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Reactions of Iminium Ligands with Alkynes. Addition of $HC\equiv CCO_2Me$ to $Os_3(CO)_{10}(\mu\text{-}H_2CNMe_2)(\mu\text{-}H)$

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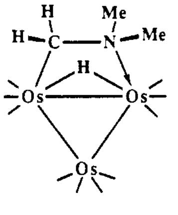
The reaction of $Os_3(CO)_{10}(\mu\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1) with $HC\equiv CCO_2Me$ has yielded three new products, $Os_3(CO)_8(\mu\text{-}CNMe_2)[\mu_3\text{-}CH_2C(CO_2Me)C(CO_2Me)CH]$ (**3**, 7%), $Os_3(CO)_9[\mu_3\text{-}Me_2NCCC(H)(CO_2Me)](\mu\text{-}H)$ (**4**, 20%), and $Os_3(CO)_9[\mu_3\text{-}H_2CNMe_2CH_2CCO_2Me]$ (**5**, 6%). Compound **4** was also obtained in a slightly higher yield (28%) from the reaction of $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**2**) and HC_2CO_2Me. Compounds **3**–**5** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Crystal data for **3**: space group, $P2_1/n$, $a = 9.998$ (3) Å, $b = 14.229$ (4) Å, $c = 17.926$ (3) Å, $\beta = 104.67$ (2)°, $R = 0.028$ for 2616 reflections. Crystal data for **4**: space group, $P\bar{1}$, $a = 10.623$ (2) Å, $b = 12.877$ (2) Å, $c = 8.531$ (2) Å, $\alpha = 102.18$ (1)°, $\beta = 102.14$ (2)°, $\gamma = 85.85$ (1)°, $R = 0.025$ for 2508 reflections. Crystal data for **5**: space group $P2_1/c$, $a = 8.778$ (4) Å, $b = 15.836$ (3) Å, $c = 16.029$ (4) Å, $\beta = 105.61$ (3)°, $R = 0.052$ for 2907 reflections. Compound **3** consists of an open cluster of three osmium atoms with a bridging (dimethylamino)carbyne ligand and a triply bridging $CH_2C(CO_2Me)C(CO_2Me)CH$ ligand. The former was formed by the removal of the two hydrogen atoms from the methylene group of the iminium ligand. The latter was formed by a tail-to-tail coupling of two $HC\equiv CCO_2Me$ molecules and the transfer of one hydrogen atom to one of the CH groups. Compound **4** contains a closed triangular cluster of metal atoms with a triply bridging $Me_2NCCC(H)CO_2Me$. This ligand was apparently formed by a C—C coupling of a rearranged $HC\equiv CCO_2Me$ ligand and a $CNMe_2$ group. Compound **5** contains a closed triangular cluster of metal atoms with a triply bridging $CH_2NMe_2CH_2CO_2Me$ ligand. This ligand was formed by a C—N coupling of the iminium ligand in **1** to a $HC\equiv CCO_2Me$ ligand that had been inserted into the metal–hydride bond in **1**.

Introduction

The formation of carbon–carbon and carbon–nitrogen bonds plays a central role in the use of organometallic compounds in organic synthesis. Eschenmoser's salt, $[H_2C{=}NMe_2]^+I^-$, has been used with great success as a reagent for the introduction of the CH_2NMe_2 group into a variety of organic substrates through the formation of carbon–carbon bonds. Although several examples of metal complexes containing the H_2CNMe_2 ligand have been reported,[1-4] there have been very few reports concerning the reactivity of this ligand toward small organic molecules. We have recently reported the synthesis and characterization of the first examples of polynuclear metal complexes containing the H_2CNMe_2 ligand.[5,6] One of these, $Os_3(CO)_{10}(\mu\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1), contains a bridging η^2-H_2CNMe_2 ligand. We have now investigated the reactivity of **1** toward the alkyne $HC\equiv CCO_2Me$ and have observed the formation of products involving both C—C and C—N bond formation. These results are reported herein.



1

Experimental Section

General Procedures. Although all the products appear to be air-stable, all the reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over molecular sieves. Methyl propiolate was purchased from Aldrich Chemical Co. and was used without further purification. $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1)[6] and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (2)[7] were prepared by the published procedures. Chromatographic separations were performed by TLC in air on silica gel, 0.25 mm, 60 F_{254}. IR spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-500 spectrometer operating at 500 MHz. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1) with Methyl Propiolate. A 30-μL (0.337-mmol) amount of methyl propiolate was added to a solution of 38.2 mg (0.042 mmol) of compound **1** dissolved in 50 mL of cyclohexane solvent at 25 °C. This solution was then refluxed for 2 h. After this time, the cyclohexane solvent was removed in vacuo, the residue was dissolved in a minimal amount of CH_2Cl_2, and the solution was chromatographed by TLC on silica gel. Elution with CH_2Cl_2/hexane, a 65/35 solvent mixture, yielded 3.0 mg of $Os_3(CO)_8(\mu\text{-}CNMe_2)[\mu_3\text{-}CH_2C(CO_2Me)C(CO_2Me)CH]$ (**3**, 7%) as a yellow band, 8.2 mg of $Os_3(CO)_9[\mu_3\text{-}Me_2NCCC(H)CO_2Me](\mu\text{-}H)$ (**4**, 20%) as a bright yellow band, and 2.3 mg of $Os_3(CO)_9[\mu_3\text{-}H_2CNMe_2CH_2CC(CO_2Me)]$ (**5**, 6%) as an orange band. Analytical and spectral data for **3**: IR (ν(CO), cm^{-1}; in hexane) 2080 (m), 2059 (s), 2002 (s), 1995 (vs), 1976 (w), 1963 (m), 1932 (w), 1732 (vw); ^1H NMR (δ; in $CDCl_3$) 8.81 (s, 1 H), 3.76 (s, 3 H), 3.62 (s, 3 H), 3.60 (s, 3 H), 3.48 (s, 3 H), 2.17 (d, 1 H, $J_{H-H} = 11.2$ Hz), 1.23 (d, 1 H, $J_{H-H} = 11.2$ Hz). Anal. Calcd for $Os_3O_{12}NC_{19}H_{15}$: C, 22.38; H, 1.48; N, 1.37. Found: C, 21.84; H, 0.99; N, 1.18. Analytical and spectral data for **4**: IR (ν(CO), cm^{-1}; in hexane) 2093 (m), 2062 (vs), 2038 (vs), 2018 (s), 1997 (m), 1981 (m), 1976 (m, sh), 1957 (w), 1724 (vw); ^1H NMR (δ; in $CDCl_3$) 3.63 (s, 3 H), 3.55 (s, 3 H), 3.26 (s, 3 H), 2.72 (s, 1 H), −19.57 (s, 1 H). Anal. Calcd for $Os_3O_{11}NC_{16}H_{11}$: C, 19.94; H, 1.15; N, 1.45. Found: C, 19.76; H, 1.18; N, 1.29. Analytical and spectral data for **5**: IR (ν(CO), cm^{-1}; in hexane) 2075 (m), 2032 (vs), 2000 (s), 1990 (m),

