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THE SYNTHESIS AND N—H ACTIVATION OF TRINUCLEAR OSMIUM ALKYLIDENIMINE COMPLEXES. THE MOLECULAR STRUCTURE OF $Os_3(CO)_{11}[NHC(CH_2)_5]$.

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Summary

Trinuclear osmium alkylidenimine complexes of the type $Os_3(CO)_{11}(NHCR_2)$ were synthesized by condensation of the ammonia complex $Os_3(CO)_{11}(NH_3)$ with ketones. The structure of the cyclohexylidenimine cluster $Os_3(CO)_{11}$—$[NHC(CH_2)_5]$ was determined by a single X-ray structure analysis. The complex crystallizes in space group $P\bar{1}$ with $a = 8.277(3)$, $b = 11.746(4)$, $c = 12.951(4)$ Å, $\alpha = 98.22(2)$, $\beta = 95.25(2)$, $\gamma = 113.81(2)°$, and $Z = 2$. The structure was refined to $R = 0.047$ for 3596 observed diffractometer data. In the solid state the osmium atoms define an isosceles triangle with the alkylidenimine ligand in an axial position. The N atom has a planar coordination geometry and the six-membered cyclohexylidene ring adopts the chair conformation. Upon heating, the N—H bond of the alkylidene ligand in $Os_3(CO)_{11}(NHCR_2)$ is activated, and the hydrogen atom transferred to the metal frame, affording alkylidenimido clusters of the type $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NCR}_2)$.

Introduction

Bond-activation reactions on transition-metal clusters have attracted great interest in the view of their possible significance for catalysis. The reaction of $Os_3(CO)_{12}$ with ethylene to yield the cluster $Os_3(CO)_9(\mu\text{-H})_2(\mu\text{-CCH}_2)$ [1,2,3] was a milestone in this chemistry. C—H activation reactions on osmium clusters are known with olefins [3], benzene [1,3], substituted arenes [4,5], pyridine [6], trialkylamines [7], trialkylphosphanes [8], aldehydes [9] and ketones [9]. However, very little is known about N—H activation on transition-

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metal clusters. Recently, we reported the preparation of the ammonia complex $Os_3(CO)_{11}(NH_3)$ and its potential for condensation and N—H activation reactions [10]. In this paper we describe the synthesis of the alkylidenimine complexes $Os_3(CO)_{11}(NHCR_2)$ (CR_2 = i-propylidene, cyclohexylidene, cyclopentylidene) (2a—2c) from $Os_3(CO)_{11}(NH_3)$ (1) and ketones, the X-ray structure analysis of the cyclohexylidenimine complex $Os_3(CO)_{11}[NHC(CH_2)_5]$ (2b), and the thermal N—H activation of these compounds yielding the corresponding alkylidenimido clusters $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NCR}_2)$ (3a—3b).

Experimental

All reactions were carried out with exclusion of air; the solvents were distilled from drying agents and saturated with purified nitrogen. For the preparative thin-layer chromatography plates coated with silica gel Merck 60 GF 254 were used.

For the spectroscopic characterization of the complexes the following instruments were employed: ^1H NMR spectra: Jeol JNM-PMX 60 and Jeol FX 90 Q; IR spectra: Perkin-Elmer 297 and Beckman 4240; mass spectra: Varian MAT CH 7 and CH 5.

Micro-analyses were performed at the Mikrolabor des Anorganisch-chemischen Instituts der Technischen Universität München. The values for hydrogen are not reliable owing to the presence of osmium.

Preparation of the compounds $Os_3(CO)_{11}(NHCR_2)$ (2a—2c)

To a solution of 225 mg (0.25 mmol) $Os_3(CO)_{11}(NH_3)$ (1) in 40 ml of CH_2Cl_2 10 ml of the corresponding ketone and 2 g of dehydrated Na_2SO_4 were added. The mixture was stirred at room temperature for about 60 h. After filtration the solvent was drawn off and the residue was taken up in CH_2Cl_2 and separated by TLC using cyclohexane/dichloromethane (3/2) as eluant. In each case the first band contained a small amount of a side-product, presumably the corresponding ketone complex $Os_3(CO)_{11}(OCR_2)$. The products 2a and 2b were found as the second (main) band, and 2c as the third band of the chromatogram. The band was taken off, and the product isolated by dissolution in CH_2Cl_2. If the band was contaminated by traces of a blue material, the product was further purified by TLC using cyclohexane/tetrahydrofuran (99/1) as eluant. After crystallization from dichloromethane/pentane (1/2), the product was dried at room temperature under high vacuum.

