Journal of Organometallic Chemistry, 213 (1981) 259—270
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE PARTIAL HYDROGENATION OF SMALL UNSATURATED MOLECULES BY OSMIUM CLUSTER COMPOUNDS. THE REACTION OF DIISOPROPYLCARBODIIMIDE WITH $H_2Os_3(CO)_{10}$ *

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(Received December 10th, 1980)

Summary

The products $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_{10}$, I, and $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCO]Os_3(CO)_9[CNCH(CH_3)_2]$, II have been obtained from the reaction of $H_2Os_3(CO)_{10}$ with diisopropylcarbodiimine. Both products have been investigated by infrared and ^{1}H NMR spectroscopies, and by single crystal X-ray diffraction analyses. For I: Space group, $P2_1/c$, a = 12.840(4), b = 15.724(4), c = 12.638(4) Å, β = 106.91(2)°, V = 2441(2) Å^3, Z = 4, ρ_{calc} = 2.66 g/cc. For 2869 reflections, R = 0.051 and R_w = 0.052. I contains an N-hydrido, N-isopropylamidinyl ligand bridging one edge of a triangular cluster of three osmium atoms. It was apparently formed by the incorporation of one carbodiimide molecule into the coordination sphere of the cluster followed by the transfer of one hydride ligand to one of the nitrogen atoms. For II: Space group $P2_1/n$; a = 13.936(7), b = 12.146(2), c = 15.509(6) Å, β = 105.20(4)°, V = 2533(3) Å^3, Z = 4, ρ_{calc} = 2.57 g/cc. For 3065 reflections, R = 0.052 and R_w = 0.057. II contains an N-hydrido, N-isopropylformamido ligand bridging one edge of a triangular cluster of three osmium atoms and an isopropylisocyanide ligand. The molecule appears to have been formed by the cleavage of an $NCH(CH_3)_2$ moiety from one carbodiimide molecule and the transfer of it together with one hydride ligand to the carbon atom of a carbonyl group. The resultant formamido ligand bridges an edge of the cluster. The remaining fragment of the carbodiimide molecule bonds to one of the metal atoms of the cluster as a terminal isocyanide ligand. When heated, I loses one mole of carbon monoxide and forms the new cluster complex $(\mu\text{-H})[\mu_3\text{-}\eta^2\text{-}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_9$ III. On the basis of electron counting schemes, III is believed to contain a triply-bridging amidinyl ligand serving as a five electron donor. Most importantly, no II was formed from I indicating that it is not a precursor to II. A mechanism for the formation of I and II is presented and discussed.

* Dedicated to the memory of Paolo Chini.

Introduction

Much attention has been focused on transition metal cluster compounds as a new source of homogeneous catalysts [1]. A key step in the use of transition metal complexes as hydrogenation catalysts is the transfer of hydrogen atoms from the metal atoms to a substrate [2]. A variety of cluster compounds have now been implicated in hydrogenation catalyses [3]. With this in mind we have been studying the reactions of a variety of small heteronuclear unsaturated molecules with hydrido transition metal carbonyl cluster compounds. The cluster compound $H_2Os_3(CO)_{10}$ has an unusually high reactivity toward donor molecules and has been shown to catalyze the hydrogenation of terminal alkenes to alkanes [4]. We have recently reported on the nature of the reaction and the accompanying transfer of hydrogen atoms from the clusters $H_2Os_3(CO)_9L$, L = CO, $P(CH_3)_2C_6H_5$, to carbon disulfide, aryl isocyanates, and isocyanides although the processes were not catalytic [5—7]. Carbodiimides, a related class of molecules, are valuable reagents and have been used in a variety of exotic organic synthesis [8]. Here we wish to report some unusual results of our studies of the reaction of $H_2Os_3(CO)_{10}$ with *N,N*-diisopropylcarbodiimide.

Experimental

General

Although the reagents and products were generally air stable, reactions were routinely performed under a prepurified nitrogen atmosphere. Hexane was purified by distillation from sodium/benzophenone. Other solvents were stored over 4 Å molecular sieves and degassed with a dispersed stream of nitrogen before use. Diisopropylcarbodiimide was obtained commercially (Aldrich) and vacuum distilled before use. Osmium carbonyl was prepared from OsO_4 [9]. Alumina for chromatography was Baker acid-washed aluminum oxide deactivated with 6% water. $H_2Os_3(CO)_{10}$ was prepared by the method of Kaesz [10].

Melting points were determined in evacuated capillary tubes by using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer (Table 1). Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX270. Mass spectra were obtained at 20 eV on a Hewlett-Packard 5985 GC/MS by using direct inlet, electron impact mode.

Reaction of $H_2Os_3(CO)_{10}$ with diisopropylcarbodiimide

A mixture of $H_2Os_3(CO)_{10}$ (211 mg, 0.25 mmol) and $[(CH_3)_2CHN]_2C$ (0.25 ml, ca. 1.6 mmol) in 40 ml of hexane was refluxed for two hours and then reduced to a yellow oil in vacuo. This residue was transferred to an alumina column using hexane and a minimum of benzene. A first yellow band was eluted with hexane/benzene (2/3, v/v), and a second yellow band was eluted with benzene and benzene/ethyl ether (4/1). Both bands were reduced to dryness and crystallized from pentane at —20° C. The first band yielded 99.6 mg (41%) of $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_{10}$, I, as pure yellow crystals. The second band yielded 75.2 mg (32%) of $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCO]Os_3(CO)_9[CNCH(CH_3)_2]$, II, as a yellow solid.

