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Bis(*tert*-butyl isocyanide)hexadecacarbonylhexaosmium

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Abstract. $Os_6(CO)_{16}(CNC_4H_9)_2$, triclinic, $P\bar{1}$, a = 9·567 (4), b = 10·583 (6), c = 19·647 (16) Å, α = 87·93 (4), β = 82·90 (4), γ = 71·56 (3)°, U = 1872·6 Å^3, Z = 2, D_x = 3·12 g cm^{-3}, μ(Mo $K\alpha$) = 196·1 cm^{-1}. The structure was refined to an R of 0·042 for 3283 unique diffractometer data. The six Os atoms form a bicapped tetrahedron, with all ligands terminal. Although the isocyanides are positioned so as to induce C_s molecular symmetry, the metal cluster shows a marked C_2 distortion.

Introduction. The compound was isolated from the pyrolysis of $Os_3(CO)_{11}$(Bu^{t}NC) in refluxing octane (Mays & Gavens, 1977). The crystal structure has been determined in order to establish the isocyanide substitution positions and to assess the effect on the $Os_6(CO)_{18}$ cluster geometry of the replacement of two carbonyl groups by isocyanides.

Black laminar crystals [principal faces (001)] were grown from dichloromethane/hexane. Intensities were determined with a Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation and a crystal 0·16 × 0·12 × 0·015 mm. Semi-empirical absorption corrections were applied on the basis of 155 azimuthal scan data for 10 independent reflexions well separated in reciprocal space; the corrections reduced the merging R for these data from 0·246 to 0·045. 5399 intensities were measured; equivalent reflexions were averaged to give 3283 unique data with $F > 6\sigma(F)$ based on counting statistics. Cell dimensions were determined by least squares from diffractometer angles for 15 reflexions. The Os atoms were located by multi-solution $\sum_2$ sign expansion, and the remaining non-hydrogen atoms from difference syntheses. The structure was refined by blocked-full-matrix least squares with anisotropic temperature factors for Os and isotropic C, N and O. The *tert*-butyl group [C(44)–C(47)] showed signs of thermal disorder, so weak constraints (in the form of extra least-squares observational equations) were applied to make the angles at the central C atom approximately tetrahedral; a common isotropic temperature factor was employed for C(45), C(46) and C(47). These constraints did not significantly affect R. Complex neutral-atom scattering factors were employed, with the weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}00035F^2]$. Refinement converged to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| =$