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Table I. Crystallographic Data for the Structural Analyses of Compounds 3–5

	3	4	5
empirical formula	$Os_3O_{12}NC_{19}H_{15}$	$Os_3O_{11}NC_{16}H_{11}$	$Os_3O_{11}NC_{16}H_{13}$
fw	1019.93	963.86	965.88
cryst syst	monoclinic	triclinic	monoclinic
lattice params			
a, Å	9.998 (3)	10.623 (2)	8.778 (4)
b, Å	14.229 (4)	12.877 (2)	15.836 (3)
c, Å	17.926 (3)	8.531 (2)	16.029 (4)
α, deg		102.18 (1)	
β, deg	104.67 (2)	102.14 (2)	105.61 (3)
γ, deg		85.85 (1)	
V, Å^3	2467 (1)	1114.8 (4)	2146 (2)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z	4	2	4
D_{calc}, g/cm^3	2.75	2.87	2.99
μ(Mo Kα), cm^{-1}	154.88	171.27	188.33
temp, °C	23	23	23
$2\theta_{max}$, deg	46.0	46.0	50.0
no. of observns ($I > 3\sigma(I)$)	2616	2508	2907
no. of variables	316	283	280
residuals: R; R_w	0.028; 0.027	0.025; 0.026	0.052; 0.057
goodness of fit indicator	1.20	1.30	2.57
max shift in final cycle	0.04	0.09	0.04
largest peak in final diff map, e/Å^3	0.82	1.83	4.69
abs cor	analytical	empirical	analytical
transmissn factors: max/min	0.74/0.15	1.00/0.52	0.24/0.07

1966 (w), 1959 (w); ^{1}H NMR (δ; in $CDCl_3$) 4.25 (d, 1 H, J_{H-H} = 10.8 Hz), 4.15 (d, 1 H, J_{H-H} = 10.8 Hz), 4.08 (d, 1 H, J_{H-H} = 11.6 Hz), 3.51 (s, 3 H), 3.08 (s, 3 H), 2.67 (d, 1 H, J_{H-H} = 11.6 Hz), 2.48 (s, 3 H). Anal. Calcd for $Os_3O_{11}NC_{16}H_{13}$: C, 19.90; H, 1.36; N, 1.45. Found: C, 18.23; H, 1.01; N, 1.22.

Reaction of $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (2) with Methyl Propiolate. A 25.6-mg (0.028-mmol) amount of compound 2 and 25 μL (0.28 mmol) of methyl propiolate were added to 15 mL of *n*-octane. The solution was refluxed for 3 h. The solvent was removed in vacuo. Workup as described above yielded 7.7 mg of compound 4 (28%).

Crystallographic Analyses. Crystals of 3 were grown by slow evaporation of solvent from hexane/CH_2Cl_2 (2/1) solutions at 25 °C. Crystals of 4 were grown by slow evaporation of hexane solutions at 25 °C. Crystals of 5 were grown by slow evaporation of solvent from benzene/CH_2Cl_2 (1/1) solutions at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All intensity measurements were made by using the standard ω-scan (moving-crystal–stationary counter) technique. Background measurements were made by a one-fourth additional scan at each end of the scan. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library (v 2.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 3 crystallized in the monoclinic crystal system with four molecular units in the unit cell. The space group $P2_1/n$ was identified uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 4 crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The bridging hydride ligand was located crystallographically and was successfully refined with an isotropic thermal parameter. All other hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 5 crystallized in the monoclinic crystal system with four molecular units in the unit cell. The space group $P2_1/c$ was determined by systematic absences observed in the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The largest peaks in a final difference Fourier synthesis were structurally insignificant residuals close to the metal atoms. See the supplementary material for the tables of structure factor amplitudes and anisotropic thermal parameters for all of the structural analyses.

Results

The three products $Os_3(CO)_8(\mu\text{-}CNMe_2)[\mu_3\text{-}CH_2C(CO_2Me)C(CO_2Me)CH]$ (3, 7%), $Os_3(CO)_9[\mu_3\text{-}Me_2NCCC(H)CO_2Me](\mu\text{-}H)$ (4, 20%), and $Os_3(CO)_9[\mu_3\text{-}H_2CNMe_2CH_2CO_2Me]$ (5, 6%) were isolated from the reaction of compound 1 with HC_2CO_2Me in refluxing cyclohexane solvent. Compound 4 was also obtained in a slightly higher yield (28%) from the reaction of 2 with HC_2CO_2Me in refluxing octane solvent. Compounds 3–5 have been characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of 3 is shown in Figure 1. Final crystallographic positional parameters are listed in Table II. Selected intramolecular bond distances and intramolecular bond angles are listed in Tables III and IV, respectively. The molecule consists of an "open" triangular cluster of three osmium atoms that has two osmium–osmium bonds. The two metal–metal

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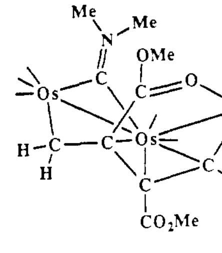
[8] (a) *International Tables for X-ray Crystallography*; Vol. IV, Kynoch Press: Birmingham, England, 1975; Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.



