Crystal and Molecular Structures of $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ *

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Both the complexes $[Os_3(CO)_{11}(NCMe)]$ (1) and $[Os_3(CO)_{10}(NCMe)_2]$ (2) crystallise in the monoclinic space group $P2_1/n$ with $Z = 4$. The cell parameters for (1) are $a = 8.284(3)$, $b = 14.787(5)$, $c = 15.944(6)$ Å, and $\beta = 102.50(2)°$, and those for (2) are $a = 8.520(3)$, $b = 20.096(6)$, $c = 12.747(4)$ Å, and $\beta = 108.77(2)°$. The structures have been solved by a combination of direct methods and Fourier-difference techniques, and refined by blocked-cascade least squares to R values of 0.039 for 1 459 diffractomer data, for (1), and 0.046 for 2 397 diffractometer data, for (2). The three Os atoms in (1) define an isosceles triangle. Two of the metal atoms are co-ordinated to two axial and two equatorial terminal carbonyl groups. The third Os atom is co-ordinated to one axial and two equatorial carbonyls and the second axial site is occupied by a linear nitrile ligand. The structure of (2) resembles that of (1) except that an axial carbonyl on an adjacent Os atom to and on the opposite side of the Os_3 plane from the co-ordinated nitrile has been replaced by the second NCMe ligand.

THE complex $[Os_3(CO)_{11}(NCMe)]$ is of importance as the starting material in substitution reactions of Os_3 clusters. It is prepared from the reaction of $[Os_3(CO)_{12}]$ with NMe_3O in the presence of MeCN.[1] It reacts with a wide range of ligands (L) to produce derivatives $[Os_3(CO)_{11}L]$ (L = two-electron donor) and with HX (X = halogen) to form $[Os_3(CO)_{11}HX]$, $[Os_3(CO)_{10}HX]$, and $[Os_3(CO)_9HI]$. Disubstituted products of the same types are obtained by reactions with $[Os_3(CO)_{10}(NCMe)_2]$. In the substituted complexes the ligand L may occupy either an axial or equatorial site. We have undertaken the structure determinations of the title complexes in order to establish the positions of substitution of these important starting materials.

EXPERIMENTAL

Yellow crystals of $[Os_3(CO)_{11}(NCMe)]$ (1) and $[Os_3(CO)_{10}(NCMe)_2]$ (2) were obtained by recrystallisation from acetonitrile. The two sets of intensity data were recorded on a Stoe four-circle diffractometer in the range $3 < 2\theta < 55°$ using Mo-K_α radiation ($\lambda = 0.710\ 69$ Å) and a 140-step ω—θ scan technique; the step scan angle was fixed at 0.01° with a counting time of 0.5 s per step. Stationary backgrounds were recorded for 17.5 s at each end of the scan range. Reflections with intensities of <10 counts s^{-1} from a 1-s pre-scan were not measured. Two check reflections were monitored every 50 measurements throughout data collection and showed no significant variation. Cell constants were derived from angular measurements of 20 strong reflections ($15 < 2\theta < 25°$). The crystal data for (1) and (2) are summarised in Table 1.

Semi-empirical absorption corrections and Lorentz polarization corrections were applied to both data sets. For each structure the Os atoms were located by multi-solution Σ_2 sign expansion, and the remaining non-hydrogen atoms from subsequent electron-density difference syntheses. The methyl groups were treated as rigid bodies

TABLE 1

Crystal data for complexes (1) and (2)

	$[Os_3(CO)_{11}(NCMe)]$	$[Os_3(CO)_{10}(NCMe)_2]$
Formula	$C_{13}H_3NO_{11}Os_3$	$C_{14}H_6N_2O_{10}Os_3$
Crystal size/mm	0.288 × 0.146 × 0.035	0.319 × 0.192 × 0.135
Molecular weight	919.76	932.81
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions		
a/Å	8.284(3)	8.520(3)
b/Å	14.787(5)	20.096(6)
c/Å	15.944(6)	12.747(4)
β/°	102.50(2)	108.77(2)
Volume/Å^3	1 906.8	2 066.4
Z	4	4
D_m	not measured	not measured
D_c/g cm^{-3}	3.20	3.00
$F(000)$	1 615.41	1 647.41
μ(Mo-K_α)/cm^{-1}	199.89	184.44
Reflections measured	3 341	3 343
Observed reflections [$F > 3\sigma(F)$]	1 459	2 397
R	0.039	0.046
$R'[= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert]$	0.035	0.038
Weighting scheme	$w = [\sigma^2(F) + 0.007\lvert F_o\rvert^2]^{-1}$	$w = [\sigma^2(F)]^{-1}$

* Undecacarbonyl(methyl cyanide)triosmium(3*Os*—*Os*) and 1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-bis(methyl cyanide)triosmium(3*Os*—*Os*).

