

An Orthometallated Phosphinocarborane Complex

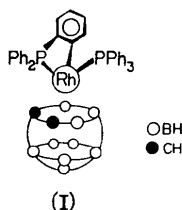
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Abstract. 3-[2-(Diphenylphosphino)phenyl-*C*¹,*P*]-3-triphenylphosphine-1,2-dicarba-3-rhoda-*closo*-dodecaborane(11) benzene solvate, $C_{38}H_{40}B_9P_2Rh.C_6H_6$, $M_r = 837.0$, monoclinic, $P2_1/c$, $a = 12.222$ (8), $b = 18.110$ (12), $c = 20.923$ (14) Å, $\beta = 109.08$ (1)°, $V = 4377$ Å³, $Z = 4$, $D_x = 1.27$, $D_m = 1.235$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 4.3$ cm⁻¹, $F(000) = 1720$, $T = 298$ K, $R = 0.065$ for 2808 observed reflections. One of the triphenylphosphine groups coordinated to Rh is monodentate. The second is bidentate and is bound to Rh through the P atom and an *ortho* atom of one of the phenyl groups. A $C_2B_9H_{11}$ fragment occupies the remaining coordination sites on Rh. The C atoms of the metallated phenyl group are coplanar with Rh and P. The greatest distance to any of these atoms from the least-squares plane through them is 0.07 Å. Variations from standard bond lengths in the four-membered ring fused to the aromatic ring are found to be in the direction of electron delocalization in the metallocycle.

Introduction. Four-membered rings are obtained by heating phenylphosphine–metal complexes containing transition metals such as iridium (Bennett & Milner, 1969), platinum (Cheney, Mann, Shaw & Slade, 1970), ruthenium (Bruce, Gardner & Stone, 1976), manganese (McKinney, Knobler, Huie & Kaesz, 1977; Deschamps, Mathey, Knobler & Jeannin, 1984), rhodium (Keim, 1968) and iron (Ikariya & Yamamoto, 1976). An orthometallated phosphinocarborane (I) containing an Rh–C–C–P four-membered ring, obtained from the reaction of [*closo*-3,3-{P(C₆H₅)₃}₂-3-H-3,1,2-RhC₂B₉H₁₁] with either isopropenyl acetate or vinyl acetate at higher temperatures, is described below.



Experimental. Title compound was prepared as described (King, Busby & Hawthorne, 1985) and recrystallized from benzene/heptane. Density measured by flotation (294 K) in distilled water/KI. Weissenberg photographs show systematic absences $l = 2n + 1$ for $h0l$ reflections, $k = 2n + 1$ for $0k0$ reflections. A transparent yellow multi-faceted crystal, $0.34 \times 0.19 \times 0.12$ mm, on a Picker FACS-1 diffractometer, Zr filter, at 298 K; orientation matrix and unit-cell dimensions by least-squares refinement of 12 reflections ($8 \leq 2\theta \leq 16^\circ$), θ - 2θ scan $2.0^\circ \text{ min}^{-1}$ in 2θ , scan range $2.2(1 + 0.692 \tan\theta)^\circ$, background measured for 20 s at each end of the scan, intensities measured for $2\theta < 45^\circ$ for the range $h = 0$ to 13, $k = 0$ to 19, $l = -21$ to 21; intensities of three standard reflections monitored every 97 reflections with 3% maximum intensity variation from average and no significant change during data collection; total of 5685 independent reflections, 2816 with $I > 3\sigma(I)$ used in structure solution and refinement; absorption corrections made (maximum and minimum factors 0.9731 and 0.9525); no correction for extinction; Rh and P atoms located by Patterson method, remaining atoms (including most H atoms) located on Fourier and difference Fourier maps.

