Inorg. Chem. **1982**, *21*, 634–639

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Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with Imidazole and Related Aromatic Heterocycles. Crystal and Molecular Structure of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}N_2C_3H_3)$[1,2]

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Received August 11, 1981

The reactions of $Os_3(CO)_{10}(NCCH_3)_2$ with imidazole, *N*-methylimidazole, 2-methylimidazole, 4-methylimidazole, benzimidazole, and pyrazole (L–H) generate products that are formulated as $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}L)$. In nearly all cases a C–H bond adjacent to the imino nitrogen is cleaved. Isomeric derivatives are formed where possible, with modest regioselectivity. The isomers do not interconvert after their formation. The complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}N_2C_3H_3)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.288$ (3) Å, $b = 17.402$ (4) Å, $c = 11.729$ (2) Å, $\beta = 94.13$ (2)°, $V = 1890.7$ (8) Å^3, and $Z = 4$. Diffraction data (Mo Kα, $2\theta = 3\text{–}40°$) were collected with a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved by conventional methods. All nonhydrogen atoms were located, and final discrepancy indices were $R_F = 5.3\%$ and $R_{wF} = 4.4\%$ for the 1769 independent reflections (none rejected). The molecule consists of a triangular cluster of osmium atoms, two of which [Os(1) and Os(2)] are each associated with three terminal carbonyl ligands, while the third [Os(3)] is associated with four. Atoms Os(1) and Os(2) are bridged by a hydride ligand (not located in this study) and by an imidazolyl ligand. The Os(1)–C–N–Os(2) bridge lies at an angle of 100.76° to the triosmium plane (i.e., the imidazolyl ligand occupies essentially axial sites on Os(1) and Os(2)). The bridged osmium–osmium bond is Os(1)–Os(2) = 2.952 (1) Å, while the nonbridged intermetallic distances are Os(1)–Os(3) = 2.881 (1) Å and Os(2)–Os(3) = 2.883 (1) Å. The structural study is marred by disorder of the imidazolyl system.

Introduction

Compounds of the formula $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}X)$ represent a common type of triosmium cluster derivative.[4] These compounds can be prepared from a variety of species X–H in reaction either directly with $Os_3(CO)_{12}$[5] or more readily and frequently more cleanly with the labile derivatives $Os_3(CO)_{10}(NCCH_3)_2$[6] and $Os_3(CO)_{10}(C_6H_8)$.[7] Particularly interesting are substances in which a C–H bond is cleaved, as in the formation of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CH{=}CHR)$ from alkenes,[6,7] $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}C(O)R)$ from aldehydes,[6b,8] or $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NC_5H_4)$ from pyridine.[6,9] We have found that the interaction of $Os_3(CO)_{10}(NCCH_3)_2$ with imidazole and several related aromatic heterocycles (L–H) proceeds analogously to provide compounds of the general type $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}L)$. This conclusion is supported by a single-crystal X-ray diffraction study of one of the imidazole reaction products.

Experimental Section

$Os_3(CO)_{12}$[10] and $H_2Os_3(CO)_{10}$[11] were prepared by published procedures. $Os_3(CO)_{10}(NCCH_3)_2$ was prepared from $H_2Os_3(CO)_{10}$ as described[6] and used directly as a crude product. Imidazole (Eastman) was recrystallized and *N*-methylimidazole (Aldrich) was distilled from BaO prior to use. 4-Methylimidazole (Aldrich) was used as received. Benzimidazole and 2-methylimidazole were kindly supplied by Professor T. B. Rauchfuss of the University of Illinois, Urbana, and were used as received. Pyrazole (Aldrich) was sublimed prior to use. Solvents were reagent grade, were stored over 4A molecular sieves (Linde), and were used without further purification. Reactions were conducted under a nitrogen atmosphere.

^1H NMR spectra were obtained on a Varian EM390 spectrometer (90 MHz) with Me_4Si as an internal reference. IR spectra were recorded on a Perkin-Elmer 281B spectrometer and were calibrated with cyclohexane (2138.5 cm^{-1}) and polystyrene film. Electron-impact mass spectra were obtained on a Varian MAT CH-5 mass spectrometer in the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences.

Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with Imidazole. $Os_3(CO)_{10}(NCCH_3)_2$, derived from 50 mg of $H_2Os_3(CO)_{10}$ (0.059 mmol), and imidazole (5 mg, 0.07 mmol) were dissolved in benzene and heated under solvent reflux for 1 h. Rotary evaporation of the solvent followed by preparative TLC of the residue (2:1 petroleum ether–dichloromethane/silica gel) gave two yellow bands. Crystallization of the faster-moving material from dichloromethane/pentane provided 8 mg (0.009 mmol, 15%) of the minor isomer, and crystallization of the slower-moving compound, also from dichloromethane/pentane, produced 30 mg (0.32 mmol, 55%) of the major isomer.

Minor isomer (1a): IR ν_{CO} (C_6H_{12}) 2106 m, 2065 vs, 2055 vs, 2022 vs, 2012 vs, 1991 s, and 1976 m cm^{-1}, ν_{NH} (CH_2Cl_2) 3427 cm^{-1}; mass spectrum (^{192}Os) m/z $924 - 28x$ ($M^+ - x$CO), $x = 0\text{–}10$. Anal. Calcd for $C_{13}H_4N_2O_{10}Os_3$: C, 16.99; H, 0.44; N, 3.05. Found: C, 17.23; H, 0.47; N, 2.91.

Major isomer (1b): IR ν_{CO} (C_6H_{12}) 2102 m, 2061 vs, 2051 vs, 2018 vs, 2006 vs, 1989 m, and 1975 w cm^{-1}, ν_{NH} (CH_2Cl_2) 3421 cm^{-1}; mass spectrum (^{192}Os) m/z $924 - 28x$ ($M^+ - x$CO), $x = 0\text{–}10$. Anal. Calcd for $C_{13}H_4N_2O_{10}Os_3$: C, 16.99; H, 0.44; N, 3.05. Found: C, 17.25; H, 0.42; N, 2.99.

Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with *N*-Methylimidazole. $Os_3(CO)_{10}(NCCH_3)_2$, derived from 50 mg of $H_2Os_3(CO)_{10}$ (0.059 mmol), was dissolved in benzene, and 1.8 μL of *N*-methylimidazole (1 equiv) was added. The mixture was refluxed for 1 h and cooled, and the solvent rotary evaporated. Preparative TLC of the residue (petroleum ether/silica gel) gave two yellow bands. Crystallization of the faster-moving compound from dichloromethane/pentane provided 11 mg (0.012 mmol, 20%) of the minor isomer. Crystallization of the slower-moving material from dichloromethane/pentane provided 32 mg (0.034 mmol, 58%) of the major isomer.

Minor isomer (2a): IR ν_{CO} (C_6H_{12}) 2105 m, 2064 vs, 2054 vs, 2021 vs, 2011 vs, 1991 s, 1976 m, 1959 w, and 1950 w cm^{-1}; mass spectrum (^{192}Os) m/z $938 - 28x$ ($M^+ - x$CO), $x = 0\text{–}10$. Anal. Calcd for $C_{14}H_6N_2O_{10}Os_3$: C, 18.02; H, 0.65; N, 3.00. Found: C, 18.41; H, 0.58; N, 3.12.

Major isomer (2b): IR ν_{CO} (C_6H_{12}) 2102 m, 2062 vs, 2051 vs, 2018 vs, 2006 vs, 1991 s, 1989 s, 1984 m, and 1973 m cm^{-1}; mass spectrum

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(1) Part 21 of the series "Structural Studies on Osmium Carbonyl Hydrides". For previous parts see ref 2.

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(^{192}Os) m/z 938 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{14}H_6N_2O_{10}Os_3$: C, 18.02; H, 0.65; N, 3.00. Found: C, 18.49; H, 0.57; N, 3.17.

Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with 2-Methylimidazole. $Os_3(CO)_{10}(NCCH_3)_2$, derived from 50 mg of $H_2Os_3(CO)_{10}$ (0.059 mmol), and 2-methylimidazole (5 mg, 0.06 mmol) were dissolved in benzene and heated under solvent reflux for 1 h. Rotary evaporation of the solvent followed by preparative TLC (4:1 petroleum ether–dichloromethane/silica gel) of the residue produced one yellow band. Crystallization of the compound from dichloromethane/pentane gave 27 mg (0.029 mmol, 50%) of $HOs_3(CO)_{10}(C_4H_5N_2)$ (**3**): IR ν_{CO} (C_6H_{12}) 2102 m, 2061 vs, 2050 vs, 2017 vs, 2005 vs, 2001 s, 1989 s, and 1973 m cm^{-1}, ν_{NH} (CH_2Cl_2) 3422 cm^{-1}; mass spectrum (^{192}Os) m/z 938 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{14}H_6N_2O_{10}Os_3$: C, 18.02; H, 0.65; N, 3.00. Found: C, 18.19; H, 0.48; N, 3.12.

Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with 4-Methylimidazole. $Os_3(CO)_{10}(NCCH_3)_2$, derived from 50 mg of $H_2Os_3(CO)_{10}$ (0.059 mmol), and 4-methylimidazole (5 mg, 0.06 mmol) were dissolved in benzene and heated under solvent reflux for 1 h. Rotary evaporation of the solvent followed by preparative TLC of the residue (4:1 petroleum ether–dichloromethane/silica gel) gave two yellow bands. Crystallization of the faster-moving material from dichloromethane/pentane provided 15 mg (0.016 mmol, 28%) of yellow crystals which, nevertheless, show ^1H NMR signals for two isomeric compounds in the approximate ratio 3:10 (see Discussion of Spectroscopic Results). Crystallization of the slower-moving compound from dichloromethane/pentane provided 13 mg (0.015 mmol, 25%) of the remaining isomer.

4a and 4b: IR ν_{CO} (C_6H_{12}) 2105 m, 2063 vs, 2054 s, 2020 vs, 2010 s, 1992 s, and 1977 m cm^{-1}, ν_{NH} (CH_2Cl_2) 3430 cm^{-1}; mass spectrum (^{192}Os) m/z 938 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{14}H_6N_2O_{10}Os_3$: C, 18.02; H, 0.65; N, 3.00. Found: C, 18.44; H, 0.56; N, 3.02.

4c: IR ν_{CO} (C_6H_{12}) 2102 m, 2061 s, 2050 vs, 2030 w, 2018 vs, 2004 vs, 1987 s, 1973 m, 1955 m, and 1940 m cm^{-1}, ν_{NH} (CH_2Cl_2) 3418 cm^{-1}; mass spectrum (^{192}Os) m/z 938 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{14}H_6N_2O_{10}Os_3$: C, 18.02; H, 0.65; N, 3.00. Found: C, 18.58; H, 0.82; N, 2.92.

Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with Benzimidazole. $Os_3(CO)_{10}(NCCH_3)_2$, derived from 50 mg of $H_2Os_3(CO)_{10}$ (0.059 mmol), and benzimidazole (9 mg, 0.08 mmol) were dissolved in benzene and heated under solvent reflux for 1 h. Rotary evaporation of the solvent followed by preparative TLC of the residue (1:1 petroleum ether–dichloromethane/silica gel) gave two yellow bands. Crystallization of the faster-moving compound from dichloromethane/pentane provided 12 mg (0.012 mmol, 21%) of the minor isomer. Crystallization of the slower-moving compound from dichloromethane/pentane provided 23 mg (0.024 mmol, 40%) of the major isomer.

Minor isomer (5a): IR ν_{CO} (C_6H_{12}) 2105 m, 2065 vs, 2056 vs, 2023 vs, 2013 vs, 2004 s, 1995 s, and 1979 m cm^{-1}, ν_{NH} (CH_2Cl_2) 3420 cm^{-1}; mass spectrum (^{192}Os) m/z 974 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{17}H_6N_2O_{10}Os_3$: C, 21.08; H, 0.62; N, 2.89. Found: C, 21.15; H, 0.67; N, 2.97.

