

Competition between N–H and C–H Activation in the Thermolysis of $\text{Os}_3(\text{CO})_{11}[\text{NHC}(\text{CH}_2)_5]$. The Molecular Structure of $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2[\mu_3\text{-NHC}(\text{CH}_2)_4\text{C}]$

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When the trinuclear cyclohexylideneimine complex $\text{Os}_3(\text{CO})_{11}[\text{NHC}(\text{CH}_2)_5]$ is heated in refluxing hydrocarbons, a competition between N–H and C–H activation is observed. Upon cleavage of the N–H bond, hydrogen transfer onto the metal framework occurs and the cluster $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})[\mu_2\text{-NC}(\text{CH}_2)_5]$ is formed. An alternative product, $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2[\mu_3\text{-NHC}(\text{CH}_2)_4\text{C}]$, is formed from the cleavage of two C–H bonds and hydrogen transfer onto the Os_3 triangle. Crystals of $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2[\mu_3\text{-NHC}(\text{CH}_2)_4\text{C}]$ are monoclinic, space group $P2_1/c$, with $Z = 4$ and cell dimensions $a = 9.479(4)$, $b = 13.498(5)$, $c = 15.943(7)$ Å, $\beta = 92.55(3)^\circ$. The structure has been solved from diffractometer data by a combination of direct methods and Fourier difference techniques and refined by blocked-cascade least-squares to $R = 0.042$ for 2882 independent observed reflections. The three Os atoms define an isosceles triangle one edge of which is bridged by a carbon atom of the six-membered ring. The third Os atom is coordinated to the nitrogen atom, in such a way that the $\text{NHC}(\text{CH}_2)_4\text{C}$ moiety caps one side of the triangle.

Introduction

Since the discovery of the reaction of ethylene with dodecacarbonyltriosmium to yield the cluster $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2(\mu_2\text{-CCH}_2)$ [1–3] considerable interest has been focused on bond activation reactions in view of their possible significance in catalytic processes. Recently we reported the N–H activation of trinuclear osmium alkylideneimine complexes [4]. In the case of the cyclohexylideneimine complex we have now isolated a C–H activated product as a side-product of the N–H activa-

tion reaction. The C–H activation in place of the expected N–H activation has been observed previously in the reaction of $\text{Os}_3(\text{CO})_{12}$ with pyrrole [5]. However, to our knowledge, the present reaction is the first case of a discrete molecule undergoing N–H and C–H activation as competing processes leading to two different products. In this paper we report the thermolysis of the cyclohexylideneimine cluster $\text{Os}_3(\text{CO})_{11}[\text{NHC}(\text{CH}_2)_5]$ (1) to give the N–H activated product $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})[\mu_2\text{-NC}(\text{CH}_2)_5]$ (2) and the C–H activated product $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2[\mu_3\text{-NHC}(\text{CH}_2)_4\text{C}]$ (3). The molecular structure of (3) is also reported.

Experimental

The thermolysis of 1 was carried out with the exclusion of air. The solvents were distilled over drying agents and saturated with purified nitrogen. For the preparative thin-layer chromatography plates coated with silicagel Merck 60 GF 254 were used. For the spectroscopic characterization the following instruments were employed:

^1H n.m.r. spectra: Bruker Cryospec WM 250; i.r. spectra: Perkin-Elmer 297 and Beckman 4240; mass spectra: Varian MAT CH7.

Thermolysis of $\text{Os}_3(\text{CO})_{11}[\text{NHC}(\text{CH}_2)_5]$ (1)

A solution of 300 mg (0.31 mmol) of 1 in 50 ml of n-heptane was refluxed at 120 °C (bath temperature). After 20 h the solvent was removed under reduced pressure, and the residue taken up in $\text{CH}_2\text{-Cl}_2$. The mixture was separated into three yellow bands by preparative t.l.c. using cyclohexane/dichloromethane (3:2) as elutant. The first band contained complex 2 as the major product, the second band contained complex 3, and the third

band the unreacted starting material *1*. The zones were separated, and the products isolated by extraction with CH₂Cl₂ and crystallization from pentane. Yields: *2*: 100 mg (34%); *3*: 30 mg (11%).