3

bonds are nearly of equal lengths, 2.8011 (9) and 2.7931 (8) Å. The Os(1)···Os(3) distance of 5.243 (1) Å clearly indicates no direct bonding exists between these atoms. A (dimethylamino)carbyne ligand bridges the Os(1)–Os(2) bond: Os(1)–C(1) = 1.99 (1) Å and Os(2)–C(1) = 2.09 (1) Å. The C(1)–N distance, 1.32 (1) Å, indicates the presence of some multiple bonding. This ligand is structurally similar to the one found in **2**.[6] The cluster also contains a triply bridging $H_2CC(CO_2Me)C(CO_2Me)CH$ ligand that was formed by a tail-to-tail coupling of two HC_2CO_2Me molecules and the addition of a hydrogen atom, presumably the hydride ligand, to the terminal carbon C(41), to form the methylene group (Os(1)–C(41) = 2.20 (1) Å). C(42), C(43), and C(44) are all bonded to Os(2) (Os(2)–C(42) = 2.27 (1) Å, Os(2)–C(43) = 2.23 (1) Å, and Os(2)–C(44) = 2.23 (1) Å) and resemble a π-allyl group, although the carbon–carbon bond between C(43) and C(44) (1.40 (1) Å) is significantly shorter than the bond between C(42) and C(43) (1.47 (1) Å). C(44) is also bonded to Os(3) (Os(3)–C(44) = 2.07 (1) Å), and the carbonyl oxygen atom of the carboxylate group on C(42) is coordinated to Os(3) (Os(3)–O(1) = 2.140 (8) Å). The positions of the hydrogen atoms of the methylene group and the single hydrogen atom on C(44) were obtained from a difference Fourier synthesis. In the ^1H NMR spectrum, the methylene protons were observed as a pair of AB doublets at 2.17 ppm (J_{H-H} = 11.2 Hz) and 1.23 ppm (J_{H-H} = 11.2 Hz). H(44) was observed at the low-field shift value of 8.81 ppm.

An ORTEP drawing of the molecular structure of **4** is shown in Figure 2. Final positional parameters are listed in Table V. Selected interatomic distances and interatomic angles are listed in Tables VI and VII, respectively. Compound **4** consists of a cluster of three osmium atoms with three osmium–osmium bonds (Os(1)–Os(2) = 2.8217 (7) Å, Os(1)–Os(3) = 2.8995 (9) Å, and Os(2)–Os(3) = 2.8766 (7) Å). The most interesting ligand is a triply bridging $Me_2NCCC(H)CO_2Me$ group. The Me_2N-substituted carbon atom C(1) is coordinated solely to Os(1) (Os(1)–C(1) = 2.07 (1) Å). The central carbon C(4) bridges the Os(2)–Os(3) bond (Os(2)–C(4) = 2.126 (9) Å and Os(3)–C(4) = 2.300 (9) Å), and carbon C(5) is coordinated only to Os(3) (Os(3)–C(5) = 2.296 (9) Å). This ligand is structurally similar to the Me_2NCCCH_2 group found in the complexes $M_3(CO)_9[\mu_3\text{-}(Me_2N)CCCH_2](\mu\text{-}H)$ (**6a**, M = Ru;[9] **6b**, M = Os[10]). The nitrogen atom is planar, and the observation of separate methyl resonances in the ^1H NMR spectrum shows that rotation about the C–N bond is slow on the NMR time scale. These properties would support the existence of carbene-like character in the carbon atom C(1) in **4** and the corresponding carbon atom in **6b**.[10]

The hydride ligand H(1) was located and refined crystallographically. It bridges the Os(2)–Os(3) bond and was observed in the characteristically high-field shift region at −19.57 ppm in the ^1H NMR spectrum. H(2) was observed as a singlet at 2.72 ppm.

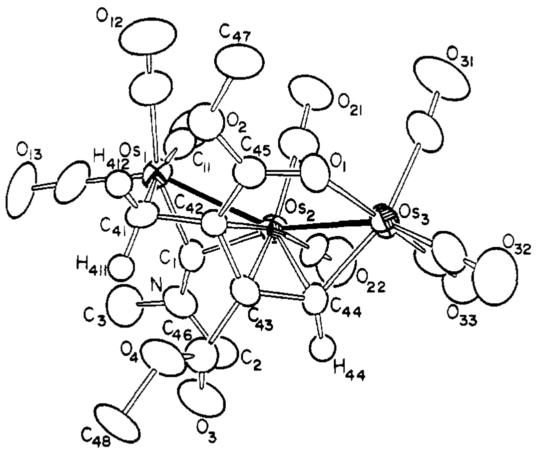


Figure 1. ORTEP drawing of $Os_3(CO)_8(\mu\text{-}CNMe_2)[\mu_3\text{-}CH_2C(CO_2Me)C(CO_2Me)CH]$ (**3**) showing 50% probability thermal ellipsoids.

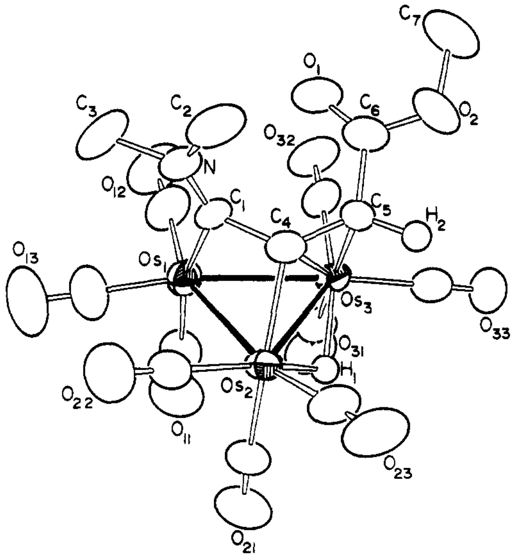


Figure 2. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}Me_2NCCC(H)(CO_2)](\mu\text{-}H)$ (**4**) showing 50% probability thermal ellipsoids.

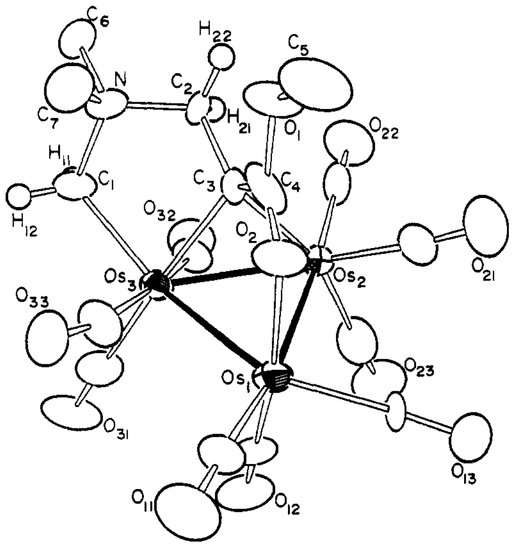


Figure 3. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}H_2CNMe_2CH_2CCO_2Me]$ (**5**) showing 50% probability thermal ellipsoids.

