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STRUCTURAL STUDIES ON OSMIUM CARBONYL HYDRIDES

XXVI *. CRYSTAL STRUCTURE OF A COMPLEX WITH A 2-METHYLIMIDAZOLYL LIGAND BOUND TO A TRIOSMIUM CLUSTER: $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

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Summary

The compound $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$ has been studied via a single-crystal X-ray diffraction study. It crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a 9.568(3), b 17.663(5), c 12.063(2) Å and β 97.72(2)°. All non-hydrogen atoms were located and the structure was refined to R_F 5.5% for all 1894 data and R_F 3.7% for those 1511 data with $|F_0| > 3\sigma(|F_0|)$. Unlike the corresponding imidazolyl complex, this 2-methylimidazolyl complex is ordered in the crystalline state. The two non-bridged Os–Os bond lengths are Os(1)–Os(3) 2.884(1) and Os(2)–Os(3) 2.892(1) Å, while the di-bridged distance is Os(1)–Os(2) 2.957(1) Å. The 2-methylimidazolyl ligand is bonded to the triosmium cluster via the linkages Os(1)–N(1) 2.153(16) Å and Os(2)–C(1) 2.089(18) Å.

Introduction

The reactions of $Os_3(CO)_{10}(NCMe)_2$ with imidazole (I) and related species have recently been described by Shapley and coworkers [4]. Included in this study was an X-ray crystallographic analysis of the unsubstituted imidazolyl derivative, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_3)$ (II).

Unfortunately, this species is disordered in the crystal (with reversal of N(3) and C(4)) and certain interatomic distances are thus subject to uncertain errors.

We have now undertaken a structural analysis of the related triosmium complex derived from 2-methylimidazole (III). The product is obtained as a single isomer [4] and is expected to be ordered in the solid state. Our results are reported below.

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* For previous parts, see ref. 1–3.

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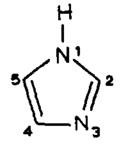
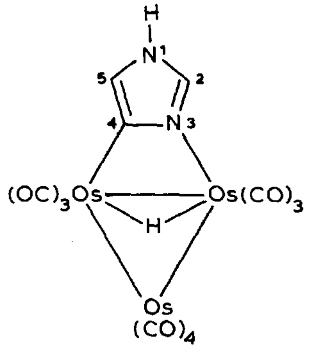


(I)



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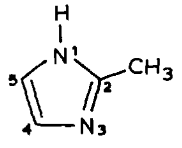

(III)

Experimental

Crystallographic study of $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}3\text{-}4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

An amber needle-shaped crystal (0.2 × 0.1 × 0.1 mm) obtained as described in ref. 4, was attached to a glass fiber and mounted on a Syntex $P2_1$ automated four circle diffractometer. Determination of cell parameters and orientation matrix and data collection were carried out as previously described [5]. Details appear in Table 1. The systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) strongly suggest the space group $P2_1/n$. Data were corrected for absorption, averaged,

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

A. Crystal parameters at 24°C

crystal system: monoclinic
space group: $P2_1/n$ (C^5_{2h}; No. 14) [a]
a 9.568(3) Å
b 17.663(5) Å
c 12.063(2) Å
β 97.72(2)°
V 2020.0(9) Å^3
$Z = 4$
mol. wt. = 932.82
ρ(calc'd) 3.07 g/cm^3

B. Collection of intensity data

diffractometer: Syntex $P2_1$
radiation; Mo-K_α ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly ordered graphite, equatorial geometry; 2θ (mono) 12.2°
reflections measured: $+h \pm k \pm l$
scan type: coupled θ (crystal)–2θ (counter)
2θ range: 4–40°
scan speed: 2°/min (in 2θ)
scan width: $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
background measurement: at beginning and end of scan; each for half of the total scan time
reflections collected: 4226 total, merged to 1894 independent data standards: 3 collected every 97 data; no significant decay absorption coefficient: μ 200.0 cm^{-1} [b]

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[a] $P2_1/n$ is a non-standard setting of $P2_1/c$ having the equipoints $\pm(x, y, z)$ and $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

[b] Data were corrected for absorption using an empirical method based upon interpolation (both in 2θ and in ϕ) between ψ-scans of close-to-axial ($\chi = 85$–$95°$) reflections. The ratio of maximum/minimum transmission was 1.8/1.

corrected for Lorentz and polarization effects and reduced to observed structure factor amplitudes.

Crystallographic calculations were performed on our in-house locally modified Syntex XTL system. The heavy atoms were located by direct methods using the program MULTAN [6]; all other non-hydrogen atoms were located from difference-Fourier syntheses. The structure was refined to convergence by full-matrix least-squares refinement. Attempts to locate hydrogen atoms by difference-Fourier methods were unsuccessful; they were included in calculated positions with d(C–H) 0.95 Å and d(Os–H) 1.87 Å.