Displacement† parameters for all H atoms were fixed, based on the displacement parameter of the attached C or B atom. Rh, two P, the C_2B_9 icosahedral fragment and the benzene of solvation were refined anisotropically. The 36 phenyl C atoms were refined isotropically and except for C(41)–C(46), the orthometallated ring, all were constrained to be members of rigid C_6H_5 groups ($C-C = 1.395$, $C-H = 1.0$ Å, $C-C-C = 120^\circ$). All H atoms, with the exception of those of the $C_2B_9H_{11}$ icosahedron, were placed in calculated positions and displacement parameters for all H were fixed at values based on those for the attached C or B. Refined by least squares on F (Busing, Martin & Levy, 1962); refinement of 286 parameters converged to $R = 0.065$, $wR = 0.070$, $w = 1/\sigma^2(F_o)$, $S = 1.88$; $(\Delta/\sigma)_{\text{max}}$ in final cycle 0.24 in a displacement parameter and 0.16 in a position parameter [both for C(71)]; maximum and minimum

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† Heretofore commonly called 'vibration parameters' or 'temperature-factor parameters'.

heights of 0.8 and -0.6 e \AA^{-3} respectively in final difference Fourier synthesis (maxima near phenyl C atoms).

Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations performed on DEC VAX 11/750 and VAX 11/780 computers using the *UCLA Crystallographic Package* (1984) (locally edited versions of *CARESS*, *PROFILE*, *MULTAN*, *ORFLS*, *ORFFE*, *ABSORB*, *ORTEP*, *SHELX*, *PLUTO* and *MG84*).

Table 1. Atomic coordinates for the orthometallated phosphinocarborhodorane complex

Equivalent isotropic displacement parameters are denoted by an asterisk. All phenyl C atoms, with the exception of the orthometallated group C(41)–C(46), have been refined as members of rigid groups.