TABLE 1

PHYSICAL AND SPECTROSCOPIC PROPERTIES

Compound	M.p. (°C)	^{1}H NMR (δ, ppm)	IR (ν(CO), cm^{-1})
$(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_{10}$, I	150.5—152.5	[a] 4.88d (^3J = 11 Hz N*H*), 3.96dsept (^3J = 11 Hz, $^3J'$ = 6 Hz, NHC*H*), 3.43sept (^3J = 6 Hz, NC*H*), 1.25d (^3J ≈ 6 Hz, NHCHC*H*$_3$), 1.15d (^3J = 6 Hz, NHCHC*H*'$_3$), 1.01d (^3J = 6 Hz, NCHC*H*$_3$), 0.83d (^3J = 7 Hz, NCHC*H*'$_3$), —14.84s (Os*H*)	[a, c] 3380w, [d] 2100m, 2055s, 2045s, 2015ms, 2000s, 1975ms
$(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCO]Os_3(CO)_9CNCH(CH_3)_2$, II	129—131	[b] Isomer A: 5.30d (^3J = 7 Hz, N*H*), 3.99dsept (^3J = 7 Hz, $^3J'$ = 6 Hz, NHC*H*), 3.41sept (^3J = 6 Hz, ≡NC*H*), 0.70d (^3J = 6 Hz, ≡NCH(C*H*$_3$)$_2$, 0.61d (^3J = 6 Hz, NHCHC*H*$_3$), 0.53d (^3J = 6 Hz, NHCHCH'$_3$), —13.32s (Os*H*) [b] Isomer B: 5.30d (^3J = 7 Hz, N*H*), 3.84dsept (^3J = 7 Hz, $^3J'$ = 6 Hz, NHC*H*), 3.30sept (^3J = 6 Hz, ≡NC*H*), 0.79d (^3J = 6 Hz, ≡NCH(C*H*$_3$)$_2$), 0.59d (^3J = 6 Hz, ≡NCH(C*H*$_3$)$_2$), —15.16s (OsH) [b, f] 5.30d (^3J = 7 Hz, NH), —14.18 (OsH)	Isomer A: [a, c] 3440w; [d, e] 2180m; [d] 2080vw; 2050s, 2040s, 2000vw; 1985s, 1980s, 1950vw; Isomer B: [a, c] 3340w; [d, e] 2170m; [d] 2080m, 2045vs, 2025s, 2010m, 2005m, 1995w, 1985m, 1975m, 1955vw
$(\mu\text{-H})[\mu_3\text{—}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_9$, III	229—230.5	[a, g] 6.11brd (^3J ≈ 6 Hz, NH), 4.39dsept (^3J ≈ 6 Hz, $^3J'$ = 6 Hz, NHC*H*), 2.68sept (^3J = 6 Hz, NCH), 1.38d (^3J = 6 Hz, NHCH(C*H*$_3$)$_2$), 1.16brd (^3J ≈ 6 Hz, NCH(C*H*$_3$)$_2$), —15.60s (OsH) [a, h] Isomer A: 6.18d (^3J = 10 Hz, NH), 4.26dsept (^3J = 10 Hz, $^3J'$ = 6 Hz, NHC*H*), 2.47sept (^3J = 7 Hz, NC*H*), 1.35d (^3J = 6 Hz, NCH(C*H*$_3$)$_2$), 1.34d (^3J ≈ 6 Hz, NHCH(C*H*$_3$)$_2$), —15.42s (OsH) [a, h] Isomer B: 6.22d (^3J = 10 Hz, NH), 4.40dsept (^3J = 10 Hz, $^3J'$ ≈ 6 Hz, NHC*H*), 2.84sept (^3J = 6 Hz, NCH), 1.34d (^3J ≈ 6 Hz, NHCH(C*H*$_3$)$_2$), 0.83d (^3J = 6 Hz, NCH(C*H*$_3$)$_2$), —15.90s (OsH)	[a, c] 3390mw, 3360w; [d] 2080m, 2060s, 2025s, 2000s, 1985ms, 1960vw, 1940w

[a] $CDCl_3$. [b] $C_6D_5CD_3$. [c] ν(NH). [d] Hexane. [e] ν(RN≡C). [f] These resonances may be due to still a third isomer. [g] 61°C. [h] —69°C. I: Mass spectrum, 20 eV ($^{12}C_{17}{}^1H_{16}{}^{14}N_2{}^{16}O_{10}{}^{190}Os_3$) molecular ion = 978 *m/e* loss of 7 (CO)'s: 950, 922, 894, 866, 838, 810, 782, parent ion = 864. II: Mass spectrum, 20 eV: ($^{12}C_{16}{}^1H_{16}{}^{14}N_2{}^{16}O_9{}^{190}Os_3$) molecular ion = 950 loss of 6 (CO)'s: 922, 894, 866, 838, 810, 782, parent ion = 864, loss of hydrogen also seems to be occurring based on shifts of isotope clusters to lower *m/e* with CO loss.

