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CARBONYL-η^5-CYCLOPENTADIENYL(1,1,4,7,7-PENTAPHENYL-1,4,7-TRIPHOSPHAHEPTANE)VANADIUM(I), η^5-$C_5H_5V(CO)PPh(CH_2CH_2PPh_2)_2$

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Summary

The molecular structure and spectroscopic properties of the title compound are reported. The complex crystallizes in the space group $P2_1/c$ with a 1807.1, b 1088.7, c 3461.6 pm and β 94.3°. The vanadium atom is centered between the two best planes spanned by the cyclopentadienyl ring and the three phosphorus atoms plus the CO ligand. The angle between the two planes is 10.5°; bond angles at the vanadium are around 77°. In solution, ^{31}P NMR, ^{51}V NMR and IR data indicate fluxional behaviour down to 200 K.

Introduction

The photo-reaction between $CpV(CO)_4$ and phosphines [1] yields complexes in which one ($CpV(CO)_3PPh_3$ [2,3]), two (*cis*-$[CpV(CO)_2(PPh_2Me)_2]$ [4]; *cis*-$[CpV(CO)_2dppe]$ [5], dppe = $Ph_2P(CH_2)_2PPh_2$) or all four CO groups ($CpV\{MeN(PF_2)_2\}_2$ [6]) have been replaced. We describe here the complex CpV(CO)triphos (triphos = $PhP(CH_2CH_2PPh_2)_2$), which is the first example of a species with three phosphorus functions coordinated to the cyclopentadienylvanadium moiety. This complex was formerly assigned a *trans*-disubstituted configuration (*trans*-$[CpV(CO)_2$triphos] [7]) on the basis of its spectroscopic data.

Structural information on transition metal derivatives of oligodentate phosphines is of interest in the context of correlations between steric factors (such as bond distances and bond angles) and phosphorus and/or metal NMR parameters [8,9]. In bi- and tricyclic structures, the steric conditions for the bridgehead phosphorus have been discussed in connection with the consistently high deshielding of the ^{31}P nucleus [10].

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Structure determination and refinement

Intensity data were collected with the help of the θ—2θ scan technique on a SYNTEX P2_1 diffractometer (Mo-K_α, graphite monochromator). Anisotropic full-matrix least squares refinement led to a final weighted R-value of 0.060 for 3937 significant ($F_0 > 3\sigma(F_0)$) reflections. All computations employed the SHELX program system [11]. Crystal data are: $C_{38}H_{34}OP_3V$ (M = 650.54) = $C_5H_5V(CO)(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)_2$, space group $P2_1/c$, a 1807.1, b 1088.7, c 3461.6 pm, β 94.3°, V 6791.2 × 10^6 pm^3, Z = 8, ρ (calculated) 1.272 g cm^{-3}, μ 4.41 cm^{-1}.

Discussion

Dark brown to black needles of CpV(CO)triphos were grown by allowing a solution of "*trans*-[CpV(CO)$_2$triphos]" (prepared as described in ref. 7) in CH_3CN (500 mg in 5 ml) to stand for three weeks at room temperature. The crystals thus obtained showed the same spectral properties as the starting product (ref. 7 and Table 1), but were only sparingly soluble in CH_3CN and toluene. A portion of one of the needles was employed in the X-ray analysis. Structural data are collected in Tables 2 and 3. Figure 1 shows an ORTEP drawing of the molecule and the numbering of atoms for one of the two independent molecules contained in the asymmetric unit.

In CpV(CO)triphos (I), which has three CO groups replaced by the weaker π-accepting phosphorus functions, the average V—CO bond length is slightly shorter and the C—O bond length slightly longer than in *cis*-[CpV(CO)$_2$dppe] (III) [12], which correlates with smaller CO stretching frequencies in the case of I. On the other hand, the differences in ^{31}P and ^{51}V NMR shift values between I and III are not significantly parallelled by differences in the bond angles at phosphorus and vanadium. The complexes exhibit large ^{31}P coordination shifts $\Delta\delta$(P) (see Table 1), i.e. high deshielding of the ^{31}P nucleus on coordination. This is commonly observed in chelate five-ring structures and considered to reflect the "normal" shielding situation (ring strains and angle distortions minimal) for the ^{31}P nucleus in chelate complexes [4,13,14].