	x	y	z	$U(\text{\AA}^2)$
Rh(3)	0.1006 (1)	0.2980 (1)	0.3977 (1)	0.0298 (4)*
P(1)	0.2054 (3)	0.2058 (2)	0.4735 (2)	0.0374 (14)*
P(2)	0.2421 (3)	0.3875 (2)	0.4296 (2)	0.0404 (14)*
C(1)	-0.0602 (10)	0.3077 (8)	0.4271 (6)	0.040 (5)*
C(2)	-0.0677 (11)	0.2373 (9)	0.3777 (7)	0.045 (6)*
B(4)	-0.0216 (13)	0.3622 (9)	0.3113 (8)	0.040 (7)*
B(5)	-0.1495 (14)	0.4005 (11)	0.3198 (9)	0.050 (7)*
B(6)	-0.1752 (15)	0.3653 (11)	0.3927 (9)	0.054 (8)*
B(7)	-0.0311 (14)	0.3847 (12)	0.3927 (8)	0.051 (9)*
B(8)	-0.0424 (14)	0.2631 (10)	0.3044 (8)	0.041 (8)*
B(9)	-0.1587 (12)	0.3226 (9)	0.2650 (8)	0.043 (7)*
B(10)	-0.2531 (13)	0.3289 (10)	0.3134 (8)	0.049 (8)*
B(11)	-0.1982 (14)	0.2723 (11)	0.3836 (9)	0.052 (8)*
B(12)	-0.1873 (14)	0.2420 (11)	0.3061 (9)	0.044 (8)*
C(71)	0.6886 (20)	0.5195 (17)	0.8339 (9)	0.128 (18)*
C(72)	0.5835 (20)	0.5574 (17)	0.8149 (9)	0.127 (16)*
C(73)	0.4848 (20)	0.5235 (17)	0.8209 (9)	0.138 (17)*
C(74)	0.4912 (20)	0.4517 (17)	0.8459 (9)	0.130 (16)*
C(75)	0.5963 (20)	0.4137 (17)	0.8649 (9)	0.138 (16)*
C(76)	0.6950 (20)	0.4476 (17)	0.8589 (9)	0.166 (22)*
C(11)	0.1322 (8)	0.1875 (4)	0.5359 (5)	0.046 (4)
C(12)	0.1261 (8)	0.2426 (4)	0.5812 (5)	0.064 (4)
C(13)	0.0644 (8)	0.2303 (4)	0.6257 (5)	0.075 (5)
C(14)	0.0089 (8)	0.1628 (4)	0.6250 (5)	0.092 (6)
C(15)	0.0150 (8)	0.1077 (4)	0.5797 (5)	0.109 (7)
C(16)	0.0767 (8)	0.1201 (4)	0.5351 (5)	0.075 (5)
C(21)	0.2107 (7)	0.1140 (5)	0.4363 (4)	0.047 (4)
C(22)	0.1376 (7)	0.0973 (5)	0.3713 (4)	0.051 (4)
C(23)	0.1436 (7)	0.0281 (5)	0.3433 (4)	0.065 (5)
C(24)	0.2227 (7)	-0.0243 (5)	0.3802 (4)	0.065 (5)
C(25)	0.2959 (7)	-0.0076 (5)	0.4452 (4)	0.076 (5)
C(26)	0.2899 (7)	0.0616 (5)	0.4732 (4)	0.057 (4)
C(31)	0.3598 (7)	0.2180 (5)	0.5211 (4)	0.035 (3)
C(32)	0.4012 (7)	0.2291 (5)	0.5909 (4)	0.051 (4)
C(33)	0.5199 (7)	0.2356 (5)	0.6244 (4)	0.067 (5)
C(34)	0.5972 (7)	0.2309 (5)	0.5881 (4)	0.068 (5)
C(35)	0.5558 (7)	0.2197 (5)	0.5183 (4)	0.064 (4)
C(36)	0.4371 (7)	0.2133 (5)	0.4848 (4)	0.052 (4)
C(41)	0.3088 (11)	0.3376 (7)	0.3791 (6)	0.039 (4)
C(42)	0.2266 (10)	0.2838 (7)	0.3515 (6)	0.038 (3)
C(43)	0.2418 (11)	0.2367 (7)	0.3046 (6)	0.046 (4)
C(44)	0.3437 (13)	0.2400 (8)	0.2855 (8)	0.064 (4)
C(45)	0.4235 (13)	0.2930 (9)	0.3141 (7)	0.069 (4)
C(46)	0.4128 (12)	0.3460 (8)	0.3614 (7)	0.062 (4)
C(51)	0.3303 (6)	0.4056 (5)	0.5160 (5)	0.044 (4)
C(52)	0.2770 (6)	0.4178 (5)	0.5647 (5)	0.062 (4)
C(53)	0.3441 (6)	0.4338 (5)	0.6312 (5)	0.079 (5)
C(54)	0.4643 (6)	0.4375 (5)	0.6490 (5)	0.078 (5)
C(55)	0.5176 (6)	0.4252 (5)	0.6003 (5)	0.078 (5)
C(56)	0.4505 (6)	0.4092 (5)	0.5337 (5)	0.062 (4)
C(61)	0.2087 (8)	0.4799 (6)	0.3952 (3)	0.048 (4)
C(62)	0.1918 (8)	0.5378 (6)	0.4350 (3)	0.068 (5)
C(63)	0.1646 (8)	0.6082 (6)	0.4073 (3)	0.082 (5)
C(64)	0.1542 (8)	0.6208 (6)	0.3398 (3)	0.072 (5)
C(65)	0.1711 (8)	0.5630 (6)	0.3000 (3)	0.057 (4)
C(66)	0.1984 (8)	0.4925 (6)	0.3277 (3)	0.051 (4)

Discussion. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1; representative bond lengths and angles are given in Table 2.* The molecular structure is shown in Fig. 1.