When octane (Octan-Fraktion, FLUKA) was used in place of heptane the solution was refluxed at 130 °C (bath temperature) for 8 h. Yields: *2*: 110 mg (38%); *3*: 30 mg (11%).

X-ray Structural Analysis of Os₃(CO)₉(μ₂-H)₂[μ₃-NHC(CH₂)₄C]

A rectangular block-shaped, pale yellow crystal with dimensions of *ca.* 0.35 × 0.31 × 0.19 mm was used for the data collection. Preliminary cell parameters were obtained *via* Weissenberg photography (Cu-Kα radiation). The crystal was transferred to a Stoe four-circle diffractometer and accurate cell parameters were determined from the angular measurement of 20 strong reflections in the range 15 < 2θ < 25°. 3408 intensities to a 2θ_{max} of 55° were recorded using graphite monochromated Mo-Kα radiation and a 140 step ω/θ scan technique; the step width was fixed at 0.01° with a counting time for each step of 0.5 s, backgrounds were measured for 17.5 s. Two standard reflections, monitored every 50 measurements, showed no decrease in intensity during data collection. The data was corrected for Lorentz polarisation effects and for absorption; an empirical method was applied based on 455 azimuthal scan data from 28 independent reflections. Transmission factors ranged from 0.304 to 0.989 for the full data set. Equivalent reflections were averaged to give 2882 unique observed reflections [*F* > 3σ(*F*)].

Crystal data: C₁₅H₁₀NO₉Os₃, *M* = 918.84, monoclinic, *a* = 9.479(4), *b* = 13.498(5), *c* = 15.943(7) Å, β = 92.55(3)°, *U* = 2037.9 Å³, *D_c* = 2.99 g cm⁻³, *Z* = 4, *F*(000) = 1627, Mo-Kα radiation (λ̄ = 0.71069 Å), μ(Mo-Kα) = 186.97 cm⁻¹, space group *P*2₁/*c* from systematic absences.

The three Os atoms were located by Σ₂ sign expansion and the remaining non-hydrogen atoms from subsequent Fourier difference syntheses. The structure was refined by blocked-cascade least squares with all the non-hydrogen atoms assigned anisotropic thermal parameters. The NH and CH₂ hydrogen atoms were placed in geometrically idealised positions (N–H, 1.08 Å; C–H, 1.08 Å) and assigned a common isotropic temperature factor. In the final cycles of refinement the weighting scheme *w* = [σ²(*F*) + 0.0012|*F_o*|²]⁻¹ was introduced since this minimised the dependence of ωΔ² on |*F_o*|² and sin θ. The final residuals for the 2882 reflections were *R* = 0.042 and *R_w* = [Σ*w*^{1/2}Δ/Σ*w*^{1/2}|*F_o*|] = 0.042. Neutral-atom scattering factors were employed [6]. The final atomic coordinates for the non-hydrogen atoms are presented in Table I and their associated anisotropic thermal parameters in Table II. The hydrogen atom

