Discussion. The structure of the title compound is shown in Fig. 1. Positional parameters and equivalent values of the anisotropic temperature factors are given in Table 1,* bond lengths and angles in Table 2. The unit cell contains four $(C_6H_5)_2Sb_2Cl_6$ moieties and four $C_{10}H_{10}N_2$ moieties. The arrangement shown in Fig. 1 resides on a center of symmetry. In this arrangement the $C_{10}H_{10}N_2$ moieties have point symmetry 2. In $(C_6H_5)_2Sb_2Cl_6$ two $C_6H_5SbCl_2$ units are linked by two bridging Cl atoms. The two non-equivalent Sb—Cl bond distances in the bridge are significantly different [difference 0·096 (1) Å] and more than 0·563 (1) Å longer than the terminal Sb—Cl bonds. The atoms bound to the Sb atom form a distorted square pyramid with C(phenyl) in the apical position. Aside from these five bonds at the Sb atom there exists an intermolecular Sb···Cl(2) ($\bar{x}$, y, $\frac{1}{2}-z$) contact [3·756 (1) Å], which is somewhat shorter than the sum of the corresponding van der Waals radii of 3·87 Å (Bondi, 1964). The distance between Sb and the Cl atom which makes this intermolecular contact is significantly longer than the other terminal Sb—Cl bond lengths, and apparently does not seriously influence the coordination spheres around the two Sb atoms of the anionic unit. *Trans* to each phenyl ligand there is ample space for the lone pair at antimony. If the intermolecular Sb···Cl contact is not considered, the atoms around Sb form a distorted pseudo-octahedron. A similar geometry is found in the anion of $[(C_6H_5)_4As][(C_6H_5)_2Sb_2Br_4]$, in which two $C_6H_5SbBr_2$ units are linked *via* two unsymmetrically bridging Br atoms with Sb—Br bond distances of 2·957 (1) and 3·187 (1) Å (Preut, Huber, Alonzo & Bertazzi, 1986). The ring atoms of the bipyridinium unit do not deviate significantly from planarity and have a torsion angle C(14)—C(15)—C(15^{ii})—C(14^{ii}) of 34·96 (2)°.

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* Lists of structure factors, anisotropic thermal parameters and a complete list of atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43201 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of $[V(CO)_3(PMe_3)_4][V(CO)_6]$*

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Abstract. Tricarbonyltetrakis(trimethylphosphine)-vanadium(1+) hexacarbonylvanadate(1−), $[V(CO)_3\{(CH_3)_3P\}_4][V(CO)_6]$, $M_r = 658·3$, monoclinic, $P2_1/n$, $a = 12·901$ (3), $b = 16·137$ (3), $c = 15·519$ (3) Å, $\beta = 95·96$ (1)°, $V = 3213·3$ Å^3, $Z = 4$, $D_x = 1·361$ Mg m^{-3}, λ(Cu $K\alpha_1$) = 1·54056 Å, $\mu = 7·22$ mm^{-1}, $F(000) = 1360$, $T = 295$ K, $R = 0·105$ for 773 observed reflections. The structure consists of pairs of ions: $V(CO)_6^-$ which is approximately octahedral, and $V(CO)_3(PMe_3)_4^+$, a hepta-coordinated vanadium cation having the configuration of a monocapped octahedron in which a PMe_3 ligand caps a face defined by three carbonyl groups.

Introduction. The title compound was prepared during an attempted synthesis of *fac*-$V(CO)_3(PMe_3)_3$ (McCall, Morton & Preston, 1985), and is an example of a comparatively rare (Drew, 1977) hepta-coordinated vanadium compound. These compounds usually have structures based on the pentagonal bipyramid (Drew, 1977, 1982), but the title compound has a structure based on a monocapped octahedron.

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Experimental. 10 ml of potassium-dried *n*-pentane were degassed in a 50 ml flask. PMe_3 (1·6 mmol) and then $V(CO)_6$ (0·8 mmol) were distilled on to the solvent. The mixture was then stirred under argon for 15 hours in the dark. Volatile compounds were removed at 273 K, leaving a yellow–brown solid which was recrystallized from CH_2Cl_2. The bright orange crystals were subjected to elemental analysis: found: C 38·7%, H 5·8%, P 18·5%; calculated for $V(CO)_3(PMe_3)_4^+V(CO)_6^-$: C 38·3%, H 5·5%, P 18·8%.