There are no unusual intermolecular distances; the shortest intermolecular distance not involving H is 3.61 Å, from C(15) to C(24) (phenyl C). The ring involving Rh, P, C(41) and C(42) is planar and all angles inside this ring are smaller than normal bond angles of the participating atoms and are remarkably similar to the values found for the four-membered ring in $(\text{CH}_2\text{C}_6\text{H}_4)_2\text{PC}_6\text{H}_3(\text{CH}_3)\text{Mn}(\text{CO})_4$ (McKinney *et al.*, 1977): Rh–P–C 85.2 (4), Mn–P–C 85.2 (3)°; P–C–C 101.2 (9), 101.5 (7)°; and C–C–Rh 105.4 (9), C–C–Mn 105.7 (7)°. The most distorted angle is that of P–Rh–C, 67.8 (4)° [P–Mn–C, 67.5 (3)°], about 25% smaller than the usual 90° angle.

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* Lists of anisotropic displacement parameters, bond distances and bond angles, H-atom parameters and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42538 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond distances (Å) and angles (°)

Rh(3)–P(1)	2.370 (3)	B(4)–B(5)	1.770 (25)
Rh(3)–P(2)	2.304 (3)	B(4)–B(7)	1.791 (25)
Rh(3)–C(1)	2.249 (14)	B(4)–B(8)	1.812 (25)
Rh(3)–C(2)	2.246 (14)	B(4)–B(9)	1.789 (20)
Rh(3)–B(4)	2.255 (14)	B(5)–B(6)	1.773 (28)
Rh(3)–B(7)	2.227 (19)	B(5)–B(7)	1.750 (20)
Rh(3)–B(8)	2.244 (14)	B(5)–B(9)	1.799 (25)
P(1)–C(11)	1.837 (12)	B(5)–B(10)	1.787 (25)
P(1)–C(21)	1.845 (10)	B(6)–B(7)	1.795 (27)
P(1)–C(31)	1.837 (8)	B(6)–B(10)	1.750 (23)
P(2)–C(41)	1.778 (13)	B(6)–B(11)	1.708 (27)
P(2)–C(51)	1.806 (9)	B(8)–B(9)	1.759 (21)
P(2)–C(61)	1.816 (11)	B(8)–B(12)	1.824 (25)
C(1)–C(2)	1.626 (21)	B(9)–B(10)	1.771 (26)
C(1)–B(6)	1.709 (21)	B(9)–B(12)	1.786 (26)
C(1)–B(7)	1.659 (25)	B(10)–B(11)	1.735 (24)
C(1)–B(11)	1.756 (19)	B(10)–B(12)	1.796 (26)
C(2)–B(8)	1.725 (23)	B(11)–B(12)	1.757 (27)
C(2)–B(11)	1.758 (23)	C(41)–C(42)	1.383 (17)
C(2)–B(12)	1.719 (18)		
B(8)–Rh(3)–C(42)	92.5 (5)	P(1)–Rh(3)–C(2)	92.4 (4)
B(7)–Rh(3)–C(42)	134.2 (6)	P(1)–Rh(3)–C(1)	101.7 (4)
B(4)–Rh(3)–C(42)	95.0 (5)	P(1)–Rh(3)–P(2)	96.4 (2)
C(2)–Rh(3)–C(42)	128.5 (5)	Rh(3)–P(1)–C(31)	120.9 (3)
C(1)–Rh(3)–C(42)	168.6 (5)	Rh(3)–P(1)–C(21)	116.0 (3)
P(2)–Rh(3)–C(42)	67.8 (4)	Rh(3)–P(1)–C(11)	108.7 (4)
P(2)–Rh(3)–B(8)	138.3 (4)	C(21)–P(1)–C(31)	99.5 (4)
P(2)–Rh(3)–B(7)	88.8 (5)	C(11)–P(1)–C(31)	106.8 (4)
P(2)–Rh(3)–B(4)	96.1 (4)	C(11)–P(1)–C(21)	103.3 (4)
P(2)–Rh(3)–C(2)	162.3 (4)	Rh(3)–P(2)–C(61)	119.0 (3)
P(2)–Rh(3)–C(1)	120.4 (4)	Rh(3)–P(2)–C(51)	124.3 (4)
P(1)–Rh(3)–C(42)	84.5 (4)	Rh(3)–P(2)–C(41)	85.2 (4)
P(1)–Rh(3)–B(8)	118.8 (5)	C(51)–P(2)–C(61)	102.3 (5)
P(1)–Rh(3)–B(7)	138.8 (5)	C(41)–P(2)–C(61)	108.7 (5)
P(1)–Rh(3)–B(4)	166.3 (4)	C(41)–P(2)–C(51)	116.6 (5)