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U
Os(1)	2129 (1)	359 (1)	2539 (1)	*
Os(2)	4849 (1)	−1009 (1)	2991 (1)	*
Os(3)	4284 (1)	1621 (1)	2532 (1)	*
Os(4)	3426 (1)	−2311 (1)	2178 (1)	*
Os(5)	4705 (1)	−394 (1)	1604 (1)	*
Os(6)	2889 (1)	1027 (1)	3811 (1)	*
C(11)	1207 (28)	111 (20)	1801 (17)	66 (7)
O(11)	502 (22)	95 (16)	1352 (13)	95 (6)
C(12)	763 (27)	7 (20)	3202 (16)	60 (7)
O(12)	−63 (23)	−378 (17)	3594 (14)	107 (7)
C(13)	1049 (25)	2207 (19)	2442 (15)	55 (6)
O(13)	391 (19)	3285 (15)	2356 (11)	75 (5)
C(21)	5972 (27)	−529 (19)	3597 (16)	61 (7)
O(21)	6772 (20)	−416 (14)	3975 (11)	75 (5)
C(22)	4409 (22)	−2314 (17)	3576 (14)	44 (5)
O(22)	4184 (18)	−3121 (14)	3954 (11)	67 (5)
C(23)	6623 (33)	−2114 (25)	2555 (19)	91 (9)
O(23)	7813 (23)	−2857 (17)	2326 (13)	101 (7)
C(31)	3865 (33)	2834 (26)	1785 (20)	87 (9)
O(31)	3575 (24)	3546 (19)	1359 (15)	106 (7)
C(32)	6293 (29)	1562 (20)	2552 (16)	64 (7)
O(32)	7472 (21)	1519 (15)	2515 (12)	82 (6)
C(33)	3688 (32)	3084 (25)	3129 (19)	88 (9)
O(33)	3464 (19)	4041 (15)	3465 (12)	79 (5)
C(41)	4809 (26)	−3998 (20)	2144 (15)	57 (6)
O(41)	5753 (19)	−5012 (14)	2137 (11)	72 (5)
C(42)	2155 (30)	−2949 (21)	2741 (18)	71 (8)
O(32)	1272 (23)	−3267 (17)	3131 (13)	103 (7)
C(43)	2642 (26)	−2724 (19)	1411 (16)	57 (7)
N(4)	2213 (23)	−2942 (17)	905 (14)	73 (6)
C(44)	1567 (29)	−3188 (22)	340 (16)	98 (10)
C(45)	2664 (40)	−4305 (33)	−103 (21)	189 (11)
C(46)	878 (41)	−1964 (32)	−82 (21)	189 (11)
C(47)	228 (36)	−3662 (35)	654 (23)	189 (11)
C(51)	5310 (31)	−1977 (25)	1064 (19)	80 (9)
O(51)	5898 (23)	−2862 (18)	735 (14)	105 (7)
C(52)	3768 (34)	537 (26)	908 (20)	90 (9)
O(52)	3154 (25)	1099 (20)	448 (15)	117 (7)
C(53)	6496 (44)	−80 (30)	1297 (23)	120 (13)
O(53)	7650 (32)	−42 (22)	1135 (17)	151 (10)
C(61)	3832 (25)	1561 (18)	4451 (15)	53 (6)
O(61)	4441 (20)	1925 (15)	4843 (12)	86 (6)
C(62)	2166 (22)	−39 (17)	4475 (14)	43 (5)
O(62)	1831 (18)	−739 (14)	4860 (11)	70 (5)
C(63)	1025 (24)	2509 (18)	4013 (14)	48 (6)
N(6)	−134 (19)	3308 (14)	4140 (11)	50 (5)
C(64)	−1604 (21)	4256 (16)	4238 (11)	45 (5)
C(65)	−1568 (27)	5575 (18)	3881 (14)	74 (8)
C(66)	−2020 (26)	4452 (20)	5009 (12)	68 (7)
C(67)	−2615 (25)	3677 (20)	3898 (14)	76 (8)

* Anisotropic thermal parameters have been deposited.

Table 2. *Bond lengths* (Å)

