

The reaction of pentafluoronitrosobenzene with $\text{Os}_3(\text{CO})_{12}$: synthesis and X-ray crystal structure of $[\text{Os}_3(\text{CO})_9(\mu_3\text{-NC}_6\text{F}_5)_2]$

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(Received June 3, 1991; accepted September 29, 1991)

Abstract

The reaction of pentafluoronitrosobenzene with $\text{Os}_3(\text{CO})_{12}$ at 125 °C in octane leads to the formation of a new bis(pentafluorophenylimido)triosmium cluster, $[\text{Os}_3(\text{CO})_9(\mu_3\text{-NC}_6\text{F}_5)_2]$ (**I**). Cluster **I** has been shown by X-ray crystallographic studies to consist of an open triosmium framework capped by triply bridging pentafluorophenylimido ligands.

Introduction

Hitherto, there has been no report on the reaction of pentafluoronitrosobenzene with metal clusters. The coordination properties of its non-fluorinated analogue, i.e. nitrosobenzene, on the other hand, have attracted considerable interest in recent years [1–7]. Imido clusters $[\text{M}_3(\text{CO})_{10}(\text{NC}_6\text{H}_5)]$ (**II**) and $[\text{M}_3(\text{CO})_9(\text{NC}_6\text{H}_5)_2]$ (**III**) have been isolated upon treatment of nitrosobenzene with $\text{M}_3(\text{CO})_{12}$ (where M = Os, Ru) [6]. The former has also been obtained by Han *et al.* [7] from the reaction of nitrosobenzene with $[\text{M}_3(\text{CO})_{11}(\text{NCMe})]$ (where M = Os, Ru). However, the X-ray structures of clusters **II** and **III** have so far not been reported. As part of our studies on the coordination properties of pentafluoronitrosobenzene, we report herein its reaction with $\text{Os}_3(\text{CO})_{12}$ which afforded an open bis(pentafluorophenylimido)triosmium cluster fully characterized as $[\text{Os}_3(\text{CO})_9(\mu_3\text{-NC}_6\text{F}_5)_2]$ (**I**).

Experimental

$\text{C}_6\text{F}_5\text{NO}$ was prepared as previously described [8] and $\text{Os}_3(\text{CO})_{12}$ as reported in the literature [9, 10]. The infrared spectrum was recorded on a Perkin-Elmer 983G infrared spectrometer. ^{19}F NMR data were obtained on a Jeol FX 90Q Fourier Transformation (90 MHz) NMR spectrometer. CDCl_3 was employed as the solvent and CF_3COOH as the internal standard. Elemental analyses for C and F were conducted by the Microanalytical Laboratory of the National University of Singapore.

Preparative details

$\text{Os}_3(\text{CO})_{12}$ (0.1913 g, 0.21 mmol), blue $\text{C}_6\text{F}_5\text{NO}$ (0.041 g, 0.21 mmol) and octane (50 ml) were placed in a two-necked 250 ml round-bottomed flask equipped with a condenser, a nitrogen inlet and a bubbler. The system was flushed with nitrogen for 10 min before commencement of stirring and heating to reflux over a period of 3 h. At the end of reflux, the dark brown reaction mixture was filtered to yield a black residue and a brownish black filtrate. The filtrate was subjected to rotary evaporation employing water bath at 70 °C to remove the octane. Dichloromethane was added to the resultant residue and thin layer chromatography in 10% dichloromethane/90% hexane carried out. The yellow band eluted (R_f , 0.42; 10 mg) and was characterized spectroscopically and crystallographically as $[\text{Os}_3(\text{CO})_9(\mu_3\text{-NC}_6\text{F}_5)_2]$ (**I**). Elemental analyses gave C, 20.97%; F, 15.97%. **I** requires C, 21.27%; F, 16.04%.

Crystal structure determination

Crystals suitable for X-ray structural analysis were obtained from hexane/dichloromethane solutions. A red crystal of $0.40 \times 0.20 \times 0.20$ mm dimensions was used for data collection. Crystal data for **I**: $[\text{C}_{21}\text{N}_2\text{O}_9\text{F}_{10}\text{Os}_3]$, triclinic, $P\bar{1}$, $a = 9.062(3)$, $b = 12.431(4)$, $c = 13.446(6)$ Å. $\alpha = 90.800(0)^\circ$, $\beta = 109.210(0)^\circ$, $\gamma = 109.650(10)^\circ$, $V = 1333.7(9)$ Å³; $Z = 4$; $D_c = 2.950$ g cm⁻³; $\mu(\text{Mo K}\alpha) = 143.98$ cm⁻¹; $T = 25$ °C. Siemens diffractometer R3m/V, Mo K α radiation. Of the 5032 data points measured ($3.0 \leq 2\theta \leq 50.0^\circ$), 4707 were independent ($R_{\text{int}} = 4.92\%$), and 3401 were considered observed [$6\sigma(F_o)$]. The structure was solved by direct methods. Refinement: all atoms anisotropic; $R(F) = 2.67\%$, $R(wF) = 2.73\%$, goodness-of-fit = 1.09, $\Delta/\sigma = 0.158$, $\Delta/\sigma_{\text{max}} = 0.029$. SHELXTL software (G.M. Sheldrick, Siemens, Madison, WI) was used for all the computations. Atomic scattering factors were obtained from *International Tables*, Vol. 4, pp. 55, 99 and 149. An empirical (psi-scan) absorption correction was performed. The ratio of the transmission coefficients was 1.28.