Major isomer (5b): IR ν_{CO} (C_6H_{12}) 2102 m, 2058 s, 2052 vs, 2018 vs, 2005 vs, 1990 m, 1982 w, 1993 w, and 1961 vw cm^{-1}, ν_{NH} (CH_2Cl_2) 3409 cm^{-1}; mass spectrum (^{192}Os) m/z 974 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{17}H_6N_2O_{10}Os_3$: C, 21.08; H, 0.62; N, 2.89. Found: C, 20.91; H, 0.80; N, 3.10.

Reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with Pyrazole. $Os_3(CO)_{10}(NCCH_3)_2$, derived from 50 mg of $H_2Os_3(CO)_{10}$ (0.059 mmol), and pyrazole (5 mg, 0.07 mmol) were dissolved in benzene and heated under solvent reflux for 1 h. Rotary evaporation of the solvent, followed by preparative TLC (4:1 petroleum ether dichloromethane/silica gel) of the residue with petroleum ether provided two yellow bands. Crystallization of these components from dichloromethane/pentane gave 26 mg (0.028 mmol, 48%) of the fast-moving major isomer and 12 mg (0.013 mmol, 22%) of the slower-moving minor isomer.

Major isomer (6a): IR ν_{CO} (C_6H_{12}) 2110 m, 2070 vs, 2061 s, 2023 vs, 2018 s, 2007 m, 1992 m, 1983 m, and 1964 w cm^{-1}; mass spectrum (^{192}Os) m/z 924 − 28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{13}H_4N_2O_{10}Os_3$: C, 16.99; H, 0.44; N, 3.05. Found: C, 17.12; H, 0.49; N, 3.12.

Minor isomer (6b): IR ν_{CO} (C_6H_{12}) 2105 m, 2063 s, 2055 s, 2022 s, 2013 s, 2004 m, 1994 s, 1979 m, 1957 m, and 1942 w cm^{-1}, ν_{NH} (CH_2Cl_2) 3405 cm^{-1}; mass spectrum (^{192}Os) m/z 924 −28x (M^+ − xCO), x = 0–10. Anal. Calcd for $C_{13}H_4N_2O_{10}Os_3$: C, 16.99; H, 0.44; N, 3.05. Found: C, 17.57; H, 0.56; N, 3.02.

Table I. Experimental Data for the X-ray Diffraction Study of (μ-H)$Os_3(CO)_{10}$(μ-3,4-η^2-$N_2C_3H_3$)

A. Crystal Parameters[a] at 24 °C

crystal system: monoclinic
space group: $P2_1/n$[b] [C_{2h}^5; No. 14]
a = 9.288 (3) Å
b = 17.402 (4) Å
c = 11.729 (2) Å
β = 94.13 (2)°
V = 1890.7 (8) Å^3
Z = 4
mol wt = 918.8
ρ(calcd) = 3.23 g/cm^3

B. Collection of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα (λ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial geometry; 2θ(mono) = 12.2°
rflctns measd: $+h+k\pm l$
scan type: coupled θ(crystal)–2θ(counter)
2θ range: 3.0–40.0°
scan speed: 2.0°/min (in 2θ)
scan width: [2.0 + $\Delta(\alpha_2 - \alpha_1)$]°
bkgd measmt: at beginning and end of scan; each for half of the total scan time
rflctns collected: 2064 total data, 1769 independent data
standards: 3 collected every 97 data; no significant decay
abs coeff: 213.6 cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 15 rflctns with 2θ = 20–30°. [b] Nonstandard setting of the space group $P2_1/c$ [C_{2h}^5; No. 14] having the equipoints ±(x, y, z) and ±($^1/_2$ + x, $^1/_2$ − y, $^1/_2$ + z).

Crystallographic Study of (μ-H)$Os_3(CO)_{10}$(μ-3,4-η^2-$N_2C_3H_3$) (1b). A yellow needle-shaped crystal (0.4 × 0.04 × 0.03 mm) 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 described previously.[12] Details appear in Table I. 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, corrected for Lorentz and polarization effects, and reduced to observed structure factor amplitudes.

Crystallization calculations were performed on our in-house locally modified Syntex XTL system. The heavy atoms were located by using direct methods (MULTAN)[13] and all other nonhydrogen atoms were located from difference-Fourier syntheses. The structure was refined to convergence by full-matrix least-squares refinement. Attempts to locate hydrogen atoms were unsuccessful. At this stage we discovered (from ORTEP-II diagrams)[14] that one carbon atom of the imidazolyl system (that bonded to Os(1)) had a very small thermal ellipsoid. We therefore interchanged the scattering factors for the C and N atoms bonded to osmium. Following refinement, the newly defined C atom now had an anomalously small thermal ellipsoid. This problem was resolved by assuming the imidazolyl ligand to be disordered about a mirror plane perpendicular to the triosmium plane and passing through Os(3), the Os(1)–Os(2) bond, the metal-bonded C–N (N–C) system, and the noncoordinated nitrogen atom.

Refinement of the disordered model led to convergence with R_F = 5.3%, R_{wF} = 4.4%, and GOF = 1.700 for all 1769 data[15] [R_F = 4.1%, R_{wF} = 4.3%, and GOF = 1.793 for those 1521 data with $|F_o| > 3\sigma(|F_o|)$].

No correction for secondary extinction was necessary, a final difference-Fourier synthesis was "clean" (ρ(max) = 0.8 e Å^{-3}, close to an osmium atom), and tests of the weighting scheme indicated that it was satisfactory. Positional and thermal parameters are listed in Tables II and III.

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(15) $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ (%); $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%); GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$; NO = number of observations; NV = number of variables.

