568 *Organometallics* 1984, *3*, 568–574

Dimethyl Azodicarboxylate Derivatives of Triosmium Carbonyl Clusters. Synthesis of $Os_3(CO)_n(CH_3OCONNCOOCH_3)$ (n = 10–12) and Characterization by Spectroscopy and X-ray Analysis

Frederick W. B. Einstein, Sophia Nussbaum, Derek Sutton,* and Anthony C. Willis

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received October 5, 1983

$Os_3(CO)_{11}(CH_3CN)$ (**1**) or $Os_3(CO)_{10}(CH_3CN)_2$ react with excess dimethyl azodicarboxylate (**2**) to yield the complex $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (**4**). In the case of **1**, a precursor, **3**, of formula $Os_3(CO)_{11}(CH_3OCONNCOOCH_3)$, has also been isolated. Complex **4** reacts quantitatively with CO at 1500 psi to give $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (**5**). The structures of **4** and **5** have been determined by single-crystal X-ray diffraction. Compound **5** is a triangular triosmium cluster with the $CH_3OCONNCOOCH_3$ group acting as a two-electron donor hydrazide ligand, bridging two (nonbonded) osmium atoms via the nitrogens. Compound **4** has a related structure, in which the ligand is now a six-electron donor, two terminal carbonyls having been replaced by coordination from the methoxycarbonyl groups of the ligand. Compound **3** is assigned an intermediate structure having only one coordinated methoxycarbonyl group. Diffraction data were collected with a Picker FACS-1 automated diffractometer using Mo Kα (graphite monochromated) radiation with $2\theta_{max} = 50°$. Compound **4** is triclinic, space group $P\bar{1}$, with a = 8.606 (1) Å, b = 9.412 (1) Å, c = 14.326 (3) Å, α = 104.50 (1)°, β = 97.90 (1)°, γ = 103.29 (1)°, V = 1069.6 Å^3, and Z = 2. The structure was refined to R_F = 0.030, R_{wF} = 0.038, for 3328 absorption-corrected reflections with $I > 2.3\sigma(I)$ and with all non-hydrogen atoms anisotropic. Selected bond lengths and angles are Os(1)–Os(2) 2.964 (1), Os(2)–Os(3) 2.970 (1), Os(1)···Os(3) 4.161 (1), Os(1)–N(5) 2.120 (6), N(4)–N(5) 1.439 (9), N(4)–C(3) 1.302 (10), C(3)–O(3) 1.281 (9), Os(1)–O(3) 2.144 (5), Os(3)–N(4) 2.128 (6), N(5)–C(6) 1.338 (10), C(6)–O(6) 1.253 (9), Os(3)–O(6) 2.144 (6) Å, and Os(1)–Os(2)–Os(3) 89.06 (2)°. Compound **5** is monoclinic, space group $P2_1/c$, with a = 12.136 (2) Å, b = 12.298 (2) Å, c = 16.027 (3) Å, β = 91.37 (1)°, V = 2391.3 Å^3, and Z = 4. The structure was refined to R_F = 0.021, R_{wF} = 0.025, for 3359 absorption-corrected reflections with $I > 2.3\sigma(I)$ and with all non-hydrogen atoms anisotropic. Selected bond lengths and angles are Os(1)–Os(2) 2.967 (1), Os(2)–Os(3) 3.008 (1), Os(1)···Os(3) 4.198 (1), Os(1)–N(5) 2.095 (5), N(4)–N(5) 1.411 (7), N(4)–C(3) 1.351 (8), C(3)–O(3) 1.220 (8), Os(3)–N(4) 2.092 (5), N(5)–C(6) 1.336 (8), C(6)–O(6) 1.226 (8) Å, and Os(1)–Os(2)–Os(3) 89.27 (2)°.

Introduction

Although numerous organic derivatives of triosmium carbonyl clusters have been synthesized, relatively little attention has been given to diazo compounds[1–4] or hydrazines.[5] In this paper we report the synthesis and structural characterization of a series of products obtained with dimethyl azodicarboxylate, of general formula $Os_3(CO)_n(CH_3OCONNCOOCH_3)$, where n = 10–12.

In the case of the complexes with n = 10 and 12, X-ray structure determinations have been carried out. The metrical details in both structures show that the diazo ligand has been incorporated as a hydrazide (i.e., the NN separation is that typical of a single bond) and that this ligand bridges the cluster across one edge of the Os_3 triangle. The Os–Os separation along this edge is increased to a non-bonded distance. The chemistry involved is therefore of some interest in exemplifying a degradation of the NN bond order in an organodiazo group by incorporation into a metal cluster. In addition, the compound with n = 12 is an example of a triosmium *dodecacarbonyl* derivative in which a triangular disposition of the metal atoms is preserved (no doubt because of the constraint imposed by the chelating organic group). This rarely observed configuration[6] contrasts with compounds such as $Os_3(CO)_{12}I_2$ or $Os_3(CO)_{12}(CH_3)_2$, which display linear Os_3 skeletons.[7] A preliminary account of this work has appeared.[8]

Experimental Section

General Data. All reactions and purifications were performed under a nitrogen atmosphere. Hexane, benzene, and acetonitrile were purified by distillation from calcium hydride. Dichloromethane was distilled from calcium sulfate and stored over 4A molecular sieve. Dimethyl azodicarboxylate (**2**) (Aldrich Chemical Co.) was distilled prior to use. $Os_3(CO)_{11}(CH_3CN)$ (**1**) and $Os_3(CO)_{10}(CH_3CN)_2$ were synthesized by a modification of the literature method,[9] using benzene instead of CH_2Cl_2 and adding Me_3NO as a solid instead of as a solution in methanol.

IR spectra were measured on a Perkin-Elmer Model 983 instrument. ^1H NMR spectra were measured at 400 MHz on a Bruker WM400 instrument and are reported in ppm referenced to Me_4Si. Mass spectra were obtained by Dr. A. M. Hogg at the University of Alberta using fast atom bombardment (xenon) of samples dispersed in thioglycerol on an AEI MS9 mass spec-

---

[1] Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 263.

[2] (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225; **1978**, *100*, 6544, 7726. (b) Keister, J. B.; Shapley, J. R. *Ibid.* **1976**, *98*, 1056.

[3] Churchill, M. R.; Wassermann, H. J. *Inorg. Chem.* **1981**, *20*, 1580.

[4] (a) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 2820. (b) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 712.

[5] Deeming, A. J.; Ghatak, I.; Owen, D. W.; Peters, R. *J. Chem. Soc., Chem. Commun.* **1982**, 392.