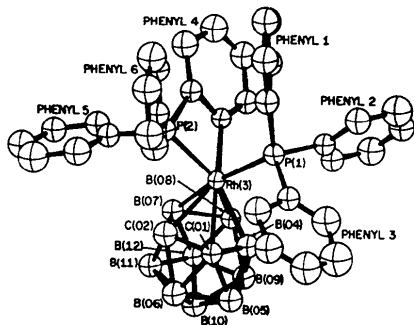


Fig. 1. View of the molecule, showing the numbering scheme. H atoms have been removed for clarity.

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Structure of Tetracarbonyl(nitrosyl)(trimethylphosphine)vanadium

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Abstract. $[V(CO)_4(NO)\{P(CH_3)_3\}]$, $M_r = 269.1$, monoclinic, $P2_1/c$, $a = 7.080(3)$, $b = 11.812(4)$, $c = 15.147(5)$ Å, $\beta = 101.33(2)^\circ$, $V = 1242(1)$ Å³, $Z = 4$, $D_x = 1.439(1)$ g cm⁻³, $\lambda(Mo K\alpha) = 0.70926$ Å, $\mu = 9.27$ cm⁻¹, $F(000) = 544$, $T = 293$ K, $R = 0.0465$ for 2221 observed reflections. The title compound is a mononuclear vanadium complex with approximate C_{4v} symmetry around the central V atom. The V–P bond length [2.543(1) Å] is the longest bonding distance ever found for a vanadium phosphine complex (large *trans* effect of the NO ligand). The V–N–O group is strictly linear. Other important bond lengths: V–C 1.996(2), V–N 1.747(2), C–O 1.139(2), N–O 1.208(3), P–C 1.822(2) Å.

Introduction. Since the early work of Hieber (Hieber, Peterhans & Winter, 1961) and Werner (1961) it has been known that carbonylnitrosyl compounds of vanadium can be isolated. Nevertheless it was only a short time ago that efficient syntheses for $[V(CO)_5NO]$ and its phosphine derivatives were established (Fjare & Ellis, 1983; Schiemann, Weiss, Näumann & Rehder, 1982) and there has been only one single-crystal X-ray structure determination carried out on a carbonylnitrosylvanadium complex (Schiemann &

Weiss, 1982). We undertook a second crystal-structure determination to ascertain the nature of the vanadium–nitrosyl bonding in such complexes.

Experimental. The title compound was synthesized by the method of Ellis (Fjare & Ellis, 1983). Satisfactory crystals were grown by adding hexane very slowly to a toluene solution of the complex at 273 K. Crystal $0.15 \times 0.4 \times 0.7$ mm. Hilger & Watts diffractometer, $\theta/2\theta$ scan mode, $4 < 2\theta < 60^\circ$, h, k, l range: $-9 \leq h \leq 9$, $0 \leq k \leq 16$, $0 \leq l \leq 21$. Cell parameters obtained by least-squares refinement from setting angles of 20 automatically centred high-angle reflections. 3549 independent, non-systematically absent (in $P2_1/c$) reflections measured, 1328 considered as unobserved [$|F| \leq 4\sigma(|F|)$]. No absorption or secondary-extinction corrections. Structure solved by Patterson and Fourier methods [*SHELX77* and *SHELXS84* (Sheldrick, 1977, 1984)]. No intensity drop of three standard reflections measured after each block of 97 reflections. H atoms from a difference Fourier map and refined with constrained C–H bond lengths of 0.96 Å, H–C–H angles of 109.5° and a common temperature factor. Least squares based on F . Scattering factors for all atoms except V included in the *SHELX77* program