The angles at vanadium are only slightly smaller than in other carbonylphosphinevanadium complexes (81.5° in HV(CO)$_4$dppe [15], 77.0 in η^3-C_3H_5V-(CO)$_3$dppe [16] and 80.8° in *cis*-[Et_4N][V(CO)$_4$*o*-$C_6H_4(PPh_2)_2$] [17] for the P—V—P angle) and cannot account for the consistently low ^{51}V shielding of I and III compared to that of the hydrido (—1690 ppm [4]), the allyl (—1490 ppm [4]) and the anionic complex (—1755 ppm [17]).

The vanadium—phosphorus bond lengths are shorter than in HV(CO)$_4$dppe (246.6 pm) and η^3-C_3H_5V(CO)$_3$dppe (247.3 pm), and also shorter in I than in III. This can be regarded to be indicative of a stronger V—P interaction in I, and thus in a decrease of ^{51}V shielding ($|\delta|$). The lower value of $\delta(^{51}V)$ for I than for III can be explained in terms of destabilization of occupied π-type molecular orbitals as CO is introduced in place of the weaker π-accepting phosphorus ligand, and a corresponding increase of the paramagnetic deshielding contribution to the overall shielding [18] in the series CpV(CO)$_4$ > CpV(CO)$_3$P > CpV-(CO)$_2$P$_2$ > CpV(CO)P$_3$.

TABLE 1

SPECTROSCOPIC AND SELECTED STRUCTURAL DATA OF CpV(CO)TRIPHOS (I), *cis*-[CpV(CO)$_2$triphos] (II) AND *cis*-[CpV(CO)$_2$dppe] (II)

Complex	ν(CO) [a] (cm^{-1})	δ(^{51}V) [b] (ppm)	δ(^{31}P) [c] (ppm)	Δδ(P) [d] (ppm)	av. V—P (Pm)	V—CO (pm)	C—O (pm)	C—Cp (Pm)	Angle PVP (°)	Angles P [e] (°)
I	1796vs, 1758s [f]	−950	+122 [g]	*ca.* 148	241.8	187.8	117.4	196.5	76.5	109.0
						183.3	123.0	195.7	76.8	
II	1862s, 1792s	−1176	+117, +105 −15.0 [h]	135, 119						
III [i]	1870s, 1799s	−1110	+112	127	244.3	189.0	116.7	192.7	76.1	109.0

[a] 0.01 THF in 0.1 mm KBr cuvettes. [b] 0.1 THF, 300 K, rel. VOCl$_3$ at 23.66 MHz. [c] 0.1 THF, 200 K, rel. H$_3$PO$_4$ at 36.44 MHz. [d] Δδ(P) = δ(^{31}P)[coord. ligand] — δ(^{31}P)[uncoord. ligand]. [e] Average angles at phosphorus. [f] Data in Nujol; 1765, ca. 1740(sh). [g] At 190 K, a second signal (+119 ppm) arises; see text for discussion. [h] The signal at −15.0 ppm (doublet, ^3J(PP) = 27 Hz), corresponds to uncoordinated PPh$_2$. [i] Data from ref. 4 and 11.