Thermolysis of (μ-H)[μ-η^2-$(CH_3)_2CHNHCNCH(CH_3)_2$]$Os_3(CO)_{10}$, I

A solution of I (79.6 mg, 0.081 mmol) in 30 ml of heptane was heated to reflux for eight hours. The resulting cloudy yellow solution was cooled and transferred directly to an alumina column. Elution with hexane/benzene (4/1 v/v) gave a small amount of starting material. A second yellow band was eluted with hexane/benzene (1/1), reduced to dryness and crystallized from CH_2Cl_2/hexane at −20°C. Pale yellow crystals of (μ-H)[μ_3-$(CH_3)_2CHNHCNCH(CH_3)_2$]-$Os_3(CO)_9$, III, (46.1 mg, 60%) were obtained. Analysis: C, 21.60; H, 1.26; N, 3.10 $C_{17}H_{16}N_2O_{10}Os_3$ calcd.: C, 20.2; H, 1.70; N, 2.95% m.p. 230°C.

Attempted reactions of I with triethylamine and diisopropylcarbodiimide

A solution of I (47.6 mg, 0.049 mmol) and triethylamine (0.2 ml, ca. 1.4 mmol) in 25 ml of hexane were heated to reflux for 8 h. No reaction occurred as evidenced by infrared spectra of the solution. The volatiles were removed in vacuo and replaced with diisopropylcarbodiimide (0.2 ml, ca. 1.3 mmol) and 25 ml of hexane. Infrared spectra of this solution showed no reaction occurred after 20 hours at reflux.

Crystallographic analysis

Crystals of I suitable for diffraction analyses were obtained by slow crystallization from a pentane solution at −20° C. Crystals of II were obtained from an ethanol solution cooled to −20° C. All crystals were mounted in thin-walled glass capillaries. All diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo-K_α-radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index and least-squares routines. The space groups were determined from the systematic absences observed during data collection. Crystal data and data collections parameters are listed in Table 2. All data processing was performed on a Digital PDP 11/45 computer by using the Enraf-Nonius SDP program library. Absorption corrections of a Gaussian integration type were done for both structures. Neutral atom scattering factors were calculated by the standard procedures [11a]. Anomalous dispersion corrections were applied to all nonhydrogen atoms [11b]. Both structures were solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were obtained either from difference Fourier syntheses or calculated on the basis of geometric considerations. Hydrogen atom contributions were included in structure factor calculations but their positions were not refined. Full-matrix least-squares refinements minimized the function $\Sigma w(|F_{obs} - F_{calc}|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F^2_{obs})/2\,F_{obs}$ and $\sigma(F^2_{obs}) = [\sigma(I_{raw})^2 + (PF^2_{obs})^2]^{1/2}/Lp$. All other atoms were refined with isotropic temperature factors only. Final fractional atomic coordinates and structure factor amplitudes are available for all structures (see supplementary material *). Interatomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables 3—6.

* Available from the authors on request.

TABLE 2

CRYSTALLOGRAPHIC DATA FOR X-RAY DIFFRACTION STUDIES

A) *Compound*	I	II
Formula	$Os_3O_{10}N_2C_{17}H_{16}$	$Os_3O_{10}N_2C_{17}H_{16}$
Temperature (±5°C)	27	27
Space group	$P2_1/c$ No. 14, $[C_{2h}^5]$	$P2_1/n$, $[C_{2h}^5]$
a (Å)	12.840(4)	13.937(7)
b (Å)	16.724(4)	12.146(2)
c (Å)	12.638(4)	15.509(6)
β (deg)	106.91(2)	105.20(4)
V (Å^3)	2441(2)	2533(3)
M. Et.	978.92	978.92
Z	4	4
ρ_{calc} (g/cc)	2.66	2.57
B) *Measurement of intensity data*		
Radiation		Mo-K_α (0.71073 Å)
Monochromator		Graphite
Detector aperture (mm)		
Horizontal (A + B tan θ):		
A	3.0	2.6
B	1.0	1.2
Vertical:	4.0	4.0
Crystal Faces:	$11\bar{1}$, $\bar{1}\bar{1}\bar{1}$, $\bar{2}21$ $2\bar{2}\bar{1}$, $2\bar{1}2$, $\bar{2}1\bar{2}$	$1\bar{1}\bar{1}$, $\bar{1}11$, $11\bar{1}$, $\bar{1}\bar{1}1$ $\bar{1}00$, 112, $1\bar{2}1$
Crystal size: (mm)	0.10 × 0.12 × 0.43	0.13 × 0.16 × 0.50
Crystal orientation:		
Direction from θ-axis; deg	normal to 101; 8.2	normal to 101; 4.7
Reflection measured	$+h$, $+k$, $\pm l$	$+h$, $+k$, $\pm l$
Max 2θ	50°	50°
Scan type	Moving crystal - stationary counter	
ω-Scan width (deg)	0.95	0.80
Background:	1/4 additional scan at each end of scan	
ω-Scan rate		
Max, °/min	10.0	10.0
Min, °/min	1.4	1.2
No reflections measured	4607	5939
Data used ($F^2 > 3.0\sigma(F)^2$)	2869	3065
C) *Treatment of data*		
Absorption		
Coefficient μ (cm^{-1})	166.2	160.1
Grid	10 × 6 × 14	12 × 6 × 12
Transmission coeff.		
max	0.25	0.18
Min.	0.03	0.09
P-factor	0.01	0.002
Final residuals R	0.051	0.052
R_w	0.050	0.057
E.s.d. of unit weight	3.92	3.73
Largest shift/error value on final cycle	0.07	0.44
Largest peaks in final diff. Fourier (e^-/Å^3)	2.6—3.4	0.6—0.7