TABLE I. Atom Coordinates (×10⁴).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Os(1)	3135(1)	3383(1)	4008(1)
Os(2)	2198(1)	1520(1)	3403(1)
Os(3)	179(1)	2686(1)	4185(1)
C(1)	5044(18)	3354(10)	3690(11)
O(1)	6185(12)	3344(9)	3488(8)
C(2)	3636(16)	4066(9)	5052(11)
O(2)	3940(14)	4450(8)	5644(8)
C(3)	2703(18)	4565(10)	3348(9)
O(3)	2402(15)	5270(8)	2992(8)
C(4)	3787(20)	894(11)	2965(10)
O(4)	4734(16)	491(10)	2712(9)
C(5)	1429(20)	344(10)	3883(10)
O(5)	1028(16)	-343(8)	4186(9)
C(6)	1134(20)	1408(12)	2339(11)
O(6)	519(18)	1352(12)	1716(9)
C(7)	-999(17)	3543(11)	4818(11)
O(7)	-1762(16)	4034(11)	5168(10)
C(8)	-1115(19)	1622(11)	4014(10)
O(8)	-1923(14)	1002(10)	3896(9)
C(9)	-369(19)	3245(14)	3127(12)
O(9)	-660(18)	3620(12)	2506(10)
N(1)	1105(12)	2050(8)	5282(7)
C(10)	2416(15)	1800(8)	5316(8)
C(11)	3129(19)	1390(11)	6114(10)
C(12)	4517(22)	1929(14)	6326(11)
C(13)	5508(17)	1903(13)	5577(11)
C(14)	4798(16)	1487(10)	4789(10)
C(15)	3292(13)	1914(8)	4594(8)

coordinates and isotropic temperature factors are given in Table III. A list of observed and calculated structure factors is available from the authors on request.

All calculations were performed on the University of Cambridge IBM 370/165 computer using a modified version of SHELX 76 written by Prof. G. M. Sheldrick [7].

Results and Discussion

The cyclohexylideneimine complex *1*, easily accessible from the ammonia complex Os₃(CO)₁₁·(NH₃) by condensation with cyclohexanone [8], reacts in refluxing hydrocarbons (heptane, octane) to yield the trinuclear clusters *2* and *3*. Complex *2* arises from cleavage of the N–H bond [4] in the imine moiety of *1* and subsequent hydrogen transfer onto the Os₃ triangle. Complex *3* is formed by cleavage of two C–H bonds in the cyclohexylidene ring of *1* and transfer of two hydrogen atoms onto the metal framework.

The thermolysis of *1* requires temperatures between 120 and 130 °C (bath temperature). In

TABLE II. Anisotropic Temperature Factors (Å² × 10³).

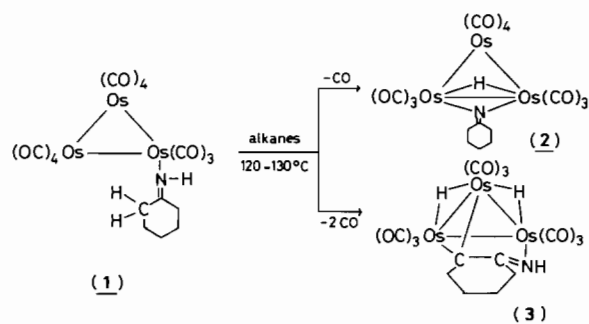
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Os(1)	18(1)	29(1)	32(1)	2(1)	2(1)	-2(1)
Os(2)	28(1)	33(1)	27(1)	-3(1)	4(1)	-3(1)
Os(3)	17(1)	42(1)	35(1)	3(1)	3(1)	1(1)
C(1)	36(9)	44(7)	54(10)	-2(7)	-8(8)	-4(7)
O(1)	15(6)	104(9)	72(8)	-11(7)	17(6)	1(6)
C(2)	33(9)	30(6)	66(11)	0(7)	-22(8)	-10(6)
O(2)	75(10)	62(6)	50(7)	-23(6)	-5(7)	-10(6)
C(3)	46(10)	49(7)	41(9)	9(7)	22(8)	-1(7)
O(3)	77(10)	59(7)	75(9)	36(6)	28(8)	23(6)
C(4)	68(13)	56(8)	36(8)	-7(7)	14(9)	11(8)
O(4)	72(11)	85(8)	85(10)	-20(8)	32(9)	20(8)
C(5)	62(12)	45(8)	41(9)	-12(7)	5(9)	9(8)
O(5)	88(11)	45(6)	85(10)	7(6)	25(9)	-18(6)
C(6)	48(11)	63(9)	44(9)	4(7)	5(8)	-25(8)
O(6)	86(12)	139(12)	52(8)	0(8)	-31(9)	-45(10)
C(7)	21(8)	66(9)	52(9)	-2(8)	-5(7)	10(7)
O(7)	70(10)	113(10)	88(10)	-42(9)	10(9)	52(9)
C(8)	41(10)	59(8)	46(9)	-8(7)	1(8)	-3(7)
O(8)	42(8)	100(9)	91(10)	-14(8)	9(8)	-34(7)
C(9)	35(10)	89(11)	52(10)	26(9)	-3(8)	10(9)
O(9)	85(13)	133(12)	80(10)	68(10)	-4(10)	2(10)
N(1)	20(6)	50(6)	25(5)	-2(5)	8(5)	-8(5)
C(10)	38(8)	22(5)	22(6)	-5(4)	-1(6)	-1(5)
C(11)	53(11)	57(8)	37(8)	19(7)	-1(8)	4(8)
C(12)	64(13)	74(10)	44(10)	11(9)	-22(9)	-9(10)
C(13)	21(8)	77(10)	62(11)	0(9)	-22(8)	10(7)
C(14)	26(8)	51(8)	55(10)	2(7)	-8(7)	15(6)
C(15)	18(6)	24(5)	28(6)	-5(5)	-9(5)	1(4)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}\cdot h^2\cdot a^{*2} + \dots + 2U_{12}\cdot h\cdot k\cdot a^*\cdot b^*)$.