An ORTEP drawing of **5** is shown in Figure 3. Final crystallographic positional parameters are listed in Table VIII. Selected intramolecular bond distances and intra-

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Table II. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.03080 (05)	0.06492 (03)	0.32663 (03)	3.06 (2)
Os(2)	−0.04830 (04)	0.18284 (03)	0.19784 (03)	2.67 (2)
Os(3)	0.02716 (05)	0.22085 (03)	0.06116 (03)	3.12 (2)
O(1)	0.1239 (07)	0.0857 (06)	0.0799 (05)	3.4 (4)
O(2)	0.1961 (07)	−0.0338 (06)	0.1596 (05)	4.2 (4)
O(3)	−0.3868 (08)	0.0433 (06)	0.1082 (06)	5.3 (5)
O(4)	−0.2563 (07)	−0.0722 (06)	0.0818 (05)	4.3 (4)
O(11)	0.1067 (10)	0.2224 (07)	0.4469 (06)	6.7 (5)
O(12)	0.3342 (10)	0.0029 (09)	0.3454 (07)	7.8 (7)
O(13)	−0.0452 (12)	−0.0831 (08)	0.4308 (07)	7.6 (6)
O(21)	0.2487 (10)	0.2454 (08)	0.2616 (07)	7.4 (6)
O(22)	−0.1558 (11)	0.3745 (07)	0.2271 (07)	7.1 (6)
O(31)	0.3223 (10)	0.3011 (08)	0.1076 (08)	8.2 (7)
O(32)	−0.0072 (10)	0.2104 (07)	−0.1118 (06)	6.0 (5)
O(33)	−0.1152 (09)	0.4094 (07)	0.0419 (06)	5.5 (5)
N	−0.2739 (09)	0.1375 (07)	0.2863 (06)	3.9 (5)
C(1)	−0.1494 (11)	0.1250 (07)	0.2756 (07)	2.8 (5)
C(2)	−0.3834 (12)	0.1947 (10)	0.2373 (08)	5.0 (7)
C(3)	−0.3143 (14)	0.0938 (11)	0.3521 (09)	5.8 (8)
C(11)	0.0809 (12)	0.1630 (10)	0.4026 (08)	4.1 (6)
C(12)	0.2233 (14)	0.0251 (10)	0.3396 (07)	4.5 (6)
C(13)	−0.0115 (14)	−0.0274 (10)	0.3927 (08)	4.6 (6)
C(21)	0.1358 (13)	0.2231 (09)	0.2356 (09)	4.9 (7)
C(22)	−0.1158 (11)	0.3024 (09)	0.2156 (07)	3.5 (6)
C(31)	0.2126 (13)	0.2756 (09)	0.0874 (08)	4.5 (6)
C(32)	0.0095 (12)	0.2119 (08)	−0.0450 (09)	3.8 (6)
C(33)	−0.0597 (12)	0.3366 (10)	0.0489 (08)	4.2 (6)
C(41)	−0.0214 (10)	−0.0321 (08)	0.2279 (07)	2.8 (5)
C(42)	−0.0157 (09)	0.0328 (08)	0.1636 (06)	2.6 (5)
C(43)	−0.1451 (10)	0.0702 (08)	0.1148 (06)	2.6 (5)
C(44)	−0.1497 (10)	0.1550 (07)	0.0742 (06)	2.6 (5)
C(45)	0.1056 (10)	0.0330 (08)	0.1312 (07)	2.8 (5)
C(46)	−0.2781 (11)	0.0144 (09)	0.1032 (07)	3.2 (5)
C(47)	0.3203 (12)	−0.0348 (11)	0.1322 (09)	5.7 (7)
C(48)	−0.3753 (11)	−0.1332 (09)	0.0652 (09)	4.7 (6)

Table III. Intramolecular Distances for 3[a]

Os(1)–C(13)	1.89 (1)	Os(3)–O(1)	2.140 (8)
Os(1)–C(11)	1.93 (1)	O(1)–C(45)	1.24 (1)
Os(1)–C(12)	1.96 (1)	O(2)–C(45)	1.32 (1)
Os(1)–C(1)	1.99 (1)	O(2)–C(47)	1.45 (1)
Os(1)–C(41)	2.20 (1)	O(3)–C(46)	1.19 (1)
Os(1)–Os(2)	2.8011 (9)	O(4)–C(46)	1.32 (1)
Os(2)–C(21)	1.88 (1)	O(4)–C(48)	1.44 (1)
Os(2)–C(22)	1.89 (1)	N–C(1)	1.32 (1)
Os(2)–C(1)	2.09 (1)	N–C(2)	1.46 (2)
Os(2)–C(44)	2.23 (1)	N–C(3)	1.48 (2)
Os(2)–C(43)	2.23 (1)	C(41)–C(42)	1.49 (1)
Os(2)–C(42)	2.27 (1)	C(42)–C(43)	1.47 (1)
Os(2)–Os(3)	2.7931 (8)	C(42)–C(45)	1.47 (1)
Os(3)–C(33)	1.85 (1)	C(43)–C(44)	1.40 (1)
Os(3)–C(32)	1.87 (2)	C(43)–C(46)	1.52 (1)
Os(3)–C(31)	1.96 (1)	O–C (av)	1.15 (1)
Os(3)–C(44)	2.07 (1)	Os(1)···C(42)	2.88 (1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Intramolecular Bond Angles for 3[a]