TABLE 3

INTERATOMIC DISTANCES WITH e.s.d.'s FOR (μ-H)[μ-η^2-(CH_3)CHNHCNCH(CH_3)$_2$]$Os_3(CO)_{10}$, I

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)—Os(2)	2.904(1)	N(1)—C(12)	1.44(1)
Os(1)—Os(3)	2.891(1)	C(12)—C(13)	1.55(1)
Os(2)—Os(3)	2.887(1)	C(12)—C(14)	1.56(1)
Os(1)—C(1)	1.84(1)	N(2)—C(22)	1.42(1)
Os(1)—C(2)	1.90(1)	C(22)—C(23)	1.56(1)
Os(1)—C(3)	1.92(1)	C(22)—C(24)	1.50(2)
Os(1)—C(11)	2.130(9)	C(1)—O(1)	1.19(1)
Os(2)—C(4)	1.87(1)	C(2)—O(2)	1.14(1)
Os(2)—C(5)	1.90(1)	C(3)—O(3)	1.16(1)
Os(2)—C(6)	1.87(1)	C(4)—O(4)	1.19(1)
Os(2)—N(1)	2.164(6)	C(5)—O(5)	1.15(1)
Os(3)—C(7)	1.98(1)	C(6)—O(6)	1.16(1)
Os(3)—C(8)	1.91(1)	C(7)—O(7)	1.13(1)
Os(3)—C(9)	1.87(1)	C(8)—O(8)	1.17(1)
Os(3)—C(10)	1.79(1)	C(9)—O(9)	1.19(1)
C(11)—N(1)	1.33(1)	C(10)—O(10)	1.22(1)
C(11)—N(2)	1.38(1)		

TABLE 4

INTERACTOMIC ANGLES WITH e.s.d.'s FOR (μ-H)[μ-η^2-(CH_3)$_2$CHNHCNCH(CH_3)$_2$]$Os_3(CO)_{10}$, I

Atoms	Angle (deg)	Atoms	Angle (deg)
Os(1)—Os(2)—Os(3)	59.89(1)	Os(1)—Os(3)—C(10)	99.1(4)
Os(2)—Os(1)—Os(3)	59.76(1)	Os(2)—Os(3)—C(7)	88.3(3)
Os(1)—Os(2)—Os(3)	60.35(1)	Os(2)—Os(3)—C(8)	100.1(3)
Os(2)—Os(1)—C(1)	141.8(3)	Os(2)—Os(3)—C(9)	88.3(4)
Os(2)—Os(1)—C(2)	104.2(4)	Os(2)—Os(3)—C(10)	159.0(4)
Os(2)—Os(1)—C(3)	116.1(3)	C(7)—Os(3)—C(8)	91.3(4)
Os(2)—Os(1)—C(11)	67.3(2)	C(7)—Os(3)—C(9)	174.1(5)
Os(3)—Os(1)—C(1)	85.1(3)	C(7)—Os(3)—C(10)	94.9(4)
Os(3)—Os(2)—C(2)	92.9(4)	C(8)—Os(3)—C(9)	94.0(5)
Os(3)—Os(1)—C(3)	175.5(3)	C(8)—Os(3)—C(10)	100.6(5)
Os(3)—Os(1)—C(11)	88.5(2)	C(9)—Os(3)—C(10)	86.6(5)
C(1)—Os(1)—C(2)	91.1(5)	Os(1)—C(1)—O(1)	177(1)
C(1)—Os(1)—C(3)	98.3(4)	Os(1)—C(2)—O(2)	179(1)
C(1)—Os(1)—C(11)	99.7(4)	Os(1)—C(3)—O(3)	176(1)
C(2)—Os(1)—C(3)	90.0(5)	Os(2)—C(4)—O(4)	176(1)
C(2)—Os(1)—C(11)	169.2(4)	Os(2)—C(5)—O(5)	174(1)
C(3)—Os(1)—C(11)	88.0(4)	Os(2)—C(6)—O(6)	170(1)
Os(1)—Os(2)—C(4)	143.4(3)	Os(3)—C(7)—O(7)	175(1)
Os(1)—Os(2)—C(5)	105.2(3)	Os(3)—C(8)—O(8)	177(1)
Os(1)—Os(2)—C(6)	115.5(4)	Os(3)—C(9)—O(9)	177(1)
Os(1)—Os(2)—N(1)	69.6(2)	Os(3)—C(10)—O(10)	172(1)
Os(3)—Os(2)—C(4)	86.3(3)	Os(1)—C(11)—N(1)	115.3(6)
Os(3)—Os(2)—C(5)	92.0(3)	Os(1)—C(11)—N(2)	127.0(6)
Os(3)—Os(2)—C(6)	175.4(4)	N(1)—C(11)—N(2)	117.6(8)
Os(3)—Os(2)—N(1)	88.2(2)	N(1)—C(12)—C913)	114.4(8)
C(4)—Os(2)—C(5)	88.6(4)	N(1)—C(12)—C(14)	114.9(8)
C(4)—Os(2)—C(6)	98.2(5)	C(13)—C(12)—C(14)	107.5(8)
C(4)—Os(2)—C(1)	97.7(4)	N(2)—C(22)—C(23)	108.5(8)
C(5)—Os(2)—C(6)	89.0(5)	N(2)—C(22)—C(24)	110.4(9)
C(5)—Os(2)—N(1)	173.7(4)	C(23)—C(22)—C(24)	111.4(9)
C(6)—Os(2)—N(1)	90.2(4)	Os(2)—N(1)—C(11)	107.6(5)
Os(1)—Os(3)—C(7)	86.0(3)	Os(2)—N(1)—C(12)	129.4(6)
Os(1)—Os(3)—C(8)	160.3(3)	C(11)—N(1)—C(12)	121.5(7)
Os(1)—Os(3)—C(9)	88.2(4)	C(11)—N(2)—C(22)	128.1(8)