TABLE 2

SELECTED STRUCTURAL DATA OF CpV(CO)triphos (MOLECULE 1 OF THE ASYMMETRIC UNIT; FOR NUMBERING OF THE ATOMS SEE FIG. 1)

Bond distances (pm)		Bond angles (°)	
V(1)—P(11)	242.9(0.4)	V(1)—C(1)—O(1)	775.6(1.0)
V(1)—P(12)	230.3(0.4)	P(11)—V(1)—C(1)	76.4(0.3)
V(1)—P(13)	244.2(0.4)	P(13)—V(1)—C(1)	78.0(0.3)
V(1)—C(1)	187.8(1.1)	P(11)—V(1)—P(12)	76.3(0.1)
C(1)—O(1)	117.4(1.3)	P(12)—V(1)—P(13)	76.7(0.1)
V(1)—C(11) to C(15)	234.7 to 229.6(1.2)	V(1)—P(11)—C(101)	120.5(0.4)
P(11)—C(101)	187.2(1.2)	V(1)—P(11)—C(107)	120.2(0.4)
P(11)—C(107)	189.0(1.3)	V(1)—P(11)—C(131)	110.7(0.4)
P(11)—C(131)	190.0(1.2)	C(101)—P(11)—C(107)	99.0(0.6)
P(12)—C(113)	187.4(1.2)	C(101)—P(11)—C(131)	101.2(0.5)
P(12)—C(132)	191.6(1.1)	C(107)—P(11)—C(131)	102.1(0.5)
P(12)—C(133)	186.8(1.3)	V(1)—P(12)—C(113)	126.3(0.4)
P(13)—C(119)	185.1(1.1)	V(1)—P(12)—C(132)	116.4(0.4)
P(13)—C(125)	186.8(1.3)	V(1)—P(12)—C(133)	126.3(0.4)
P(13)—C(134)	188.6(1.3)	C(113)—P(12)—C(132)	96.7(0.5)
C(131)—C(132)	156.4(1.5)	C(113)—P(12)—C(133)	100.3(0.5)
C(133)—C(134)	144.9(1.8)	C(132)—P(12)—C(133)	9.4(0.6)
C—C in Cp—ligand	145.0 to 150.0 (1.7)	B(1)—P(13)—C(119)	118.3(0.4)
		V(1)—P(13)—C(125)	101.3(0.5)
V(1)—plane 1	196.5	V(1)—P(13)—C(134)	114.8(0.4)
V(1)—plane 2	108.9	C(119)—P(13)—C(125)	101.3(0.5)
		C(119)—P(13)—C(134)	103.7(0.6)
		C(125)—P(13)—C(134)	99.1(0.6)

SQ-planes (deviations (pm) in brackets)

Plane 1:	C(11) (—0.7)	C(12) (0.2)	C(13) (—0.3)	C(14) (—0.7)	C(15) (0.9)
Plane 2:	C(1) (—22.5)	P(11) (20.0)	P(12) (—17.1)	P(13) (19.6)	

Angle between normals of plane 1 and 2: 10.5°

cis-[CpV(CO)$_2$triphos] (II) shows the expected two typically broadened (interaction with the ^{51}V nucleus, $I = 7/2$) ^{31}P resonances, corresponding to the PPh$_2$ and the PPh group. The half width $\Delta\nu_{1/2}$ at 200 K is 215 Hz. In contrast, there is only one signal observed for I in the temperature range of 290 to 200 K. The signal is rather broad at 290 K ($\Delta\nu_{1/2}$ 1200 Hz) and sharpens rapidly as the temperature is lowered (265 K: 930 Hz, 240 K: 370 Hz, 215 K: 230 Hz, 200 K: 135 Hz) due to partial decoupling of the ^{51}V and ^{31}P nuclei as the quadrupolar relaxation time decreases (rotational reorientation rates increase). While partial decoupling due to quadrupolar relaxation accounts for the comparatively sharp signals of I and II, there is an additional decrease of $\Delta\nu_{1/2}$ for I relative to II by ca. 80 Hz (at 200 K). This leads to the assumption that I is non-rigid on the NMR time scale. Fluxionality provides an additional decoupling mechanism and further accounts for the presence of only one signal. The ^{51}V resonance of I in turn is dynamically broadened ($\Delta\nu_{1/2}$ 1080 Hz) compared to that of II (750 Hz). Finally at 190 K two ^{31}P NMR signals are ob-

(Continued on p. 78)