Table II. Positional Parameters for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}N_2C_3H_3)$

atom	x	y	z	atom	x	y	z
Os(1)	0.41407 (8)	0.33640 (5)	0.19169 (7)	O(31)	0.1799 (20)	0.4075 (11)	−0.1494 (15)
Os(2)	0.17569 (9)	0.35422 (5)	0.34302 (7)	O(32)	0.0708 (17)	0.21320 (90)	0.0517 (14)
Os(3)	0.13137 (8)	0.38376 (5)	0.10115 (7)	O(33)	−0.1921 (16)	0.4154 (10)	0.1133 (14)
O(11)	0.7055 (15)	0.2991 (11)	0.3106 (14)	O(34)	0.2022 (17)	0.55215 (89)	0.1562 (12)
O(12)	0.3896 (18)	0.1770 (11)	0.0848 (18)	C/N(1)	0.4264 (19)	0.4429 (12)	0.2821 (14)
O(13)	0.5197 (17)	0.4127 (10)	−0.0184 (14)	C/N(2)	0.3201 (20)	0.4499 (13)	0.3534 (15)
O(21)	0.2484 (17)	0.3193 (13)	0.5933 (15)	C(2)	0.5101 (24)	0.5046 (15)	0.2930 (21)
O(22)	0.0005 (20)	0.2085 (10)	0.3026 (15)	N(2)	0.4575 (21)	0.5529 (11)	0.3710 (16)
O(23)	−0.0778 (17)	0.4558 (10)	0.3796 (14)	C(3)	0.3351 (26)	0.5170 (17)	0.4062 (19)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
C(11)	0.5951 (25)	0.3098 (13)	0.2677 (18)	3.74 (45)	C(32)	0.0971 (25)	0.2779 (16)	0.0720 (20)	4.85 (54)
C(12)	0.3924 (28)	0.2444 (17)	0.1258 (22)	5.68 (59)	C(33)	−0.0684 (26)	0.4010 (13)	0.1073 (19)	4.36 (49)
C(13)	0.4798 (23)	0.3788 (14)	0.0619 (20)	4.28 (48)	C(34)	0.1799 (24)	0.4887 (15)	0.1406 (19)	4.23 (49)
C(21)	0.2197 (25)	0.3344 (14)	0.4994 (23)	4.71 (52)	H(12)	0.34189 (0)	0.29415 (0)	0.32124 (10)	4.0000 (0)
C(22)	0.0631 (26)	0.2629 (16)	0.3154 (20)	4.69 (54)	H(2)	0.59481 (0)	0.51555 (0)	0.25316 (0)	4.0000 (0)
C(23)	0.0134 (26)	0.4143 (14)	0.3666 (19)	4.35 (50)	H(3)	0.27259 (0)	0.53653 (0)	0.45949 (0)	4.0000 (0)
C(31)	0.1617 (25)	0.3952 (14)	−0.0543 (24)	5.21 (55)					

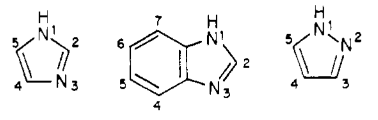
Table IV. ^{1}H NMR Data for Imidazole and Related Compounds[a]

compd	signals[b,c]	assignt
imidazole	7.70 (s, 1 H)	C(2)-H
	7.13 (s, 2 H)	C(4)-H, C(5)-H
N-methylimidazole	7.37 (s, 1 H)	C(2)-H
	6.98 (br, 1 H)	C(5)-H
	6.78 (br, 1 H)	C(4)-H
	3.60 (s, 3 H)	N-CH_3
2-methylimidazole	6.94 (s, 2 H)	C(4)-H, C(5)-H
	2.42 (s, 3 H)	C(2)-CH_3
4-methylimidazole	7.56 (s, 1 H)	C(2)-H
	6.75 (s, 1 H)	C(5)-H
	2.27 (s, 3 H)	C(4)-CH_3
benzimidazole	8.03 (s, 1 H)	C(2)-H
	7.55 (m, 2 H)	C(4)-H
	7.15 (m, 2 H)	C(5)-H
pyrazole	7.61 (d, 2 H_a)	C(3)-H, C(5)-H
	6.31 (t, 1 H_b, J_{ab} = 1.9 Hz)	C(4)-H

[a] Data for all compounds except benzimidazole from: Batterham, T. J. "NMR Spectra of Simple Heterocycles"; Wiley: New York, 1973. [b] Chemical shifts (δ) downfield from internal $SiMe_4$. [c] Solutions in $CDCl_3$, except benzimidazole is in CD_2Cl_2/$(CD_3)_2CO$.

Discussion of Spectroscopic Results

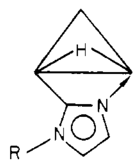
The numbering schemes for the ring positions in imidazole, benzimidazole, and pyrazole are as follows:



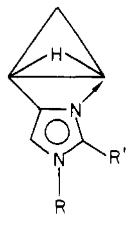
The ^{1}H NMR spectral data observed for these compounds and the three possible methyl-substituted imidazoles are shown in Table IV. The N–H resonances, when observable, are broad and have concentration-dependent chemical shifts, due to self-association equilibria. These interactions promote proton exchange between the two nitrogen atoms, which in turn equilibrates C(4)/C(5) in imidazole and its 2-methyl and 4(5)-methyl derivatives, C(4)/C(7) and C(5)/C(6) in benzimidazole, and C(3)/C(5) in pyrazole. The C(2)–H resonances in imidazole and its derivatives appear significantly downfield of the resonances for protons at C(4) or C(5).

The interaction of these heterocycles (L–H) with $Os_3(CO)_{10}(NCCH_3)_2$ (approximately 1:1) in refluxing benzene provides compounds that are readily formulated as "metalated" derivatives $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$. Isomeric compounds are formed in cases where inequivalent C–H bonds may be cleaved. We have deduced the configurations of the products by comparing their ^{1}H NMR spectra (Table V) with those of the unmodified heterocycles. In addition we have assumed that the aromaticity of the heterocyclic rings would be retained in the derivatives, i.e., that coordination of the "imino" nitrogen (N(3) in imidazole) would be preferred over coordination of the "amino" nitrogen.[16]

The reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with imidazole leads to two isomeric derivatives. Both isomers show evidence for the presence of N–H, i.e., a low-field, broad proton resonance. The minor isomer does not have the resonance expected for C(2)–H, which implies that it has structure **1a**. In contrast the major isomer has a signal for C(2)–H but not for C(4)–H, which suggests structure **1b**. The reaction of *N*-methylimidazole also produces two isomers. Again the spectrum of the minor isomer lacks the C(2)–H signal, and it is assigned structure **2a**. By analogy the major isomer must be **2b**.