Os(2)–Os(1)	2·784 (3)	Os(3)–Os(1)	2·787 (3)
Os(4)–Os(1)	2·781 (3)	Os(5)–Os(1)	2·797 (3)
Os(6)–Os(1)	2·860 (4)	Os(3)–Os(2)	2·800 (3)
Os(4)–Os(2)	2·861 (3)	Os(5)–Os(2)	2·788 (3)
Os(6)–Os(2)	2·775 (3)	Os(5)–Os(3)	2·754 (3)
Os(6)–Os(3)	2·842 (3)	Os(5)–Os(4)	2·820 (3)
C(11)–Os(1)	1·854 (35)	C(12)–Os(1)	1·843 (28)
C(13)–Os(1)	1·917 (20)	C(21)–Os(2)	1·880 (32)
C(22)–Os(2)	1·881 (23)	C(23)–Os(2)	1·854 (28)
C(31)–Os(3)	1·909 (36)	C(32)–Os(3)	1·909 (29)
C(33)–Os(3)	1·872 (32)	C(41)–Os(4)	1·853 (19)
C(42)–Os(4)	1·814 (31)	C(52)–Os(5)	1·814 (37)
C(53)–Os(5)	1·870 (44)	C(61)–Os(6)	1·835 (30)
C(62)–Os(6)	1·903 (24)	C(63)–Os(6)	1·975 (19)
N(4)–C(43)	1·179 (43)	Os(4)–C(43)	1·886 (32)
C(44)–N(4)	1·405 (44)	C(45)–C(44)	1·523 (41)
C(46)–C(44)	1·522 (43)	C(47)–C(44)	1·569 (49)
C(64)–N(6)	1·441 (23)	C(63)–N(6)	1·166 (24)
C(65)–C(64)	1·547 (29)	C(66)–C(64)	1·521 (32)
C(67)–C(64)	1·524 (37)	O(11)–C(11)	1·178 (43)
O(12)–C(12)	1·190 (37)	O(13)–C(13)	1·133 (24)
O(21)–C(21)	1·165 (39)	O(22)–C(22)	1·166 (29)
O(23)–C(23)	1·204 (33)	O(31)–C(31)	1·108 (44)
O(32)–C(32)	1·107 (36)	O(33)–C(33)	1·177 (37)
O(41)–C(41)	1·162 (24)	O(42)–C(42)	1·190 (39)
O(51)–C(51)	1·110 (35)	O(52)–C(52)	1·178 (46)
O(53)–C(53)	1·123 (53)	O(61)–C(61)	1·164 (38)
O(62)–C(62)	1·129 (30)	Os(5)–C(51)	1·906 (30)

0·039 and $R = 0·042$. Positional and isotropic thermal parameters are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The Os_6 cluster forms a bicapped tetrahedron consistent with extended Wade theory (Wade 1975; Eady, Johnson & Lewis, 1975). The two isocyanides replace two of the carbonyls in the Os_4 plane of $Os_6(CO)_{18}$, reducing the ligand symmetry from approximately C_{2v} (Mason, Thomas & Mingos, 1973) to C_s. The Os–Os lengths, however, conform much more closely to C_2 (mean deviation 0·007 Å) than to C_s (0·047 Å); a similar but less pronounced trend can be seen in $Os_6(CO)_{18}$ (0·011 and 0·018 Å respectively). The C_2 distortion is particularly clear in the Os_4 basal plane, and contradicts the expected *trans* effect of the isocyanide ligands. The cluster dimensions in $Os_6(CO)_{18}$ and the bis(isocyanide) derivative are compared in Fig. 1. The carbonyl arrangement (Fig. 2) is also approximately C_2 (C_s would be less staggered); this may well be the dominating factor in determining the distortion of the metal cluster. Substitution of isocyanides on Os(4) and Os(6) slightly lengthens the mean Os–Os bond involving these atoms (2·823 Å relative to 2·812 Å in the carbonyl); replacement of one carbonyl in $Os_6(CO)_{18}$ by an O_2C- substituent (a much weaker π acceptor) has a larger effect in the same direction (2·877 Å for the substituted Os, 2·814 Å for the other; Eady, Guy, Johnson, Lewis, Malatesta & Sheldrick, 1976). The mean Os–Os distances in the central Os_4 tetrahedron are the same (2·782, 2·785 and 2·783 Å) in all three compounds. The Os–C–O and Os–C–N angles have typical values in the range 170–180°, but as found in $Os_5(CO)_{16}$ (Reichert & Sheldrick, 1977) two of the largest deviations from linearity are associated with short C···Os interactions [Os(5)–C(51)–O(51) 167·6°, C(51)···Os(4) 2·74 Å; Os(3)–C(33)–O(33) 171·7°, C(33)···Os(6) 2·78 Å]. The isocyanide ligands are also approximately linear at N [C–N–C 174·4, 174·5°; C–N (mean) 1·17 (2) Å] analogous to the terminal isocyanides in $Pt_3(CNBu^t)_6$ [mean N–C 1·15 (3) Å; the bridging isocyanides are bent at N with mean C–N–C 132·7°; Green, Howard, Murray, Spencer & Stone, 1977].