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V(1)	0,74920(10)	0.4420(2)	0,71578(5)	0,0379(13)	0,0354(13)	0,0402(14)	0.0007(12)	0.0052(10)	—0,0017(12)
C(1)	0,6474(6)	0,4784(10)	0,7098(3)	0,037(8)	0,028(8)	0,054(9)	—0,002(7)	0,013(7)	—0,002(7)
O(1)	0,5841(4)	0,5008(7)	0,7035(2)	0,031(5)	0,069(7)	0,094(7)	0,004(5)	0,007(5)	0,012(5)
C(11)	0,7683(7)	0,5455(11)	0,6579)3)	0,6579(3)	0,065(9)	0,051(10)	0,005(9)	0,027(7)	—0,014(9)
C(12)	0,7955(6)	0,4207(10)	0,6548(3)	0,042(9)	0,043(9)	0,039(9)	0.004(7)	0,021(7)	—0,004(7)
C(13)	0,8572(6)	0,4011(12)	0,6857(3)	0,027(8)	0,094(11)	0,033(9)	—0,005(8)	—0,004(7)	—0,030(8)
C(14)	0,8658(6)	0,5155(12)	0,7070(3)	0,032(8)	0,056(10)	0,058(10)	0,023(8)	0,007(7)	—0,001(8)
C(15)	0,8119(7)	0,6062(11)	0,6896(3)	0,069(10)	0,070(10)	0,034(9)	—0,005(8)	0,013(8)	—0,026(9)
P(11)	0,6925(2)	0,2463(3)	0,69725(9)	0,043(2)	0,044(2)	0,049(2)	0,001(2)	—0,008(2)	—0,003(2)
C(101)	0,6135(6)	0,2390(12)	0,6591(4)	0,039(9)	0,041(9)	0,074(11)	—0,034(9)	—0,019(8)	0,010(8)
C(102)	0,6136(7)	0,3248(13)	0,6278(4)	0,067(11)	0,082(11)	0,053(10)	0,002(9)	—0,021(9)	0,019(9)
C(103)	0,5558(8)	0,3129(15)	0,5974(4)	0,055(10)	0,122(14)	0,062(11)	—0,010(11)	—0,023(9)	0,009(10)
C(104)	0,5017(8)	0,218(2)	0,5984(4)	0,054(11)	0,12(2)	0,082(13)	—0,046(12)	0,032(11)	0,019(11)
C(105)	0,5025(8)	0,1365(13)	0,6316(5)	0,062(12)	0,089(13)	0,098(14)	—0,040(11)	—0,012(11)	0,006(10)
C(106)	0,5577(7)	0,1466(12)	0,6622(4)	0,045(10)	0,079(12)	0,126(15)	—0,033(11)	—0,013(10)	—0,022(9)
C(107)	0,7511(7)	0.1171(11)	0,6769(4)	0,052(10)	0,037(9)	0,059(11)	0,017(8)	0,003(8)	0,014(8)
C(108)	0,8232(7)	0,1076(11)	0,6988(3)	0,047(9)	0,044(9)	0,043(9)	0,024(7)	0,005(7)	0,005(8)
C(109)	0,8696(7)	0.0089(12)	0,6881(4)	0,074(11)	0,041(9)	0,063(11)	0,020(8)	0,027(9)	0,012(9)