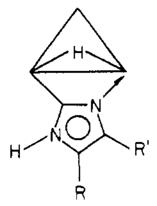


1a, R = H
2a, R = CH_3

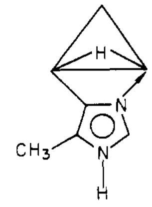


1b, R = H; R' = H
2b, R = CH_3; R' = H
3, R = H; R' = CH_3

Treatment of $Os_3(CO)_{10}(NCCH_3)_2$ with 2-methylimidazole gives only a single derivative, since coordination of C(2) is blocked. The ^{1}H NMR spectrum of this compound is consistent with structure **3**. In contrast, reaction at C(2) is possible with 4(5)-methylimidazole, but this produces two isomers, depending on whether the methyl group ends up at C(4) or C(5). A total of three isomers is expected, allowing for reaction also at C(5), and in fact three products are observed. Two of these products were not separated by chromatography or crystallization. Their NMR spectra indicate structures **4a**



4a, R = CH_3; R' = H
b, R = H; R' = CH_3



4c

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(16) Doonan, D. J.; Balch, A. L. *J. Am. Chem. Soc.* **1975**, *97*, 1403.

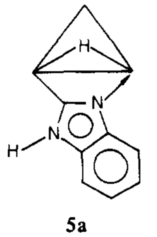
Table V. ^1H NMR Data for Triosmium Derivatives

compd	signals[a,b]	assignt
1a	8.75 (br, 1 H_a)	N-H
	6.80 (t, 1 H_b, J_{ab} = 1.7 Hz)	C(4)-H
	6.67 (t, 1 H_c, J_{ac}, J_{bc} = 1.7 Hz)	C(5)-H
	−15.17 (s, 1 H)	Os-H
1b	9.10 (br, 1 H_a)	N-H
	7.60 (s, 1 H)	C(2)-H
	6.44 (d, 1 H_b, J_{ab} = 2.0 Hz)	C(5)-H
	−15.23 (s, 1 H)	Os-H
2a	6.72 (d, 1 H_a)	C(4)-H
	6.49 (d, 1 H_b, J_{ab} = 1.4 Hz)	C(5)-H
	3.46 (s, 3 H)	$N-CH_3$
	−15.13 (s, 1 H)	Os-H
2b	7.38 (s, 1 H)	C(2)-H
	6.25 (s, 1 H)	C(5)-H
	3.62 (s, 3 H)	$N-CH_3$
	−15.35 (s, 1 H)	Os-H
3	8.45 (br, 1 H_a)	N-H
	6.38 (d, 1 H_b, J_{ab} = 2.4 Hz)	C(5)-H
	2.34 (s, 3 H)	$C(2)-CH_3$
	−15.26 (s, 1 H)	Os-H
4a, 4b	8.4 (br, 1 H)	N-H
	6.44 (s, 1 H)	C-H
	2.22 (s, 3 H)	$C-CH_3$
	−15.17 (s, 1 H)	Os-H
	8.5 (br, 1 H)	N-H
	6.33 (s, 1 H)	C-H
	1.95 (s, 3 H)	$C-CH_3$
	−15.10 (s, 1 H)	Os-H
4c	8.55 (br, 1 H)	N-H
	7.54 (s, 1 H)	C(2)-H
	2.22 (s, 3 H)	$C(5)-CH_3$
	−15.25 (s, 1 H)	Os-H
5a	9.30 (br, 1 H)	N-H
	7.35–6.95 (m, 4 H)	C-H
	−15.03 (s, 1 H)	Os-H
5b	9.45 (br, 1 H)	N-H
	8.14 (s, 1 H)	C(2)-H
	7.72 (dd, 1 H_a)	
	7.07 (d, 1 H_b, J_{ab} = 6.6 Hz)	C-H
	6.99 (d, 1 H_c, J_{ac} = 2.0 Hz)	
	−13.74 (s, 1 H)	Os-H
6a	7.16 (d, 2 H_a)	C(3)-H, C(5)-H
	5.91 (d, 1 H_b, J_{ab} = 3.3 Hz)	C(4)-H
	−13.47 (s, 1 H)	Os-H
6b	8.90 (br, 1 H)	N-H
	7.15 (d, 1 H_a)	C(2)-H
	6.22 (d, 1 H_b, J_{ab} = 3.0 Hz)	C(3)-H
	−15.05 (s, 1 H)	Os-H

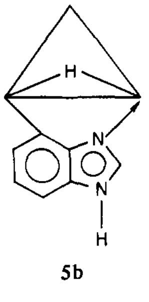
[a] Chemical shifts (δ) downfield from internal $SiMe_4$.
[b] Solutions in $CDCl_3$, except compounds **1b**, **5a**, and **5b** are in CD_2Cl_2.

and **4b** but do not allow individual assignments. Presumably, isomer **4a** is the more abundant for steric reasons. The third, chromatographically separable product shows evidence for a proton at C(2), consistent with structure **4c**.

Only one product was expected with benzimidazole, that derived from addition of the C(2)–H bond. This compound (**5a**) in fact is observed, but a second product is formed in greater amounts. The NMR spectrum of this compound shows a resonance for a proton at C(2) but displays evidence for only three benzo ring protons; structure **5b** is indicated.