C(13)–Os(1)–C(1)	105.4 (5)	C(33)–Os(3)–Os(2)	93.1 (4)
C(13)–Os(1)–C(41)	91.3 (5)	C(32)–Os(3)–C(44)	102.8 (5)
C(13)–Os(1)–Os(2)	150.8 (4)	C(32)–Os(3)–O(1)	91.2 (4)
C(11)–Os(1)–C(1)	93.3 (5)	C(32)–Os(3)–Os(2)	154.5 (3)
C(11)–Os(1)–C(41)	171.8 (5)	C(31)–Os(3)–C(44)	160.0 (5)
C(11)–Os(1)–Os(2)	96.8 (4)	C(31)–Os(3)–O(1)	87.5 (4)
C(12)–Os(1)–C(1)	157.3 (5)	C(31)–Os(3)–Os(2)	108.4 (4)
C(12)–Os(1)–C(41)	86.6 (5)	C(44)–Os(3)–O(1)	86.6 (3)
C(12)–Os(1)–Os(2)	109.5 (4)	C(44)–Os(3)–Os(2)	51.9 (3)
C(1)–Os(1)–C(41)	84.1 (4)	O(1)–Os(3)–Os(2)	84.3 (2)
C(1)–Os(1)–Os(2)	48.1 (3)	C(45)–O(1)–Os(3)	121.1 (7)
C(41)–Os(1)–Os(2)	75.7 (3)	C(45)–O(2)–C(47)	116 (1)
C(21)–Os(2)–C(1)	118.4 (6)	C(46)–O(4)–C(48)	115.6 (9)
C(21)–Os(2)–C(44)	124.7 (5)	C(1)–N–C(2)	125 (1)
C(21)–Os(2)–C(43)	132.6 (5)	C(1)–N–C(3)	121 (1)
C(21)–Os(2)–C(42)	100.9 (5)	N–C(1)–Os(1)	140.1 (9)
C(21)–Os(2)–Os(3)	78.4 (5)	N–C(1)–Os(2)	132.7 (8)
C(21)–Os(2)–Os(1)	80.8 (4)	Os(1)–C(1)–Os(2)	86.6 (4)
C(22)–Os(2)–C(1)	89.4 (4)	C(42)–C(41)–Os(1)	100.7 (7)
C(22)–Os(2)–C(44)	103.7 (4)	C(43)–C(42)–C(45)	117 (1)
C(22)–Os(2)–C(43)	130.3 (4)	C(43)–C(42)–C(41)	119.1 (8)
C(22)–Os(2)–C(42)	167.6 (4)	C(43)–C(42)–Os(2)	69.8 (6)
C(22)–Os(2)–Os(3)	99.3 (4)	C(45)–C(42)–C(41)	120 (1)
C(22)–Os(2)–Os(1)	116.1 (4)	C(45)–C(42)–Os(2)	107.1 (7)
C(1)–Os(2)–C(44)	114.7 (4)	C(41)–C(42)–Os(2)	109.8 (7)
C(1)–Os(2)–C(43)	87.8 (4)	C(44)–C(43)–C(42)	122.0 (9)
C(1)–Os(2)–C(42)	86.3 (4)	C(44)–C(43)–C(46)	118 (1)
C(1)–Os(2)–Os(3)	161.1 (3)	C(44)–C(43)–Os(2)	71.4 (6)
C(1)–Os(2)–Os(1)	45.3 (3)	C(42)–C(43)–C(46)	120 (1)
C(44)–Os(2)–C(43)	36.6 (4)	C(42)–C(43)–Os(2)	72.2 (6)
C(44)–Os(2)–C(42)	67.9 (4)	C(46)–C(43)–Os(2)	133.1 (7)
C(44)–Os(2)–Os(3)	47.0 (2)	C(43)–C(44)–Os(3)	122.1 (7)
C(44)–Os(2)–Os(1)	132.5 (3)	C(43)–C(44)–Os(2)	72.0 (6)
C(43)–Os(2)–C(42)	38.0 (4)	Os(3)–C(44)–Os(2)	81.1 (4)
C(43)–Os(2)–Os(3)	73.8 (3)	O(1)–C(45)–O(2)	120 (1)
C(43)–Os(2)–Os(1)	96.0 (3)	O(1)–C(45)–C(42)	126 (1)
C(42)–Os(2)–Os(3)	81.7 (3)	O(2)–C(45)–C(42)	113 (1)
C(42)–Os(2)–Os(1)	68.2 (3)	O(3)–C(46)–O(4)	124 (1)
Os(3)–Os(2)–Os(1)	139.15 (2)	O(3)–C(46)–C(43)	127 (1)
C(33)–Os(3)–C(44)	91.6 (4)	O(4)–C(46)–C(43)	108.9 (9)
C(33)–Os(3)–O(1)	177.4 (4)	O–C–Os (av)	177 (1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

molecular bond angles are listed in Tables IX and X, respectively. The structure of 5 consists of a triangular cluster of osmium atoms with normal metal–metal bond distances: Os(1)–Os(2) = 2.791 (1) Å, Os(1)–Os(3) = 2.785 (1) Å, and Os(2)–Os(3) = 2.735 (2) Å. The most interesting ligand in 5 is a $CH_2(NMe_2)CH_2CCO_2Me$ group that bridges all three metal atoms. The methylene group C(1) is coordinated only to Os(3). The Os(3)–C(1) distance of 2.18 (2) Å is not significantly different from the Os–C distance of 2.19 (2) Å to the carbon atom of the iminium ligand in 1. Carbon C(3) serves as a bridge across the Os(2)–Os(3) bond (Os(2)–C(3) = 2.22 (2) Å and Os(3)–C(3) = 2.18 (2) Å). The carbonyl oxygen atom of the CO_2Me group is coordinated to Os(1). The Os(1)–O(2) distance of 2.15 (1) Å is similar to that observed for compound 3. The nitrogen atom is formally positively charged, but all of the C–N distances indicate normal single-bond distances within experimental error C(1)–N = 1.54 (2) Å and C(2)–N = 1.47 (2) Å). The distance between C(3) and the carboxylate carbon atom C(4) (1.38 (3) Å) is slightly shorter than the corresponding distances in 3 (1.47 (1) Å) and 4 (1.50 (1) Å) and could indicate the existence of a partial multiple bonding between C(3) and C(4). Compound 5 contains two slightly nonlinear semibridging carbonyl ligands on atom Os(3) (Os(3)–C(32)–O(32) = 162 (2)° and Os(3)–C(33)–O(33) = 165 (2)°). The positions of the methylene hydrogen atoms on C(1) and C(2) were obtained from a difference Fourier synthesis, but they were not refined. Due to their inequivalence, they were observed as two pairs of AB doublets, one at 4.25 and 4.15 ppm (J_{H-H} = 10.8 Hz) and the other at 4.08 and 3.51 ppm (J_{H-H} = 11.6 Hz) in the ^1H NMR spectrum.