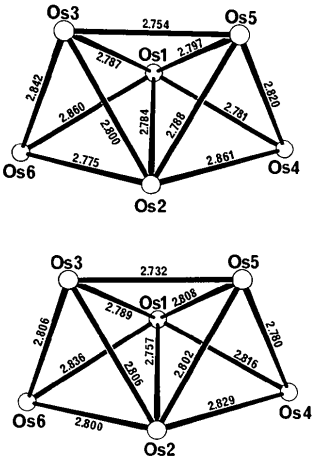

Fig. 1. Os_6 cluster dimensions in $Os_6(CO)_{16}(CNBu^t)_2$ and $Os_6(CO)_{18}$ (Mason, Thomas & Mingos, 1973).

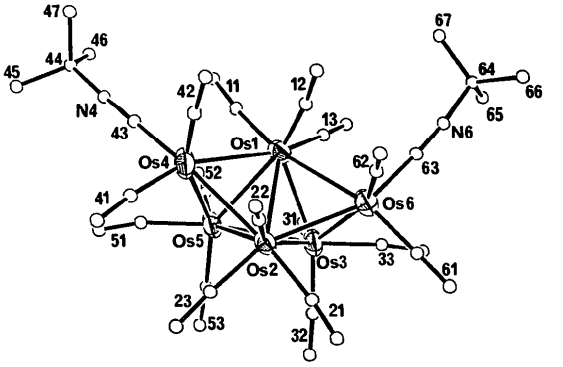

Fig. 2. *ORTEP* diagram of $Os_6(CO)_{16}(CNBu^t)_2$, showing the atom labelling and 50% probability ellipsoids for the anisotropic atoms.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33385 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond angles* (°)