Refinement led to convergence with R_F 5.5%, R_{wF} 4.1% and GOF = 1.08 for all 1894 independent data (R_F 3.7%, R_{wF} 3.8% and GOF = 1.13 for those 1511 data with $|F_0| > 3\sigma(|F_0|)$]. A final difference-Fourier synthesis was "clean" (ρ_{max} 1.1

TABLE 2

FINAL POSITIONAL PARAMETERS AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B_{iso}
Os(1)	0.09640(8)	0.32986(5)	0.29882(6)	
Os(2)	0.33112(8)	0.33569(5)	0.16267(6)	
Os(3)	0.37624(8)	0.37279(5)	0.39828(6)	
O(11)	−0.1967(14)	0.2892(10)	0.1826(10)	
O(12)	0.1164(18)	0.1772(9)	0.4142(16)	
O(13)	0.0015(16)	0.4074(10)	0.4986(12)	
O(21)	0.2568(16)	0.2970(10)	−0.0833(11)	
O(22)	0.4982(19)	0.1902(10)	0.2124(14)	
O(23)	0.5784(15)	0.4353(11)	0.1277(12)	
O(31)	0.3516(16)	0.4006(9)	0.6440(12)	
O(32)	0.2969(16)	0.5397(8)	0.3393(11)	
O(33)	0.6901(15)	0.4046(11)	0.3993(12)	
O(34)	0.4324(16)	0.2033(9)	0.4498(12)	
C(11)	−0.079(2)	0.3056(11)	0.2246(15)	3.7(4)
C(12)	0.109(2)	0.2376(16)	0.3743(19)	5.7(5)
C(13)	0.037(2)	0.3745(15)	0.4238(20)	5.6(5)
C(21)	0.285(2)	0.3120(13)	0.0152(18)	4.8(5)
C(22)	0.440(2)	0.2410(15)	0.1960(17)	5.0(5)
C(23)	0.490(2)	0.3957(14)	0.1422(18)	5.4(5)
C(31)	0.359(2)	0.3909(13)	0.5504(19)	5.1(5)
C(32)	0.321(2)	0.4813(14)	0.3554(18)	4.7(5)
C(33)	0.563(2)	0.3899(12)	0.4006(16)	4.7(5)
C(34)	0.408(2)	0.2624(14)	0.4332(16)	4.1(5)
N(1)	0.0968(16)	0.4304(9)	0.1979(12)	4.2(3)
C(1)	0.2079(18)	0.4335(10)	0.1388(14)	2.9(4)
C(2)	0.200(2)	0.4986(13)	0.0793(18)	5.4(5)
N(2)	0.0775(16)	0.5376(10)	0.1131(12)	4.4(4)
C(3)	0.0184(19)	0.4963(12)	0.1835(15)	4.0(4)
C(4)	−0.108(2)	0.5166(13)	0.2321(18)	5.7(5)
H(Os)	0.1637	0.2805	0.1786	2.5
H(2)	0.2600	0.5151	0.0275	6.0
HN(2)	0.0455	0.5862	0.0873	6.0
H(4A)	−0.1300	0.4773	0.2807	6.0
H(4B)	−0.0916	0.5623	0.2732	6.0
H(4C)	−0.1844	0.5233	0.1741	6.0

TABLE 3

FINAL ANISOTROPIC THERMAL PARAMETERS [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	3.14(4)	3.08(4)	3.58(4)	−0.09(3)	0.69(3)	−0.26(3)
Os(2)	3.53(4)	3.50(4)	3.03(4)	−0.12(3)	0.65(3)	−0.51(3)
Os(3)	3.19(4)	3.25(4)	3.06(4)	0.04(3)	0.39(3)	−0.48(3)
O(11)	4.3(8)	8.6(10)	4.6(7)	−2.5(7)	−0.5(6)	0.7(7)
O(12)	7.5(10)	4.8(9)	10.8(12)	0.4(8)	2.3(9)	3.1(9)
O(13)	6.8(8)	7.4(10)	5.3(7)	0.7(8)	1.5(7)	−1.0(7)
O(21)	6.5(9)	9.4(11)	3.9(7)	−0.4(8)	0.0(6)	−2.1(7)
O(22)	9.7(12)	5.9(10)	7.1(9)	4.6(9)	0.4(8)	−1.0(8)
O(23)	5.0(8)	9.2(12)	7.5(9)	−2.9(8)	1.3(7)	−1.5(8)
O(31)	8.5(10)	7.2(10)	5.0(8)	0.5(8)	2.3(7)	−0.7(7)
O(32)	8.0(9)	2.7(7)	6.2(8)	1.1(7)	−2.3(7)	0.0(6)
O(33)	4.8(8)	11.1(13)	6.7(9)	−1.6(8)	1.6(7)	−0.6(9)
O(34)	7.9(10)	3.5(8)	7.0(9)	2.5(7)	2.3(7)	−0.5(7)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form: $\exp\left(-0.25\left(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23}\right)\right)$.