Discussion

The reaction of 1 with HC_2CO_2Me has yielded three new cluster complexes (see Scheme I). Compound 3 was formed by a combination of several transformations. These include the tail-to-tail coupling of two HC_2CO_2Me molecules, a transformation of the dimethyliminium ligand to a (dimethylamino)carbyne ligand, as in the known transformation of 1 to 2,[6] the addition of one hydrogen atom to one of the carbon atoms (C(41)) of the coupled alkynes, and the elimination of H_2.

The sequence of these events cannot be accurately predicted at this time, but the transformation of 1 to 2[6]

Table V. Positional Parameters and *B*(eq) Values for 4

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.15376 (04)	0.23030 (03)	0.72155 (05)	3.69 (2)
Os(2)	0.25861 (04)	0.07212 (03)	0.89958 (05)	3.00 (2)
Os(3)	0.39454 (04)	0.26611 (03)	0.95688 (05)	2.99 (2)
O(1)	0.1923 (08)	0.4467 (06)	1.1926 (10)	5.4 (4)
O(2)	0.3451 (08)	0.4135 (06)	1.4032 (10)	5.9 (4)
O(11)	0.2891 (11)	0.1264 (08)	0.4385 (11)	7.6 (5)
O(12)	0.0899 (11)	0.4505 (08)	0.6442 (14)	8.8 (6)
O(13)	−0.0981 (11)	0.1382 (10)	0.5228 (14)	10.7 (7)
O(21)	0.3732 (09)	−0.0809 (07)	0.6348 (12)	7.2 (5)
O(22)	−0.0118 (09)	−0.0138 (07)	0.8017 (12)	6.7 (4)
O(23)	0.3384 (09)	−0.0570 (07)	1.1687 (11)	6.4 (4)
O(31)	0.5248 (09)	0.2456 (08)	0.6640 (12)	7.2 (5)
O(32)	0.3465 (08)	0.5004 (06)	0.9428 (12)	6.5 (4)
O(33)	0.6534 (08)	0.2841 (06)	1.1973 (11)	5.8 (4)
N(1)	−0.0055 (08)	0.2797 (06)	1.0020 (11)	3.7 (4)
C(1)	0.0997 (09)	0.2580 (07)	0.9467 (12)	3.2 (4)
C(2)	−0.0172 (11)	0.2770 (09)	1.1696 (15)	5.0 (5)
C(3)	−0.1257 (12)	0.3101 (11)	0.8983 (17)	6.3 (6)
C(4)	0.2171 (09)	0.2224 (07)	1.0415 (11)	2.9 (4)
C(5)	0.3012 (09)	0.2744 (07)	1.1789 (11)	2.9 (4)
C(6)	0.2718 (11)	0.3872 (08)	1.2551 (14)	3.9 (5)
C(7)	0.3295 (15)	0.5237 (11)	1.4857 (17)	7.7 (7)
C(11)	0.2404 (13)	0.1679 (10)	0.5454 (15)	5.4 (6)
C(12)	0.1179 (13)	0.3688 (11)	0.6744 (16)	5.8 (6)
C(13)	−0.0007 (14)	0.1730 (11)	0.5980 (15)	6.1 (6)
C(21)	0.3264 (11)	−0.0270 (08)	0.7297 (14)	4.5 (5)
C(22)	0.0899 (11)	0.0188 (08)	0.8352 (14)	4.2 (5)
C(23)	0.3141 (10)	−0.0061 (08)	1.0707 (14)	4.1 (5)
C(31)	0.4712 (11)	0.2513 (08)	0.7707 (15)	4.5 (5)
C(32)	0.3635 (10)	0.4146 (09)	0.9520 (14)	4.3 (5)
C(33)	0.5572 (11)	0.2775 (07)	1.1110 (14)	3.9 (5)
H(1)	0.403 (08)	0.113 (06)	0.908 (09)	3.0

Table VI. Intramolecular Distances for 4[a]

Os(1)–C(13)	1.86 (1)	Os(3)–C(33)	1.93 (1)
Os(1)–C(12)	1.90 (1)	Os(3)–C(5)	2.296 (9)
Os(1)–C(11)	1.93 (1)	Os(3)–C(4)	2.300 (9)
Os(1)–C(1)	2.07 (1)	Os(3)–H(1)	1.92 (8)
Os(1)–Os(2)	2.8217 (7)	O(1)–C(6)	1.21 (1)
Os(1)–Os(3)	2.8995 (9)	O(2)–C(6)	1.33 (1)
Os(2)–C(22)	1.89 (1)	O(2)–C(7)	1.46 (1)
Os(2)–C(23)	1.91 (1)	N(1)–C(1)	1.29 (1)
Os(2)–C(21)	1.94 (1)	N(1)–C(2)	1.47 (1)
Os(2)–C(4)	2.126 (9)	N(1)–C(3)	1.47 (1)
Os(2)–Os(3)	2.8766 (7)	C(1)–C(4)	1.44 (1)
Os(2)–H(1)	1.65 (8)	C(4)–C(5)	1.39 (1)
Os(3)–C(31)	1.90 (1)	C(5)–C(6)	1.50 (1)
Os(3)–C(32)	1.92 (1)	O–C (av)	1.14 (1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Intramolecular Bond Angles for 4[a]