X-ray diffraction intensity measurements were carried out at 295 K with graphite-monochromatized Cu $K\alpha$ radiation on a poor quality crystal of approximate dimensions 0·1 × 0·1 × 0·1 mm which was the only crystal available after repeated attempts at recrystallization. Lattice parameters were obtained from 74 reflections, $2\theta < 74°$. 2597 unique reflections were measured on a Picker diffractometer using the $\theta/2\theta$ scan mode and profile analysis (Grant & Gabe, 1978). Range of *hkl*: $-11 < h < 11$, $0 < k < 14$, $0 < l < 14$. $2\theta < 120°$. Only 773 of these reflections have $I(\text{net}) > 2{\cdot}5\sigma[I(\text{net})]$, and this small number, which is a result of high thermal motion, coupled with poor crystal quality, caused problems in the structure solution and severely limited the accuracy obtained (see high residual values). The crystal was mounted in a capillary tube with Si grease and therefore could not be measured for absorption corrections. Three standard reflections showed a decline of 9%.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares using unit weights with anisotropic thermal parameters for V and P and isotropic thermal parameters for C and O. A subsequent difference map revealed positions of at least one H atom on each methyl C atom, and the remaining H atoms were then fixed at their calculated positions (C—H = 1·08 Å, sp^3 hybridization). The 36 hydrogen atoms were included in the last least-squares cycle with isotropic temperature factors related to the thermal motions of the methyl C atom to which they are bonded, but were not refined. Refinement was performed with unit weights and counting statistics weights. The overall geometry with the former weighting scheme is more reasonable and the parameters quoted are for unit weights. $\sum w(|F_o| - |F_c|)^2$ was minimized for 175 parameters. The final residual values are high and result from the poor quality

Table 1. *Atomic parameters x, y, z and B_{iso} with e.s.d.'s referring to the last digit printed*

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

	x	*y*	*z*	B_{iso}
V(1)	0·2423 (6)	0·3409 (5)	0·8746 (6)	4·2 (5)
V(2)	0·7378 (7)	0·6028 (6)	0·6411 (6)	5·7 (6)
P(1)	0·2263 (12)	0·2290 (9)	0·9768 (12)	7·1 (11)
P(2)	0·2298 (11)	0·4906 (9)	0·9343 (11)	6·5 (10)
P(3)	0·1265 (10)	0·3796 (8)	0·7372 (10)	5·4 (8)
P(4)	0·4009 (11)	0·3590 (11)	0·7926 (13)	8·8 (12)
O(1)	0·255 (3)	0·1832 (24)	0·776 (3)	8·3 (11)
O(2)	0·026 (3)	0·351 (3)	0·945 (3)	10·4 (13)
O(3)	0·422 (3)	0·3670 (20)	1·0197 (23)	6·6 (9)
O(4)	0·913 (3)	0·6325 (24)	0·794 (3)	9·4 (12)
O(5)	0·922 (3)	0·5571 (25)	0·536 (3)	10·3 (13)
O(6)	0·7216 (24)	0·4293 (24)	0·7204 (24)	7·3 (10)
O(7)	0·591 (3)	0·5568 (24)	0·478 (3)	9·1 (12)
O(8)	0·735 (4)	0·779 (3)	0·558 (3)	12·6 (15)
O(9)	0·567 (3)	0·6590 (23)	0·7533 (25)	8·0 (10)
C(1)	0·247 (3)	0·251 (3)	0·819 (3)	3·6 (11)
C(2)	0·096 (5)	0·341 (4)	0·904 (4)	9·4 (18)
C(3)	0·356 (3)	0·353 (3)	0·963 (3)	4·6 (12)
C(4)	0·852 (4)	0·621 (3)	0·731 (4)	7·2 (16)
C(5)	0·850 (4)	0·565 (3)	0·577 (4)	7·5 (17)
C(6)	0·725 (4)	0·499 (4)	0·691 (4)	6·9 (16)
C(7)	0·648 (4)	0·568 (3)	0·541 (4)	7·5 (16)
C(8)	0·743 (4)	0·711 (4)	0·592 (4)	6·7 (16)
C(9)	0·636 (5)	0·650 (4)	0·701 (4)	8·5 (17)
C(11)	0·115 (4)	0·152 (4)	0·942 (4)	9·0 (17)
C(12)	0·331 (5)	0·160 (4)	0·990 (4)	11·1 (20)
C(13)	0·219 (4)	0·256 (4)	1·092 (4)	9·1 (18)
C(21)	0·222 (4)	0·492 (3)	1·051 (4)	7·2 (15)
C(22)	0·339 (4)	0·567 (3)	0·926 (4)	8·6 (17)
C(23)	0·114 (4)	0·553 (3)	0·892 (3)	6·8 (15)
C(31)	0·117 (4)	0·303 (3)	0·650 (4)	7·2 (15)
C(32)	0·162 (4)	0·465 (3)	0·672 (3)	6·3 (14)
C(33)	−0·007 (4)	0·398 (4)	0·748 (4)	9·0 (17)
C(41)	0·452 (5)	0·458 (4)	0·761 (4)	11·5 (21)
C(42)	0·508 (5)	0·305 (4)	0·848 (5)	11·8 (21)
C(43)	0·407 (5)	0·313 (4)	0·691 (4)	10·3 (20)