Results and discussion

The bis(pentafluorophenylimido) cluster, $[\text{Os}_3(\text{CO})_9(\mu_3\text{-NC}_6\text{F}_5)_2]$ (**I**) (Fig. 1) was obtained upon heating pentafluoronitrosobenzene and $\text{Os}_3(\text{CO})_{12}$ in refluxing octane for 3 h in an inert nitrogen atmosphere. The infrared spectrum of **I** in cyclohexane exhibits carbonyl stretching frequencies at 2104(w), 2083(vs), 2068(m,sh), 2062(vs), 2035(m), 2018(s,sh), 2014(vs), 2005(m) and 1992(w) cm⁻¹. Pentafluorophenyl ring vibrations are located at 1512 and 1491 cm⁻¹ as a doublet, and a band at 998 cm⁻¹ is assigned to C–N stretching [11]. The ¹⁹F NMR spectrum exhibits four sets of signals at δ –65.90 (m, 2F), –72.11 (m, 1F), –84.80 (m, 3F) and –85.95 (m, 4F) ppm corresponding to 10 fluorine atoms and thus indicates the presence of two pentafluorophenyl rings. This is in contrast to the ¹⁹F NMR spectrum

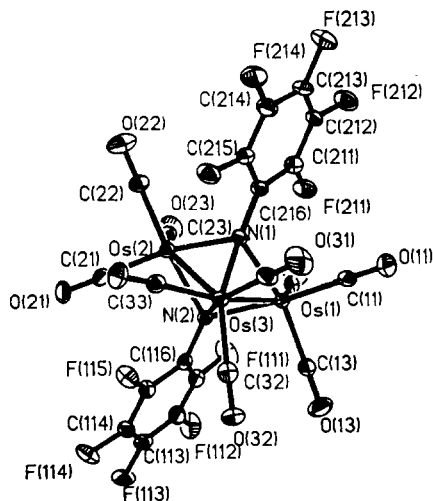


Fig. 1. The ORTEP drawing of $\text{Os}_3(\text{CO})_9(\mu_3\text{-NC}_6\text{F}_5)_2$.

characteristic of a C_6F_5 ring such as that of $\text{C}_6\text{F}_5\text{NO}$ which exhibits three sets of signals at δ -66.08 (m, 1F), -83.81 (m, 2F) and -84.68 (m, 2F) ppm.

The molecular geometry of **I** was established by a single crystal X-ray structural analysis. Atomic coordinates, and selected bond lengths and angles are given in Tables 1 and 2 respectively. The molecular structure comprises a three osmium atoms capped by pentafluorophenylimido ligands above and below the plane containing the osmium atoms. Nine terminally bound carbon monoxide ligands are present and the C–O bond lengths of 1.109–1.140 Å fall within the range for typical C–O bonds. Os(1) and Os(2) atoms are at a non-bonded distance of 3.367 Å. The Os(2)–Os(3) bond (2.752 Å) is found to be significantly longer than the Os(1)–Os(3) bond (2.648 Å) but both are shorter than the average Os–Os bond in the parent $\text{Os}_3(\text{CO})_{12}$ cluster (2.877 Å) [12]. The C–N(1) and C–N(2) distances of 1.416 Å and 1.410 Å are typical of C–N single bonds [13]. The Os–C distances and Os–C–O angles lie in the range of 1.89(1)–1.94(1) Å and of 174.6(9)–178.0(1)° respectively. The Os–N(1) and Os–N(2) bonds show little variation except for Os(3)–N(1) (2.185 Å) which is somewhat longer than the Os(3)–N(2) bond (2.157 Å). The Os(3)–N(1)–C(216) (125.7°) and Os(3)–N(2)–C(116) (128.8°) bond angles are not equal, and the pentafluorophenyl ring attached to N(1) and that attached to N(2) are inclined at a different angle with respect to the triosmium plane (88.5° and 95.9°). In addition, the dihedral angle between the two mean planes containing pentafluorophenylimido groups is found to be 7.9°. It is therefore evident that the two C_6F_5 rings are not symmetrical with respect to the triosmium plane.