C(110)	0,8446(9)	—0,0758(13)	0,6594(4)	0,116(15)	0,073(12)	0,039(10)	0,008(9)	0,020(10)	0,015(11)
C(111)	0,7718(9)	—0,0646(12)	0,6404(3)	0,102(12)	0,052(10)	0,038(10)	0,001(8)	—0,003(9)	0,016(10)
C(112)	0,7232(8)	0,0351(13)	0,6503(4)	0,124(13)	0,046(9)	0,045(10)	—0,009(8)	0,019(9)	0,010(10)
C(131)	0,6494(6)	0,1727(10)	0,7400(3)	0,052(9)	0,065(9)	0,047(9)	0,017(8)	0,010(7)	—0,018(8)
C(132)	0,7124(6)	0,1677(10)	0,7735(3)	0,056(9)	0,047(8)	0,069(10)	0,016(8)	—0,007(8)	—0,011(7)
P(12)	0,7624(2)	0.3230(3)	0,77438(9)	0,047(2)	0,051(2)	0,043(2)	0,008(2)	0,006(2)	0,008(2)
C(113)	0,8517(6)	0,2684(10)	0,7997(3)	0,060(10)	0,034(8)	0,028(9)	0,002(7)	—0,008(7)	0,000(7)
C(114)	0,9169(7)	0,2920(10)	0,7810(3)	0,035(8)	0,050(9)	0,051(9)	—0,015(7)	0,001(8)	—0,010(7)
C(115)	0,9853(6)	0,2463(12)	0,7985(4)	0,044(9)	0.073(10)	0,049(9)	—0,001(9)	—0,001(8)	—0,002(9)
C(116)	0,9881(7)	0,1797(12)	0,8332(4)	0,059(10)	0,069(10)	0,042(10)	—0,012(9)	0,000(8)	—0,017(9)
C(117)	0,9213(8)	0,1615(11)	0,8516(3)	0,081(12)	0,045(9)	0,056(10)	0,008(8)	—0,003(9)	0,010(9)
C(118)	0,8517(7)	0,2033(11)	0,8342(4)	0,089(12)	0,042(9)	0,039(9)	0,016(7)	—0,10(8)	0,013(8)
C(133)	0,7185(7)	0,3964(12)	0,8157(4)	0,112(12)	0,073(11)	0,057(10)	0,009(9)	0,049(9)	0,060(10)
C(134)	0,7232(9)	0,5293(12)	0,8159(4)	0,25(2)	0,037(9)	0,043(10)	0,015(9)	0,063(11)	0,002(11)
P(13)	0,7366(2)	0,5949(3)	0,76648(9)	0,060(2)	0,044(2)	0,037(2)	—0,004(2)	0,009(2)	0,001(2)
C(119)	0,6616(6)	0,7104(9)	0,7593(4)	0,024(7)	0,030(8)	0,062(10)	—0,028(8)	0,008(7)	—0,007(6)
C(120)	0,6241(7)	0,7502(13)	0,7912(4)	0,045(9)	0,069(10)	0,083(12)	—0,037(10)	0,009(9)	0,005(9)
C(121)	0,5640(8)	0,8384(14)	0,7848(5)	0,079(12)	0,080(13)	0,109(15)	—0,019(12)	0,032(11)	0,004(10)