TABLE III. Hydrogen Atom Coordinates (×10⁴) and Isotropic Temperature Factors (Å² × 10³).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i>
H(1)	475(12)	1933(8)	5821(7)	75(18)
H(11a)	2432(19)	1483(11)	6626(10)	75(18)
H(11b)	3343(19)	612(11)	6028(10)	75(18)
H(12a)	4291(22)	2691(14)	6477(11)	75(18)
H(12b)	5042(22)	1576(14)	6862(11)	75(18)
H(13a)	6414(17)	1449(13)	5748(11)	75(18)
H(13b)	5852(17)	2649(13)	5451(11)	75(18)
H(14a)	5446(16)	1654(10)	4267(10)	75(18)
H(14b)	4713(16)	694(10)	4859(10)	75(18)

refluxing heptane the conversion of *1* into both *2* and *3* is incomplete even after 20 h; in octane *1* has completely reacted after 8 h, but considerable decomposition is observed. The relative yields of *2* and *3* are approximately 3:1 and are independent of the solvent used. The activation of the N–H bond in *1* appears to be favoured compared with the activation of the two C–H bonds in *1*.



The novel cluster *3* is obtained as air-stable yellow crystals which melt with decomposition at 147–148 °C. The i.r. spectrum of *3* in the carbonyl region only displays absorptions due to terminal carbonyl groups (ν_{CO} 2095w, 2070vs, 2041vs, 2012vs, 1997s, 1987m, 1974w, 1967m cm⁻¹ in pentane). The imine group is easily recognised in the i.r. spectrum by two characteristic ν_{NH} absorptions at 3385 and 3375 cm⁻¹ (KBr pellet), and the cyclohexylidene ring gives rise to several bands in the CH region (ν_{CH} 2955m, 2920sh, 2895vw, 2885vw, 2845vw cm⁻¹ in KBr).

TABLE IV. Bond Lengths (Å).