TABLE 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	$U(\text{eq})^a$
Os(1)	3234(1)	3168(1)	7976(1)	30(1)
Os(2)	-741(1)	1373(1)	6684(1)	29(1)
Os(3)	867(1)	2301(1)	8795(1)	29(1)
N(1)	717(9)	3077(6)	7334(5)	29(3)
N(2)	1565(8)	1429(6)	7728(5)	25(3)
C(11)	4246(13)	4776(9)	8443(8)	43(5)
C(12)	3910(12)	3290(8)	6744(9)	40(4)
C(13)	5180(13)	2962(8)	8894(9)	43(5)
C(21)	-1915(12)	-282(9)	6530(8)	40(4)
C(22)	-2842(13)	1572(9)	6001(8)	40(5)
C(23)	-485(12)	1225(8)	5367(8)	38(4)
C(31)	1076(13)	3628(8)	9631(7)	42(5)
C(32)	2117(13)	1827(9)	10030(8)	43(5)
C(33)	-1312(13)	1398(8)	8823(8)	38(4)
O(11)	4831(10)	5738(7)	8756(7)	71(4)
O(12)	4245(10)	3347(7)	6016(6)	63(4)
O(13)	6303(10)	2805(7)	9470(7)	71(4)
O(21)	-2615(9)	-1228(6)	6456(6)	58(4)
O(22)	-4073(11)	1673(8)	5573(7)	75(5)
O(23)	-202(10)	1161(7)	4618(6)	60(4)
O(31)	1244(12)	4455(7)	10095(7)	79(5)
O(32)	2922(10)	1549(7)	10746(6)	61(4)
O(33)	-2534(9)	894(7)	8891(6)	57(4)
C(111)	3136(12)	264(8)	7418(8)	37(4)
C(112)	3548(13)	-698(9)	7473(9)	46(5)
C(113)	2877(13)	-1540(8)	8007(8)	43(5)
C(114)	1734(13)	-1450(8)	8414(8)	42(4)
C(115)	1310(12)	-474(8)	8341(8)	37(4)
C(116)	2030(11)	445(8)	7849(7)	34(4)
C(211)	897(12)	4843(8)	6516(7)	36(4)
C(212)	439(13)	5771(8)	6261(8)	42(5)
C(213)	-771(13)	5939(9)	6559(9)	47(5)
C(214)	-1547(13)	5140(8)	7108(8)	43(5)
C(215)	-1084(11)	4210(8)	7336(7)	34(4)
C(216)	198(12)	4019(8)	7076(7)	35(4)
F(111)	3768(9)	1044(5)	6844(5)	67(4)
F(112)	4622(8)	-794(5)	7028(6)	72(4)
F(113)	3265(8)	-2507(5)	8060(5)	65(3)
F(114)	965(8)	-2307(5)	8864(5)	58(3)
F(115)	175(7)	-445(5)	8754(5)	50(3)
F(211)	2054(7)	4703(5)	6149(5)	54(3)
F(212)	1204(8)	6543(5)	5726(5)	62(3)
F(213)	-1222(9)	6852(5)	6324(6)	72(4)
F(214)	-2721(8)	5304(5)	7426(5)	62(3)
F(215)	-1923(7)	3452(5)	7839(5)	55(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2

Selected bond lengths (Å) and bond angles (°)

Os(1)–Os(3)	2.648 (1)	Os(1)–N(1)	2.118 (8)
Os(1)–N(2)	2.126 (6)	Os(2)–N(1)	2.075 (6)
Os(2)–Os(3)	2.752 (1)	Os(3)–N(2)	2.157 (9)
Os(2)–N(2)	2.076 (7)	N(1)–C(216)	1.410 (13)
Os(3)–N(1)	2.185 (7)	N(2)–C(116)	1.416 (13)
Os(3)–Os(1)–N(1)	53.2 (2)	Os(3)–Os(2)–N(1)	51.5 (2)
N(1)–Os(1)–N(2)	69.7 (3)	N(1)–Os(2)–N(2)	71.6 (3)
Os(3)–Os(2)–N(2)	50.7 (2)	Os(1)–N(1)–Os(2)	106.9 (4)
Os(1)–N(1)–Os(3)	75.9 (2)	Os(2)–N(1)–Os(3)	80.4 (2)
Os(1)–N(2)–Os(3)	76.4 (2)	Os(1)–N(2)–Os(2)	106.5 (3)
Os(3)–Os(1)–N(2)	52.3 (2)	Os(2)–N(2)–Os(3)	81.1 (3)

Supplementary material is available from: The director, Cambridge Crystallographic Data Centre, Chemistry Department, Lensfield Road, Cambridge, UK.

Acknowledgement

We thank the National University of Singapore for a research grant. One of us (K.K. Ong) is grateful to the University for a research scholarship.

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