e$^-$/Å^3, close to Os(3)), and tests of the weighting scheme indicated that it was satisfactory. Positional and thermal parameters are listed in Tables 2 and 3.

The analytical form of the scattering factor of the neutral atoms were used in all calculations; these were corrected for both the real and anomalous terms of

TABLE 4

INTRAMOLECULAR DISTANCES (Å) WITH e.s.d. FOR $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

Atoms	Distance	Atoms	Distance
(A) Osmium – osmium distances			
Os(1)–Os(2)	2.957(1)	Os(1)–Os(3)	2.884(1)
Os(2)–Os(3)	2.892(1)		
(B) Osmium – bridging imidazolyl ligand distances			
Os(1)–N(1)	2.153(16)	Os(2)–C(1)	2.089(18)
(C) Osmium – carbonyl distances			
Os(1)–C(11)	1.847(20)	Os(2)–C(23)	1.898(24)
Os(1)–C(12)	1.863(27)	Os(3)–C(31)	1.891(23)
Os(1)–C(13)	1.857(24)	Os(3)–C(32)	2.037(25)
Os(2)–C(21)	1.822(22)	Os(3)–C(33)	1.805(22)
Os(2)–C(22)	1.982(26)	Os(3)–C(34)	2.010(25)
(D) Carbon – oxygen distances			
C(11)–O(11)	1.202(24)	C(23)–O(23)	1.127(29)
C(12)–O(12)	1.168(32)	C(31)–O(31)	1.154(27)
C(13)–O(13)	1.161(28)	C(32)–O(32)	1.069(29)
C(21)–O(21)	1.213(26)	C(33)–O(33)	1.249(26)
C(22)–O(22)	1.062(31)	C(34)–O(34)	1.082(29)
(E) Distances within the imidazolyl ring			
N(1)–C(1)	1.358(22)	N(2)–C(3)	1.305(25)
N(1)–C(3)	1.383(26)	C(3)–C(4)	1.458(29)
C(1)–C(2)	1.352(29)		
C(2)–N(2)	1.463(27)		

anomalous dispersion. All values are from International Tables for X-ray Crystallography, Volume 4.

Description of the molecular geometry of $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

The crystal contains an ordered arrangement of discrete molecular units which are mutually separated by normal Van der Waals' distances. The molecular geometry and atomic labeling scheme are illustrated in Fig. 1. Interatomic distances and angles are collected in Tables 4 and 5; intramolecular planes and dihedral angles are listed in Table 6.

The molecule contains a triangular core of osmium atoms; Os(3) is linked to four terminal carbonyl ligands, while Os(1) and Os(2) are each bonded to three terminal carbonyl ligands. In addition Os(1) and Os(2) are bridged by a μ-3,4-η^2-(*N*,*C*)-$C_3N_2H_2(2\text{-}CH_3)$ ligand and by a μ-hydride ligand (which was not located directly from the X-ray diffraction study).