Complex	Yield	Formula	Micro-analyses Found (Calcd.) (%)		
			C	H	N
2a	50 mg (21%)	$C_{14}H_7NO_{11}Os_3$ (923.81)	18.52 (17.97)	1.08 (0.76)	1.56 (1.50)
2b	150 mg (61%)	$C_{17}H_{11}NO_{11}Os_3$ (975.87)	20.92 (20.92)	1.60 (1.14)	1.44 (1.44)
2c	35 mg (15%)	$C_{16}H_9NO_{11}Os_3$ (961.81)	19.69 (19.98)	1.07 (0.95)	1.47 (1.46)

Preparation of the compounds $Os_3(CO)_{10}(H)(NCR_2)$ (3a—3b)

0.1 mmol of **2a** or **2b** was dissolved in 50 ml of octane (Oktan-Fraktion, Fluka) and refluxed at 125°C. After 8—9 h the solvent was drawn off, and the residue taken up in CH_2Cl_2. The product was separated by TLC using cyclohexane/dichloromethane (3/2) as eluant. The first yellow (main) band was taken off, and the product separated by dissolution in CH_2Cl_2 and crystallization from a dichloromethane/pentane (1/2) mixture. The yellow crystals were dried at room temperature under high vacuum.

Complex	Yield	Formula	Micro-analyses Found (Calcd.) (%)		
			C	H	N
3a	15 mg (16%)	$C_{13}H_7NO_{10}Os_3$ (907.41)	17.10 (17.20)	1.55 (0.78)	1.54 (1.54)
3b	35 mg (38%)	$C_{16}H_9NO_{10}Os_3$ (935.82)	20.43 (20.28)	1.21 (1.17)	1.46 (1.48)

X-ray structural analysis of $Os_3(CO)_{11}[NHC(CH_2)_5]$

Crystal data: $C_{17}H_{11}NO_{11}Os_3$, mol. wt. 975.87, Triclinic, $a = 8.277(3)$, $b = 11.746(4)$, $c = 12.951(4)$ Å, $\alpha = 98.22(2)$, $\beta = 95.25(2)$, $\gamma = 113.81(2)$ °, $U = 1124.5$ Å^3, $d_c = 2.88$ g cm^{-3}, $Z = 2$. Space group $P\bar{1}$ from successfull refinement. Graphite monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 169.52 cm^{-1}. Intensity data was recorded from a crystal of dimensions 0.462 × 0.269 × 0.231 mm.

Orange-yellow crystals of $Os_3(CO)_{11}[NHC(CH_2)_5]$ were deposited as rectangular blocks from hexane. A suitable single crystal was mounted on a glass fibre and its crystal system determined *via* Weissenberg (Cu-K_α) photography. The crystal was transferred to a Stoe four-circle diffractometer, and accurate cell parameters determined from the angular measurement of 20 strong reflections in the range $20 < 2\theta < 30^c$. 4380 intensities to a $2\theta_{max}$ of 60° were measured using graphite-monochromated Mo-K_α radiation and a 140 step ω/θ scan technique. Two standard reflections, measured at regular intervals throughout the course of data collection, showed no significant reduction in intensity. Lp corrections, and an empirical absorption correction based on a pseudoellipsoid model and 350 azimuthal scan data from 40 independent reflections, were applied. Equivalent reflections were averaged to give 3596 unique observed $[F > 3\sigma(F)]$ intensities.

The three Os atom positions were located by multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms from a subsequent electron-density difference synthesis. The structure was refined by blocked-cascade least squares with all the non-hydrogen atoms assigned anisotropic thermal parameters. The hydrogen atom coordinated to nitrogen, and those on the cyclohexylidene ring were placed in idealised positions and were constrained to ride 1.08 Å from the coordinated atom. All the H atoms were assigned a common isotropic temperature factor. The weighting scheme $w = [\sigma^2(F) + 0.001|F|^2]^{-1}$ was introduced and refinement continued until the maximum shift/e.s.d. for every parameter was less than 0.004. The final residuals were $R = 0.047$ and $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0|] = 0.047$. A final electron-density difference map showed no significant regions of electron density. Final atomic coordinates for the non-