TABLE 2

Atomic co-ordinates (× 10^4) for $[Os_3(CO)_{11}(NCMe)]$ (1) *

	x/a	y/b	z/c
Os(1)	4 337(1)	−131(1)	2 328(1)
Os(2)	4 474(1)	1 798(1)	2 278(1)
Os(3)	6 929(1)	838(1)	3 490(1)
N(1)	5 971(22)	1 779(10)	1 390(15)
C(1)	6 762(34)	1 830(14)	810(24)
C(2)	7 690(37)	1 887(19)	210(23)
C(11)	5 138(32)	−1 341(15)	2 705(18)
O(11)	5 537(24)	−2 058(10)	2 847(14)
C(12)	2 319(36)	−199(16)	1 451(20)
O(12)	1 140(26)	−203(16)	955(16)
C(13)	3 025(36)	−122(16)	3 232(20)
O(13)	2 210(25)	−162(13)	3 729(13)
C(14)	5 656(31)	−126(14)	1 439(18)
O(14)	6 351(27)	−196(12)	907(15)
C(21)	5 282(37)	2 996(17)	2 641(20)
O(21)	5 830(31)	3 673(11)	2 798(17)
C(22)	2 671(35)	2 080(15)	1 328(20)
O(22)	1 657(30)	2 256(15)	773(16)
C(23)	3 023(31)	1 839(15)	3 047(18)
O(23)	2 073(26)	1 882(14)	3 438(15)
C(31)	8 145(31)	1 882(14)	3 992(18)
O(31)	8 997(23)	2 450(13)	4 311(13)
C(32)	8 026(31)	−213(14)	4 060(17)
O(32)	8 730(25)	−815(14)	4 412(14)
C(33)	8 273(27)	794(14)	2 636(15)
O(33)	9 129(21)	747(12)	2 139(14)
C(34)	5 507(27)	927(14)	4 326(15)
O(34)	4 774(24)	1 060(11)	4 824(13)
H(21)	7 044(37)	1 942(19)	−453(23)
H(22)	8 468(37)	1 294(19)	289(23)
H(23)	8 443(37)	2 481(19)	390(23)

* Estimated standard deviations are in parentheses in Tables 2—4.

TABLE 3

Atomic co-ordinates (× 10^4) for $[Os_3(CO)_{10}(NCMe)_2]$ (2)

	x/a	y/b	z/c
Os(1)	−298(1)	1 550(1)	3 756(1)
Os(2)	2 072(1)	950(1)	2 867(1)
Os(3)	−1 153(1)	1 268(1)	1 429(1)
N(1)	2 903(18)	1 900(7)	2 545(12)
C(1)	3 391(21)	2 387(8)	2 353(15)
C(2)	3 913(28)	3 061(10)	2 107(20)
N(2)	−2 089(17)	301(6)	1 585(11)
C(3)	−2 687(26)	−197(9)	1 505(16)
C(4)	−3 454(29)	−846(9)	1 470(19)
C(11)	−2 113(23)	2 011(8)	3 915(16)
O(11)	−3 181(20)	2 311(8)	4 033(15)
C(12)	1 166(21)	1 495(8)	5 229(14)
O(12)	2 087(18)	1 470(7)	6 134(11)
C(13)	−1 319(23)	713(9)	3 821(15)
O(13)	−1 961(18)	214(6)	3 968(11)
C(14)	559(23)	2 389(8)	3 509(15)
O(14)	1 047(21)	2 907(6)	3 421(12)
C(21)	3 010(22)	579(8)	1 843(15)
O(21)	3 491(20)	345(7)	1 158(14)
C(22)	3 973(25)	880(9)	4 224(17)
O(22)	5 069(19)	833(6)	5 024(14)
C(23)	1 255(20)	118(8)	3 125(14)
O(23)	883(15)	−407(5)	3 298(10)
C(31)	−781(22)	963(8)	124(15)
O(31)	−566(21)	813(6)	−695(13)
C(32)	−3 392(24)	1 585(8)	1 047(15)
O(32)	−4 682(16)	1 806(6)	810(11)
C(33)	−443(22)	2 099(8)	1 171(15)
O(33)	−98(17)	2 621(5)	917(12)
H(21)	5 100(28)	3 026(10)	1 975(20)
H(22)	4 015(28)	3 389(10)	2 797(20)
H(23)	3 006(28)	3 257(10)	1 371(20)
H(41)	−3 809(29)	−1 038(9)	635(19)
H(42)	−4 541(29)	−800(9)	1 726(19)
H(43)	−2 582(29)	−1 182(9)	2 021(19)