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

V(1)–P(1)	2·426 (19)	P(2)–C(22)	1·89 (6)
V(1)–P(2)	2·599 (16)	P(2)–C(23)	1·86 (5)
V(1)–P(3)	2·550 (16)	P(3)–C(31)	1·83 (6)
V(1)–P(4)	2·536 (17)	P(3)–C(32)	1·80 (5)
V(1)–C(1)	1·70 (5)	P(3)–C(33)	1·77 (6)
V(1)–C(2)	1·99 (7)	P(4)–C(41)	1·81 (7)
V(1)–C(3)	1·91 (5)	P(4)–C(42)	1·79 (7)
V(2)–C(4)	1·95 (6)	P(4)–C(43)	1·75 (7)
V(2)–C(5)	1·94 (6)	O(1)–C(1)	1·28 (6)
V(2)–C(6)	1·86 (6)	O(2)–C(2)	1·16 (8)
V(2)–C(7)	1·92 (7)	O(3)–C(3)	1·18 (6)
V(2)–C(8)	1·91 (6)	O(4)–C(4)	1·20 (8)
V(2)–C(9)	1·85 (6)	O(5)–C(5)	1·18 (8)
P(1)–C(11)	1·93 (6)	O(6)–C(6)	1·21 (7)
P(1)–C(12)	1·74 (7)	O(7)–C(7)	1·17 (8)
P(1)–C(13)	1·85 (6)	O(8)–C(8)	1·22 (8)
P(2)–C(21)	1·82 (6)	O(9)–C(9)	1·27 (8)