TABLE 1

ATOM COORDINATES ($\times 10^4$)

	x/a	*y/b*	*z/c*
Os(1)	11679(1)	3044(1)	886(1)
Os(2)	8369(1)	2345(1)	1722(1)
Os(3)	11770(1)	3443(1)	3126(1)
C(11)	11533(18)	4662(13)	930(9)
O(11)	11551(14)	5618(9)	909(8)
C(12)	10545(21)	2498(13)	−580(10)
O(12)	9919(18)	2164(11)	−1442(8)
C(13)	11888(18)	1484(12)	1010(10)
O(13)	12122(16)	582(9)	1049(9)
C(14)	14093(20)	3735(13)	742(12)
O(14)	15586(17)	4199(12)	649(10)
C(21)	6805(18)	1898(14)	390(12)
O(21)	5899(16)	1595(12)	−401(9)
C(22)	6702(23)	1886(16)	2657(13)
O(22)	5671(21)	1558(14)	3213(11)
C(23)	8359(16)	681(13)	1506(10)
O(23)	8231(16)	−355(9)	1356(8)
C(24)	8575(18)	4050(14)	2056(11)
O(24)	8649(15)	5039(11)	2262(10)
C(31)	10743(20)	3575(16)	4376(10)
O(31)	10114(21)	3588(15)	5107(9)
C(32)	14208(19)	3953(13)	3680(11)
O(32)	15660(16)	4183(11)	4028(10)
C(33)	11372(20)	1763(13)	3193(10)
O(33)	11208(16)	781(10)	3302(9)
N(1)	12264(18)	5435(11)	3226(9)
C(1)	13548(21)	6467(15)	3101(12)
C(2)	15218(24)	6503(17)	2730(13)
C(3)	16801(29)	7443(17)	3492(16)
C(4)	16861(28)	8742(17)	3802(17)
C(5)	15152(34)	8634(18)	4142(17)
C(6)	13408(36)	7704(16)	3357(16)

hydrogen and hydrogen atoms are listed in Tables 1 and 2, respectively, while the associated anisotropic thermal parameters may be found in Table 3.

Complex neutral-atom scattering factors [11] were employed throughout the structure solution and refinement. Calculations were performed on the University of Cambridge IBM 370/165 computer using programs written by Professor G.M. Sheldrick. The molecular diagram was drawn using PLUTO written by Dr. W.D.S. Motherwell. Copies of observed and calculated structure factor tables may be obtained from the authors.

Results and Discussion

The ammonia complex 1, easily accessible from $Os_3(CO)_{12}$ and NH_3 by aminoxide-induced carbonyl substitution [10], reacts in dichloromethane with ketones to produce the alkylidenimine complexes 2a—2c.

$$Os_3(CO)_{11}(NH_3) + O{=}CR_2 \rightarrow Os_3(CO)_{11}(NH{=}CR_2) + H_2O$$

(1) acetone 2a: $R_2 = (CH_3)_2$
cyclohexanone 2b: $R_2 = (CH_2)_5$
cyclopentanone 2c: $R_2 = (CH_2)_4$

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS (Å^2 $\times10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	52(1)	44(1)	41(1)	9(1)	12(1)	25(1)
Os(2)	46(1)	49(1)	46(1)	6(1)	7(1)	23(1)
Os(3)	50(1)	52(1)	38(1)	3(1)	4(1)	22(1)
C(11)	61(8)	62(8)	43(6)	14(5)	9(5)	34(6)
O(11)	84(7)	55(6)	83(7)	21(5)	20(6)	39(6)
C(12)	86(10)	53(7)	48(7)	7(6)	13(7)	41(7)
O(12)	124(10)	88(8)	46(6)	1(5)	−4(6)	56(8)
C(13)	54(7)	52(7)	55(7)	11(6)	14(6)	26(6)
O(13)	103(8)	58(6)	84(7)	26(5)	30(6)	50(6)
C(14)	61(8)	59(8)	73(9)	28(7)	25(7)	38(7)
O(14)	80(8)	105(9)	107(9)	45(7)	21(7)	57(7)
C(21)	44(7)	74(9)	65(8)	14(7)	14(6)	27(7)
O(21)	75(8)	91(8)	75(7)	13(6)	−17(6)	25(6)
C(22)	83(11)	73(9)	80(10)	11(8)	29(9)	48(9)
O(22)	124(11)	111(10)	111(10)	39(8)	71(9)	57(9)
C(23)	41(6)	63(8)	47(6)	4(6)	3(5)	21(6)
O(23)	93(8)	52(6)	74(6)	−2(5)	−7(6)	37(6)
C(24)	53(8)	68(8)	66(8;	1(6)	9(6)	37(7)
O(24)	74(7)	70(7)	110(9)	−1(6)	1(6)	48(6)
C(31)	62(9)	93(10)	44(7)	11(7)	11(6)	35(8)
O(31)	153(13)	158(12)	68(7)	42(8)	64(8)	102(11)
C(32)	55(8)	53(7)	63(8)	0(6)	3(6)	26(6)
O(32)	68(7)	85(8)	101(9)	1(6)	−7(6)	35(6)
C(33)	68(9)	53(8)	44(7)	6(6)	−6(6)	12(6)
O(33)	90(8)	68(7)	69(7)	21(5)	−3(6)	25(6)
N(1)	80(8)	56(7)	50(6)	−3(5)	−2(6)	37(6)
C(1)	64(9)	61(8)	71(9)	−6(7)	8(7)	22(7)
C(2)	76(11)	81(10)	73(10)	6(8)	19(8)	24(9)
C(3)	104(15)	79(12)	100(14)	15(10)	28(12)	10(11)
C(4)	106(15)	68(11)	97(13)	0(9)	25(11)	−18(10)
C(5)	171(21)	61(11)	109(15)	5(10)	38(15)	24(12)
C(6)	180(21)	53(10)	97(13)	15(9)	19(14)	43(12)