[6] Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4104.

[7] Kelland, J. W.; Norton, J. R. *J. Organomet. Chem.* **1978**, *149*, 185. Gochin, M.; Moss, J. R. *Ibid.* **1980**, *192*, 409. Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

[8] Einstein, F. W. B.; Nussbaum, S.; Sutton, D.; Willis, A. C. *Organometallics* **1983**, *2*, 1259.

[9] Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407.

[10] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

0276-7333/84/2303-0568$01.50/0

Table I. IR, ^{1}H NMR, and Mass Spectroscopic Data for Compounds 3-5

compound	ν(CO)[a]	ν(ligand)[b]	δ[c]	*m/e*
3, $Os_3(CO)_{11}(CH_3OCONNCOOCH_3)$	2134 mw, 2095 s 2060 sh, 2040 sh 2020 m, 2007 sbr	1658, 1530 1472	3.64 s 3.82 s	
4, $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$	2014 w, 2078 s, 2050 s 2005 vs, 1996 w, 1982 w	1518, 1484	3.86 s	1002[d]
5, $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$	2123 s, 2075 s, 2062 s 2026 m, 1995 mw	1633, 1443	3.64 s	1058[d]

[a] In hexane. [b] In C_2Cl_4. [c] In $CDCl_3$. [d] Based on ^{192}Os.

Table II. Crystal and Diffraction Data for Compounds 4 and 5

compound	4	5
formula	$Os_3(CO)_{10}(C_4H_6N_2O_4)$	$Os_3(CO)_{12}(C_4H_6N_2O_4)$
formula wt	996.80	1052.82
space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
a, Å	8.606 (1)	12.136 (2)
b, Å	9.412 (1)	12.298 (2)
c, Å	14.326 (3)	16.027 (3)
α, deg	104.50 (1)	90
β, deg	97.90 (1)	91.37 (1)
γ, deg	103.29 (1)	90
V, Å^3	1069.6	2391.3
Z	2	4
D_{calcd}, g cm^{-3}	3.095	2.924
μ, cm^{-1}	189.10	169.30
cryst dimens, mm	0.21 × 0.17 × 0.07	0.12 × 0.11 × 0.27
take-off angle, deg	5	5
scan type	θ-2θ	θ-2θ
scan rate, deg min^{-1}	2	2
scan width, deg[a]	1.4	1.2
background count[b]	0.25	0.10
line profile analysis[c]	no	yes
2θ max, deg	50	50
no. reflctns mead	3779	4235
no. reflctns obsd ($I > 2.3\sigma(I)$)	3328	3359
no. variables	299	335
final R_F	0.030	0.021
final R_{wF}	0.038	0.025
GOF[d]	1.299	1.024

[a] Also corrected for dispersion. [b] Stationary-crystal stationary-counter background count at each side of the scan, expressed as a fraction of total scan time. [c] Grant, D. F.; Gabe, E. J. *J. Appl. Crystallgr.* **1978**, *11*, 114. [d] GOF = $((\Sigma w(|F_o| - |F_c|)^2/(\text{no. of observations} - \text{no. of variables}))^{1/2}$.

trometer. The spectroscopic properties of **3**–**5** are listed in Table I.

Preparation of $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (4). (a) From $Os_3(CO)_{11}(CH_3CN)$. $Os_3(CO)_{11}(CH_3CN)$ (**1**; 25 mg, 0.027 mmol) was suspended in 10 mL of benzene at room temperature. $CH_3OCONNCOOCH_3$ (**2**; 10 μL, 0.07 mmol) was added and the mixture was stirred for 1 h. It was then heated to 70 °C for 20 min and concentrated to 2 mL. The mixture was chromatographed on a silica gel column (15 × 2 cm) under nitrogen pressure. The excess dimethyl azodicarboxylate was eluted with hexane and then **4** was eluted with 1:1 hexane–benzene and was recrystallized from hexane: yield 14 mg, 50%; yellow crystals, mp 104 °C dec. Anal. Calcd: C, 16.77; H, 0.59; N, 2.75. Found: C, 17.02; H, 0.57; N, 2.76%.

(b) From $Os_3(CO)_{10}(CH_3CN)_2$. $Os_3(CO)_{10}(CH_3CN)_2$ (100 mg, 0.11 mmol) was dissolved in 100 mL of benzene and $CH_3OCONNCOOCH_3$ (0.2 mL) was added. The mixture was stirred for 1 h at room temperature. Benzene was then evaporated and **4** was separated by column chromatography as above: yield 95 mg, 87%.

Preparation of $Os_3(CO)_{11}(CH_3OCONNCOOCH_3)$ (3). $Os_3(CO)_{11}(CH_3CN)$ (**1**; 100 mg, 0.11 mmol) was added to 20 mL of benzene followed by 0.1 mL (0.7 mmol) of **2**. The reaction was stirred at room temperature for 1 h. During that time the ν(CO) IR absorptions belonging to **1** disappeared and finally only those of **3** were present. The solution was then cooled to 15 °C and poured onto a cellulose column (15 × 2 cm). It was washed down with cold hexane under N_2 pressure, until the intense orange band due to **2** was removed, leaving a yellow band on the column. The solvent was then changed to hexane–benzene (1:1) and first a (ca. 30 mL) fraction was collected followed by the yellow band. Both fractions were immediately cooled to −78 °C to preserve them for later IR characterization. The first fraction contained small amounts of **1**, **2**, and **4**. The second fraction contained pure **3**. It was kept at −78 °C until required, and then the solvents were evaporated at ice temperature to give **3** as a yellow solid.

The isolated **3** was heated to 70 °C in benzene and completely transformed to **4** over 10 min (monitored by IR and NMR).

Preparation of $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (5). $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (**4**; 50 mg, 0.05 mmol) was dissolved in 10 mL of CH_2Cl_2 in a Parr bomb and pressurized with 1500 psi of CO for 24 h. The transformation to **5** was quantitative by IR. The solvent was evaporated and the product was recrystallized from pentane–dichloromethane as yellow crystals, mp 126 °C dec. Anal. Calcd: C, 18.16; H, 0.56; N, 2.65. Found: C, 18.31; H, 0.50; N, 2.38%.

Reaction of $Os_3(CO)_{11}(CH_3OCONNCOOCH_3)$ (3) with CO. A slow stream of CO was passed through freshly prepared **3** in CH_2Cl_2 at 0 °C. The reaction was monitored by IR. The transformation to **5** was complete after 30 h, and no other compound was detected by IR during the reaction. A sample of **3** kept at the same temperature under nitrogen converted to a mixture of **3**, **4**, and unidentified decomposition products after 30 h.