5a

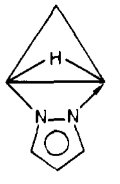


5b

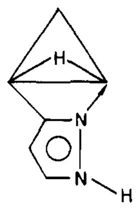
Table VI. Intramolecular Distances (Å) with Esd's

atoms	dist	atoms	dist
(A) Osmium–Osmium Distances			
Os(1)–Os(2)	2.952 (1)	Os(1)–Os(3)	2.881 (1)
Os(2)–Os(3)	2.883 (1)		
(B) Osmium-Bridging Imidazole Ligand Distances			
Os(1)–C/N(1)	2.134 (20)	Os(2)–C/N(2)	2.136 (22)
(C) Osmium–Carbonyl Distances			
Os(1)–C(11)	1.903 (23)	Os(2)–C(23)	1.871 (24)
Os(1)–C(12)	1.783 (28)	Os(3)–C(31)	1.876 (27)
Os(1)–C(13)	1.835 (28)	Os(3)–C(32)	1.897 (28)
Os(2)–C(21)	1.882 (27)	Os(3)–C(33)	1.886 (25)
Os(2)–C(22)	1.917 (27)	Os(3)–C(34)	1.930 (26)
(D) Carbon–Oxygen Distances			
C(11)–O(11)	1.125 (27)	C(23)–O(23)	1.132 (29)
C(12)–O(12)	1.266 (34)	C(31)–O(31)	1.160 (32)
C(13)–O(13)	1.193 (29)	C(32)–O(32)	1.173 (32)
C(21)–O(21)	1.145 (32)	C(33)–O(33)	1.183 (29)
C(22)–O(22)	1.116 (32)	C(34)–O(34)	1.135 (30)
(E) Distances within the Imidazolyl Ring			
C/N(1)–C(2)	1.327 (32)	C/N(2)–C(3)	1.324 (36)
C(2)–N(2)	1.359 (31)	C/N(1)–C/N(2)	1.345 (25)
N(2)–C(3)	1.386 (32)		

Treatment of $Os_3(CO)_{10}(NCCH_3)_2$ with pyrazole provided a test of whether the N–H bond, now adjacent to the more basic imino nitrogen center, could undergo addition to the Os_3 triangle. Two products are obtained from the reaction. The NMR spectrum of the major one is consistent with the symmetrical structure **6a**, which indeed is derived from N–H bond addition. The minor product, for which the NMR data indicate retention of the N–H bond, is assigned structure **6b**. The behavior of these compounds during chromatography also is consistent with their proposed structures. Compound **6a** moves readily with petroleum ether, whereas **6b** is mobile only when the eluting solvent contains a more polar solvent such as dichloromethane. The weakly acidic N–H group apparently interacts with the silica gel surface, since the same effect is observed in comparing analogous N–H and $N-CH_3$ imidazole derivatives (**1a**,**b** vs. **2a**,**b**).



6a



6b

In early experiments concerning the reaction between $Os_3(CO)_{10}(NCCH_3)_2$ and imidazole, it was observed that longer reaction times increased the relative yield of **1a** with respect to **1b** but decreased the total yield of isolated products. Heating solutions of pure **1b** or **2b** at the synthesis temperature (ca. 80 °C), either in the presence or in the absence of excess base, produced only the starting material and cluster decomposition. Decomposition was suppressed under ca. 2 atm of carbon monoxide, and there was no evidence for the formation of $Os_3(CO)_{12}$. These results imply that product formation is kinetically determined and essentially irreversible. The formation of the 2-pyridyl derivative $HOs_3(CO)_{10}(\mu-NC_5H_4)$ was found to be irreversible also.[9]

The modest regioselectivity displayed in the addition of imidazole and its derivatives to the Os_3 triangle invites attention. In each case where a choice is possible, a proton other

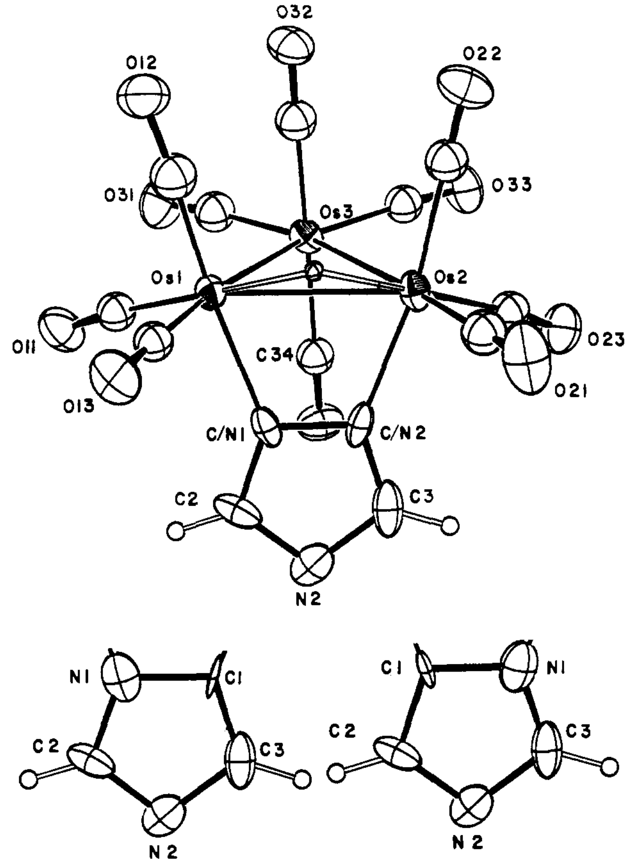


Figure 1. Labeling of atoms in the (μ-H)$Os_3(CO)_{10}$(μ-3,4-η^2-$N_2C_3H_3$) molecule. The molecule is projected onto the imidazolyl plane. The entire molecule (disordered model) is shown at the top. The two partial images show the results of refining the two possible *ordered* models. (Note the unrealistic thermal ellipsoids on the bridging carbon atoms.)

than the one at C(2) is added preferentially. Since C(2)–H should be the most acidic C–H bond, acidity does not appear to be the controlling property. Rather these results suggest that the C(2)–H bond may be slightly stronger than the other accessible C–H bonds.

Crystal and Molecular Structure of (μ-H)$Os_3(CO)_{10}$(μ-3,4-η^2-$N_2C_3H_3$) (1b)

The crystal is composed of discrete monomeric molecular units which are mutually separated by normal van der Waals distances. Figure 1 shows the molecular geometry and the system used for labeling atoms. Figure 2 provides a stereoscopic view of the molecule. Interatomic distances and angles are presented in Tables VI and VII, while the three important intramolecular planes are defined in Table VIII.