The non-bridged osmium–osmium bond lengths, Os(1)–Os(3) 2.884(1) Å and

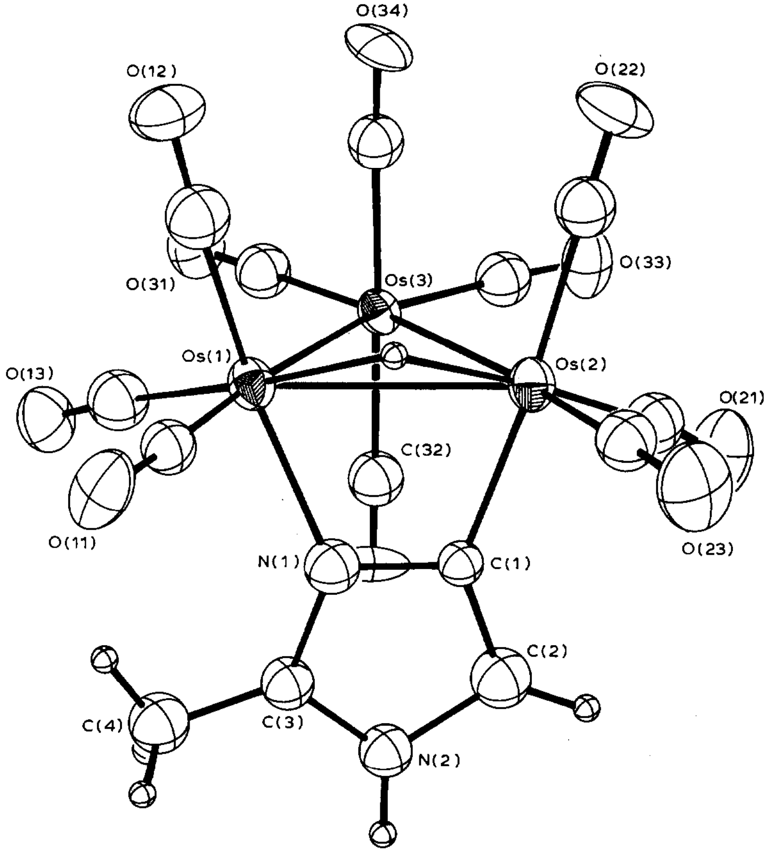

Fig. 1. Atomic labeling scheme and molecular geometry of the 2-methylimidazolyl complex $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$. This is an ORTEP-II diagram with the hydride ligand shown in its estimated position. (Note that the labeling of atoms within the 2-methylimidazolyl ligand does not correspond to the IUPAC numbering scheme, cf. structure III.)

TABLE 5

INTRAMOLECULAR ANGLES (degree) WITH e.s.d. FOR $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

(A) Osmium - osmium - osmium angles			
Os(3)-Os(1)-Os(2)	59.34(3)	Os(2)-Os(3)-Os(1)	61.57(3)
Os(1)-Os(2)-Os(3)	59.09(3)		
(B) Angles involving the bridging imidazolyl ligand			
Os(2)-C(1)-N(1)	111.2(12)	Os(1)-N(1)-C(1)	113.0(11)
Os(2)-C(1)-C(2)	140.0(15)	Os(1)-N(1)-C(3)	136.3(12)
C(1)-Os(2)-Os(1)	69.4(5)	N(1)-Os(1)-Os(2)	66.3(4)
C(1)-Os(2)-Os(3)	87.4(5)	N(1)-Os(1)-Os(3)	86.9(4)
C(1)-Os(2)-C(21)	89.9(8)	N(1)-Os(1)-C(11)	89.3(7)
C(1)-Os(2)-C(22)	175.3(8)	N(1)-Os(1)-C(12)	173.1(9)
C(1)-Os(2)-C(23)	88.1(8)	N(1)-Os(1)-C(13)	97.7(8)
(C) Osmium - osmium - carbon (carbonyl) angles			
Os(2)-Os(1)-C(11)	116.7(6)	Os(3)-Os(2)-C(22)	89.2(7)
Os(2)-Os(1)-C(12)	107.2(8)	Os(3)-Os(2)-C(23)	89.1(7)
Os(2)-Os(1)-C(13)	140.8(7)	Os(1)-Os(3)-C(31)	104.7(7)
Os(3)-Os(1)-C(11)	175.4(6)	Os(1)-Os(3)-C(32)	86.8(6)
Os(3)-Os(1)-C(12)	91.7(8)	Os(1)-Os(3)-C(33)	155.6(7)
Os(3)-Os(1)-C(13)	85.4(7)	Os(1)-Os(3)-C(34)	86.5(6)
Os(1)-Os(2)-C(21)	115.7(7)	Os(2)-Os(3)-C(31)	166.2(7)
Os(1)-Os(2)-C(22)	105.9(7)	Os(2)-Os(3)-C(32)	87.9(6)
Os(1)-Os(2)-C(23)	140.7(7)	Os(2)-Os(3)-C(33)	94.0(7)
Os(3)-Os(2)-C(21)	174.8(7)	Os(2)-Os(3)-C(34)	89.1(6)
(D) Carbon(carbonyl) - osmium - carbon(carbonyl) angles			
C(11)-Os(1)-C(12)	91.7(10)	C(31)-Os(3)-C(32)	92.0(9)
C(11)-Os(1)-C(13)	97.7(10)	C(31)-Os(3)-C(33)	99.7(10)
C(12)-Os(1)-C(13)	89.0(11)	C(31)-Os(3)-C(34)	89.5(9)
C(21)-Os(2)-C(22)	93.2(10)	C(32)-Os(3)-C(33)	94.0(9)
C(21)-Os(2)-C(23)	95.3(10)	C(32)-Os(3)-C(34)	173.3(9)
C(22)-Os(2)-C(23)	95.2(10)	C(33)-Os(3)-C(34)	92.1(9)
(E) Osmium - carbon - oxygen angles			
Os(1)-C(11)-O(11)	175.9(17)	Os(2)-C(23)-O(23)	175.3(21)
Os(1)-C(12)-O(12)	175.1(22)	Os(3)-C(31)-O(31)	178.4(20)
Os(1)-C(13)-O(13)	175.0(21)	Os(3)-C(32)-O(32)	175.1(20)
Os(2)-C(21)-O(21)	179.0(18)	Os(3)-C(33)-O(33)	177.2(18)
Os(2)-C(22)-O(22)	179.0(22)	Os(3)-C(34)-O(34)	176.1(19)
(F) Angles within the imidazolyl ligand			
C(1)-N(1)-C(3)	110.5(15)	C(2)-N(2)-C(3)	110.6(16)
N(1)-C(1)-C(2)	108.7(16)	N(2)-C(3)-N(1)	106.1(16)
C(1)-C(2)-N(2)	104.0(17)		