X-ray Data Collection. Crystals of **4** and **5** were obtained by crystallization from hexane and pentane–CH_2Cl_2, respectively. Well-formed, single crystals of suitable size were selected and sealed in thin-walled capillaries. X-ray photographs taken with Cu Kα radiation (λ = 1.5418 Å) revealed the Laue symmetry (and the systematic absences for **5**) and gave approximate unit cell dimensions.

The crystals were then transferred to a Picker FACS-I four-circle automated diffractomer where graphite-monochromatized

Table III. Atomic Coordinates for $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (4)

atom	x	y	z	B_{equiv},[a] Å^2	atom	x	y	z	B_{equiv},[a] Å^2
Os(1)	0.09953 (3)	0.24393 (3)	0.25432 (2)	2.816	C(32)	0.5742 (10)	0.8184 (10)	0.4448 (7)	3.8
Os(2)	0.23019 (4)	0.44860 (4)	0.13944 (2)	3.292	O(32)	0.6530 (9)	0.9193 (8)	0.5067 (5)	5.6
Os(3)	0.44318 (4)	0.66610 (3)	0.32493 (2)	2.973	C(33)	0.5894 (11)	0.7413 (10)	0.2491 (7)	4.3
C(11)	0.2046 (10)	0.1140 (10)	0.1818 (7)	3.7	O(33)	0.6749 (9)	0.7803 (10)	0.2027 (6)	7.2
O(11)	0.2723 (8)	0.0397 (7)	0.1380 (5)	5.2	C(1)	−0.0642 (11)	0.6723 (11)	0.4152 (7)	4.7
C(12)	0.0241 (10)	0.1083 (9)	0.3283 (6)	3.8	O(2)	0.1038 (6)	0.6675 (6)	0.4250 (4)	3.6
O(12)	−0.0250 (9)	0.0213 (8)	0.3670 (5)	5.7	C(3)	0.1326 (9)	0.5351 (9)	0.3859 (5)	3.1
C(13)	−0.0948 (10)	0.1565 (10)	0.1544 (6)	3.7	O(3)	0.0131 (6)	0.4158 (6)	0.3440 (4)	3.3
O(13)	−0.2123 (8)	0.1077 (9)	0.0966 (5)	5.4	N(4)	0.2858 (7)	0.5371 (7)	0.3946 (5)	3.0
C(21)	0.1159 (11)	0.2910 (11)	0.0212 (6)	4.2	N(5)	0.3002 (7)	0.3834 (7)	0.3686 (5)	2.8
O(21)	0.0558 (9)	0.1984 (9)	−0.0508 (5)	5.9	C(6)	0.4527 (9)	0.3850 (9)	0.3583 (6)	3.2
C(22)	0.0368 (11)	0.5115 (10)	0.1667 (6)	4.0	O(6)	0.5589 (6)	0.4992 (6)	0.3557 (4)	3.5
O(22)	−0.0780 (8)	0.5489 (9)	0.1778 (5)	6.0	O(7)	0.4836 (6)	0.2515 (7)	0.3525 (3)	4.2
C(23)	0.2981 (13)	0.6009 (13)	0.0767 (7)	5.2	C(8)	0.6440 (12)	0.2377 (12)	0.3390 (8)	5.5
O(23)	0.3328 (11)	0.6947 (10)	0.0387 (6)	8.1	H(1A)	−0.1220	0.6128	0.3505	5.8
C(24)	0.4292 (11)	0.3860 (11)	0.1443 (6)	4.3	H(1B)	−0.0704	0.7744	0.4242	5.8
O(24)	0.5441 (8)	0.3456 (9)	0.1448 (5)	6.3	H(1C)	−0.1146	0.6334	0.4621	5.8
C(31)	0.3149 (10)	0.7911 (9)	0.2976 (6)	3.5	H(8A)	0.6303	0.1328	0.3073	6.9
O(31)	0.2325 (9)	0.8651 (8)	0.2811 (5)	5.8	H(8B)	0.7212	0.2724	0.3996	6.9
					H(8C)	0.6849	0.2970	0.2979	6.9

[a] $B_{equiv} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ for anisotropic atoms.

Mo Kα radiation was used. Accurate cell dimensions were obtained by least-squares (λ(Mo Kα_1) = 0.7093 Å) from the setting angles of a number of reflections, widely separated in reciprocal space, which were accurately centered on the detector: 26 with $28° < 2\theta < 37°$ for 4 and 18 with $29° < 2\theta < 34°$ for 5. Crystal data and details of the data collections are given in Table II. The intensities of a unique data set were collected in each case. Two standards were measured after every 75 reflections to check stability. A gradual decrease in intensity was observed in each case (8% for 4, 2% for 5) so the data were scaled appropriately. Reflections where $I > 2.3\sigma(I)$ were regarded as observed and used in the structure solution and refinement. Analytic absorption corrections were applied to each data set (T = 0.242–0.073 for 4, 0.244–0.181 for 5).

Determination and Refinement of the Structures. In both structures, the coordinates of the Os atoms were determined from the three-dimensional Patterson map. Fourier maps phased by these atoms revealed all remaining non-hydrogen atoms. The non-hydrogen atoms were refined, first with isotropic temperature factors and then with anisotropic temperature factors. The coordinates of the hydrogen atoms of the methyl groups were calculated (assuming staggered conformations and r_{C-H} = 0.95 Å). These atoms were assigned isotropic temperature factors of 1.25 times the isotropic equivalent of the temperature factors of the C atoms to which they were attached and included in subsequent structure factor calculations, though their parameters were not refined. Secondary extinction parameters[11] were included in the refinements. Both structures were refined to completeness (all shift:error ratios < 0.01). The largest features in final difference maps were all located close to the Os atoms.

Refinement was by block-diagonal least-squares analysis minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma(F))^2 + n \times 10^{-4}F^2]^{-1}$ (n = 5 for 4, n = 3 for 5). Neutral-atom scattering factors with anomalous dispersion corrections[12] were used throughout. Computer programs[13] were run on a PDP-8e computer.

Final positional parameters and associated B_{equiv} are reported in Tables III and IV for 4 and 5, respectively. Bond lengths and angles for both compounds are given side-by-side in Table V to allow comparisons to be drawn. The atomic labeling is shown on ORTEP diagrams in Figures 1 and 2. Tables of anisotropic thermal parameters and calculated and observed structure factors are available as supplementary material.