Table VII. Intramolecular Angles (Deg) with Esd's

(A) Osmium–Osmium–Osmium Angles			
Os(3)–Os(1)–Os(2)	59.23 (3)	Os(2)–Os(3)–Os(1)	61.61 (3)
Os(1)–Os(2)–Os(3)	59.15 (3)		
(B) Angles Involving the Bridging Imidazolyl Ligand			
Os(1)–C/N(1)–C/N(2)	111.9 (14)	Os(2)–C/N(2)–C/N(1)	112.3 (14)
Os(1)–C/N(1)–C(2)	139.6 (16)	Os(2)–C/N(2)–C(3)	139.4 (17)
C/N(1)–Os(1)–Os(2)	68.0 (5)	C/N(2)–Os(2)–Os(1)	67.7 (5)
C/N(1)–Os(1)–Os(3)	87.1 (5)	C/N(2)–Os(2)–Os(3)	87.8 (5)
C/N(1)–Os(1)–C(11)	87.9 (8)	C/N(2)–Os(2)–C(21)	89.8 (9)
C/N(1)–Os(1)–C(12)	174.6 (10)	C/N(2)–Os(2)–C(22)	171.3 (9)
C/N(1)–Os(1)–C(13)	93.1 (9)	C/N(2)–Os(2)–C(23)	93.7 (9)
(C) Osmium–Osmium–Carbon (Carbonyl) Angles			
Os(2)–Os(1)–C(11)	114.8 (7)	Os(3)–Os(2)–C(22)	86.8 (7)
Os(2)–Os(1)–C(12)	106.8 (9)	Os(3)–Os(2)–C(23)	89.2 (7)
Os(2)–Os(1)–C(13)	139.9 (7)	Os(1)–Os(3)–C(31)	101.1 (8)
Os(3)–Os(1)–C(11)	173.4 (7)	Os(1)–Os(3)–C(32)	85.7 (8)
Os(3)–Os(1)–C(12)	91.5 (9)	Os(1)–Os(3)–C(33)	154.8 (7)
Os(3)–Os(1)–C(13)	85.9 (7)	Os(1)–Os(3)–C(34)	89.5 (7)
Os(1)–Os(2)–C(21)	116.6 (8)	Os(2)–Os(3)–C(31)	162.7 (8)
Os(1)–Os(2)–C(22)	103.6 (7)	Os(2)–Os(3)–C(32)	90.8 (8)
Os(1)–Os(2)–C(23)	142.6 (7)	Os(2)–Os(3)–C(33)	93.6 (7)
Os(3)–Os(2)–C(21)	175.7 (8)	Os(2)–Os(3)–C(34)	85.3 (7)
(D) Carbon (Carbonyl)–Osmium–Carbon (Carbonyl) Angles			
C(11)–Os(1)–C(12)	93.0 (11)	C(31)–Os(3)–C(32)	87.9 (11)
C(11)–Os(1)–C(13)	98.7 (10)	C(31)–Os(3)–C(33)	103.7 (10)
C(12)–Os(1)–C(13)	92.0 (11)	C(31)–Os(3)–C(34)	94.8 (10)
C(21)–Os(2)–C(22)	95.2 (11)	C(32)–Os(3)–C(33)	90.5 (10)
C(21)–Os(2)–C(23)	94.5 (10)	C(32)–Os(3)–C(34)	174.9 (10)
C(22)–Os(2)–C(23)	93.0 (10)	C(33)–Os(3)–C(34)	93.0 (10)
(E) Osmium–Carbon–Oxygen Angles			
Os(1)–C(11)–O(11)	175.1 (20)	Os(2)–C(23)–O(23)	174.4 (21)
Os(1)–C(12)–O(12)	173.8 (22)	Os(3)–C(31)–O(31)	175.5 (22)
Os(1)–C(13)–O(13)	174.1 (20)	Os(3)–C(32)–O(32)	177.3 (21)
Os(2)–C(21)–O(21)	177.1 (22)	Os(3)–C(33)–O(33)	176.7 (20)
Os(2)–C(22)–O(22)	177.4 (22)	Os(3)–C(34)–O(34)	174.6 (20)
(F) Angles within the Imidazolyl Ligand			
C/N(2)–C/N(1)–C(2)	108.5 (19)	N(2)–C(3)–C/N(2)	108.6 (21)
C/N(1)–C(2)–N(2)	109.2 (20)	C(3)–C/N(2)–C/N(1)	108.3 (19)
C(2)–N(2)–C(3)	105.3 (19)		

The molecule is based upon a triangular arrangement of osmium atoms, one of which, [Os(3)], is associated with four terminal carbonyl ligands, while the other two osmium atoms [Os(1) and Os(2)] are each linked to three terminal carbonyl ligands and are mutually bridged both by a μ-hydride ligand and the μ-3,4-η^2-$N_2C_3H_3$ ligand. As mentioned in the Experimental Section, the bridging imidazolyl ligand is disordered such that images **7** and **8** overlap to form the composite image **9**.

The crystallographic evidence for this model is shown clearly in Figure 1. Due to this disorder we have been unable to locate directly any of the hydrogen atoms, and their locations (on the noncoordinated CNC system) must be derived from the spectroscopic results.

