Synthesis of Triosmium Clusters containing Amidine Ligands: *X*-Ray Structural Characterization of $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ †

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Reactions of $[Os_3(CO)_{10}(NCMe)_2]$ with amidines have been used to synthesize the complexes $[Os_3(\mu\text{-}H)(CO)_{10}\{NHC(Me)NH\}]$ (1) and $[Os_3(\mu\text{-}H)(CO)_{10}\{NPhC(Ph)NH\}]$ (2); these amidine clusters have been thermally decarbonylated to the corresponding nonacarbonyl compounds of which $[Os_3(\mu\text{-}H)(CO)_9(MeCN_2H_2)]$ (3), alone, exists as two tautomeric forms in $CDCl_3$ solution at 20 °C. The structure of $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4) was established by *X*-ray crystallography. The complex crystallises in the monoclinic space group $P2_1/c$ with a = 20.002(10), b = 14.492(7), c = 17.999(6) Å, β = 102.80(3)°, and Z = 8. The structure was solved by a combination of direct methods and Fourier-difference techniques, and refined to R = 0.047 for 3 565 unique, observed diffractometer data. There are two independent but structurally similar molecules of (4) per asymmetric unit. In each molecule the Os atoms define an isosceles triangle one edge of which is bridged by the protonated nitrogen atom of the NPhC(Ph)NH ligand; the other N atom is terminally bound to the third Os atom in an axial site. In this way the amidino-ligand caps one triangular face of the metal framework and formally donates five electrons to the cluster.

Amidines will co-ordinate to metals in a variety of monomeric,[1,2] dimeric,[3] and cluster[4] systems but, prior to this work, clusters containing these ligands had not been structurally characterized. Previous research[5,6] has shown that the triazene ligands, R–N–N=N–R, derived from azides, will bridge osmium–osmium bonds in triosmium systems and that on heating extrusion of dinitrogen occurs to give nitrene clusters. Amidines are related to triazenes by replacement of N with isoelectronic C–R fragments and clearly clusters containing these ligands might be structurally and chemically similar; this research was undertaken in order to investigate the extent of this similarity.

Results and Discussion

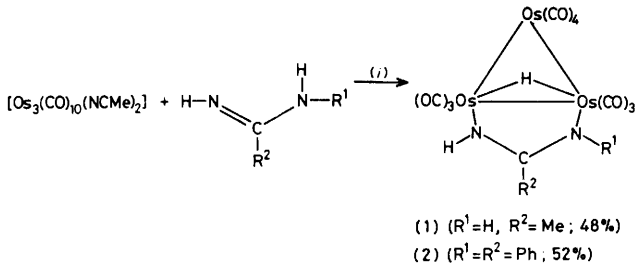
Amidines can readily be co-ordinated to a triosmium frame by displacement of the labile acetonitrile ligands of an activated cluster (Scheme 1). The complexes were characterized by ^1H n.m.r., i.r., mass spectral (Table 1) and analytical data. Reports of similar reactions using five-membered ring heterocycles[7] and 2-substituted pyridines[8,9] have appeared recently and these syntheses underline the value of $[Os_3(CO)_{10}(NCMe)_2]$ as a precursor to organotriosmium clusters.

Complexes (1) and (2) are analogous to the triazenido-clusters $[Os_3(CO)_{10}(HN_3R)]$ (R = Me,[10] Ph,[6] Bu^n,[6] cyclo-C_6H_{11},[6] or CH_2Ph[6]) but, unlike these, when heated they decarbonylate to systems in which the amidine is intact (Scheme 2). Similar decarbonylation reactions have been observed[8] for the 2-substituted pyridine systems $[Os_3(\mu\text{-}H)(CO)_{10}(NHC_5H_4N)]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(SC_5H_4N)]$. The N^2-diphenylamidine cluster (4) was also prepared by reaction of N^2-phenylbenzamidine with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (40% yield, see Experimental section).

$$[Os_3(\mu\text{-}H)(CO)_{10}\{NR^1C(R^2)NH\}] \xrightarrow{(i)} [Os_3(\mu\text{-}H)(CO)_9(R^2CN_2HR^1)]\ (3)\ (R^1 = H,\ R^2 = Me;\ 70\%)$$

$$\text{or } [Os_3(\mu\text{-}H)(CO)_9\{NR^1C(R^2)NH\}]\ (4)\ (R^1 = R^2 = Ph;\ 80\%)$$