Os(3)–Os(1)–Os(2)	60·3 (1)	Os(4)–Os(1)–Os(2)	61·9 (1)	Os(5)–Os(4)–C(43)	100·5 (9)	Os(5)–Os(4)–Os(1)	59·9 (1)
Os(4)–Os(1)–Os(3)	110·7 (1)	Os(5)–Os(1)–Os(2)	59·9 (1)	Os(5)–Os(4)–Os(2)	58·8 (1)	C(41)–Os(4)–C(43)	90·2 (12)
Os(5)–Os(1)–Os(3)	59·1 (1)	Os(5)–Os(1)–Os(4)	60·7 (1)	C(41)–Os(4)–Os(1)	157·9 (9)	C(41)–Os(4)–Os(2)	98·8 (10)
Os(6)–Os(1)–Os(2)	58·9 (1)	Os(6)–Os(1)–Os(3)	60·4 (1)	C(41)–Os(4)–Os(5)	111·3 (8)	C(42)–Os(4)–C(43)	89·8 (15)
Os(6)–Os(1)–Os(4)	113·7 (1)	Os(6)–Os(1)–Os(5)	108·3 (1)	C(42)–Os(4)–Os(1)	97·0 (8)	C(42)–Os(4)–Os(2)	108·8 (11)
C(11)–Os(1)–Os(2)	132·9 (6)	C(11)–Os(1)–Os(3)	127·3 (9)	C(42)–Os(4)–Os(5)	156·8 (7)	C(42)–Os(4)–C(41)	89·2 (11)
C(11)–Os(1)–Os(4)	74·6 (7)	C(11)–Os(1)–Os(5)	84·1 (9)	Os(2)–Os(5)–Os(1)	59·8 (1)	Os(3)–Os(5)–Os(1)	60·3 (1)
C(11)–Os(1)–Os(6)	167·2 (8)	C(12)–Os(1)–Os(2)	103·7 (9)	Os(3)–Os(5)–Os(2)	60·7 (1)	Os(4)–Os(5)–Os(1)	59·4 (1)
C(12)–Os(1)–Os(3)	134·6 (9)	C(12)–Os(1)–Os(4)	93·1 (7)	Os(4)–Os(5)–Os(2)	61·4 (1)	Os(4)–Os(5)–Os(3)	110·5 (1)
C(12)–Os(1)–Os(5)	153·1 (6)	C(12)–Os(1)–Os(6)	74·8 (11)	C(51)–Os(5)–Os(1)	123·5 (9)	C(51)–Os(5)–Os(2)	110·6 (10)
C(12)–Os(1)–C(11)	95·5 (14)	C(13)–Os(1)–Os(2)	134·0 (8)	C(51)–Os(5)–Os(3)	168·6 (10)	C(51)–Os(5)–Os(4)	67·8 (10)
C(13)–Os(1)–Os(3)	76·3 (9)	C(13)–Os(1)–Os(4)	158·3 (9)	C(52)–Os(5)–Os(1)	93·1 (11)	C(52)–Os(5)–Os(2)	151·9 (10)
C(13)–Os(1)–Os(5)	111·0 (8)	C(13)–Os(1)–Os(6)	87·8 (10)	C(52)–Os(5)–Os(3)	100·8 (11)	C(52)–Os(5)–Os(4)	113·3 (11)
C(13)–Os(1)–C(11)	84·8 (12)	C(13)–Os(1)–C(12)	95·8 (11)	C(52)–Os(5)–C(51)	90·0 (15)	C(53)–Os(5)–Os(1)	145·6 (12)
Os(3)–Os(2)–Os(1)	59·9 (1)	Os(4)–Os(2)–Os(1)	59·0 (1)	C(53)–Os(5)–Os(2)	105·0 (15)	C(53)–Os(5)–Os(3)	85·3 (13)
Os(4)–Os(2)–Os(3)	108·0 (1)	Os(5)–Os(2)–Os(1)	60·3 (1)	C(53)–Os(5)–Os(4)	144·4 (9)	C(53)–Os(5)–C(51)	90·3 (15)
Os(5)–Os(2)–Os(3)	59·0 (1)	Os(5)–Os(2)–Os(4)	59·9 (1)	C(53)–Os(5)–C(52)	93·5 (18)	Os(2)–Os(6)–Os(1)	59·2 (1)
Os(6)–Os(2)–Os(1)	61·9 (1)	Os(6)–Os(2)–Os(3)	61·3 (1)	Os(3)–Os(6)–Os(1)	58·5 (1)	Os(3)–Os(6)–Os(2)	59·8 (1)
Os(6)–Os(2)–Os(4)	113·8 (1)	Os(6)–Os(2)–Os(5)	111·0 (1)	C(61)–Os(6)–Os(1)	162·5 (8)	C(61)–Os(6)–Os(2)	111·3 (6)
C(21)–Os(2)–Os(1)	131·9 (6)	C(21)–Os(2)–Os(3)	84·3 (8)	C(61)–Os(6)–Os(3)	104·2 (9)	C(62)–Os(6)–Os(1)	104·7 (9)
