 (2)
Pd-C(1)-C(2)	120.0 (2)	C(11)-C(12)-C(13)	122.8 (3)
Pd-C(1)-C(5)	135.5 (2)	C(11)-C(12)-C(14)	115.4 (3)
C(2)-C(1)-C(5)	59.1 (2)	C(13)-C(12)-C(14)	112.4 (3)
C(1)-C(2)-C(3)	118.0 (3)	C(11)-C(12)-C(15)	60.0 (2)
C(1)-C(2)-C(4)	120.7 (3)	C(13)-C(12)-C(15)	121.5 (3)
C(3)-C(2)-C(4)	113.1 (3)	C(14)-C(12)-C(15)	115.3 (3)
C(1)-C(2)-C(5)	60.1 (2)	C(11)-C(15)-C(12)	59.6 (2)
C(3)-C(2)-C(5)	118.2 (3)	C(11)-C(15)-C(16)	117.8 (2)
C(4)-C(2)-C(5)	117.0 (3)	C(12)-C(15)-C(16)	119.7 (2)
C(1)-C(5)-C(2)	60.8 (2)	C(15)-C(16)-C(17)	123.9 (2)
C(1)-C(5)-C(6)	129.1 (2)	C(15)-C(16)-C(20)	128.5 (2)
C(2)-C(5)-C(6)	123.9 (3)	C(17)-C(16)-C(20)	60.4 (2)
C(5)-C(6)-C(7)	120.3 (2)	C(16)-C(17)-C(18)	117.8 (2)
C(5)-C(6)-C(10)	118.5 (2)	C(16)-C(17)-C(19)	117.1 (2)
C(7)-C(6)-C(10)	59.6 (2)	C(18)-C(17)-C(19)	112.8 (2)
C(6)-C(7)-C(8)	116.4 (3)	C(16)-C(17)-C(20)	59.9 (2)
C(6)-C(7)-C(9)	121.3 (3)	C(18)-C(17)-C(20)	118.3 (2)
C(8)-C(7)-C(9)	112.1 (2)	C(19)-C(17)-C(20)	121.2 (3)
C(6)-C(7)-C(10)	60.3 (2)	Pd-C(20)-C(16)	133.5 (2)
C(8)-C(7)-C(10)	116.0 (3)	Pd-C(20)-C(17)	119.6 (2)
C(9)-C(7)-C(10)	121.7 (3)	C(16)-C(20)-C(17)	59.8 (2)

C(6)-C(15) are 3.696 (4) and 3.291 (4) Å respectively. This indicates a preferred interaction between C(1) and C(20) which facilitates the reductive elimination of the hydrocarbon part of the molecule. It is interesting to know that in the case of (III) reductive elimination can be achieved even in boiling diethyl ether while (IIa) and (IIb) eliminate only at *ca* 473 K with a comparable rate.

Unusually short intermolecular distances were not observed.

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is probably due to a conjugative effect induced by the unsaturated character of the cyclopropyl groups.

The nonbonding distance between the two α -C atoms C(1) and C(20) [3.039 (4) Å] is *ca* 0.3 Å shorter than the sum of the van der Waals radii. The comparable transannular distances C(5)-C(16) and

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Structure of Lithium Diisopropylthiocarbamate Trihydrate, Li⁺.C₇H₁₄NS₂⁻.3H₂O

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Abstract. $M_r = 237.3$, triclinic, $P\bar{1}$, $a = 6.143$ (1), $b = 8.488$ (1), $c = 12.796$ (1) Å, $\alpha = 95.71$ (1), $\beta = 101.32$ (1), $\gamma = 93.73$ (1)°, $V = 648.5$ (1) Å³, $Z = 2$,

$D_m = 1.224$ (5), $D_x = 1.215$ (1) Mg m⁻³, Cu K α , $\lambda = 1.5418$ Å, $\mu = 3.5$ mm⁻¹, $F(000) = 256$, $T = 295$ K, $R = 0.047$ for 920 reflections. Pairs of distorted tetrahedra [Li(H₂O)₄]⁺₂ are formed by edge sharing and these polyhedra are connected to layers parallel to the

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