Os(1)—Os(2)	2.823(2)	Os(1)—Os(3)	2.980(2)
Os(1)—C(1)	1.901(17)	Os(1)—C(2)	1.943(16)
Os(1)—C(3)	1.945(14)	Os(1)—C(15)	2.194(11)
Os(2)—Os(3)	2.812(2)	Os(2)—C(4)	1.888(18)
Os(2)—C(5)	1.921(15)	Os(2)—C(6)	1.940(17)
Os(2)—C(15)	2.189(12)	Os(3)—C(7)	1.924(16)
Os(3)—C(8)	1.901(16)	Os(3)—C(9)	1.898(18)
Os(3)—N(1)	2.106(10)	C(1)—O(1)	1.142(21)
C(2)—O(2)	1.104(20)	C(3)—O(3)	1.137(18)
C(4)—O(4)	1.138(23)	C(5)—O(5)	1.120(19)
C(6)—O(6)	1.131(22)	C(7)—O(7)	1.145(22)
C(8)—O(8)	1.143(21)	C(9)—O(9)	1.137(24)
N(1)—C(10)	1.286(18)	C(10)—C(11)	1.519(20)
C(10)—C(15)	1.457(18)	C(11)—C(12)	1.528(26)
C(12)—C(13)	1.553(26)	C(13)—C(14)	1.507(23)
C(14)—C(15)	1.558(19)		

The ^1H n.m.r. spectrum of **3** (in CDCl_3) exhibits the resonances of the cyclohexylidene protons at δ 1.56 (m,2), 1.72(m,2), 1.92(t,2), 2.24(m,2) ppm, two

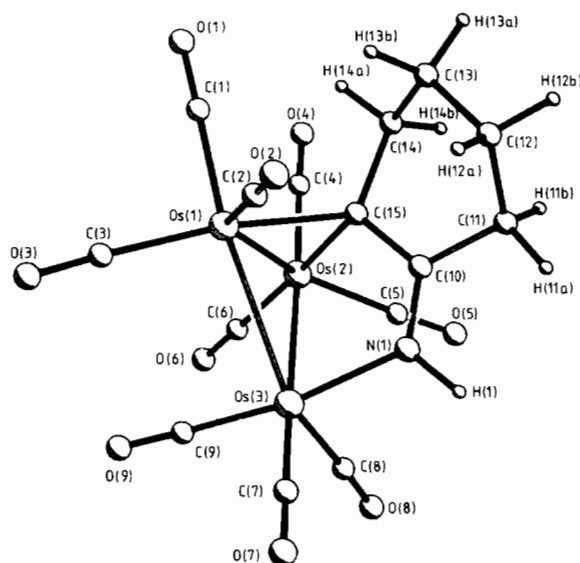


Fig. 1. The molecular structure of $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2[\mu_3\text{-NHC}(\text{CH}_2)_4\text{C}]$ (**3**) including the atom numbering scheme.

TABLE V. Bond Angles (deg.).