TABLE 5

INTERATOMIC DISTANCES WITH e.s.d.'s FOR $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCO]Os_3(CO)_9[CNCH(CH_3)_2]$, II

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)—Os(2)	2.915(1)	N(2)—C(12)	1.51(1)
Os(1)—Os(3)	2.894(1)	C(12)—C(13)	1.42(2)
Os(2)—Os(3)	2.859(1)	C(12)—C(14)	1.53(2)
Os(1)—C(1)	1.92(1)	C(1)—O(1)	1.16(1)
Os(1)—C(2)	1.81(1)	C(2)—O(2)	1.19(1)
Os(1)—C(3)	1.86(1)	C(3)—O(3)	1.16(1)
Os(1)—C(11)	2.068(9)	C(5)—O(5)	1.19(1)
Os(2)—C(4)	2.01(1)	C(6)—O(6)	1.19(1)
Os(2)—C(5)	1.87(1)	C(7)—O(7)	1.16(1)
Os(2)—C(6)	1.85(1)	C(8)—O(8)	1.19(1)
Os(2)—O(11)	2.172(6)	C(9)—O(9)	1.16(1)
Os(3)—C(7)	1.95(1)	C(10)—O(10)	1.16(1)
Os(3)—C(8)	1.84(1)	C(4)—N(1)	1.17(2)
Os(3)—C(9)	1.93(1)	N(1)—C(15)	1.77(3)
Os(3)—C(10)	1.91(1)	C(15)—C(16)	1.32(4)
C(11)—O(11)	1.31(1)	C(15)—C(17)	1.58(4)
C(11)—N(2)	1.36(1)		

TABLE 6

INTERATOMIC ANGLES WITH e.s.d.'s FOR $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCO]Os_3(CO)_9[CNCH(CH_3)_2]$, II

Atoms	Angle (deg)	Atoms	Angle (deg)
Os(2)—Os(1)—Os(3)	58.96(2)	Os(1)—Os(3)—C(9)	86.1(3)
Os(1)—Os(2)—Os(3)	60.15(2)	Os(1)—Os(3)—C(10)	93.3(3)
Os(1)—Os(3)—Os(2)	60.88(2)	Os(2)—Os(3)—C(7)	84.0(4)
Os(2)—Os(1)—C(1)	106.6(4)	Os(2)—Os(3)—C(8)	98.0(4)
Os(2)—Os(1)—C(2)	116.7(4)	Os(2)—Os(3)—C(9)	89.3(4)
Os(2)—Os(1)—C(3)	139.8(4)	Os(2)—Os(3)—C(10)	160.1(3)
Os(2)—Os(1)—C(11)	66.4(3)	C(7)—Os(3)—C(8)	92.7(5)
Os(3)—Os(1)—C(1)	89.9(4)	C(7)—Os(3)—C(9)	171.6(5)
Os(3)—Os(1)—C(2)	174.8(4)	C(7)—Os(3)—C(10)	93.9(5)
Os(3)—Os(1)—C(3)	86.0(4)	C(8)—Os(3)—C(9)	91.7(4)
Os(3)—Os(1)—C(11)	87.6(3)	C(8)—Os(3)—C(10)	101.8(5)
C(1)—Os(1)—C(2)	94.3(5)	C(9)—Os(3)—C(10)	92.3(5)
C(1)—Os(1)—C(3)	91.0(5)	Os(1)—C(11)—O(11)	119.1(7)
C(1)—Os(1)—C(11)	172.8(4)	Os(1)—C(11)—N(2)	129.7(7)
C(2)—Os(1)—C(3)	97.0(5)	O(11)—C(11)—N(2)	111.2(8)
C(2)—Os(1)—C(11)	87.9(5)	C(11)—N(2)—C(12)	124.5(9)
C(3)—Os(1)—C(11)	95.5(4)	B(2)—C(12)—C(13)	113(1)
Os(1)—Os(2)—C(4)	108.7(4)	N(2)—C(12)—C(14)	105(1)
Os(1)—Os(2)—C(5)	108.1(4)	C(13)—C(12)—C(14)	111(1)
Os(1)—Os(2)—C(6)	145.4(4)	Os(1)—C(1)—O(1)	172(1)
Os(1)—Os(2)—O(11)	68.7(2)	Os(1)—C(2)—O(2)	177(1)
Os(3)—Os(2)—C(4)	167.8(4)	Os(1)—C(3)—O(3)	176(1)
Os(3)—Os(2)—C(5)	95.7(4)	Os(2)—C(4)—N(1)	173(1)
Os(3)—Os(2)—C(6)	91.0(4)	Os(2)—C(5)—O(5)	178(1)
Os(3)—Os(2)—O(11)	87.5(2)	Os(2)—C(6)—O(6)	176(1)
C(4)—Os(2)—C(5)	92.6(5)	Os(3)—C(7)—O(7)	175(1)
C(4)—Os(2)—C(6)	97.6(5)	Os(3)—C(8)—O(8)	179(1)
C(4)—Os(2)—O(11)	83.4(4)	Os(3)—C(9)—O(9)	177(1)
C(5)—Os(2)—C(6)	92.3(5)	Os(3)—C(10)—O(10)	175(1)
C(5)—Os(2)—O(11)	173.6(4)	C(4)—N(1)—C(15)	161(2)
C(6)—Os(2)—O(11)	93.2(4)	N(1)—C(15)—C(16)	83(2)
Os(1)—Os(3)—C(7)	87.3(4)	N(1)—C(15)—C(17)	84(2)
Os(1)—Os(3)—C(8)	158.8(4)	C(16)—C(15)—C(17)	101(3)