Os(2)-Os(3) 2.892(1) Å (average 2.888 ± 0.006 Å) are similar to those found in the disordered unsubstituted imidazolyl complex (Os(1)-Os(3) 2.881(1) Å and Os(2)-Os(3) 2.883(1) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_3)$ [4]) and to the average osmium-osmium bond length in the parent carbonyl (Os-Os = 2.877 ± 0.003 Å in $Os_3(CO)_{12}$ [7]).

The dibridged Os(1)-Os(2) distance in the present complex is 2.957(1) Å, i.e., some 0.07 Å longer than the non-bridged osmium-osmium bond lengths. The dibridged osmium-osmium distance in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_3)$ is 2.952(1) Å [4], in good agreement with the present value.

TABLE 6

LEAST SQUARES PLANES WITHIN $[(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_2(2\text{-}CH_3)]$

Plane 1: $-0.1849x+0.9579y-0.2196z-4.7155=0$ [a]	
Os(1)	0.000 Å
Os(2)	0.000 Å
Os(3)	0.000 Å
Plane 2: $-0.4781x-0.4328y-0.7643x+5.4046=0$ [a]	
N(1)	0.017(15) Å
C(1)	−0.021(18) Å
C(2)	0.015(22) Å
N(2)	−0.005(15) Å
C(3)	−0.007(19) Å
Plane 3: $-0.4726x-0.4533y-0.7558z+5.5387=0$ [a]	
Os(1)	−0.0088(7) Å
Os(2)	0.0089(7) Å
N(1)	0.019(15) Å
C(1)	−0.020(17) Å
Dihedral angles (degrees)	
Plane 1/2	99.11°
1/3	100.42°
2/3	1.31°

[a] Equations to planes are in an orthonormal coordinate system.

The previous structural study of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}C_3N_2H_3)$ [4] suffered from a disorder problem such that the osmium–carbon and osmium–nitrogen bonds were disordered; the resulting Os–C/N distances were 2.134(20) and 2.136(22) Å. The present 2-methylimidazolyl derivative is no longer disordered in the crystalline state and we can now obtain the individual osmium–ligand bond distances, which are Os(1)–N(1) 2.153(16) Å and Os(2)–C(1) 2.089(18) Å. (Note that the average of these two values is 2.121 Å, in reasonable agreement with the disordered Os–C/N distances mentioned above.) A similar difference in osmium–nitrogen and osmium–carbon distances is found within the HC=NPh ligand of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}HC{=}NPh)Os_3(CO)_9(P(OMe)_3)$ [8], in which Os–N 2.150(6) Å and Os–C 2.078(9) Å. Although the normally accepted covalent radius for single-bonded nitrogen is less than that for carbon (i.e., 0.70 versus 0.77 Å [9]) and the same holds true for double-bonded atoms (0.62 versus 0.67 Å [9]), these values refer to atoms in a similarly charged environment i.e., NR_2 versus CR_3, rather than to the present situation of $\gg$N:→Os versus $\gg$C–Os in which the nitrogen atom is involved in a polar donor–acceptor bond whereas the carbon atom is associated with a C–Os σ-bond.

As can be seen in Table 6, the Os(1)–N(1)–C(1)–Os(2) system is close to planar and makes a dihedral angle of 100.42° with the triosmium plane. The imidazolyl ring is close to coplanar with the Os(1)–N(1)–C(1)–Os(2) system, the calculated deviation being only 1.31°.

All other distances and angles in the molecule are normal (see Tables 4 and 5).

Additional data

A table of observed and calculated structure factor amplitudes is available upon request from M.R.C.

Acknowledgments

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