TABLE 3 (continued)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(122)	0,5470(7)	0,8830(12)	0,7472(5)	0,079(12)	0,051(10)	0,092(13)	0,010(11)	−0,013(11)	−0,022(9)
C(123)	0,5875(8)	0,8462(11)	0,7148(4)	0,080(12)	0,048(10)	0,081(13)	−0,016(9)	0,013(10)	−0,007(8)
C(124)	0,6445(7)	0,7592(11)	0,7224(4)	0,080(11)	0,033(8)	0,060(10)	0,019(8)	−0,003(8)	0,018(8)
C(125)	0,8188(7)	0,6948(12)	0,7793(3)	0,059(10)	0,050(10)	0,043(9)	−0,039(8)	−0,001(8)	−0,002(8)
C(126)	0,8155(7)	0,8228(12)	0,7719(3)	0,064(10)	0,050(10)	0,032(9)	−0,017(8)	0,007(7)	−0,017(9)
C(127)	0,8801(7)	0,9007(12)	0,7813(3)	0,043(9)	0,104(12)	0,031(9)	−0,018(8)	0,007(7)	−0,006(10)
C(128)	0,9436(8)	0,8432(15)	0,7999(4)	0,055(11)	0,094(14)	0,056(11)	−0,036(10)	0,023(8)	−0,008(10)
C(129)	0,9443(8)	0,716(2)	0,8084(4)	0,068(12)	0,089(13)	0,074(12)	−0,059(11)	−0,024(9)	0,007(10)
C(130)	0,8815(8)	0,6376(13)	0,7986(4)	0,062(11)	0,1111(13)	0,063(11)	−0,037(10)	−0,033(9)	0,048(11)
V(2)	0,71279(10)	0,0467(2)	0,48189(5)	0,0383(13)	0,0452(13)	0,0357(13)	−0,0229(13)	0,0032(10)	0,0033(12)
C(2)	0,6833(6)	0,0201(11)	0,4307(4)	0,033(8)	0,047(9)	0,064(10)	−0,001(9)	0,009(8)	0,009(7)
O(2)	0,6611(4)	0,0057(7)	0,3966(2)	0,059(6)	0,082(7)	0,050(7)	−0,018(6)	−0,003(5)	0,005(8)
C(21)	0,6050(6)	−0,0461(13)	0,5003(3)	0,043(10)	0,071(10)	0,036(9)	0,003(9)	0,022(7)	−0,015(9)
C(22)	0,6689(7)	−0,1210(12)	0,5141(4)	0,055(10)	0,090(11)	0,033(9)	0,019(9)	0,027(8)	−0,005(9)
C(23)	0,7147(7)	−0,0427(13)	0,5424(3)	0,068(10)	0,062(10)	0,045(9)	0,023(9)	0,018(8)	0,003(10)
C(24)	0,6798(6)	0,0756(12)	0,5451(3)	0,032(9)	0,091(12)	0,027(8)	0,020(8)	0,013(7)	−0,009(9)
C(25)	0,6119(6)	0,0733(11)	0,5190(3)	0,042(9)	0,058(10)	0,033(8)	−0,014(8)	0,025(7)	−0,003(7)
P(21)	0,8006(2)	−0,1047(3)	0,46242(10)	0,043(2)	0,049(2)	0,052(2)	−0,004(2)	0,008(2)	0,004(2)
C(201)	0,7709(7)	−0,2245(10)	0,4262(3)	0,080(10)	0,029(8)	0,029(8)	0,004(7)	−0,004(8)	0,021(8)
C(202)	0,6965(7)	−0,2657(11)	0,4222(4)	0,046(9)	0,033(8)	0,081(11)	0,004(8)	−0,005(8)	−0,013(8)
C(203)	0,6728(8)	−0,3550(12)	0,3941(4)	0,109(14)	0,042(10)	0,069(12)	−0,004(9)	−0,033(10)	0,003(9)
C(204)	0,7246(9)	−0,4022(12)	0,3680(4)	0,086(12)	0,058(11)	0,060(11)	0,005(9)	−0,007(10)	0,034(10)
C(205)	0,7982(9)	−0,3631(13)	0,3728(4)	0,092(13)	0,072(12)	0,056(11)	−0,004(9)	0,004(10)	0,020(11)
C(206)	0,8245(6)	−0,2740(12)	0,4020(4)	0,065(10)	0,070(11)	0,031(8)	−0,003(8)	0,017(8)	0,027(9)
C(207)	0,8469(6)	−0,2041(13)	0,5018(4)	0,031(8)	0,070(11)	0,052(10)	0,005(9)	0,021(7)	0,023(8)
C(208)	0,8357(7)	−0,3354(12)	0,5032(4)	0,080(12)	0,031(9)	0,082(13)	−0,018(9)	0,008(9)	−0,006(8)
C(209)	0,8665(8)	−0,4067(13)	0,5333(4)	0,080(12)	0,107(14)	0,055(11)	−0,003(11)	−0,032(9)	0,009(11)