$(\mu$-H)[μ-η^2-$(CH_3)_2$CHNHCO]$Os_3(CO)_9$[CNCH$(CH_3)_2$], II. Not knowing its identity originally, atom O(11) was initially refined as a nitrogen atom. It developed the unusually low temperature factor of 1.96. Refinement as an oxygen atom subsequently produced the more reasonable value of 3.7(5). In addition, elemental analyses indicated the presence of only two nitrogen atoms per formula equivalent. Difficulties were encountered in the refinement of the isopropyl group of the isocyanide ligand. Large temperature factors and relatively poor structural quality suggested the presence of conformational disorder; however, several attempts to refine disorder models were unsuccessful. The reported values are considered the best which could be obtained, but we believe some of them (e.g. N(1)—C(15) = 1.77(3) Å) should not be taken too literally.

Results

Two products were isolated from the reaction of diisopropylcarbodiimide with $H_2Os_3(CO)_{10}$. They were characterized as $(\mu$-H)[μ-η^2-$(CH_3)_2$CHNHCNCH-$(CH_3)_2$]$Os_3(CO)_{10}$, I and $(\mu$-H)[μ-η^2-$(CH_3)_2$CHNHCO]$Os_3(CO)_9$[CNCH$(CH_3)_2$], II, on the basis of IR and ^{1}H NMR spectroscopies, and X-ray crystallographic analyses. At 98°C, I lost one mole of carbon monoxide and was converted into the compound $(\mu$-H)[μ_3-$(CH_3)_2$CHNHCNCH$(CH_3)_2$]$Os_3(CO)_9$, III.

Descriptions of the structures

$(\mu$-H)[μ-η^2-$(CH_3)_2$CHNHCNCH$(CH_3)_2$]$Os_3(CO)_{10}$, I. The molecular structure of I is shown in Fig. 1. The molecule contains a triangular cluster of three osmium atoms. The Os—Os bond distances which span the small range 2.887(1)—2.904(1) Å are only slightly longer than average Os—Os bond distance of 2.877(1) Å found in $Os_3(CO)_{12}$ [12]. There are ten linear carbonyl ligands distributed such that Os(1) and Os(2) have three each and Os(3) has four.

The most interesting ligand is an amidinyl ligand which bridges the Os(1)—Os(2) edge of the cluster in a diaxial coordination arrangement (i.e. two coordination sites which are essentially perpendicular to the plane of the three metal atoms). Atom C(11) is bonded solely to the metal atom Os(1), Os(1)—C(11) = 2.130(9) Å while atom N(1) is bonded solely to the metal atom Os(2), Os(2)—N(1) = 2.164(6) Å. The distances C(11)—N(1) = 1.33(1) Å and C(11)—N(2) = 1.38(1) Å indicate partial multiple bonding most likely in the form of electron delocalization across the N(1)—C(11)—N(2) unit. A hydrogen atom is believed to be bonded to atom N(2). Although it was not observed crystallographically, an absorption which was observed at 3380 cm^{-1} is characteristic of such an N—H stretching vibration. ^{1}H NMR spectra revealed the presence of a metal-hydride ligand. This ligand was not observed crystallographically, but a large cavity circumscribed by the four carbonyl ligands C(2)—O(2), C(3)—O(3), C(5)—O(5) and C(6)—O(6) seems to suggest that the hydride ligand occupies a bridging position across the Os(1)—Os(2) bond on the opposite side of the cluster from the amidinyl ligand.

The crystal consists of discrete molecules of I. The two shortest intermolecular contacts were between carbonyl oxygen atoms at 3.06(1) and 3.12(1) Å.

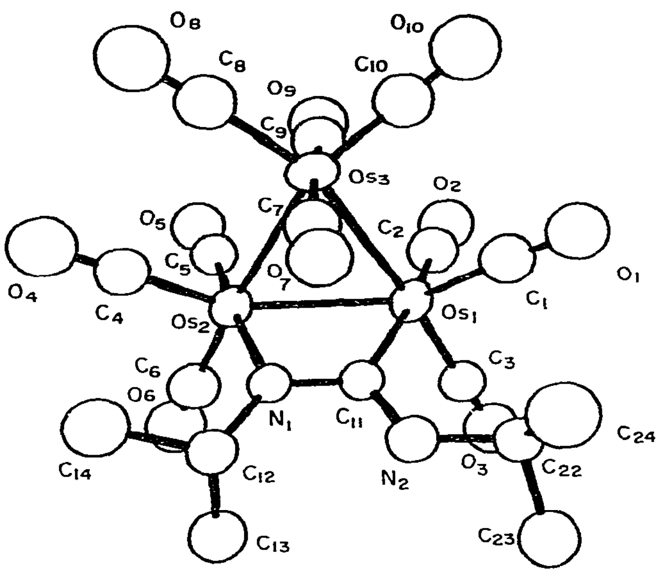


Fig. 1. An ORTEP diagram of $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_{10}$, I, showing 50% probability ellipsoids.