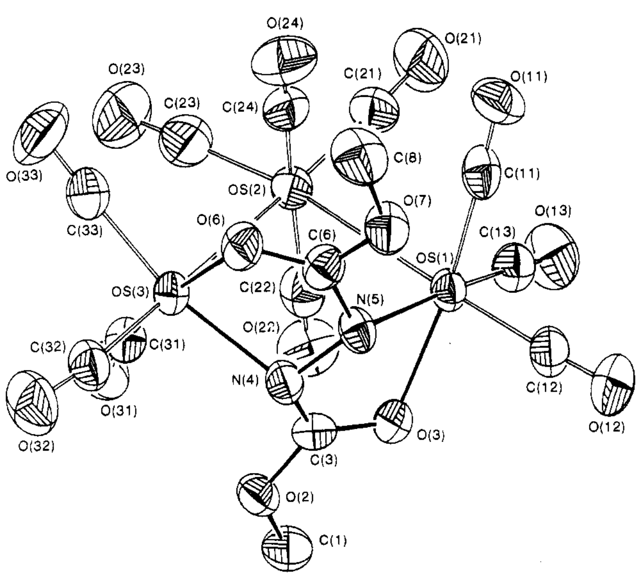


Figure 1. The structure of $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (4).

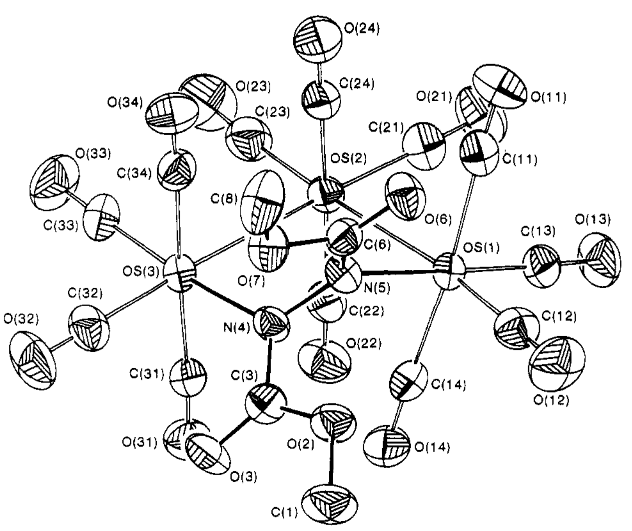


Figure 2. The structure of $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (5).

Results and Discussion

The reactions of dimethyl azodicarboxylate (2) with the labile triosmium carbonyl clusters $Os_3(CO)_{11}(CH_3CN)$ (1)

---

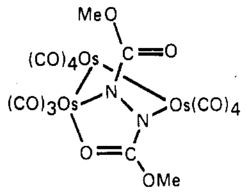
(11) Larson, A. C. "Crystallographic Computing"; Munksgaard: Copenhagen, 1970; p 291.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99, 149.

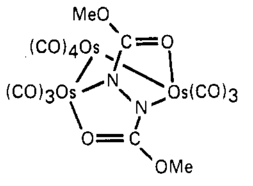
(13) Larson, A. C.; Gabe, E. J. "Computing in Crystallography"; Schenk, H., et al., Eds.; Delft University Press: Holland, 1978.

and $Os_3(CO)_{10}(CH_3CN)_2$ are summarized as follows. Under mild conditions, **1** is converted to the enneacarbonyl complex **3** in virtually quantitative yield (by IR) in about 1 h. Complex **3** transforms slowly in solution to the decacarbonyl **4**, but it can be obtained in spectroscopically pure condition if isolated quickly by flash chromatography on cellulose. Some decomposition occurs on the column. The instability has precluded recrystallization or growing X-ray quality crystals of **3** and limits the available methods of identification. Compound **4** is obtained fairly cleanly by increasing the temperature to 70 °C for a further 20 min, whereas maintaining the solution of **3** at room temperature longer than 1 h results in substantial decomposition as well as **4**. Alternatively, compound **4** can be obtained quantitatively (as determined by IR) from the reaction of the bisacetonitrile complex $Os_3(CO)_{10}(CH_3CN)_2$ with excess **2**. Some decomposition of **4** occurs on a silica column, but the products do not elute under the conditions used. Both **3** and **4** may be carbonylated to the dodecacarbonyl complex **5**. This occurs under mild conditions for **3** (1 atm, room temperature). The decacarbonyl **4** requires a high pressure of CO (1500 psi) and is unchanged under 1 atm of CO. We could not detect the enneacarbonyl **3** as an observable intermediate, and if it were formed, it would be expected to convert rapidly to **4** at high CO pressure.

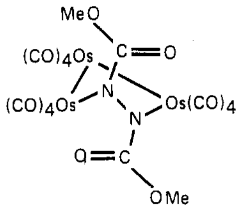
Two of these compounds, the decacarbonyl **4** and the dodecacarbonyl **5**, have been subjected to complete analysis by MS, IR, NMR, and X-ray crystallography. Their structures are assured. That of the enneacarbonyl **3** rests upon IR and NMR evidence only. But we can observe a clear similarity between features in the spectra of **3** with ones in **4** and **5**, which correspond to specific structural features in each case. This makes us confident of the structure proposed for **3** also, and it agrees with the observed chemistry. We shall discuss the structures of **4** and **5** and then **3**.



[3]



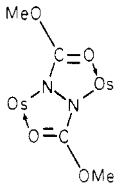
[4]



[5]

$Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (4). The molecular structure deduced from X-ray crystallography is shown in Figure 1. It consists of a triangular $Os_3(CO)_{10}$ fragment with the azo ligand spanning one edge. However, there has not merely been ligand substitution of the two acetonitrile groups in $Os_3(CO)_{10}(CH_3CN)_2$ (or an acetronitrile and a CO group in **1**). Rather, this Os–Os edge has been lengthened to a nonbonding distance of 4.1615 (7) Å. The ligand forms two five-membered chelate rings with these Os atoms to which it is bound in tetradentate fashion through the two N atoms and the methoxycarbonyl oxygens.

An examination of the bond lengths in the azo ligand supports the view that it is bound as a hydrazide and that the complexation can be described quite well by the formal valence representation A. The N–N bond length (1.439 (9) Å) is that of a single bond, compared with ca. 1.23 Å for a double bond,[14] and is similar to that observed[15] for a copper(II) dibenzoylhydrazine complex (1.436 Å). The N–C distance is close to a single-bond value and is similar to values in the copper complex[15] and the arylformamido complex $HOs_3(CO)_{10}(ArNCHO)$.[16] The C–O distance in the coordinated carbonyl group compares with similar distances in the above two complexes and in $Os_5C(CO)_{14}(COOMe)$.[17] Consequently, we view each N atom to supply one electron to the cluster, replacing the electrons of the formal Os–Os bond in the parent cluster. The ligand is a six-electron donor.