with idealised bond parameters (C–H 1.08 Å, H–C–H 109.5°); the H atoms were assigned a common isotropic temperature factor. The structures were refined by blocked-cascade least squares, with Os, N, O, and the nitrile C atoms assigned anisotropic temperature factors, until convergence was reached.

Complex neutral-atom scattering factors [2] were employed in both structure refinements. Final atomic co-ordinates for (1) and (2) are given in Tables 2 and 3, respectively, while full details of bond parameters, thermal parameters, molecular planes, and observed and calculated structure factors may be found in Supplementary Publication No. SUP 23188 (32 pp.).* All computing was carried out on the University of Cambridge IBM 370/165 computer using programs written by Professor G. M. Sheldrick. The figures were drawn with the PLUTO program.

RESULTS AND DISCUSSION

The molecular structures of (1) and (2) are shown in Figures 1 and 2 respectively; selected bond parameters are listed in Table 4. There are no short intermolecular contacts in either structure. In both complexes the

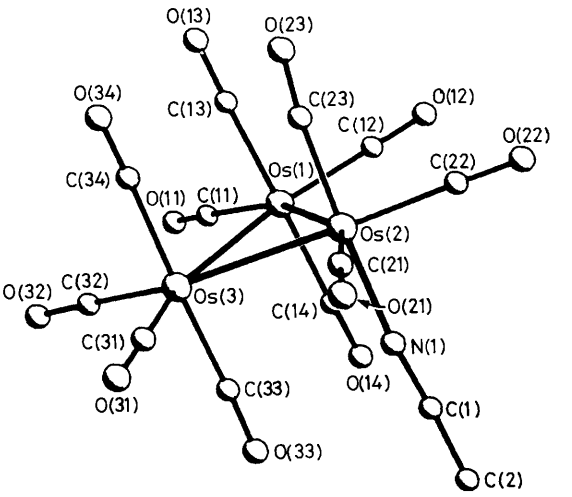

FIGURE 1 The molecular structure of $[Os_3(CO)_{11}(NCMe)]$ (1) showing the atom numbering scheme

Os atoms define isosceles triangles with the nitrile ligands occupying axial co-ordination sites. All the carbonyl groups are terminal and linear.

In (1), the two shorter Os–Os bonds [mean 2.859(2) Å] are associated with the metal atom which is co-ordinated to the nitrile ligand. These distances are significantly shorter than the average Os–Os distance of 2.877(3) Å in the parent binary carbonyl, $[Os_3(CO)_{12}]$.[3] The long bond is significantly longer than that found in $[Os_3(CO)_{12}]$. In (2), the shortest Os–Os bond is the one between the two metal atoms bearing the nitrile ligands. This bond is shorter than the short bonds in (1), while the two longer bonds [mean 2.877(2) Å] in (2) are in close agreement to the average Os–Os bond distance in $[Os_3(CO)_{12}]$.[3] Similar, although less marked trends have been

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

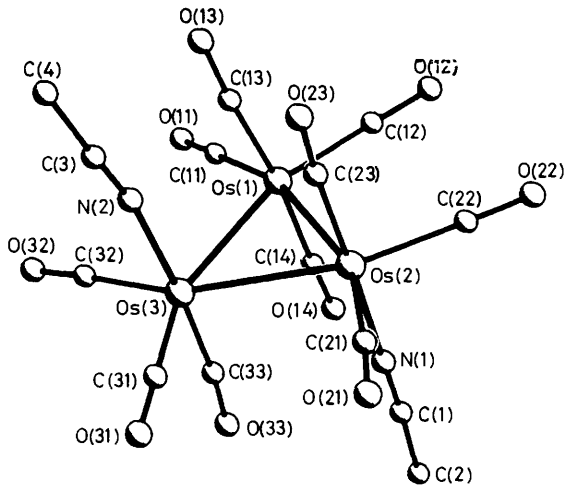

FIGURE 2 The molecular structure of $[Os_3(CO)_{10}(NCMe)_2]$ (2) showing the atom numbering scheme