C(13)–Os(1)–Os(2)	103.1 (4)	C(5)–Os(3)–Os(1)	94.1 (2)
C(13)–Os(1)–Os(3)	163.3 (4)	C(4)–Os(3)–Os(2)	46.9 (2)
C(12)–Os(1)–Os(2)	158.4 (4)	C(4)–Os(3)–Os(1)	61.1 (2)
C(12)–Os(1)–Os(3)	100.2 (4)	Os(2)–Os(3)–Os(1)	58.49 (2)
C(11)–Os(1)–Os(2)	91.6 (4)	C(6)–O(2)–C(7)	115 (1)
C(11)–Os(1)–Os(3)	92.5 (4)	C(1)–N(1)–C(2)	124 (1)
C(1)–Os(1)–Os(2)	68.8 (2)	C(1)–N(1)–C(3)	121 (1)
C(1)–Os(1)–Os(3)	75.8 (3)	C(2)–N(1)–C(3)	114.2 (9)
Os(2)–Os(1)–Os(3)	60.35 (2)	N(1)–C(1)–C(4)	123 (1)
C(22)–Os(2)–Os(1)	84.2 (3)	N(1)–C(1)–Os(1)	137.3 (8)
C(22)–Os(2)–Os(3)	141.3 (3)	C(4)–C(1)–Os(1)	98.6 (6)
C(23)–Os(2)–Os(1)	163.4 (3)	C(5)–C(4)–C(1)	131.5 (8)
C(23)–Os(2)–Os(3)	112.6 (3)	C(5)–C(4)–Os(2)	124.1 (7)
C(21)–Os(2)–Os(1)	99.3 (3)	C(5)–C(4)–Os(3)	72.2 (5)
C(21)–Os(2)–Os(3)	106.6 (3)	C(1)–C(4)–Os(2)	103.7 (6)
C(4)–Os(2)–Os(1)	64.1 (2)	C(1)–C(4)–Os(3)	111.3 (6)
C(4)–Os(2)–Os(3)	52.1 (2)	Os(2)–C(4)–Os(3)	81.0 (3)
Os(1)–Os(2)–Os(3)	61.16 (2)	C(4)–C(5)–C(6)	120 (1)
C(31)–Os(3)–Os(2)	103.8 (3)	C(4)–C(5)–Os(3)	72.5 (5)
C(31)–Os(3)–Os(1)	85.3 (4)	C(6)–C(5)–Os(3)	111.3 (6)
C(32)–Os(3)–Os(2)	140.8 (3)	O(1)–C(6)–O(2)	124 (1)
C(32)–Os(3)–Os(1)	86.4 (3)	O(1)–C(6)–C(5)	126 (1)
C(33)–Os(3)–Os(2)	117.3 (3)	O(2)–C(6)–C(5)	110 (1)
C(33)–Os(3)–Os(1)	175.3 (3)	Os(2)–H(1)–Os(3)	107 (1)
C(5)–Os(3)–C(4)	35.2 (3)	O–C–Os (av)	177 (1)
C(5)–Os(3)–Os(2)	73.4 (2)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table VIII. Positional Parameters and *B*(eq) Values for 5

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.66944 (11)	0.189326 (48)	0.849831 (54)	2.79 (3)
Os(2)	0.461828 (97)	0.091454 (47)	0.724485 (53)	2.51 (3)
Os(3)	0.746411 (93)	0.138539 (45)	0.699887 (48)	2.21 (3)
O(1)	0.7768 (21)	−0.06957 (79)	0.87195 (89)	4.0 (7)
O(2)	0.7544 (18)	0.06712 (77)	0.89960 (78)	3.1 (6)
O(11)	0.9320 (23)	0.2784 (10)	0.9815 (11)	5.3 (9)
O(12)	0.5603 (23)	0.34671 (97)	0.7499 (11)	5.5 (9)
O(13)	0.4304 (27)	0.2086 (12)	0.9551 (14)	7 (1)
O(21)	0.3469 (22)	0.0181 (11)	0.8719 (11)	5.4 (9)
O(22)	0.2657 (21)	−0.0318 (11)	0.5932 (11)	5.4 (8)
O(23)	0.2121 (22)	0.2324 (11)	0.6747 (14)	7 (1)
O(31)	0.7956 (25)	0.30762 (92)	0.6171 (12)	6 (1)
O(32)	0.5038 (21)	0.11156 (98)	0.52355 (99)	4.7 (8)
O(33)	1.0543 (19)	0.1709 (10)	0.8360 (11)	4.4 (8)
N	0.8666 (21)	−0.03785 (93)	0.6735 (11)	3.1 (7)
C(1)	0.8715 (25)	0.0513 (11)	0.6366 (13)	2.9 (8)
C(2)	0.7154 (22)	−0.0486 (11)	0.6959 (12)	2.1 (7)
C(3)	0.6891 (21)	0.0211 (11)	0.7556 (12)	2.0 (7)
C(4)	0.7329 (26)	0.0114 (14)	0.8442 (14)	4 (1)
C(5)	0.8232 (35)	−0.0870 (15)	0.9630 (18)	5 (1)
C(6)	0.8764 (29)	−0.0994 (13)	0.6032 (17)	4 (1)
C(7)	1.0065 (27)	−0.0507 (15)	0.7539 (16)	4 (1)
C(11)	0.8358 (28)	0.2433 (13)	0.9317 (14)	3 (1)
C(12)	0.6030 (31)	0.2868 (12)	0.7885 (16)	4 (1)
C(13)	0.5176 (31)	0.1990 (14)	0.9140 (22)	6 (1)
C(21)	0.3904 (26)	0.0505 (13)	0.8165 (14)	3.2 (9)
C(22)	0.3420 (25)	0.0130 (14)	0.6426 (15)	3 (1)
C(23)	0.3084 (28)	0.1811 (17)	0.6957 (18)	5 (1)
C(31)	0.7806 (27)	0.2454 (14)	0.6467 (12)	3 (1)
C(32)	0.5740 (27)	0.1192 (12)	0.5958 (14)	3 (1)
C(33)	0.9335 (25)	0.1617 (12)	0.7954 (13)	2.9 (8)

probably does not occur first in the formation of **3** since no **3** was obtained from the independently performed reaction of **2** with HC_2CO_2Me.

In contrast, a higher yield of **4** was obtained from the reaction of **2** and HC_2CO_2Me. This strongly suggests that the **1** to **2** transformation probably does occur prior to the formation of **4**. The formation of **4** could be viewed as a combination of a rearrangement of HC_2CO_2Me to a $C{=}C(H)CO_2Me$ group and a C—C coupling to the carbyne ligand. Once again, it is not possible to predict which step occurs first. It is known that cluster complexes can transform terminal alkynes into substituted vinylidene ligands by 1,2-hydrogen shifts;[12] thus, the formation of the $C{=}C(H)CO_2Me$ grouping could precede the coupling to the carbyne ligand. On the other hand, it is also known that alkylidyne ligands will couple to alkynes,[11] and the grouping expected from the combination of HC_2CO_2Me and $CNMe_2$ (i.e. $Me_2NCC(H)C(CO_2Me)$) was reported recently in the complex $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Me_2NCC(H)C(CO_2Me)](\mu\text{-}OMe)$.[13] However, this ligand would then have to rearrange by a hydrogen shift to yield **4**. This seems unlikely, since the related compound **6a** actually rearranges in a reverse of the required direction to yield $Ru_3(CO)_9[\mu_3\text{-}Me_2NCC(H)CH](\mu\text{-}H)$.[9] The formation of **5** represents a novel transformation in which a C–N bond