A

In essence, the Os–Os bond and the NN π-bond have been broken and two new Os–N bonds have been made. A possible mechanism for this transformation is discussed later in the paper.

The IR spectrum shows, in addition to the expected terminal ν(CO) absorptions, bands at 1518 and 1484 cm^{-1} associated with *coordinated* carbonyl groups of the ligand. The ^{1}H NMR spectrum is a singlet at δ 3.86 assigned to the equivalent methoxy groups adjacent to these *coordinated* carbonyls. These values are altered considerably when the methoxycarbonyl groups become detached from the Os atoms in **5** (vide infra), so providing a useful probe for the structure of **3**.

$Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (5). The X-ray structure of this is shown in Figure 2. It is essentially related to that of **4** by having the extra two carbon monoxide groups occupying the sites previously filled by the coordinated methoxycarbonyls in **4**. Important features have generally been retained, such as the N–N single bond (1.411 (7) Å) and the long nonbonded Os···Os distance (4.1979 (7) Å). The complex can thus be viewed as derived from $Os_3(CO)_{12}$ by the replacement of one Os–Os bond by a bridging two-electron donor hydrazide ligand. The conformation of the ligand is, however, considerably altered from that in **4** as the methoxycarbonyl groups are now nonbonding and directed away from the center of the molecule. The C(3)–N(4)–N(5)–C(6) torsion angle is 76.2 (7)° (cf. −167.6 (7)° for **4**) and the C=O distances tend to be shorter than in **4** as expected. The Os(2)–Os(3) bond length (3.0078 (6) Å) is appreciably longer than the other Os–Os distances in either structure (2.9638 (6), 2.9704 (7) Å for **4**; 2.9672 (6) Å for **5**), presumably because the adjacent atoms are eclipsed across the Os–Os bond, whereas in the other cases, they are closer to staggered (torsion angles X–Os–Os–Y ≈ 30°). A similar effect, with com-

---

[14] Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 5313.

[15] Baker, R. J.; Nyburg, S. C.; Szymanski, J. T. *Inorg. Chem.* **1971**, *10*, 138.

[16] Adams, R. D.; Golembeski, N. M. *J. Organomet. Chem.* **1979**, *171*, C21. Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *Inorg. Chem.* **1981**, *20*, 1242.

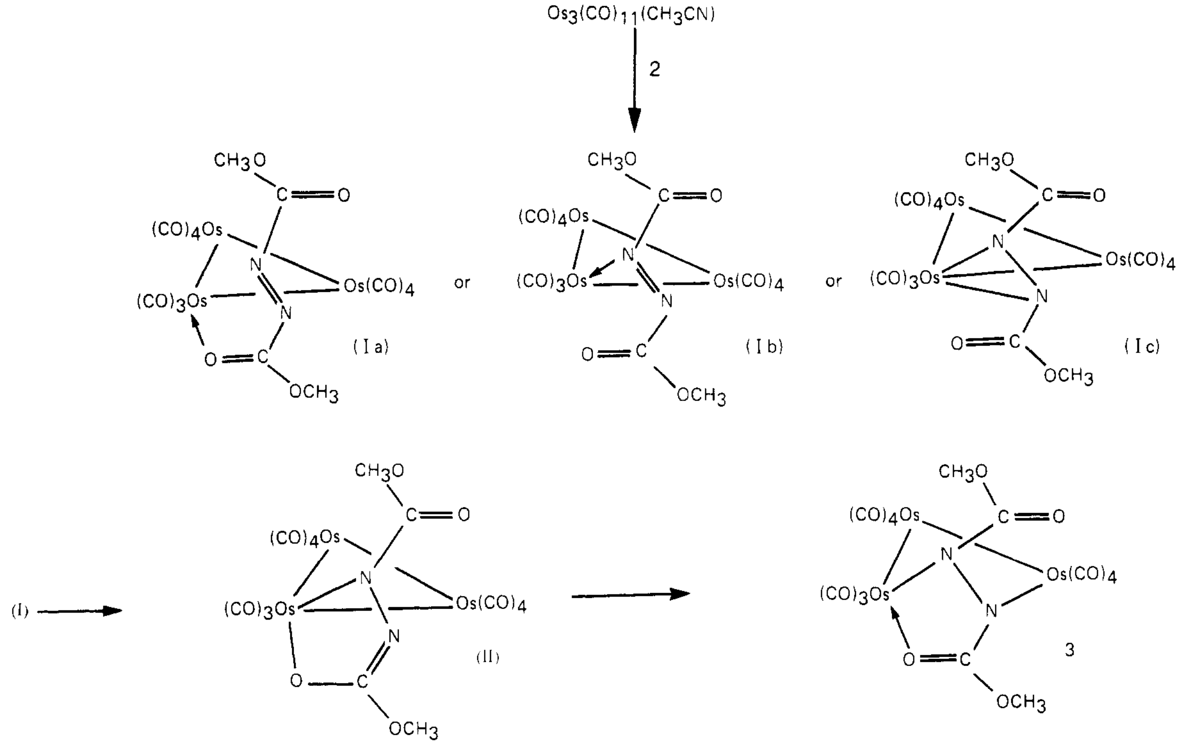
[17] Braga, D.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1982**, 966.

Table IV. Atomic Coordinates for $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (5)