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

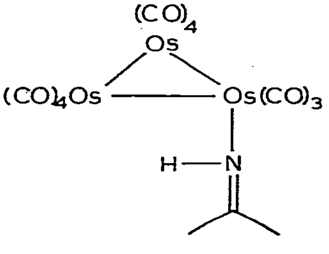
TABLE 3

HYDROGEN ATOM COORDINATES ($\times10^4$) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 $\times10^3$)

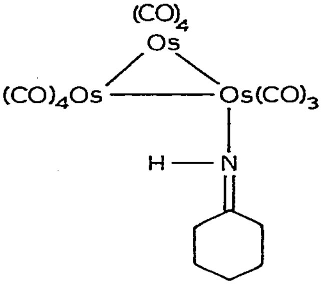
	x/a	y/b	z/c	U
H(10)	11134(18)	5602(11)	3437(9)	94(15)
H(21)	15213(24)	5574(17)	2652(13)	94(15)
H(22)	15275(24)	6784(17)	1970(13)	94(15)
H(31)	16830(29)	7056(17)	4199(16)	94(15)
H(32)	17983(29)	7550(17)	3149(16)	94(15)
H(41)	17084(28)	9218(17)	3139(17)	94(15)
H(42)	17944(28)	9280(17)	4454(17)	94(15)
H(51)	15064(34)	8310(18)	4883(17)	94(15)
H(52)	15180(34)	9571(18)	4254(17)	94(15)
H(61)	13354(36)	8070(16)	2642(16)	94(15)
H(62)	12225(36)	7587(16)	3703(16)	94(15)

The condensation is performed in the presence of dehydrating agents such as sodium sulphate; the reaction proceeds at room temperature and in contrast to classical condensation reactions without acid or base catalysis. Addition of HCl leads to the cluster compounds $Os_3(CO)_{11}(\mu\text{-H})(Cl)$ [12] and $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-Cl})$ [12,13] instead of the alkylidenimine complexes; using HBF_4 the products 2a—2c are obtained only in very low yields. If NaOH or $NaOCH_3$ is added, formation of $Na[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-CO})]$ [14] is observed. These findings are inconsistent with the view that condensation reactions of coordinated ammonia proceed via a NH_2^- complex intermediate [15]. Traces of side-products which seem to be the ketone complexes $Os_3(CO)_{11}(OCR_2)$ [$R_2 = (CH_3)_2, (CH_2)_5, (CH_2)_4$] [16] are suggestive of a dissociative mechanism which involves the cleavage of the bond between the ammonia ligand and the cluster, the condensation of the free ammonia and the ketone via nucleophilic attack, and the subsequent coordination of the resulting alkylidenimine molecule with the unsaturated $Os_3(CO)_{11}$ fragment.

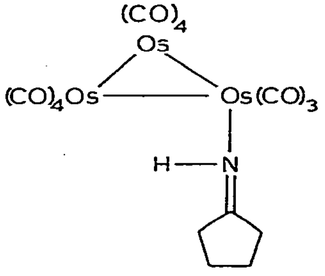
The alkylidenimine complexes 2a—2c are obtained as yellow, air-stable crystals, which decompose rather indistinctly above 170 °C.