$(\mu$-H$)[\mu$-η^2-$(CH_3)_2CHNHCO]Os_3(CO)_9CNCH(CH_3)_2$, II. The molecular structure of II is shown in Fig. 2. The molecule contains a triangular cluster of three osmium atoms. The Os—Os bonding distaces are normal and range from 2.859 to 2.915 Å. The most interesting ligand is an *N*-hydrido-*N*-isopropylcarboxamido group which bridges the Os(1)—Os(2) edge of the cluster in a diaxial coordination position. The carbon atom C(11) is bonded solely to the metal atom Os(1), Os(1)—C(11) = 2.068(9) Å, while the oxygen atom O(11) is bonded solely to the metal atom Os(2), Os(2)—O(11) = 2.172(6) Å. These distances are very similar to those found for the carboxamido complex (μ-H)(μ-p-$CH_3C_6H_4NHCO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$, IV, Os—C = 2.121(7) Å and Os—O = 2.141(4) Å, which was formed from the reaction of p-tolylisocyanate with $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ [6b]. The C(11)—O(11) and C(11)—N(2) distances of 1.31(1) are 1.36(1) Å, respectively, are similar to the corresponding distances 1.254(9) and 1.345(8) Å found in IV [6b]. Although it was not observed crystallographically, an absorption at 3340 cm^{-1} in the infrared spectrum strongly indicates the presence of a hydrogen atom bonded to the nitrogen atom N(2). A hydride ligand (δ = —15.16 ppm in ^{1}H NMR spectral) was not observed crystallographically either, but a large cavity in the ligand structure, circumscribed by ligands C(1)—O(1), C(2)—O(2), C(6)—O(6) and the isocyanide, C(4)—N(1), strongly indicates that the hydride ligand bridges the Os(1)—Os(2) bond.

The cluster contains nine linear carbonyl ligands and one linear isopropylisocyanide ligand. The isocyanide ligand, supported also by its C—N stretching vibration observed at 2170 cm^{-1} in the infrared spectrum, is located in an equatorial coordination site on Os(2). As observed in other isocyanide osmium cluster compounds [13], the Os—C bond distance to the isocyanide ligand at 2.01(1) Å is slightly longer than the osmium—carbonyl bonding distances. The

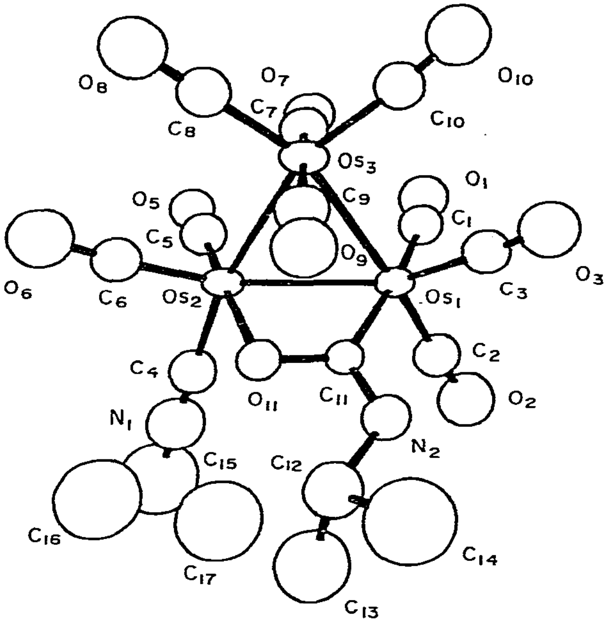


Fig. 2. An ORTEP diagram of $(\mu\text{-H})[\mu\text{-}\eta^2\text{-}(CH_3)_2CHNHCO]Os_3(CO)_9[CNCH(CH_3)_2]$, II showing 50% probability ellipsoids.

large temperature factors and poor structural quality of the isopropyl group seemed to suggest conformational disorder; however, numerous attempts to refine disorder models were unsuccessful.

The ^{1}H NMR spectrum of II showed that it exists as a mixture of two slowly interconverting isomers. IIA and IIB, in solution (cf. Table 1). However, a spectrum of freshly dissolved crystals showed that the isomer examined crystallographically was IIB. Interestingly, spectra of material crystallized from hexane solvent showed it consisted largely of isomer IIa.

When refluxed in heptane solvent, I lost one mole of carbon monoxide and formed the product $(\mu\text{-H})[\mu\text{-}(CH_3)_2CHNHCNCH(CH_3)_2]Os_3(CO)_9$, III, in 60% yield. The ^{1}H NMR spectrum of III showed that it exists in solution as two rapidly interconverting isomers at ambient temperature. However, at $-69°$C separate resonances were observed for each isomer. These resonances broadened and coalesced reversibly, as the temperature was raised to 61°C (cf. Table 1).

