

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

Table 1. Atomic parameters

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}/U_{iso}(\text{\AA}^2)$
V	0.22339 (7)	0.14840 (4)	0.21074 (3)	0.0427 (5)
C(1)	0.1236 (5)	0.2757 (3)	0.2750 (2)	0.062 (4)
O(1)	0.0650 (5)	0.3459 (2)	0.3138 (2)	0.101 (4)
C(2)	0.4930 (5)	0.1948 (3)	0.2624 (2)	0.058 (3)
O(2)	0.6467 (4)	0.2185 (3)	0.2945 (2)	0.096 (4)
C(3)	-0.0467 (5)	0.1109 (3)	0.1517 (2)	0.064 (4)
O(3)	-0.2021 (4)	0.0878 (3)	0.1204 (2)	0.103 (4)
C(4)	0.3196 (5)	0.0282 (3)	0.1375 (2)	0.064 (4)
O(4)	0.3719 (5)	-0.0436 (3)	0.0985 (2)	0.118 (4)
N	0.2167 (4)	0.0540 (2)	0.2989 (2)	0.052 (3)
O(5)	0.2122 (4)	-0.0115 (2)	0.3597 (2)	0.080 (3)
P	0.2340 (1)	0.2893 (1)	0.0849 (1)	0.048 (1)
C(5)	0.4116 (6)	0.2613 (4)	0.0157 (3)	0.093 (5)
C(6)	0.0103 (5)	0.3078 (3)	0.0032 (2)	0.065 (4)
C(7)	0.2908 (6)	0.4346 (3)	0.1224 (3)	0.077 (4)
H(1)	0.5352 (24)	0.2606 (23)	0.0555 (17)	0.099 (5)
H(2)	0.3882 (47)	0.1890 (11)	-0.0133 (17)	0.099 (5)
H(3)	0.4095 (44)	0.3192 (17)	-0.0290 (15)	0.099 (5)
H(4)	-0.0899 (32)	0.3302 (23)	0.0340 (18)	0.099 (5)
H(5)	-0.0201 (45)	0.2351 (11)	-0.0243 (18)	0.099 (5)
H(6)	0.0213 (45)	0.3626 (17)	-0.0423 (14)	0.099 (5)
H(7)	0.4113 (19)	0.4354 (27)	0.1646 (14)	0.099 (5)
H(8)	0.1905 (30)	0.4620 (27)	0.1512 (16)	0.099 (5)
H(9)	0.2997 (38)	0.4822 (23)	0.0720 (13)	0.099 (5)

(Sheldrick, 1977); for V from *International Tables for X-ray Crystallography* (1974). 164 parameters. Final conventional R factor 0.0465 for 2221 structure factors; $wR = 0.0442$; $w = 1.5599/\sigma^2(|F|) + 0.0004F^2$. Final difference map showed no peak higher than 0.5 or less than -0.3 e \AA^{-3} ; all Δ/σ values < 0.01 . Plots performed with *ORTEPII* (Johnson, 1976).

Discussion. Table 1 gives the atomic parameters,* Table 2 the bond distances and corresponding angles. Fig. 1 shows the mononuclear vanadium complex with approximate C_{4v} symmetry around the central V atom. The angles at V are all close to the ideal values of 90 and 180°, the most significantly different being C(1)–V–C(4) [175.5 (1)°]. The four CO groups are nearly linear [angles between 176.8 (3) and 177.8 (3)°]. The V–P bond length [2.543 (1) Å] is the longest bonding distance ever found for a vanadium phosphine complex, thus reflecting the large *trans* effect of the nitrosyl ligand. Normally V–P lengths around 2.45 Å are observed. A similar long V–P distance [2.525 (3) Å] is found for the nitrosyl complex [V(CO)₃(NO)(PMe₃)₂] (Schiemann & Weiss, 1982). The V–C bond lengths are normal [average 1.996 (2) Å] compared with those found for [V(CO)₆] (Bellard, Rubinson & Sheldrick, 1979). The same holds for the C–O distances [average 1.139 (3) Å]. The V–N–O group is strictly linear [179.9 (1)°]. The V–N distance [1.747 (3) Å] is shorter than that found for [V(CO)₃(NO)(PMe₃)₂] [1.809 (10) Å] (Schiemann & Weiss, 1982) but longer than those for [V(CN)₅(NO)]³⁻ [1.66 (4) Å] (Jagner & Vannerberg, 1970) and [V(CN)₆(NO)]⁴⁻ [1.680 (16) Å] (Drew & Pygall, 1977). Fig. 2 shows the unit-cell contents.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42537 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

V–P	2.543 (1)	P–C(6)	1.821 (3)
V–N	1.747 (2)	P–C(7)	1.827 (4)
V–C(1)	1.995 (4)	N–O(5)	1.208 (3)
V–C(2)	1.992 (4)	C(1)–O(1)	1.140 (4)
V–C(3)	1.995 (4)	C(2)–O(2)	1.136 (4)
V–C(4)	2.002 (4)	C(3)–O(3)	1.142 (4)
P–C(5)	1.819 (3)	C(4)–O(4)	1.136 (4)
P–V–N	178.8 (1)	C(2)–V–C(4)	90.5 (1)
P–V–C(1)	86.4 (1)	C(3)–V–C(4)	89.7 (2)
P–V–C(2)	87.0 (1)	V–P–C(5)	116.0 (1)
P–V–C(3)	88.6 (1)	V–P–C(6)	116.0 (1)
P–V–C(4)	89.2 (1)	V–P–C(7)	114.7 (1)
N–V–C(1)	92.5 (1)	C(5)–P–C(6)	103.7 (2)
N–V–C(2)	92.5 (1)	C(5)–P–C(7)	102.4 (2)
N–V–C(3)	91.9 (1)	C(6)–P–C(7)	102.0 (2)
N–V–C(4)	91.9 (1)	V–N–O(5)	179.9 (1)
C(1)–V–C(2)	90.3 (1)	V–C(1)–O(1)	177.6 (3)
C(1)–V–C(3)	89.2 (2)	V–C(2)–O(2)	177.4 (3)
C(1)–V–C(4)	175.5 (1)	V–C(3)–O(3)	177.8 (3)
C(2)–V–C(3)	175.6 (1)	V–C(4)–O(4)	176.8 (3)