(2a)



(2b)



(2c)

The alkylidenimine ligand in 2a—2c is easily recognized in the IR spectrum by a characteristic ν(N—H) absorption between 3308 and 3323 cm^{-1} and a typical ν(N=C) band between 1630 and 1647 cm^{-1}. In the carbonyl region the infrared spectra show the typical $Os_3(CO)_{11}L$ pattern; only absorptions of terminal CO ligands are observed. The ^1H NMR spectra exhibit the NH proton resonances as broad multiplets between δ 9.17 and 9.25 ppm, the signals of the alkylidene groups lie in the range between δ 1.71 and 2.76 ppm. As expected, the two methyl groups in 2a are non-equivalent, giving rise to two resonances of equal intensity at δ 2.48 and 2.25 ppm. As the signal at δ 2.48 ppm appears as a doublet, this resonance is assigned to the methyl groups *trans* with respect to the hydrogen atom of the NH moiety. Similarly, two different signals are observed for the two CH_2 groups of the cyclopentylidene ring vicinal to the N=C double bond in 2c, whereas the signal of the corresponding CH_2 groups in 2b is not resolved. The ^1H NMR and IR data of the compounds 2a—2c are presented in Table 4.

In the mass spectra of the complexes 2a—2c the molecular ions (*m/e* related to ^{192}Os: 2a 941, 2b 981, 2c 967) as well as the ions of the fragments $Os_3(CO)_{11}(NH)$ and $Os_3(CO)_n$ (n = 11—0) appear showing the typical Os_3 isotope pattern.

TABLE 4

^{1}H NMR AND IR DATA OF THE ALKYLIDENIMINE COMPLEXES $Os_3(CO)_{11}(NHCR_2)$ [R_2 = $(CH_3)_2$: 2a; R_2 = $(CH_2)_5$: 2b; R_2 = $(CH_2)_4$: 2c] AND THE ALKYLIDENIMIDO COMPLEXES $Os_3(CO)_{10}(\mu$-$H)(\mu$-$NCR_2)$ [R_2 = $(CH_3)_2$: 3a; R_2 = $(CH_2)_5$: 3b]

Complex	ν(C≡O) (cm^{-1}) [a]	ν(N—H) (cm^{-1}) [b]	ν(N=C) (cm^{-1}) [b]	δ (ppm) [c]
2a	2102w, 2050s, 2032vs, 2021m, 1997vs, 1977(sh), 1963vw, 1950vw	3308	1630	9.25 (m,1), 2.48 (d, 3), 2.25 (s, 3)
2b	2104w, 2050s, 2032vs, 2018m, 2000s, 1995(sh), 1982m, 1955(sh)	3323	1638	9.18 (m,1), 2.62 (m, 4), 1.71 (m,6)
2c	2100w, 2046s, 2035vs, 2018m, 1997s, 1987m, 1967vw, 1953vw	3321	1647	9.17 (m,1), 2.76 (dt, 2), 2.48 (dt,2), 1.91 (m, 4)
3a	2102w, 2065vs, 2054s, 2022vs, 2009s, 1993vs, 1979w	—	1655	2.44 (s,6), —15.00 (s,1)
3b	2104w, 2063vs, 2055s, 2020vs, 2008s, 1998vs, 1984w	—	1645	2.67 (m,4), 1.67 (m, 6), —15.00 (s,1)

[a] In pentane. [b] KBr pellet. [c] In $CDCl_3$.

The structure of complex 2b was solved by a single crystal X-ray structure analysis. The molecular structure of $Os_3(CO)_{11}[NHC(CH_2)_5]$ is shown in Fig. 1, which includes the atom numbering scheme adopted. Lists of bond lengths and inter-bond angles can be found in Tables 5 and 6, respectively. The complex exists in the solid state as discrete, neutral molecules separated by normal Van der