Os(2)—Os(1)—Os(3)	57.9(1)	Os(2)—Os(1)—C(1)	100.3(4)
Os(3)—Os(1)—C(1)	158.2(4)	Os(2)—Os(1)—C(2)	141.0(4)
Os(3)—Os(1)—C(2)	105.3(5)	C(1)—Os(1)—C(2)	92.2(7)
Os(2)—Os(1)—C(3)	119.4(4)	Os(3)—Os(1)—C(3)	97.7(5)
C(1)—Os(1)—C(3)	93.0(7)	C(2)—Os(1)—C(3)	96.4(6)
Os(2)—Os(1)—C(15)	49.8(3)	Os(3)—Os(1)—C(15)	73.8(3)
C(1)—Os(1)—C(15)	92.7(5)	C(2)—Os(1)—C(15)	93.1(5)
C(3)—Os(1)—C(15)	168.7(6)	Os(1)—Os(2)—Os(3)	63.9(1)
Os(1)—Os(2)—C(4)	106.3(5)	Os(3)—Os(2)—C(4)	169.9(5)
Os(1)—Os(2)—C(5)	136.0(5)	Os(3)—Os(2)—C(5)	90.5(5)
C(4)—Os(2)—C(5)	95.8(7)	Os(1)—Os(2)—C(6)	120.7(5)
Os(3)—Os(2)—C(6)	95.4(5)	C(4)—Os(2)—C(6)	92.0(7)
C(5)—Os(2)—C(6)	95.4(7)	Os(1)—Os(2)—C(15)	50.0(3)
Os(3)—Os(2)—C(15)	77.6(3)	C(4)—Os(2)—C(15)	94.3(6)
C(5)—Os(2)—C(15)	91.6(6)	C(6)—Os(2)—C(15)	170.1(5)
Os(1)—Os(3)—Os(2)	58.3(1)	Os(1)—Os(3)—C(7)	115.5(5)
Os(2)—Os(3)—C(7)	172.4(5)	Os(1)—Os(3)—C(8)	145.9(5)
Os(2)—Os(3)—C(8)	87.8(5)	Os(1)—Os(3)—C(9)	90.7(6)
Os(2)—Os(3)—C(9)	89.6(6)	C(7)—Os(3)—C(8)	98.2(7)
C(7)—Os(3)—C(9)	94.9(7)	C(8)—Os(3)—C(9)	91.3(7)
Os(1)—Os(3)—N(1)	81.3(3)	Os(2)—Os(3)—N(1)	82.7(3)
C(7)—Os(3)—N(1)	92.2(6)	C(8)—Os(3)—N(1)	93.1(6)
C(9)—Os(3)—N(1)	171.0(6)	Os(1)—C(1)—O(1)	179.0(11)
Os(1)—C(2)—O(2)	179.0(14)	Os(1)—C(3)—O(3)	176.4(14)
Os(2)—C(4)—O(4)	177.9(14)	Os(2)—C(5)—O(5)	177.2(17)
Os(2)—C(6)—O(6)	179.4(17)	Os(3)—C(7)—O(7)	176.2(14)
Os(3)—C(8)—O(8)	177.7(13)	Os(3)—C(9)—O(9)	176.6(18)
Os(3)—N(1)—C(10)	120.5(9)	N(1)—C(10)—C(11)	121.5(12)
N(1)—C(10)—C(15)	121.5(11)	C(11)—C(10)—C(15)	116.9(12)
C(10)—C(11)—C(12)	111.0(13)	C(11)—C(12)—C(13)	111.3(14)
C(12)—C(13)—C(14)	112.8(14)	C(13)—C(14)—C(15)	113.6(12)
Os(1)—C(15)—Os(2)	80.2(4)	Os(1)—C(15)—C(10)	113.7(7)
Os(2)—C(15)—C(10)	113.3(9)	Os(1)—C(15)—C(14)	117.6(8)
Os(2)—C(15)—C(14)	118.5(9)	C(10)—C(15)—C(14)	110.6(11)

doublets for the two non-equivalent hydrides at $\delta - 13.56(\text{d},1)$, $-13.61(\text{d},1)$ ppm [$J_{\text{H-H}} 1.7$ Hz], and the resonance of the NH proton as a broad singlet at $\delta 6.24$ ppm. In the mass spectrum of **3** the molecular ion at m/e 925 (related ^{192}Os) and the fragments of the sequence $\text{Os}_3(\text{CO})_n\text{H}_2[\text{NHC}(\text{CH}_2)_4\text{C}]$ ($n = 9-0$) are observed, showing the characteristic Os_3 isotope pattern.

The molecular structure of **3** is shown in Fig. 1. Bond lengths and interbond angles not involving the hydrogen atoms are presented in Tables IV and V respectively. The three Os atoms define an isosceles triangle with one edge of $2.980(1)$ Å [Os(1)–Os(3)] and two edges [Os(1)–Os(2), Os(2)–Os(3)] with an average distance of $2.817(4)$ Å. The Os(1)–Os(2) edge is symmetrically bridged by the C(15) atom of the six-membered ring, and by a μ_2 -H ligand, from the distribution of the carbonyl groups. These two Os atoms are also bonded to three terminal carbonyl ligands. The third metal atom Os(3) is also bonded to three terminal carbonyl groups and to the N(1) atom of the cyclohexylideneimine ligand. This organic group, therefore, caps one side of the Os_3 triangle. A second bridging hydride is considered to span the Os(1)–Os(3) bond from the distribution of the carbonyls which bend away from the edge.