Scheme 2. Decarbonylation reactions: (*i*) hexane, 140 °C, 24 h, for (3); heptane, 97 °C, 6 h, for (4)



(1) (R^1=H, R^2= Me; 48%)
(2) (R^1=R^2= Ph; 52%)

Scheme 1. Formation of the decacarbonyl clusters: (*i*) benzene, 20 °C, 12 h

The acetamidine cluster (3) displays three N–H signals and two Os–H resonances in its ^1H n.m.r. spectrum at 20 °C which is consistent with approximately equal amounts of two tautomeric forms as shown in Figure 1. There is no indication of tautomerism in the ^1H n.m.r. spectrum of the N^2-phenylbenzamidine cluster (4) and only one tautomer was observed in the *X*-ray crystallographic study of this compound.

In the solid state, molecules of $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4) are separated by normal van der Waals distances. There are two independent but structurally similar molecules in the asymmetric unit and one of these is illustrated in Figure 2. Selected bond lengths and angles for the two molecules are presented in Table 2.

The amidine unit lies over a triangle of osmiums in which

† Nonacarbonyl-μ-hydrido-(μ_3-N^2-phenylbenzamidino-$N^1N^1N^2$)-*triangulo*-triosmium.

Supplementary data available (No. SUP 23575, 39 pp.): structure factors, thermal parameters, bond distances and angles, least-squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Spectral data for the amidine clusters

Compound	*m/z* (M^+ ^{192}Os)	Solvent	^{1}H n.m.r. (δ/p.p.m.) N–H (br, s)	Os–H (s, 1 H)	Other	ν(CO) (hexane solution)/cm^{-1}
(1)	914	$CDCl_3$	3.94 (1 H)	−13.36	2.00 (s, 3 H)	2 107w, 2 065s, 2 055s, 2 021s, 2 006s, 1 994m, 1 984m, 1 973w
(2)	1 052	$(CD_3)_2CO$	6.27 (1 H)	−12.49	7.29—6.73 (m, 10 H)	2 105w, 2 065s, 2 051s, 2 020s, 2 003s, 1 994m, 1 982m, 1 972m
(3)	886	$CDCl_3$ [a]	3.62 (2 H)	−11.72	1.46 (s, 3 H)	2 084m, 2 053s, 2 024s, 1 995s, 1 984 (sh), 1 946m
		$CDCl_3$ [b]	6.92 (1 H), 4.31 (1 H)	−14.17	1.63 (s, 3 H)	
(4)	1 024	CD_2Cl_2	4.58 (1 H)	−11.75	7.31—6.74 (m, 10 H)	2 083m, 2 068w, 2 052s, 2 027s, 1 996s, 1 978s, 1 952w

[a] Isomer (3a). [b] Isomer (3b).

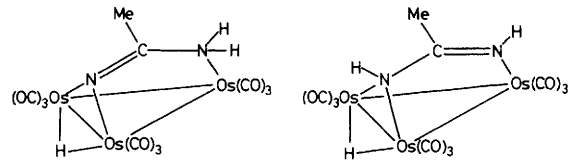


Figure 1. Tautomeric forms of $[Os_3(\mu\text{-}H)(CO)_9(MeCN_2H_2)]$ (3) in $CDCl_3$ solution at 20 °C