C(210)	0.9080(7)	−0.3457(14)	0.5642(4)	0.061(10)	0.080(12)	0.062(12)	−0.010(10)	−0.015(8)	0.012(9)
C(211)	0.9185(7)	−0.2149(14)	0.5643(4)	0.046(10)	0.071(12)	0.086(13)	−0.024(10)	−0.001(9)	0.010(9)
C(212)	0.8875(6)	−0.1427(12)	0.5331(4)	0.019(8)	0.087(12)	0.062(11)	−0.019(10)	−0.015(7)	0.014(8)
C(321)	0.8818(6)	−0.0347(12)	0.4393(4)	0.049(9)	0.062(9)	0.086(11)	0.005(9)	0.026(8)	−0.018(8)
C(232)	0.9037(7)	0.0809(12)	0.4570(4)	0.068(11)	0.101(12)	0.125(13)	−0.087(11)	0.069(9)	−0.030(9)
P(22)	0.8263(2)	0.1611(3)	0.48131(9)	0.043(2)	0.057(2)	0.049(2)	−0.007(2)	0.007(2)	−0.009(2)
C(213)	0.8835(7)	0.2140(11)	0.5258(4)	0.048(10)	0.041(9)	0.058(11)	−0.019(8)	−0.016(8)	0.009(7)
C(214)	0.9476(7)	0.2905(12)	0.5206(4)	0.040(9)	0.061(11)	0.093(12)	0.011(9)	−0.008(9)	−0.001(8)
C(215)	0.9903(7)	0.3355(12)	0.5545(5)	0.059(11)	0.066(10)	0.090(13)	−0.016(11)	−0.043(10)	0.001(9)
C(216)	0.9673(8)	0.3307(13)	0.5907(4)	0.050(11)	0.072(12)	0.085(13)	−0.006(10)	−0.015(10)	0.023(9)
C(217)	0.9061(7)	0.2260(13)	0.5952(4)	0.048(10)	0.079(12)	0.068(11)	−0.012(9)	−0.005(9)	0.006(9)
C(218)	0.8630(7)	0.1784(12)	0.5626(4)	0.052(10)	0.090(11)	0.048(10)	−0.017(10)	−0.002(9)	0.013(9)
C(233)	0.8201(6)	0.3130(10)	0.4545(4)	0.061(9)	0.049(9)	0.063(9)	0.019(8)	−0.016(8)	−0.023(8)
C(234)	0.7456(6)	0.3137(10)	0.4277(3)	0.062(9)	0.069(9)	0.046(9)	0.011(8)	0.013(7)	−0.035(8)
P(23)	0.6716(2)	0.2443(3)	0.45711(9)	0.051(2)	0.042(2)	0.041(2)	−0.003(2)	−0.002(2)	0.001(2)
C(219)	0.5863(7)	0.2539(13)	0.4229(4)	0.057(10)	0.053(9)	0.062(11)	−0.013(9)	−0.011(8)	0.012(9)
C(220)	0.5255(7)	0.1781(12)	0.4325(3)	0.042(9)	0.085(11)	0.062(10)	−0.046(9)	−0.009(8)	0.007(9)
C(221)	0.4580(7)	0.1892(13)	0.4074(4)	0.072(12)	0.066(11)	0.066(11)	−0.011(9)	−0.021(9)	0.021(9)
C(222)	0.4537(8)	0.272(2)	0.3756(5)	0.079(13)	0.090(15)	0.10(2)	−0.025(12)	−0.009(12)	0.030(11)
C(223)	0.5141(9)	0.3425(15)	0.3679(4)	0.100(14)	0.12(2)	0.049(11)	0.014(10)	−0.049(11)	0.022(12)
C(224)	0.5841(9)	0.3361(12)	0.3909(4)	0.13(2)	0.062(11)	0.078(13)	0.018(10)	−0.022(11)	0.008(10)
C(225)	0.6545(7)	0.3732(10)	0.4907(4)	0.049(9)	0.033(9)	0.051(10)	−0.006(7)	0.023(8)	−0.007(7)
C(226)	0.7028(6)	0.3787(11)	0.5252(3)	0.056(9)	0.050(9)	0.021(8)	−0.013(7)	0.014(7)	−0.017(7)
C(227)	0.6963(7)	0.4813(13)	0.5502(4)	0.082(12)	0.061(11)	0.057(11)	0.014(9)	0.027(9)	0.003(9)
C(228)	0.6425(8)	0.5710(13)	0.5411(4)	0.071(12)	0.068(12)	0.066(12)	−0.005(10)	0.022(9)	−0.022(10)
C(229)	0.5944(7)	0.5645(13)	0.5078(5)	0.074(11)	0.047(11)	0.091(13)	0.015(10)	0.035(10)	0.002(9)
C(230)	0.6004(6)	0.4618(12)	0.4821(4)	0.068(11)	0.023(8)	0.102(12)	−0.015(9)	0.030(9)	−0.006(8)