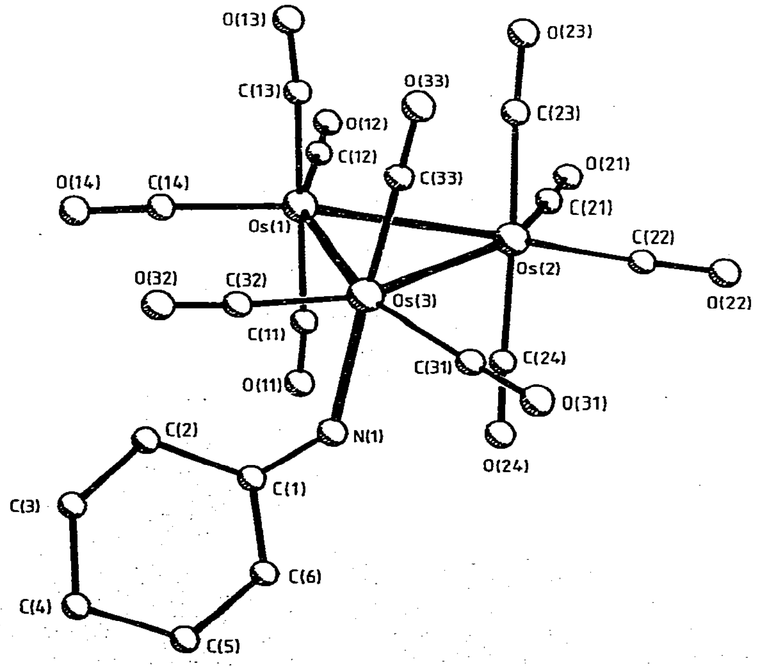


Fig. 1. The molecular structure of $Os_3(CO)_{11}[NHC(CH_2)_5]$, the hydrogen atoms have been omitted for clarity.

TABLE 5

BOND LENGTHS (Å)

Os(1)—Os(2)	2.887(2)	Os(1)—C(11)	1.947(17)
Os(1)—Os(3)	2.860(2)	Os(1)—C(12)	1.933(13)
Os(2)—Os(3)	2.890(2)	Os(1)—C)13)	1.935(16)
Os(3)—N(1)	2.189(13)	Os(1)—C(14)	1.867(15)
C(11)—O(11)	1.121(20)	Os(2)—C(21)	1.927(14)
C(12)—O(12)	1.129(16)	Os(2)—C(22)	1.885(18)
C(13)—O(13)	1.158(21)	Os(2)—C(23)	1.930(16)
C(14)—O(14)	1.158(20)	Os(2)—C(24)	1.921(17)
C(21(—O(21)	1.131(18)	Os(3)—C(31)	1.911(15)
C(22(—O(22)	1.149(24)	Os(3)—C(32)	1.893(15)
C(23)—O(23)	1.164(19)	Os(3)—C(33)	1.881(16)
C(24)—O(24)	1.130(21)	N(1)—C(1)	1.293(18)
C(31)—O(31)	1.123(21)	C(1)—C(2)	1.491(28)
C(32)—O(32)	1.150(20)	C(1)—C(6)	1.497(30)
C(33)—O(33)	1.137(21)	C(2)—C(3)	1.482(22)
C(3)—C(4)	1.501(31)	C(4)—C(5)	1.482(38)
C(5)—C(6)	1.565(29)		

TABLE 6

BOND ANGLES (deg.)

Os(2)—Os(1)—Os(3)	60.4(1)	Os(2)—Os(1)—C(11)	83.5(4)
Os(1)—Os(2)—Os(3)	59.4(1)	Os(3)—Os(1)—C(11)	87.4(4)
Os(1)—Os(3)—Os(2)	60.3(1)	Os(2)—Os(1)—C(12)	95.0(5)
C(11)—Os(1)—C(12)	90.3(6)	Os(3)—Os(1)—C(12)	155.4(5)
C(11)—Os(1)—C(13)	173.7(5)	Os(2)—Os(1)—C(13)	94.5(4)
C(12)—Os(1)—C(13)	95.8(6)	Os(3)—Os(1)—C(13)	86.4(4)
C(11)—Os(1)—C(14)	92.7(7)	Os(2)—Os(1)—C(14)	163.7(4)
C(12)—Os(1)—C(14)	100.9(7)	Os(3)—Os(1)—C(14)	103.7(4)
C(13)—Os(1)—C(14)	87.6(7)	Os(1)—Os(2)—C(21)	97.0(5)
C(21)—Os(2)—C(23)	90.6(6)	Os(3)—Os(2)—C(21)	155.6(4)
C(22)—Os(2)—C(23)	91.3(7)	Os(1)—Os(2)—C(22)	161.1(6)
C(21)—Os(2)—C(24)	95.1(7)	Os(3)—Os(2)—C(22)	102.9(5)
C(22)—Os(2)—C(24)	88.6(7)	C(21)—Os(2)—C(22)	101.3(7)
C(23)—Os(2)—C(24)	174.2(5)	Os(1)—Os(2)—C(23)	83.4(4)
C(31)—Os(3)—C(32)	102.4(6)	Os(3)—Os(2)—C(23)	92.0(3)
C(31)—Os(3)—C(33)	90.5(7)	Os(1)—Os(2)—C(24)	94.8(4)
C(32)—Os(3)—C(33)	88.3(7)	Os(3)—Os(2)—C(24)	82.3(4)
Os(1)—Os(3)—N(1)	92.5(3)	Os(1)—Os(3)—C(31)	153.7(5)
Os(2)—Os(3)—N(1)	97.3(3)	Os(2)—Os(3)—C(31)	94.2(4)
C(31)—Os(3)—N(1)	84.4(6)	Os(1)—Os(3)—C(32)	103.7(5)
C(32)—Os(3)—N(1)	89.8(6)	Os(2)—Os(3)—C(32)	162.5(5)
C(33)—Os(3)—N(1)	174.1(5)	Os(1)—Os(3)—C(33)	93.5(4)
Os(3)—N(1)—C(1)	137.0(14)	Os(2)—Os(3)—C(33)	86.1(4)
N(1)—C(1)—C(2)	123.2(17)	Os(1)—C(11)—O(11)	174.6(13)
N(1)—C(1)—C(6)	119.7(18)	Os(1)—C(12)—O(12)	177.9(17)
C(2)—C(1)—C(6)	117.1(15)	Os(1)—C(13)—O(13)	175.0(12)
C(1)—C(2)—C(3)	109.8(16)	Os(1)—C(14)—O(14)	177.8(16)
C(2)—C(3)—C(4)	116.3(21)	Os(2)—C(21)—O(21)	177.3(16)
C(3)—C(4)—C(5)	109.6(16)	Os(2)—C(22)—O(22)	177.3(16)
C(4)—C(5)—C(6)	115.9(19)	Os(2)—C(23)—O(23)	175.5(11)
C(1)—C(6)—C(5)	106.5(21)	Os(2)—C(24)—O(24)	178.0(13)
Os(3)—C(31)—O(31)	176.5(17)	Os(3)—C(33)—O(33)	175.1(12)
Os(3)—C(32)—O(32)	175.5(14)		