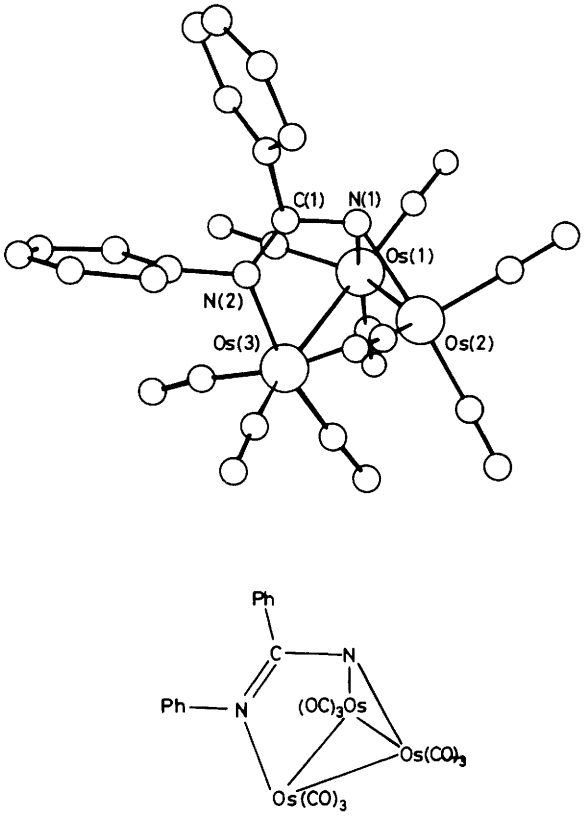


Figure 2. The molecular structure of $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4) showing the atom-numbering scheme

all the Os–Os bonds are equal, within the limits of experimental error, and average 2.79 Å. Hydrogen atoms were not located from difference maps but the trigonal pyramidal

Table 2. Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4)

	Molecule 1	Molecule 2
Os(1)–Os(2)	2.808(2)	2.806(3)
Os(1)–Os(3)	2.778(3)	2.782(3)
Os(2)–Os(3)	2.801(3)	2.793(3)
Os(1)–N(1)	2.198(23)	2.132(19)
Os(2)–N(1)	2.193(23)	2.188(20)
Os(3)–N(2)	2.141(22)	2.174(20)
N(1)–C(1)	1.417(39)	1.464(37)
N(2)–C(1)	1.243(36)	1.242(40)
Os(3)–Os(1)–Os(2)	60.2(1)	60.0(1)
Os(3)–Os(2)–Os(1)	59.4(1)	59.6(1)
Os(2)–Os(3)–Os(1)	60.4(1)	60.4(1)
Os(1)–N(1)–Os(2)	79.5(8)	81.0(7)
Os(3)–N(2)–C(1)	119.0(20)	120.6(20)
N(1)–C(1)–N(2)	121.7(25)	115.3(20)
Dihedral angle between phenyl groups (°)	57.1	55.8

geometry about N(1) indicates that a proton is attached and N(1) may therefore be considered to act as a three electron donor symmetrically spanning the Os(1)–Os(2) bond with an average Os–N(1) (bridge) distance of 2.178 Å. The geometry about N(2) is essentially planar with the N(2)–Os(3) bond distances averaging 2.156 Å. The two phenyl groups are attached to C(1) and N(2) and the C(1)–N(2) distance of 1.243 Å is appreciably shorter than the average C(1)–N(1) bond length of 1.441 Å; however there does not appear to be any extensive delocalisation through this bond since the aromatic rings are twisted with respect to one another, the dihedral angle being 56°. A molecule with a similar geometry to (4), $[Os_3(\mu\text{-}H)(CO)_9(NHC_5H_4N)]$, has been reported [9] and it was shown that the pyridyl nitrogen co-ordinates in a terminal fashion to an osmium atom whilst the amino-function spans an Os–Os bond; the Os–N bond lengths for the planar and for the tetrahedrally hybridized nitrogen atoms are comparable in these compounds. The bond connecting the amino-group to the aromatic ring in $[Os_3(\mu\text{-}H)(CO)_9(NHC_5H_4N)]$ is short (1.392 Å) as found for the C(1)–N(2) distance in structure (4). When nitrogen caps a triosmium face, as in $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$,[5,6] the average Os–N distance is only 2.08 Å; presumably the capping ligand here is relatively free to adopt the orientation that maximizes bonding to the metals whereas the amidine and 2-amino-pyridine ligands discussed above are more constrained due to their bidentate co-ordination mode.

Experimental

A Varian CFT 20 80 MHz spectrometer was used for the ^1H n.m.r. recordings, a Perkin-Elmer 257 for the i.r., and an A.E.I. MS12 spectrometer for the mass spectral data. Solvents were dried and distilled before use. All the complexes were recrystallized by slow evaporation from dichloromethane–hexane solutions at 0 °C under dinitrogen. Satisfactory C, H, and N analyses were obtained for all the new compounds reported in this paper.