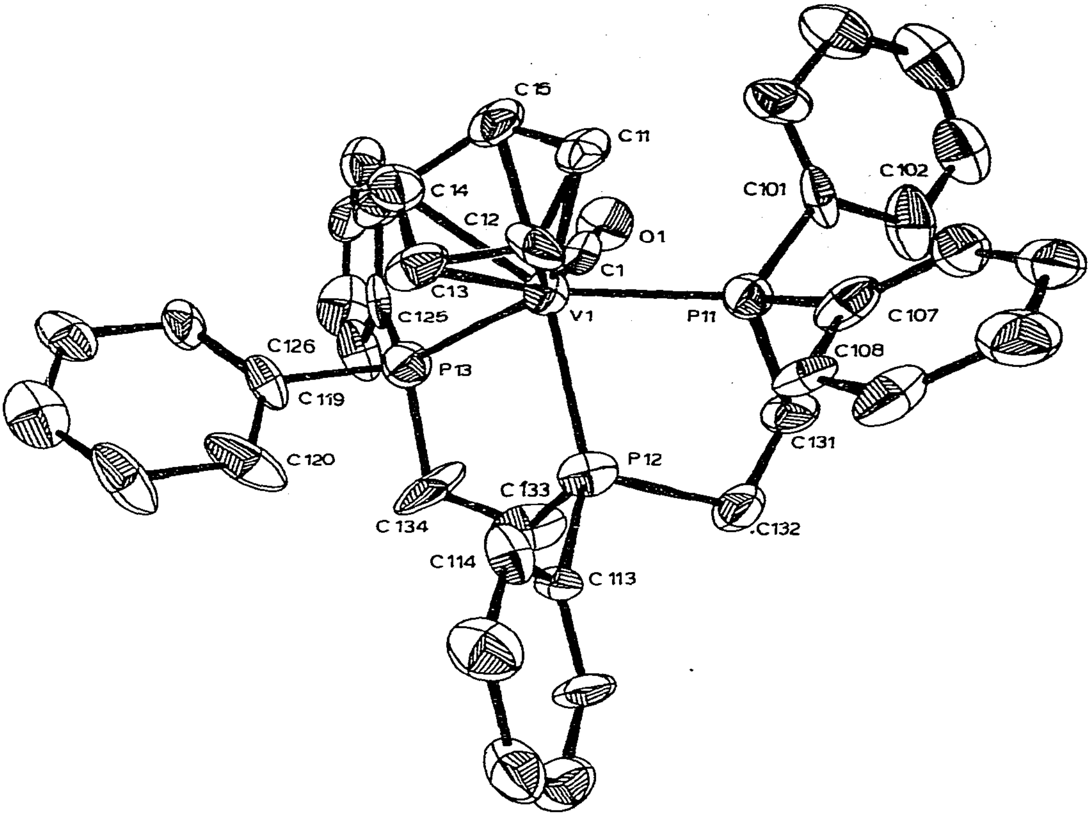

Fig. 1. ORTEP drawing and numbering (atom 1 of the asymmetric unit only) of atoms of CpV(CO)triphos.

served for I (PPh_2: +121.8 ppm, $\Delta\nu_{1/2}$ 100 Hz; PPh: +118.7 ppm, $\Delta\nu_{1/2}$ 190 Hz; ratio of integrals 2/1).

If I exhibits fluxional behaviour because the two resonances of the different phosphorus groups are averaged to a single absorption, the CO group must be *trans* and *cis* to the central PPh group of the triphos ligand. Hence the observation of two IR bands in the CO stretching region.

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