TABLE 7

HYDROGEN BOND ANGLES (deg.)

Os(3)—N(1)—H(10)	111.6(4)	H(10)—N(1)—C(1)	111.4(11)
C(1)—C(2)—H(21)	109.7(10)	C(1)—C(2)—H(22)	108.9(10)
H(21)—C(2)—C(3)	110.0(13)	H(22)—C(2)—C(3)	108.9(11)
C(2)—C(3)—H(31)	107.1(11)	C(2)—C(3)—H(32)	108.1(12)
H(31)—C(3)—C(4)	108.3(12)	H(32)—C(3)—C(4)	107.4(12)
C(3)—C(4)—H(41)	109.6(12)	C(3)—C(4)—H(42)	108.9(12)
H(41)—C(4)—C(5)	110.1(13)	H(42—C(4)—C(5)	109.0(10)
C(4)—C(5)—H(51)	109.0(13)	C(4)—C(5)—H(52)	107.2(11)
H(51)—C(5)—C(6)	107.0(11)	H(52)—C(5)—C(6)	108.2(14)
C(1)—C(6)—H(61)	109.2(10)	C(5)—C(6)—H(61)	109.3(11)
C(1)—C(6)—H(62)	110.9(12)	C(5)—C(6)—H(62)	111.4(14)

Waals' distances. The shortest non-bonded intermolecular contact is between O(14) and O(24) [related by the symmetry operation $(1 + x, y, z)$] at a distance of 2.861 Å.

The three Os atoms define the vertices of an isosceles triangle. Two of the metal atoms are coordinated to four terminal carbonyl groups, two axial and two equatorial. The third Os atom is bonded to three carbonyls and the $NHC(CH_2)_5$ group which occupies an axial coordination site. The N atom of this group may be considered as formally sp^2 hybridized, and has a planar coordination geometry. The six-membered cyclohexylidene ring adopts the chair conformation.