atom	x	y	z	B_{equiv},[a] Å^2	atom	x	y	z	B_{equiv},[a] Å^2
Os(1)	0.39940 (2)	0.54038 (2)	0.29509 (2)	2.401	C(32)	0.0289 (6)	0.6101 (6)	0.0776 (5)	3.8
Os(2)	0.17838 (2)	0.57929 (2)	0.36449 (2)	2.620	O(32)	−0.0078 (5)	0.6220 (5)	0.0119 (3)	5.9
Os(3)	0.08414 (2)	0.59386 (2)	0.18956 (2)	2.493	C(33)	−0.0591 (5)	0.6116 (6)	0.2359 (5)	3.6
C(11)	0.3972 (6)	0.3902 (6)	0.3387 (4)	3.4	O(33)	−0.1444 (4)	0.6181 (5)	0.2625 (4)	5.8
O(11)	0.3994 (5)	0.3062 (4)	0.3656 (3)	5.0	C(34)	0.0634 (5)	0.4361 (6)	0.1866 (4)	3.3
C(12)	0.5355 (6)	0.5193 (6)	0.2362 (5)	3.8	O(34)	0.0501 (4)	0.3458 (4)	0.1807 (3)	4.5
O(12)	0.6150 (5)	0.5112 (6)	0.2020 (4)	6.3	C(1)	0.4381 (7)	0.6381 (7)	−0.0055 (5)	5.2
C(13)	0.4734 (6)	0.5867 (5)	0.3952 (5)	3.4	O(2)	0.3900 (4)	0.5899 (4)	0.0653 (3)	3.8
O(13)	0.5191 (5)	0.6088 (4)	0.4556 (3)	4.8	C(3)	0.2854 (5)	0.6199 (6)	0.0811 (4)	3.1
C(14)	0.3856 (5)	0.6891 (5)	0.2532 (4)	3.1	O(3)	0.2350 (4)	0.6905 (4)	0.0426 (3)	4.0
O(14)	0.3810 (4)	0.7746 (4)	0.2275 (3)	4.3	N(4)	0.2436 (4)	0.5672 (4)	0.1472 (3)	2.7
C(21)	0.2482 (6)	0.5648 (6)	0.4715 (4)	3.8	N(5)	0.3118 (4)	0.4898 (4)	0.1878 (3)	2.4
O(21)	0.2866 (5)	0.5552 (5)	0.5365 (3)	5.6	C(6)	0.3256 (5)	0.3930 (5)	0.1515 (4)	2.9
C(22)	0.2016 (6)	0.7365 (6)	0.3587 (4)	3.3	O(6)	0.3881 (4)	0.3221 (4)	0.1780 (3)	3.7
O(22)	0.2106 (5)	0.8275 (4)	0.3565 (3)	4.6	O(7)	0.2596 (4)	0.3794 (4)	0.0840 (3)	3.5
C(23)	0.0368 (6)	0.5969 (6)	0.4117 (5)	4.4	C(8)	0.2631 (6)	0.2728 (7)	0.0460 (6)	5.0
O(23)	−0.0453 (5)	0.6042 (6)	0.4442 (4)	7.3	H(1A)	0.5119	0.6109	−0.0110	5.7
C(24)	0.1617 (6)	0.4244 (5)	0.3521 (4)	3.5	H(1B)	0.4409	0.7155	−0.0006	5.7
O(24)	0.1484 (4)	0.3327 (4)	0.3488 (4)	5.2	H(1C)	0.3968	0.6205	−0.0556	5.7
C(31)	0.1145 (5)	0.7514 (5)	0.1899 (4)	2.9	H(8A)	0.2130	0.2723	−0.0021	4.7
O(31)	0.1285 (4)	0.8416 (4)	0.1850 (3)	4.3	H(8B)	0.2394	0.2178	0.0846	4.7
					H(8C)	0.3353	0.2542	0.0288	4.7

[a] $B_{equiv} = 8\pi^2(U_{11} + U_{22} + U_3)/3$ for anisotropic atoms.

Scheme I



parable distances, occurs in $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$.[6]

The IR spectrum of **5** in the ν(CO) region is relatively simple, and in the methoxycarbonyl region the absorptions of the *uncoordinated* COOMe group are seen at 1633 and 1443 cm^{-1}. In the ^{1}H NMR, the resonance for the *uncoordinated* $COOCH_3$ groups is a singlet at δ 3.64, shifted upfield from the resonance of the *coordinated* $COOCH_3$ groups in **4**.

$Os_3(CO)_{11}(CH_3OCONNCOOCH_3)$ (3). The structure of this complex, deduced from IR and ^{1}H NMR spectroscopic results, is intermediate between those of **4** and **5** and derived from **4** by the replacement of only one of the coordinated $COOCH_3$ groups by a CO ligand. Thus, the compound exhibits two sharp singlet methyl resonances of equal intensity at δ 3.82 and 3.64, at the respective positions established for resonances of coordinated and uncoordinated $COOCH_3$ groups in **4** and **5**. It also exhibits IR absorptions at 1658, 1530, and 1472 cm^{-1}, suggesting both coordinated and free carbonyl groups to be present. Because both **4** and **5** exhibit the nonbonded Os(1)···Os(3) distances, and the uptake of CO by **3** to give **5** occurs under such mild conditions, it is almost certain that the Os(1)···Os(3) bond is absent in **3** also.

A possible mechanism of formation of **3** and **4** from $Os_3(CO)_{11}(CH_3CN)$ is shown in Scheme I. The first step is presumably loss of CH_3CN and coordination of the dimethyl azodicarboxylate (**2**) as a two-electron donor (I). Possible structures for I include the following: Ia, bonded through a carbonyl; Ib, bonded through a nitrogen atom; or Ic bonded through the π-system of the diazo group.

Table V. Bond Lengths (Å) and Angles (deg) for $Os_3(CO)_{10}(CH_3OCONNCOOCH_3)$ (4) and $Os_3(CO)_{12}(CH_3OCONNCOOCH_3)$ (5)