P(1)–V(1)–P(2)	116·5 (6)	C(8)–V(2)–C(9)	83·3 (24)
P(1)–V(1)–P(3)	130·3 (6)	V(1)–P(1)–C(11)	113·9 (19)
P(1)–V(1)–P(4)	122·8 (6)	V(1)–P(1)–C(12)	115·7 (22)
P(1)–V(1)–C(1)	72·9 (15)	V(1)–P(1)–C(13)	118·2 (20)
P(1)–V(1)–C(2)	72·6 (19)	C(11)–P(1)–C(12)	99 (3)
P(1)–V(1)–C(3)	73·7 (14)	C(11)–P(1)–C(13)	108 (3)
P(2)–V(1)–P(3)	91·0 (6)	C(12)–P(1)–C(13)	98 (3)
P(2)–V(1)–P(4)	98·9 (6)	V(1)–P(2)–C(21)	112·2 (17)
P(2)–V(1)–C(1)	170·4 (16)	V(1)–P(2)–C(22)	120·5 (18)
P(2)–V(1)–C(2)	79·8 (18)	V(1)–P(2)–C(23)	117·1 (17)
P(2)–V(1)–C(3)	73·8 (14)	C(21)–P(2)–C(22)	100·3 (24)
P(3)–V(1)–P(4)	89·1 (6)	C(21)–P(2)–C(23)	102·4 (23)
P(3)–V(1)–C(1)	80·5 (15)	C(22)–P(2)–C(23)	101·6 (24)
P(3)–V(1)–C(2)	72·9 (19)	V(1)–P(3)–C(31)	116·3 (18)
P(3)–V(1)–C(3)	155·9 (15)	V(1)–P(3)–C(32)	119·9 (17)
P(4)–V(1)–C(1)	76·5 (15)	V(1)–P(3)–C(33)	116·8 (20)
P(4)–V(1)–C(2)	161·9 (20)	C(31)–P(3)–C(32)	95·9 (24)
P(4)–V(1)–C(3)	75·3 (14)	C(31)–P(3)–C(33)	101 (3)
C(1)–V(1)–C(2)	101·9 (23)	C(32)–P(3)–C(33)	103·1 (25)
C(1)–V(1)–C(3)	112·6 (20)	V(1)–P(4)–C(41)	124·7 (21)
C(2)–V(1)–C(3)	120·8 (23)	V(1)–P(4)–C(42)	108·9 (23)
C(4)–V(2)–C(5)	82·4 (23)	V(1)–P(4)–C(43)	121·1 (22)
C(4)–V(2)–C(6)	85·9 (23)	C(41)–P(4)–C(42)	106 (3)
C(4)–V(2)–C(7)	166·8 (23)	C(41)–P(4)–C(43)	94 (3)
C(4)–V(2)–C(8)	95·3 (23)	C(42)–P(4)–C(43)	97 (3)
C(4)–V(2)–C(9)	95·6 (24)	V(1)–C(1)–O(1)	177 (4)
C(5)–V(2)–C(6)	91·7 (23)	V(1)–C(2)–O(2)	158 (5)
C(5)–V(2)–C(7)	85·1 (23)	V(1)–C(3)–O(3)	173 (4)
C(5)–V(2)–C(8)	91·5 (23)	V(2)–C(4)–O(4)	172 (4)
C(5)–V(2) C(9)	174·2 (25)	V(2)–C(5)–O(5)	167 (5)
C(6)–V(2)–C(7)	90·2 (23)	V(2)–C(6)–O(6)	176 (4)
C(6)–V(2)–C(8)	176·7 (22)	V(2)–C(7)–O(7)	172 (5)
C(6)–V(2)–C(9)	93·6 (25)	V(2)–C(8)–O(8)	172 (5)
C(7)–V(2)–C(8)	89·3 (23)	V(2)–C(9)–O(9)	161 (5)
C(7)–V(2)–C(9)	97·2 (24)		

of the data. Final $R = 0{\cdot}105$, $wR = 0{\cdot}119$, $S = 3{\cdot}21$; maximum $\Delta/\sigma = 0{\cdot}03$, max. and min. heights in final difference Fourier synthesis $= 0{\cdot}52$ and $-0{\cdot}45$ e Å^{-3}, respectively. All computations were performed using the *NRCVAX* system of programs (Gabe, Lee & Le Page, 1985). Atomic parameters of non-H atoms are given in Table 1, and Table 2 shows relevant bond lengths and angles.*

Discussion. The unit of the crystallographic structure consists of a pair of vanadium-centered ions, $[V(CO)_3(PMe_3)_4]^+.[V(CO)_6]^-$. In each of these species, the central atom has satisfied the effective atomic number rule by attaining the electronic structure of krypton. The structure of the cation is of particular interest since it contains hepta-coordinated vanadium.

A stereo diagram of the cation is given in Fig. 1 and its geometry is summarized in Table 3. The V(1)—P (ave. 2·528 Å, $\sigma = 0{\cdot}017$ Å) and V—C (ave. 1·89 Å, $\sigma = 0{\cdot}06$ Å) bond lengths do not differ significantly from those reported for $V(CO)_3(NO)(PMe_3)_2$ (Schiemann & Weiss, 1982) and $V(CO)_4(NO)(PMe_3)$ (Töfke & Behrens, 1986). The bond from V(1) to P(1) is significantly shorter and therefore stronger than the remaining V—P bonds.