Within the triosmium system, the doubly bridged Os(1)–Os(2) bond length is 2.952 (1) Å—i.e., 0.070 Å longer than the average nonbridged distance of 2.882 [1] Å [Os(1)–Os(3)

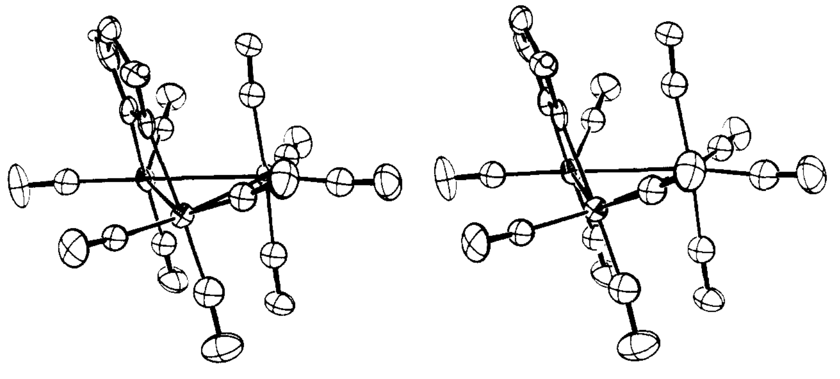
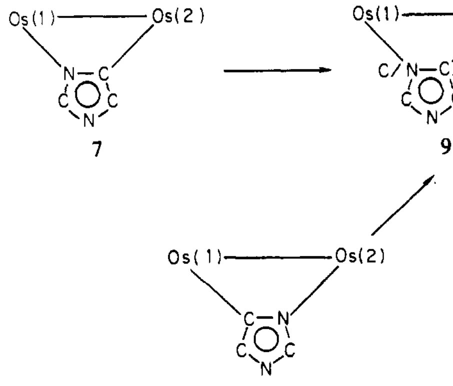


Figure 2. Stereoscopic view of the (μ-H)$Os_3(CO)_{10}$(μ-3,4-η^2-$N_2C_3H_3$) molecule.



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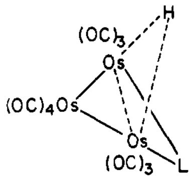
= 2.881 (1) Å and Os(2)–Os(3) = 2.883 (1) Å]. These values may be compared to the average bond length of 2.877 [3] Å found in the parent compound, $Os_3(CO)_{12}$.[17]

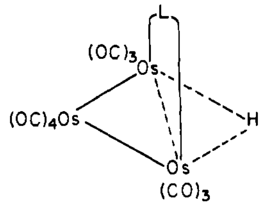
The present cluster has a formal electron count of 48 electrons (considering metals and ligands as neutral, we have three d^8 metal atoms, two electrons from each of the ten carbonyl ligands, three electrons from the bridging imidazolyl ligand, and one electron from the bridging hydride). This is consistent with the observed triangular cluster shape. The bridging hydride ligand was not located, but a conspicuously large cavity along the Os(1)–Os(2) vector, circumscribed by the four carbonyl groups C(12)–O(12), C(13)–O(13), C(21)–O(21), and C(22)–O(22), seems to suggest its probable location [in a diequatorial site trans to carbonyl groups C(11)–O(11) and C(23)–O(23)]. Unsupported bridging hydride ligands generally produce increases of the order of 0.1–0.15 Å on the associated metal–metal bonds.[17,18] However, this effect can be counterbalanced and completely nullified by supplementary bridging ligands.[19,20] In the present case, while the Os(1)–Os(2) bond length is the longest in the molecule, its extension is not as large as would be expected in the presence of a single unsupported bridging hydride ligand. Thus, the hydride lengthening effect is partially inhibited by the presence of the imidazolyl ligand, which also bridges the Os(1)–Os(2) vector.

We have previously carried out extensive crystallographic studies on $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$ molecules of type **10** (see ref 2c and discussion therein) in which the ligand L and hydride ligand each occupy "semiaxial" bridging positions. Here, the ligand L forms a one-atom bridge between the two osmium atoms.



10

Although the present molecule has a similar stoichiometry, it is of a different molecular architecture, with the ligand L spanning two strictly axial coordination sites and the hydride ligand occupying a diequatorial bridging site (see **11**). Here the ligand L participates in a two-atom bridge between the osmium atoms.



11

The triosmium plane is nearly perpendicular to the imidazolyl ring (see Table VI). The dihedral plane between the two is 100.88 (79.12)°. Deviation of atoms from selected planes is also shown in Table VIII. In summary, there are two equatorial carbonyls and one axial carbonyl (trans to the imidazole ligand) on each of the bridged osmium atoms and two equatorial and two axial ligands (trans to each other) on the unbridged osmium atom.

The μ-η^2 imidazolyl ring is composed of the two disordered atoms, C/N(1) and C/N(2), and three ordered atoms, C(2), N(2), and C(3). The C/N–Os bond lengths are identical with C/N(1)–Os(1) = 2.134 (20) Å and C/N(2)–Os(2) = 2.136 (22) Å. These bond lengths are similar to those found in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$,[21] [Os(1)–N = 2.111 (6) Å and Os(3)–C(17) = 2.090 (8) Å] and in $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}HC{=}NC_6H_5)Os_3(CO)_9(P(OCH_3)_3)$[22] [Os(1)–N = 2.150 (6) Å and Os(3)–C(17) = 2.075 (9) Å].

The distance between the two disordered atoms is 1.345 (25) Å, which is approximately 0.07 Å longer than the corresponding C–N distance of 1.278 (10) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$[21] and only 0.025 Å longer than the C–N distance of 1.320 (10) Å in $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}HC{=}NC_6H_5)Os_3(CO)_9(P(OCH_3)_3)$.[22]

Distances within the imidazolyl ring range from C/N(2)–C(3) = 1.324 (36) Å to N(2)–C(3) = 1.386 (32) Å. All other bond distances and angles are within their expected ranges.

Acknowledgment. This research was supported by the National Science Foundation (Grant Nos. CHE 81-00140 to J.R.S. and CHE 80-23448 to M.R.C.). J.R.S. acknowledges the Alfred P. Sloan Foundation for a research fellowship and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award.

Registry No. **1a**, 79840-13-4; **1b**, 79840-14-5; **2a**, 79840-15-6; **2b**, 79840-16-7; **3**, 79840-17-8; **4a**, 79840-18-9; **4b**, 79840-07-6; **4c**, 79840-08-7; **5a**, 79840-09-8; **5b**, 79840-10-1; **6a**, 79840-11-2; **6b**, 79840-12-3; $Os_3(CO)_{10}(NCCH_3)_2$, 61817-93-4.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Table III), and selected planes (Table VIII) (12 pages). For ordering information, see any current masthead page.

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