C(21)–Os(2)–Os(4)	167·5 (6)	C(21)–Os(2)–Os(5)	128·5 (8)	C(62)–Os(6)–Os(2)	98·3 (7)	C(62)–Os(6)–Os(3)	156·6 (6)
C(21)–Os(2)–Os(6)	73·4 (7)	C(22)–Os(2)–Os(1)	103·2 (7)	C(62)–Os(6)–C(61)	90·8 (12)	C(63)–Os(6)–Os(1)	94·1 (9)
C(22)–Os(2)–Os(3)	152·1 (6)	C(22)–Os(2)–Os(4)	75·7 (9)	C(63)–Os(6)–Os(2)	153·2 (8)	C(63)–Os(6)–Os(3)	106·6 (8)
C(22)–Os(2)–Os(5)	135·1 (8)	C(22)–Os(2)–Os(6)	91·6 (7)	C(63)–Os(6)–C(61)	93·9 (11)	C(63)–Os(6)–C(62)	89·8 (9)
C(22)–Os(2)–C(21)	94·4 (12)	C(23)–Os(2)–Os(1)	133·1 (12)	Os(4)–C(43)–N(4)	175·5 (24)	C(44)–N(4)–C(43)	174·4 (26)
C(23)–Os(2)–Os(3)	111·3 (10)	C(23)–Os(2)–Os(4)	86·2 (12)	C(45)–C(44)–N(4)	110·4 (24)	C(46)–C(44)–C(45)	112·0 (28)
C(23)–Os(2)–Os(5)	75·7 (12)	C(23)–Os(2)–Os(6)	159·8 (11)	C(46)–C(44)–N(4)	115·0 (24)	C(47)–C(44)–N(4)	105·3 (28)
C(23)–Os(2)–C(21)	87·4 (14)	C(23)–Os(2)–C(22)	96·4 (12)	C(47)–C(44)–C(45)	108·7 (26)	C(47)–C(44)–C(46)	104·8 (26)
Os(2)–Os(3)–Os(1)	59·8 (1)	Os(5)–Os(3)–Os(1)	60·6 (1)	Os(6)–C(63)–N(6)	174·5 (20)	C(63)–N(6)–C(64)	174·5 (25)
Os(5)–Os(3)–Os(2)	60·3 (1)	Os(6)–Os(3)–Os(1)	61·1 (1)	C(65)–C(64)–N(6)	108·7 (17)	C(66)–C(64)–N(6)	106·5 (18)
Os(6)–Os(3)–Os(2)	58·9 (1)	Os(6)–Os(3)–Os(5)	110·1 (1)	C(66)–C(64)–C(65)	111·1 (17)	C(67)–C(64)–N(6)	107·2 (16)
C(31)–Os(3)–Os(1)	102·3 (12)	C(31)–Os(3)–Os(2)	147·2 (10)	C(67)–C(64)–C(65)	109·6 (19)	C(67)–C(64)–C(66)	113·6 (19)
C(31)–Os(3)–Os(5)	87·2 (11)	C(31)–Os(3)–Os(6)	139·9 (9)	O(11)–C(11)–Os(1)	172·2 (18)	O(12)–C(12)–Os(1)	171·6 (20)
C(32)–Os(3)–Os(1)	151·2 (6)	C(32)–Os(3)–Os(2)	92·6 (8)	O(13)–C(13)–Os(1)	176·8 (26)	O(21)–C(21)–Os(2)	170·7 (16)
C(32)–Os(3)–Os(5)	99·9 (9)	C(32)–Os(3)–Os(6)	113·9 (9)	O(22)–C(22)–Os(2)	177·1 (22)	O(23)–C(23)–Os(2)	174·5 (32)
C(32)–Os(3)–C(31)	97·3 (14)	C(33)–Os(3)–Os(1)	112·5 (10)	O(31)–C(31)–Os(3)	177·8 (28)	O(32)–C(32)–Os(3)	175·1 (28)
C(33)–Os(3)–Os(2)	122·9 (10)	C(33)–Os(3)–Os(5)	170·9 (10)	O(33)–C(33)–Os(3)	171·7 (27)	O(41)–C(41)–Os(4)	174·8 (24)
C(33)–Os(3)–Os(6)	68·6 (10)	C(33)–Os(3)–C(31)	88·6 (15)	O(42)–C(42)–Os(4)	174·8 (20)	O(51)–C(51)–Os(5)	167·6 (28)
C(33)–Os(3)–C(32)	88·7 (13)	Os(1)–Os(4)–C(43)	110·9 (6)	O(52)–C(52)–Os(5)	177·6 (29)	O(53)–C(53)–Os(5)	171·9 (28)
Os(2)–Os(4)–C(43)	159·2 (8)	Os(2)–Os(4)–Os(1)	59·1 (1)	O(61)–C(61)–Os(6)	178·0 (22)	O(62)–C(62)–Os(6)	175·1 (15)

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