We believe III is similar to I except that it has one less carbonyl ligand and probably contains a μ_3-amidinyl ligand serving as a five-electron donor. This is also supported by the mass spectrum which shows the expected molecular ion. The relationship between I and III is probably similar to that between the molcules $(\mu\text{-H})(\mu\text{-HCHC}_6H_5)Os_3(CO)_{10}$ and $(\mu\text{-H})(\mu_3\text{-HCNC}_6H_5)Os_3(CO)_9$ [7].

Discussion

Mononuclear metal hydride complexes react with carbodiimides with transfer of a hydride ligand to the carbon atom of the carbodiimide and form complexes containing chelating formamidinato ligands [14].

In contrast we find that $H_2Os_3(CO)_{10}$ reacts with diisopropylcarbodiimide with a transfer of a hydrogen atom from the cluster to a nitrogen atom and forms the complex I containing an amidinyl ligand which bridges an edge of the cluster. In a similar process complexes containing bridging carboxamido ligands were formed by transfer of a hydrogen atom from the cluster to the nitrogen atom of the reagent when the clusters $H_2Os_3(CO)_9L$; L = CO, $P(CH_3)_2C_6H_5$ were reacted with arylisocyanates [6b].

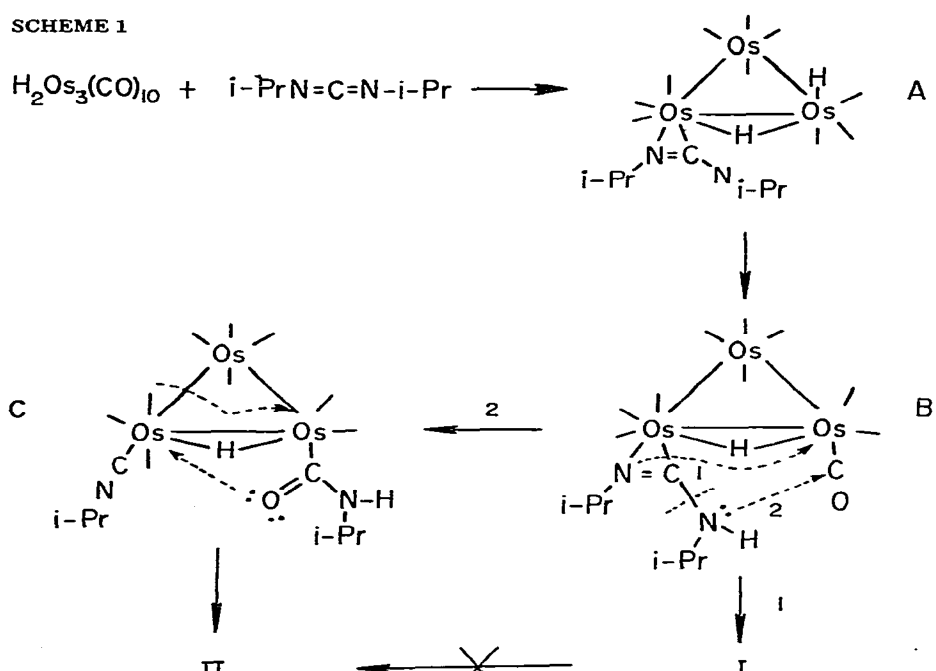
II on the other hand was a most unexpected product. Overall, the formation of II involves the cleavage of a $(CH_3)_2CHN$ moiety from the carbodiimide molecule, and the transfer of it together with a hydride ligand to the carbon atom of a carbonyl ligand. The resulting carboxamido ligand bridges an edge of the cluster. The remaining portion of the carbodiimide bonds to the cluster as an isocyanide ligand.

Although the metal induced cleavage of NR fragments from carbodiimide molecules has been observed previously [15], to the best of our knowledge this is the first example of a transfer to a carbonyl ligand.

We have shown that I is not an intermediate in the formation of II since I is thermolytically transformed into III and no II is formed. It is, thus, believed that I and II are formed by independent, competing reactions.

A tentative mechanism for the formation of I and II is shown in Scheme 1. It is believed that $H_2Os_3(CO)_{10}$ reacts initially with diisopropylcarbodiimide with formation of an intermediate adduct, A, containing a carbodiimide ligand. A variety of adducts of $H_2Os_3(CO)_{10}$ with donor molecules have been character-

SCHEME 1



ized [4b,16]. The coordination behavior of carbodiimides has been investigated previously [17]. Transfer of a hydride ligand from the cluster to the uncoordinated nitrogen atom of the carbodiimide ligand might produce an intermediate like B containing an amidinyl ligand. A shift of the coordinated nitrogen atom to one of the adjacent osmium atoms would produce I.

On the other hand attack of the amino portion of the amidinyl ligand upon a carbon atom of a carbonyl ligand followed by cleavage of the amidinyl C—N bond might produce an intermediate C containing a carboxamido ligand. It has been shown previously that primary and secondary amines do react with carbonyl ligands in $Os_3(CO)_{12}$ to form complexes containing bridging carboxamido ligands [18]. Attack of the carboxamido oxygen atom in C on the osmium atom which contains the isocyanide ligand could induce a shift of one carbonyl ligand, would form a bridging carboxamido ligand, and complete the formation of II.

Acknowledgements

This work was supported by the Division of Basic Energy Science, U.S. Department of Energy, under Contract No. DE-AC02-78ER04900, and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported in part under Grant No. CHE-7916210 from the Chemistry Division pf the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetroxide and Dr. B.F.G. Johnson, Cambridge, for converting it into $Os_3(CO)_{12}$ for us.

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