	4	5		4	5
Os(1)-Os(2)	2.9638 (6)	2.9672 (6)	Os(1)-Os(2)-C(21)	88.9 (3)	86.3 (2)
Os(2)-Os(3)	2.9704 (7)	3.0078 (6)	Os(1)-Os(2)-C(22)	78.3 (3)	90.5 (2)
Os(1)···Os(3)	4.1615 (7)	4.1979 (7)	Os(1)-Os(2)-C(23)	171.2 (3)	177.0 (2)
Os(1)-C(11)	1.877 (9)	1.975 (7)	Os(1)-Os(2)-C(24)	91.7 (3)	84.0 (2)
Os(1)-C(12)	1.914 (8)	1.940 (7)	Os(3)-Os(2)-C(21)	171.4 (3)	175.4 (2)
Os(1)-C(13)	1.909 (8)	1.907 (7)	Os(3)-Os(2)-C(22)	93.5 (3)	87.1 (2)
Os(1)-C(14)		1.954 (7)	Os(3)-Os(2)-C(23)	87.4 (3)	92.1 (3)
Os(1)-O(3)	2.144 (5)		Os(3)-Os(2)-C(24)	77.2 (3)	85.7 (2)
Os(1)-N(5)	2.120 (6)	2.095 (5)	C(21)-Os(2)-C(22)	94.2 (4)	94.2 (3)
Os(2)-C(21)	1.911 (9)	1.903 (7)	C(21)-Os(2)-C(23)	95.8 (4)	92.3 (3)
Os(2)-C(22)	1.946 (10)	1.957 (7)	C(21)-Os(2)-C(24)	94.6 (4)	92.5 (3)
Os(2)-C(23)	1.900 (11)	1.907 (8)	C(22)-Os(2)-C(23)	93.9 (4)	92.2 (3)
Os(2)-C(24)	1.933 (10)	1.925 (7)	C(22)-Os(2)-C(24)	166.5 (4)	171.0 (3)
Os(3)-C(31)	1.861 (9)	1.972 (7)	C(23)-Os(2)-C(24)	95.4 (4)	93.4 (3)
Os(3)-C(32)	1.940 (8)	1.910 (7)	Os(2)-Os(3)-C(31)	82.6 (3)	89.4 (2)
Os(3)-C(33)	1.901 (9)	1.919 (7)	Os(2)-Os(3)-C(32)	176.0 (3)	176.9 (2)
Os(3)-C(34)		1.957 (7)	Os(2)-Os(3)-C(33)	88.8 (3)	88.5 (2)
Os(3)-O(6)	2.144 (6)		Os(2)-Os(3)-C(34)		90.5 (2)
Os(3)-N(4)	2.128 (6)	2.092 (5)	Os(2)-Os(3)-O(6)	92.9 (1)	
C(1)-O(2)	1.446 (10)	1.411 (8)	Os(2)-Os(3)-N(4)	84.3 (2)	87.7 (1)
O(2)-C(3)	1.326 (10)	1.353 (8)	C(31)-Os(3)-C(32)	93.4 (4)	87.8 (3)
C(3)-O(3)	1.281 (9)	1.220 (8)	C(31)-Os(3)-C(33)	90.0 (4)	93.3 (3)
C(3)-N(4)	1.302 (10)	1.351 (8)	C(31)-Os(3)-C(34)		176.4 (3)
N(4)-N(5)	1.439 (9)	1.411 (7)	C(31)-Os(3)-O(6)	171.8 (3)	
N(5)-C(6)	1.338 (10)	1.336 (8)	C(31)-Os(3)-N(4)	98.7 (3)	88.9 (2)
C(6)-O(6)	1.253 (9)	1.226 (8)	C(32)-Os(3)-C(33)	91.1 (4)	92.9 (3)
C(6)-O(7)	1.327 (10)	1.354 (8)	C(32)-Os(3)-C(34)		92.2 (3)
O(7)-C(8)	1.450 (11)	1.440 (9)	C(32)-Os(3)-O(6)	91.1 (3)	
C(11)-O(11)	1.136 (11)	1.120 (9)	C(32)-Os(3)-N(4)	96.5 (3)	91.0 (3)
C(12)-O(12)	1.134 (10)	1.125 (9)	C(33)-Os(3)-C(34)		90.3 (3)
C(13)-O(13)	1.133 (10)	1.137 (9)	C(33)-Os(3)-O(6)	96.7 (4)	
C(14)-O(14)		1.131 (8)	C(33)-Os(3)-N(4)	168.1 (3)	175.5 (3)
C(21)-O(21)	1.135 (11)	1.137 (9)	C(34)-Os(3)-N(4)		87.5 (2)
C(22)-O(22)	1.140 (12)	1.124 (9)	O(6)-Os(3)-N(4)	74.0 (2)	
C(23)-O(23)	1.153 (13)	1.138 (9)	C(1)-O(2)-C(3)	117.9 (6)	116.2 (6)
C(24)-O(24)	1.138 (12)	1.141 (9)	O(2)-C(3)-O(3)	119.9 (7)	124.2 (6)
C(31)-O(31)	1.144 (11)	1.126 (8)	O(2)-C(3)-N(4)	115.7 (7)	112.8 (6)
C(32)-O(32)	1.125 (11)	1.144 (9)	O(3)-C(3)-N(4)	124.4 (7)	123.0 (6)
C(33)-O(33)	1.119 (11)	1.132 (8)	Os(1)-O(3)-C(3)	109.3 (5)	
C(34)-O(34)		1.126 (9)	Os(3)-N(4)-C(3)	121.2 (5)	123.2 (4)
Os(2)-Os(1)-C(11)	83.3 (3)	89.9 (2)	Os(3)-N(4)-N(5)	108.3 (4)	119.5 (4)
Os(2)-Os(1)-C(12)	177.3 (3)	172.8 (2)	C(3)-N(4)-N(5)	110.0 (6)	117.3 (5)
Os(2)-Os(1)-C(13)	89.6 (3)	92.8 (2)	Os(1)-N(5)-N(4)	108.8 (4)	117.3 (4)
Os(2)-Os(1)-C(14)		84.7 (2)	Os(1)-N(5)-C(6)	120.1 (5)	123.7 (4)
Os(2)-Os(1)-O(3)	92.2 (1)		N(4)-N(5)-C(6)	109.7 (6)	118.6 (5)
Os(2)-Os(1)-N(5)	84.9 (2)	84.8 (1)	N(5)-C(6)-O(6)	124.9 (8)	124.5 (6)
C(11)-Os(1)-C(12)	94.4 (4)	93.8 (3)	N(5)-C(6)-O(7)	113.0 (6)	112.7 (5)
C(11)-Os(1)-C(13)	90.5 (4)	89.5 (3)	O(6)-C(6)-O(7)	122.1 (7)	122.8 (6)
C(11)-Os(1)-C(14)		174.3 (3)	Os(3)-O(6)-C(6)	109.5 (5)	
C(11)-Os(1)-O(3)	171.8 (3)		C(6)-O(7)-C(8)	118.3 (7)	115.1 (6)
C(11)-Os(1)-N(5)	99.4 (3)	90.1 (2)	Os(1)-C(11)-O(11)	177.6 (7)	177.1 (6)
C(12)-Os(1)-C(13)	91.8 (4)	93.4 (3)	Os(1)-C(12)-O(12)	175.9 (8)	177.4 (7)
C(12)-Os(1)-C(14)		91.4 (3)	Os(1)-C(13)-O(13)	177.9 (8)	176.4 (6)
C(12)-Os(1)-O(3)	89.9 (3)		Os(1)-C(14)-O(14)		177.6 (6)
C(12)-Os(1)-N(5)	94.1 (3)	89.0 (3)	Os(2)-C(21)-O(21)	176.2 (8)	177.6 (7)
C(13)-Os(1)-C(14)		92.5 (3)	Os(2)-C(22)-O(22)	176.5 (8)	177.1 (6)
C(13)-Os(1)-O(3)	96.4 (3)		Os(2)-C(23)-O(23)	177.0 (11)	175.7 (7)
C(13)-Os(1)-N(5)	168.1 (3)	177.6 (3)	Os(2)-C(24)-O(24)	178.0 (8)	176.1 (6)
C(14)-Os(1)-N(5)		87.6 (2)	Os(3)-C(31)-O(31)	178.2 (7)	175.4 (6)
O(3)-Os(1)-N(5)	73.3 (2)		Os(3)-C(32)-O(32)	170.9 (8)	177.2 (7)
Os(1)-Os(2)-Os(3)	89.06 (2)	89.27 (2)	Os(3)-C(33)-O(33)	177.5 (9)	177.4 (7)
			Os(3)-C(34)-O(34)		176.5 (6)