Preparations of $[Os_3(\mu\text{-}H)(CO)_{10}\{NHC(Me)NH\}]$ (1) *and* $[Os_3(\mu\text{-}H)(CO)_{10}\{NPhC(Ph)NH\}]$ (2).—The complex $[Os_3(CO)_{10}(NCMe)_2]$ (*ca.* 100 mg) and the amidine (1.1 equivalents) were stirred in benzene (50 cm^3) at 20 °C for 12 h. Removal of the solvent at 20 °C and thin-layer chromatography (t.l.c.) [dichloromethane–hexane eluant; 1 : 4 for (1), 1 : 10 for (2)] gave the amidine clusters (1) and (2) as yellow-orange bands.

Preparations of $[Os_3(\mu\text{-}H)(CO)_9(MeCN_2H_2)]$ (3) *and* $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4).—The clusters (1) or (2) (*ca.* 50 mg) were thermally decarbonylated [hexane (50 cm^3), 140 °C, 24 h for (1); heptane (50 cm^3) under argon, 97 °C, 6 h for (2)]. Removal of solvent and t.l.c. [dichloromethane–hexane eluant; 9 : 1 for (1), 1 : 1 for (2)] gave the products (3) and (4) respectively as yellow-orange bands. Cluster (4) was also prepared by reacting $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (35 mg) and N^2-phenylbenzamidine (1.5 equivalents) in methylbenzene (7 cm^3) at 110 °C for 45 min using the same separation procedure as given above.

Molecular Structure Determination of $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4).—Yellow crystals of (4) were deposited from CH_2Cl_2–hexane by slow evaporation. A suitable single crystal with dimensions *ca.* 0.25 × 0.22 × 0.17 mm was mounted on a glass fibre, and unit-cell dimensions and space group determined *via* precession (Mo) *X*-ray photography. Intensity data were recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-K_α radiation and a 96 step $\omega/2\theta$ scan technique. The scan speed varied from 2.5° min^{-1} to 29.3° min^{-1} depending upon the intensity of the reflection in a 1-s pre-scan; reflections registering <7 counts s^{-1} were not remeasured. Two check reflections were monitored periodically throughout the data collection and showed no significant variation. Accurate cell parameters were obtained from the centred positions of 15 strong reflections in the range $15 < 2\theta < 25°$.

The 4 409 measured reflections in the range $3 < 2\theta < 50°$ were profile fitted,[11] and Lorentz polarisation factors applied. A semi-empirical absorption correction was also applied, and equivalent reflections averaged to give 3 565 unique observed reflections [$F > 3\sigma(F)$].

Crystal data. $C_{22}H_{12}N_2O_9Os_3$, $M = 1\,018.94$, Monoclinic, $a = 20.002(10)$, $b = 14.492(7)$, $c = 17.999(6)$ Å, $\beta = 102.80(3)°$, $U = 5\,088(4)$ $Å^3$, $D_c = 2.66$ g cm^{-3}, $Z = 8$, D_m = not measured, $F(000) = 3\,663$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 149.86 cm^{-1}, space group $P2_1/c$ from systematic absences.

The six independent Os-atom positions from the two molecules in the asymmetric unit were located by multi-solution Σ_2 sign expansion. The remaining non-hydrogen atoms were