The overall structure of **3** closely resembles that of $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2(\text{NHC}_6\text{H}_3\text{F})$ [9] and is similar to that postulated for a number of clusters with the general formula $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2\text{R}$ [10]. The long Os(1)–Os(3) bond is similar in length to the long Os–Os bond ($2.996(4)$ Å) in $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2(\text{NHC}_6\text{H}_3\text{F})$ [9], and the bond-lengthening effect of an edge-bridging hydride in cluster complexes is well established [11]. The average *cis* Os–Os–C (carbonyl) angle for the carbonyl groups adjacent to the Os(1)–Os(3) edge is $110(2)^\circ$ compared to the angle of $92(2)^\circ$ for the carbonyls adjacent to the unbridged Os(2)–Os(3) edge. This unbridged edge is *ca.* 0.07 Å shorter than the average metal–metal distance of $2.877(3)$ Å in the parent carbonyl, $\text{Os}_3(\text{CO})_{12}$ [12], but similar in length to the unbridged Os–Os bond of $2.810(4)$ Å in $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2(\text{NHC}_6\text{H}_3\text{F})$ [9]. The shortening of this metal–metal bond may be due to the overall capping effect of the $\text{NHC}(\text{CH}_2)_4\text{C}$ ligand. The third metal–metal bond, Os(1)–Os(2), which is bridged by a carbon atom of the six-membered ring and by a hydride as evidenced by the average *cis* Os–Os–C(carbonyl) angle of $120(1)^\circ$ for this edge, is very similar in length to the unbridged bond, Os(2)–Os(3). This suggests that the bond lengthening effect of the hydride is almost exactly counterbalanced by the shortening effect of the organic group. Similar trends have been observed in $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2\text{NHC}_6\text{H}_3\text{F}$ [9].

Five of the six C–C bonds in the six-membered ring exhibit distances which are not significantly different from the idealised C–C single bond value.

The sixth bond C(10)–C(15) is somewhat shorter and the adjacent N(1)–C(10) bond displays a double bond character. The two Os–C(15) distances (average $2.19(1)$ Å) are somewhat shorter than the comparative distances (average $2.23(1)$ Å) in $\text{Os}_3(\text{CO})_9\text{H}_2(\mu_3\text{-OC}_6\text{H}_3)\text{CH}_2\text{Ph}$ [13]. The Os(3)–N(1) distance is also slightly shorter than the value of $2.164(13)$ Å in $\text{Os}_3(\text{CO})_9\text{H}[\mu_3\text{-NC}_5\text{H}_4(\text{NH})]$ [14] where the N atom which is axially coordinated to the metal atom is also formally sp^2 hybridized. The carbonyl C(9)O(9) *trans* to this Os(3)–N(1) bond has an Os(3)–C(9) distance of $1.898(18)$ Å which may indicate some competition between N(1) and C(9)O(9) for back-donation of electron density from the metal orbitals.

None of the carbonyl groups in **3** deviate from linearity by more than 5° . The four carbonyl groups lying approximately in the plane of the Os_3 triangle are orientated so that they are *trans* to metal–metal bonds. These four Os–C distances average $1.90(1)$ Å, which is significantly shorter than the average value of $1.94(1)$ Å for the four carbonyls on Os(1) and Os(2) which are pseudo-*trans* to the C(15)–Os and the Os–H (bridging the Os(1)–Os(2) edge) bonds. This would indicate a delocalisation of electron density over the Os(1)Os(2)C(15)H unit permitting competition with these four carbonyl groups for back-donation of metal electron density, and causing a lengthening of these Os–C (carbonyl) bonds. The carbonyl C–O bond lengths average $1.13(3)$ Å.

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