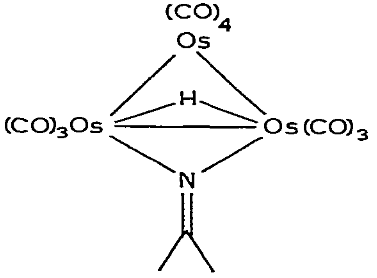
The structure may be considered as derived from that of the parent binary carbonyl, $Os_3(CO)_{12}$ [17], by the replacement of one axial carbonyl by the nitrogen coordinated ligand. Two of the Os—Os distances in $Os_3(CO)_{11}[NHC(CH_2)_5]$ are similar to the average metal—metal distance of 2.877(3) Å in $Os_3(CO)_{12}$ [17], while the third is slightly shorter. All the carbonyl groups are essentially linear although there is a small difference in Os—C—O angle between the equatorial (mean 177°) and axial (mean 175°) groups. This difference is not statistically significant but the trend may suggest that there is a slight increase in bending of the axial groups to reduce ligand—ligand repulsions. There is, perhaps, a significant difference between the equatorial (mean 1.90 Å) and axial (mean 1.93 Å) Os—C(carbonyl) distances in this cluster. The greater length of the axial Os—C bonds may be explained in terms of the greater competition between two *trans* carbonyls for back donation of electron density from the same metal orbital. The equatorial carbonyls are approximately *trans* to Os—Os bonds, which are not good π-acceptors, so that the back donated electron density is taken up by the Os—C bond, causing it to shorten. The Os—C(carbonyl) bond *trans* to the nitrogen donor ligand does not fit into this pattern. It is *ca.* 0.05 Å shorter than the average value for the other axial carbonyls. This suggests that the $NHC(CH_2)_5$ ligand is a poor π-acceptor and does not compete effectively with the carbonyl for the back donated electron density. The Os—N distance is similar in length to the values of 2.156(6) and 2.162(6) Å reported for the Os—N$(sp)^2$ single bonds in $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}p\text{-}CH_3C_6H_4NCHO)$ and $Os_3(CO)_9(\mu\text{-}H)(PMe_2Ph)(\mu\text{-}p\text{-}CH_3C_6H_4NHCO)$ [18], respectively. This is consistent with there being little back donation from the metal to this Os—N bond. The N(1)—C(1) bond distance is close to that expected for a formal double bond, and the bond parameters of the cyclohexylidene ring do not deviate significantly from the normal values.

The N—H bond in the alkylidenimine complexes **2a**—**2c** can be activated thermally. Upon heating in octane solution the N—H bond is cleaved and the hydrogen transferred as a hydride bridge onto the metal framework under elimination of carbon monoxide, yielding the alkylidenimido complexes $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NCR}_2)$ ($R_2 = (CH_3)_2$: **3a**, $R_2 = (CH_2)_5$: **3b**). **3b** is formed in significantly higher yield than **3a**. In the case of cyclopentylidenimine complex **2c** a reaction was observed, but the expected complex $Os_3(CO)_{10}(\mu\text{-H})[\mu\text{-NC(CH}_2)_4]$ (**3c**) could not be isolated.

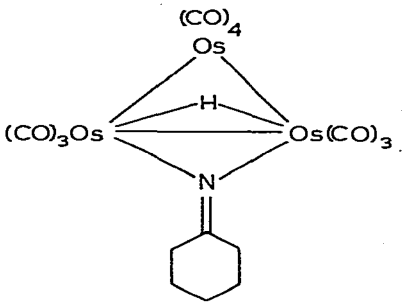
$$Os_3(CO)_{11}(NH{=}CR_2) \xrightarrow{125^\circ C} Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-N}{=}CR_2) + CO$$

(**2a**: $R_2 = (CH_3)_2$, (**3a**: $R_2 = (CH_3)_2$,
2b: $R_2 = (CH_2)_5$) **3b**: $R_2 = (CH_2)_5$)

The alkylidenimido clusters **3a**—**3b** form yellow air-stable crystals which decompose indistinctly between 170 and 200 °C.



(3a)



(3b)

The IR spectra of **3a**—**3b** exhibit in the carbonyl region seven absorptions of terminal CO ligands in the typical $Os_3(CO)_{10}(\mu\text{-L})(\mu\text{-L}')$ pattern; a band at 1655 or 1645 cm^{-1}, respectively, is attributed to the ν(N=C) vibration. In the ^1H NMR spectra apart from the resonances of the aliphatic protons the μ-hydride signal is observed at $\delta -15.00$ ppm for both compounds. The appearance of only one singlet for the two methyl groups in **3a** (in contrast to the two singlets in **2a**) clearly demonstrates the C_s symmetry of the molecule. The ^1H NMR and IR data for **3a** and **3b** are given in Table 4.

In the mass spectra of **3a**—**3b** the molecular ions appear at *m/e* 913 and 953, respectively (related to ^{192}Os). All the ions of the sequences $Os_3(CO)_n(H)(NCR_2)$ and $Os_3(CO)_n(H)$ (n = 10—0) are observed. Molecular ion and fragment ions show the characteristic Os_3 isotope pattern.

The bridging alkylidenimido ligand $\mu\text{-NCR}_2$ in **3a** and **3b** is isomeric to the bridging aminocarbyne ligand $\mu\text{-CNR}_2$ to be found in the cluster $Os_3(CO)_{10}(\mu\text{-H})[\mu\text{-CN(CH}_3)_2]$ [7]. Like the aminocarbyne ligand, the alkylidenimido moiety can be considered as a three-electron donor to satisfy the eighteen-electron rule for the metal atoms of the cluster triangle.

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