Table 3. Atom co-ordinates (× 10^4) for $[Os_3(\mu\text{-}H)(CO)_9\{NPhC(Ph)NH\}]$ (4)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	2 655(1)	9 262(1)	6 991(1)	Os(4)	2 457(1)	10 904(1)	469(1)
Os(2)	1 698(1)	9 142(1)	5 594(1)	Os(5)	3 113(1)	11 090(1)	2 010(1)
Os(3)	1 327(1)	9 900(1)	6 876(1)	Os(6)	3 805(1)	10 298(1)	989(1)
C(11)	3 049(16)	10 402(22)	7 248(17)	C(41)	2 734(15)	13 940(21)	4 547(17)
O(11)	3 323(12)	11 139(17)	7 413(13)	O(41)	2 876(12)	13 829(16)	3 961(13)
C(12)	2 652(15)	9 046(21)	8 005(17)	C(42)	2 091(17)	9 789(25)	146(19)
O(12)	2 642(10)	8 884(14)	8 663(12)	O(42)	1 838(13)	9 033(19)	−24(15)
C(13)	3 479(17)	8 662(23)	6 955(18)	C(43)	1 569(21)	11 499(27)	193(22)
O(13)	3 998(12)	8 281(16)	6 917(13)	O(43)	1 056(14)	11 791(18)	24(14)
C(21)	1 531(17)	10 182(24)	4 968(19)	C(51)	2 540(23)	11 689(33)	2 569(26)
O(21)	1 463(12)	10 873(18)	4 662(13)	O(51)	2 232(14)	12 016(19)	2 973(16)
C(22)	2 052(18)	8 461(25)	4 848(20)	C(52)	3 922(21)	13 474(28)	7 576(23)
O(22)	2 340(14)	8 074(20)	4 446(16)	O(52)	4 451(17)	13 171(23)	7 909(19)
C(23)	769(17)	8 792(23)	5 303(18)	C(53)	3 218(18)	10 008(26)	2 596(20)
O(23)	209(12)	8 560(15)	5 164(12)	O(53)	3 258(13)	9 330(19)	2 923(14)
C(31)	1 333(15)	10 274(21)	7 884(17)	C(61)	4 636(18)	10 027(25)	1 631(20)
O(31)	1 281(12)	10 568(17)	8 453(14)	O(61)	5 153(15)	9 835(20)	2 065(16)
C(32)	1 623(14)	11 028(20)	6 601(16)	C(62)	4 032(12)	14 927(17)	5 036(14)
O(32)	1 824(11)	11 739(16)	6 375(13)	O(62)	4 159(11)	9 845(15)	−548(12)
C(33)	410(15)	10 091(21)	6 510(16)	C(63)	3 444(15)	9 152(23)	1 088(17)
O(33)	−187(12)	10 261(16)	6 258(13)	O(63)	3 206(11)	8 439(16)	1 225(13)
N(1)	2 009(12)	8 097(16)	6 484(13)	N(3)	2 987(10)	12 059(14)	1 056(11)
C(1)	1 512(13)	7 879(19)	6 908(15)	C(2)	3 608(14)	12 347(19)	816(16)
N(2)	1 141(11)	8 483(15)	7 098(12)	N(4)	4 050(10)	13 262(14)	5 845(11)
C(111)	1 321(15)	6 832(20)	6 918(17)	C(311)	3 669(13)	13 340(18)	619(14)
C(112)	1 638(18)	6 384(26)	7 588(21)	C(312)	3 164(18)	13 599(25)	−70(20)
C(113)	1 489(23)	5 376(33)	7 751(26)	C(313)	3 239(18)	14 498(25)	−354(20)
C(114)	1 062(21)	5 032(29)	7 148(25)	C(314)	3 754(21)	15 046(29)	−25(24)
C(115)	789(26)	5 408(38)	6 451(30)	C(315)	4 193(26)	14 771(37)	650(29)
C(116)	915(23)	6 360(33)	6 282(25)	C(316)	4 229(16)	13 880(22)	1 017(17)
C(211)	613(12)	8 213(17)	7 527(14)	C(411)	4 666(17)	11 952(23)	572(19)
C(212)	−25(16)	7 903(22)	7 112(18)	C(412)	4 678(14)	12 033(19)	−170(15)
C(213)	−512(16)	7 645(21)	7 600(18)	C(413)	5 280(16)	12 265(21)	−442(18)
C(214)	−294(20)	7 697(26)	8 391(22)	C(414)	5 868(16)	12 455(22)	155(18)
C(215)	304(18)	7 995(25)	8 735(20)	C(415)	5 893(16)	12 390(22)	924(19)
C(216)	820(16)	8 214(23)	8 325(18)	C(416)	5 254(17)	12 111(23)	1 169(19)

located from subsequent difference electron-density maps. The structure was refined by blocked full-matrix least squares, with the Os atoms assigned anisotropic thermal parameters and the other non-hydrogen atoms individual isotropic thermal parameters. The H atoms were not located. The converged residuals were $R = 0.047$ and $R' = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.052$. A final difference map only showed ripple peaks of *ca.* 1.5 e A^{-3} in the region of the Os atoms.

Complex neutral-atom scattering factors were employed throughout.[12] Computations were performed on the University of Cambridge IBM 370/165, using SHELX 76.[13] Atomic fractional co-ordinates are listed in Table 3.

Acknowledgements

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