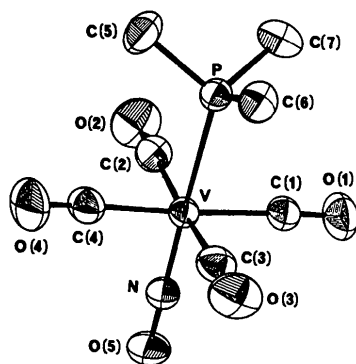


Fig. 1. ORTEP plot of the molecular structure.

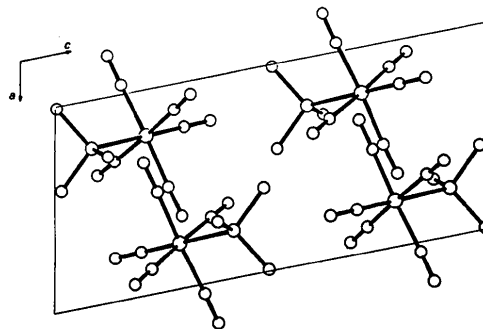


Fig. 2. Contents of the unit cell (projection on ac).

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Structures of Heptadecacarbonyl(triphenylphosphine)hexaosmium(0) and Hexadecacarbonylbis(triphenylphosphine)hexaosmium(0)

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Abstract. $[\text{Os}_6(\text{CO})_{17}\{\text{P}(\text{C}_6\text{H}_5)_3\}]$ (I), $M_r = 1879.47$, triclinic, $P\bar{1}$, $a = 9.122$ (4), $b = 14.542$ (7), $c = 16.569$ (7) Å, $\alpha = 74.07$ (4), $\beta = 87.10$ (3), $\gamma = 71.83$ (3)°, $V = 2006.6$ Å³, $Z = 2$, $D_x = 3.11$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 19.02$ mm⁻¹, $F(000) = 1700$, $T = 290$ K, $R = 0.038$ for 5896 reflections. $[\text{Os}_6(\text{CO})_{16}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (II), $M_r = 2113.9$, monoclinic, $C2/c$, $a = 17.472$ (4), $b = 18.064$ (2), $c = 17.688$ (3) Å, $\beta = 104.29$ (2)°, $V = 5409.0$ Å³, $Z = 4$, $D_x = 2.60$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 14.18$ mm⁻¹, $F(000) = 3824$, $T = 296$ K, $R = 0.039$ for 4895 reflections. The six Os atoms, in both (I) and (II), define a bicapped tetrahedron closely related to that in the parent carbonyl, $\text{Os}_6(\text{CO})_{18}$. The triphenylphosphine ligands are terminally bound to one, in (I), or both, in (II), of the capping Os atoms, and in each case the Os–P vector lies approximately *trans* to the longest Os–Os bond [2.998 (4) Å in (I) and 2.943 (1) Å in (II)]. Two terminal carbonyl groups are also bound to these metal atoms, while the other metal atoms are each coordinated to three carbonyl groups. In (I) the Os atoms and carbonyl groups are also linked by a network of incipient bridge bonds, a feature which is also observed in (II).

Introduction. The introduction of the labile acetonitrile ligand into triosmium cluster carbonyls greatly enhances their reactivity under mild reaction conditions. The

clusters $\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)$ and $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ have become important as starting materials in a wide variety of cluster reactions (Johnson, Lewis & Pippard, 1981; Tachikawa & Shapley, 1977; Deeming, Ghatak, Owen & Peters, 1982; Mayr, Lin, Boag & Kaesz, 1982). It has recently been found possible to activate higher nuclearity osmium clusters with acetonitrile in a similar manner to the trinuclear systems (Gómez-Sal, Johnson, Kamarudin, Lewis & Raithby, 1985). In this paper we report the reaction of the activated complexes $\text{Os}_6(\text{CO})_{18-n}(\text{NCCH}_3)_n$, $n = 1, 2$, with triphenylphosphine to afford the clusters $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ (I) and $\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II), the X-ray crystal structures of which have been determined.

Experimental. (I) Reaction of $\text{Os}_6(\text{CO})_{18}$ with slight excess of $(\text{CH}_3)_3\text{NO}$ (1.1 equivalents) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ at 195 K affords the complex $\text{Os}_6(\text{CO})_{17}(\text{NCCH}_3)$. This product is used *in situ* in the reaction with triphenylphosphine (1 equivalent) to give $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{C}_6\text{H}_5)_3]$ as the major product. Purification and recrystallization from CH_2Cl_2 , black block-shaped single crystals obtained. Synthesis of (II) is similar to that of (I) except that two equivalents of $(\text{CH}_3)_3\text{NO}$ are used to generate the complex $\text{Os}_6(\text{CO})_{16}(\text{NCCH}_3)_2$, which is then reacted with an excess of triphenylphosphine to give $\text{Os}_6(\text{CO})_{16}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in 25% yield. After purification, dark brown long brick-shaped single