observed in the metal–metal distances in $[Ru_3(CO)_{11}(CNBu^t)]$.[4] All the Os atoms exhibit a distorted octahedral co-ordination geometry. There is no systematic distortion of the ligand polyhedron in the equatorial Os_3 plane of either cluster caused by the presence of the axial nitrile ligand, but the axial Os–Os–C and Os–Os–N angles for the metal atoms bound to the nitrile ligand are slightly wider than the Os–Os–C angles for the all-carbonyl bound metal atoms.

TABLE 4

Selected bond distances (Å) and angles (°) for complexes (1) and (2)

	$[Os_3(CO)_{11}(NCMe)]$	$[Os_3(CO)_{10}(NCMe)_2]$
Os(1)–Os(2)	2.856(2)	2.879(2)
Os(1)–Os(3)	2.894(2)	2.875(2)
Os(2)–Os(3)	2.861(2)	2.842(2)
Os(2)–N(1)	2.074(23)	2.122(15)
Os(3)–N(2)		2.133(13)
N(1)–C(1)	1.246(44)	1.121(23)
N(2)–C(3)		1.112(22)
Os(3)–Os(1)–Os(2)	57.9(1)	59.2(1)
Os(3)–Os(2)–Os(1)	60.8(1)	60.3(1)
Os(2)–Os(3)–Os(1)	59.2(1)	60.5(1)
Os(1)–Os(2)–N(1)	92.2(4)	91.1(5)
Os(3)–Os(2)–N(1)	90.6(5)	89.2(3)
Os(1)–Os(3)–N(2)		93.5(4)
Os(2)–Os(3)–N(2)		92.8(3)
Os(2)–N(1)–C(1)	173.6(17)	176.7(16)
Os(3)–N(2)–C(3)		169.9(14)

An examination of the Os–C(carbonyl) distances for the Os atoms not co-ordinated to the nitrile ligands indicates that the axial Os–C bond lengths [mean 1.964 Å for (1) and 1.906 Å for (2)] are significantly longer than the equatorial ones [mean 1.935 Å for (1) and 1.881 Å for (2)]. This trend may be attributed to the fact that there is greater competition between two axial carbonyls than between an equatorial carbonyl and an Os atom for back donation of electron density from the same metal orbital. In (1) the equatorial Os–C(carbonyl) distances (mean 1.933 Å) for metal atoms associated with axial nitriles are similar to those where the metal is co-ordinated to axial carbonyls. However, in (2) these equatorial distances are slightly longer (mean 1.937 Å) than equivalent distances around Os atoms co-ordinated to axial carbonyls. In both clusters the axial Os–C(carbonyl) distances *trans* to the nitrile are the shortest metal–ligand bonds in the structures [1.895 Å for (1) and an average of 1.861 Å for (2)]. For these bonds the carbonyl is in direct competition with the nitrile which is a good σ-donor but a poor π-acceptor. Therefore, the carbonyl, which is a good π-acceptor ligand, receives most of the back-donated electron density from the metal orbital and this results in the short metal–carbon bond.

The nitrile ligands in the two complexes are approximately linear and the N–C bond lengths [1.25(5) Å for (1) and an average of 1.12(3) Å for (2)] indicate triple-bond character. This is consistent with there being little π-bonding in the Os–N bonds since it is localised in N–C bonds. However, the high estimated standard deviations on the N–C and C–C bonds makes a useful comparison of these bond parameters between the two structures difficult. There are no other examples of nitriles co-ordinated to osmium cluster complexes but the Os–N distances [2.074(23) Å in (1) and an average of 2.128(20) Å in (2)] in these two nitrile clusters are similar to values in the range 2.16—2.22 Å in a number of Os complexes [5] where the metal–nitrogen bonds are considered to be single. The presence of these relatively weakly co-ordinated nitrile ligands, when compared to the multiple-bond character of the metal–carbonyl bonds, is consistent with the easy substitution of these nitrogen-co-ordinated ligands by other reactive groups and small molecules.

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