Compound I is then suggested to rearrange to **3** through the intermediacy of the metallocycle II in which the Os–Os bond is still present. It this scheme is correct, then the suggested intermediates I and II must be short-lived and rapidly give rise to **3**, for when the reaction was monitored by ^1H NMR in $CDCl_3$ at 10 °C, the signal at δ 2.76 due to the CH_3CN ligand in **1** decreased, with a corresponding smooth increase in the signals at δ 3.64 and 3.82 due to the formation of **3** alone and at δ 1.98 (free CH_3CN). No other methyl signals could be detected. Thermal loss of CO from **3** to give **4** also occurs with no detectable intermediate. After the complete disappearance of **1**, the temperature was raised to 35 °C, and this produced a smooth decrease in the signals of **3** and an increase in a new signal at δ 3.87 from **4**.

An attempt to synthesize compound **5** directly from $Os_3(CO)_{12}$ and excess **2** in benzene at 80 °C gave no evidence of reaction over 24 h. Similarly, **5** showed no reaction with PPh_3 (by NMR) over 3 h at 50 °C in $CDCl_3$. Compound **5** did not transform to **4** under these conditions but did so quantitatively when heated alone in benzene at 70 °C for 5 h. Treatment of **5** in benzene with excess

Me_3NO in methanol at room temperature converted it to a mixture of osmium compounds of which **4** was the major constituent (IR). Other products were not identified except to note that **3** was not present. UV irradiation of a solution of **5** in CH_2Cl_2 in Pyrex led to general decomposition.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council Canada through a Strategic Grant. Mass spectra by xenon fast atom bombardment were kindly carried out at the University of Alberta by Dr. A. M. Hogg.

Registry No. **1**, 65702-94-5; **3**, 86409-58-7; **4**, 86409-59-8; **5**, 86409-60-1; $Os_3(CO)_{10}(CH_3CN)_2$, 61817-93-4.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Hexamethylsilirane. 5. Conversion to Five-Membered Ring Silicon Compounds by "Two-Atom" Insertion Reactions of Aryl Olefins, 1,3-Dienes, and Conjugated Acetylenes[1]

Dietmar Seyferth,* Don P. Duncan, Mark L. Shannon, and Emma W. Goldman

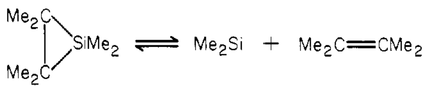
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received September 21, 1983

Hexamethylsilirane reacts, under mild conditions, with styrene, α-methylstyrene, terminal 1,3-dienes, conjugated terminal acetylenes, and benzyne with insertion of a C=C or C≡C bond into an Si—C bond of the silirane ring to give a silacyclopentane or silacyclopentene (in the case of the acetylenes). Byproducts derived from Me_2Si addition to these substrates also are obtained.

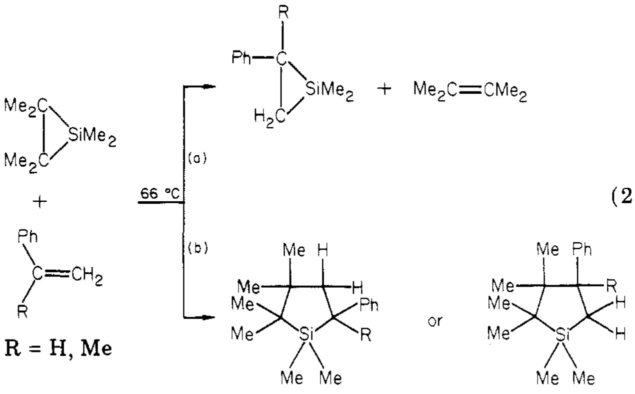
Introduction

In earlier papers of this series we have reported that hexamethylsilirane decomposes at temperatures as low as 65–75 °C with extrusion of dimethylsilylene (eq 1).[1,2] The



(1)

dimethylsilylene thus generated was found to insert into the Si—H bonds of organosilicon hydrides and into the Si—O bonds of methoxysilanes, hexamethylcyclotrisiloxane, and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane and to add to the C=C bonds of internal olefins to give new siliranes.[1] During the course of an investigation of the scope of the formation of siliranes by the addition of hexamethylsilirane-derived dimethylsilylene to olefins we carried out the thermolysis of hexamethylsilirane in the presence of styrene and α-methylstyrene. The expected reaction was Me_2Si addition to the C=C bond of the styrene (eq 2a). However, what was found instead was that the major product was that of a ring expansion process: the insertion of both carbon atoms of the C=C bonds of styrene and α-methylstyrene into an Si—C bond of the silirane ring to give a silacyclopentane (eq 2b).[2] Such an apparent [3 + 2] cycloaddition, which we shall call a "two-atom insertion", was unexpected and very interesting in terms of mechanistic considerations and synthetic organosilicon chemistry, and thus we undertook to investigate the scope and, if possible, the mechanism of such two-atom insertions in more detail.



1 **2**

(2)

Results and Discussion

We shall address ourselves first to the structure of the two-atom insertion products in the case of styrene and α-methylstyrene. In our initial report,[2] structure **1** was given; this assignment was based on proton NMR-based reasoning[3] which later considerations disputed.[4] The application of ^{13}C NMR spectroscopy allowed us to settle this question of structure.[5]

During the course of this investigation it was found that styrene reacts with hexamethylsilirane even at room temperature. An overnight reaction at 25 °C gave the same product (in 47% yield) as was obtained in the reaction carried out at 66 °C as well as a minor (6% yield) product

---

[1] (a) Part 4: Seyferth, D.; Wiseman, G. H.; Annarelli, D. C.; Shannon, M. L. *J. Organomet. Chem.*, in press. (b) Preliminary communications: Seyferth, D.; Duncan, D. P.; Vick, S. C. *Ibid.* **1977**, *125*, C5. Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *Ibid.* **1977**, *135*, C37.

[2] Seyferth, D.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, *117*, C51.

[3] Annarelli, D. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1976.

[4] Duncan, D. P. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

[5] Goldman, E. W. Ph.D. Thesis, Massachusetts Institute of Technology, 1983.