In $V(CO)_3(PMe_3)_4^+$, one could regard V(1) as being at the center of a distorted octahedron with the seventh ligand, $P(1)Me_3$, capping the C(1), C(2), C(3) face. The resulting monocapped octahedron retains its C_{3v} symmetry. The strength of the V(1)—$P(1)Me_3$ interaction is reflected in the significant distortion of the carbonyls from ideal octahedral positions: the P(1)—V(1)—C(1,2,3) angles are ~75°, whereas they would be 55° (Drew, 1977) if the seventh ligand $P(1)Me_3$ had not distorted the octahedral C—V(1)—C angles. These C—V(1)—C angles are also all larger than 90°, the C—V(1)—P angles are less than the expected 180° but the P(*n*)—V(1)—P(*m*) angles are not decreased. Similar interbond angles have been observed for the mono-capped octahedral structures of $W(CO)_4Br_3^-$ (Drew & Wolters, 1972) and $Mo(PPhMe_2)_3Br_4$ (Drew & Wilkins, 1972). It would appear that hepta-coordinated molecules $MX(4)Y(3)$ adopt a high C_{3v} symmetry structure in which the capping ligand X occupies the least sterically crowded face. It is also noteworthy that the M—X(cap) bond of such species is considerably shorter than the other M—X bonds. No satisfactory explanation of this phenomenon has yet been presented. In the structure of the title compound, distortions from C_{3v} symmetry in $V(CO)_3(PMe_3)_4^+$ arise mainly because of a displacement of the carbon atom C(2) of the carbonyl group C(2)—O(2) towards the $P(3)Me_3$ ligand. This displacement is probably an artifact of the refinement and does not have any chemical significance. $V(CO)_6^-$ is a six-coordinate vanadium anion in an octahedral configuration with normal bond lengths and angles.

The formation of the ionic title compound from $V(CO)_6$ and PMe_3 parallels the preparation of $V(CO)_3$-diars)$_2^+$.$V(CO)_6^-$ from $V(CO)_6$ and diars (o-phenylene-bisdimethylarsine) (Ellis & Faltynek, 1975), and casts further doubt on the dimeric formulation $[V(CO)_4\{P(C_6H_{11})_3\}_2]_2$ for the product of the reaction between $V(CO)_6$ and $P(C_6H_{11})_3$ (Hieber & Winter, 1964).

Table 3. *Geometry of the* $[V(CO)_3(PM3_3)_4]^+$ *polyhedron*

L—V(1)—L	Number in polyhedron	Mean angle (°)*	$L\cdots L$ (Å)
P(1)†—V(1)—C	3	73·0	2·59
P(1)—V(1)—Pn‡	3	123·2	4·38
C—V(1)—C	3	111·7	3·09
P*n*—V(1)—P*n*	3	93·0	3·75
$\lvert C—V(1)—Pn\rvert_{trans}$	3	162·8	4·37
$\lvert C—V(1)—Pn\rvert_{cis}$	6	76·5	2·79

* Mean e.s.d.'s for angles: P—V(1)—C 1·6, P—V(1)—P 0·6, C—V(1)—C 2·1°; bonds: P—C 0·05, P—P 0·02, C—C 0·07 Å.
† $P(1)Me_3$ ligand caps the C(1,2,3) face.
‡ n = 2,3,4; PMe_3 ligands defining the uncapped face.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43322 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

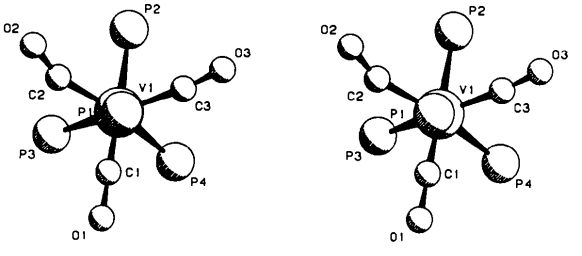

Fig. 1. Stereo diagram of the cation $[V(CO)_3(PMe_3)_4]^+$ with numbering scheme. PMe_3 C atoms have been omitted for clarity.

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