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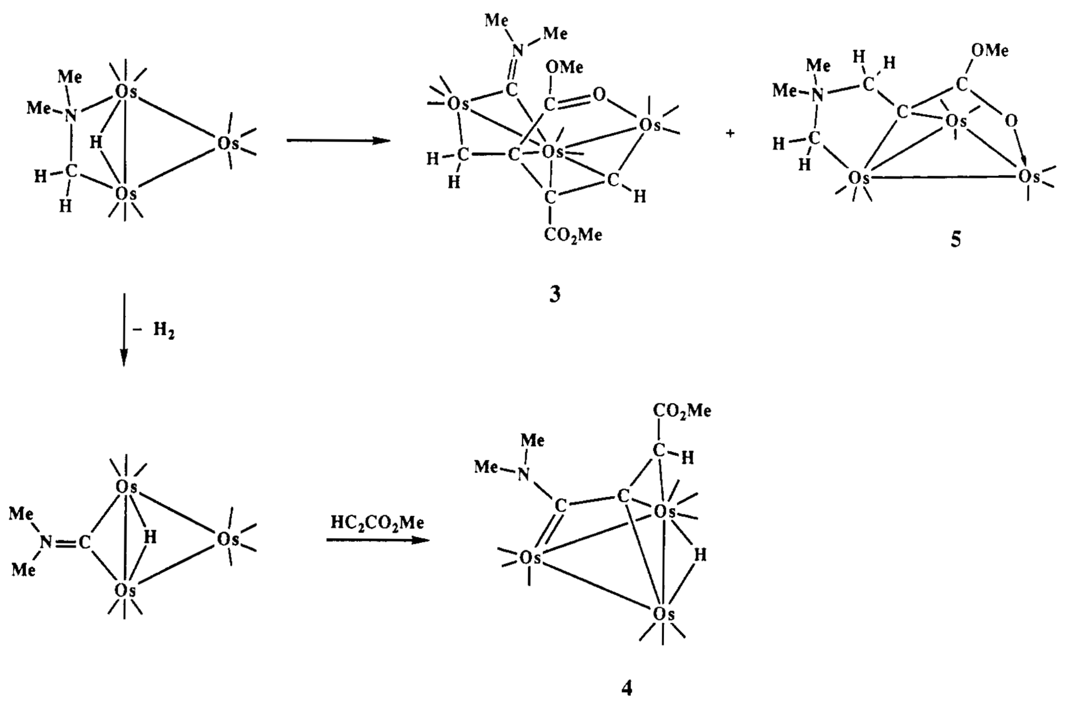
[12] (a) von Schnering, C.; Albiez, T.; Bernhardt, W.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 479. (b) Roland, E.; Vahrenkamp, H. *J. Mol. Catal.* **1983**, *21*, 233.

[13] Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 2300.

Scheme I



Scheme II

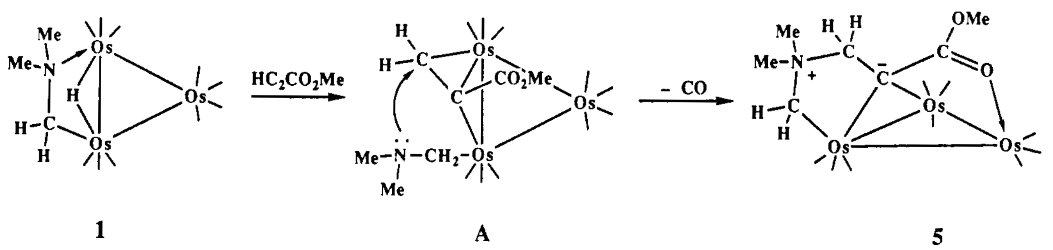


Table IX. Intramolecular Distances for 5[a]

Os(1)–C(12)	1.84 (2)	Os(3)–C(33)	1.96 (2)
Os(1)–C(11)	1.89 (2)	Os(3)–C(1)	2.18 (2)
Os(1)–C(13)	1.90 (2)	Os(3)–C(3)	2.18 (2)
Os(1)–O(2)	2.15 (1)	O(1)–C(4)	1.38 (2)
Os(1)–Os(3)	2.785 (1)	O(1)–C(5)	1.43 (3)
Os(1)–Os(2)	2.791 (1)	O(2)–C(4)	1.23 (3)
Os(2)–C(21)	1.87 (2)	N–C(2)	1.47 (2)
Os(2)–C(22)	1.90 (2)	N–C(6)	1.51 (3)
Os(2)–C(23)	1.93 (3)	N–C(7)	1.54 (3)
Os(2)–C(3)	2.22 (2)	N–C(1)	1.54 (2)
Os(2)–Os(3)	2.735 (2)	C(2)–C(3)	1.52 (2)
Os(3)–C(32)	1.95 (2)	C(3)–C(4)	1.38 (3)
Os(3)–C(31)	1.95 (2)	O–C (av)	1.15 (2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 5[a]

C(12)–Os(1)–O(2)	169.4 (8)	C(3)–Os(3)–Os(2)	52.3 (5)
C(11)–Os(1)–O(2)	91.4 (8)	C(3)–Os(3)–Os(1)	75.9 (5)
C(13)–Os(1)–O(2)	95.5 (9)	Os(2)–Os(3)–Os(1)	60.74 (4)
O(2)–Os(1)–Os(3)	85.4 (4)	C(4)–O(1)–C(5)	119 (2)
O(2)–Os(1)–Os(2)	82.0 (4)	C(4)–O(2)–Os(1)	114 (1)
Os(3)–Os(1)–Os(2)	58.76 (3)	C(2)–N–C(6)	110 (2)
C(21)–Os(2)–C(3)	96.9 (8)	C(2)–N–C(7)	110 (2)
C(22)–Os(2)–C(3)	97.1 (8)	C(2)–N–C(1)	109 (1)
C(23)–Os(2)–C(3)	162.1 (8)	C(6)–N–C(7)	110 (2)
C(3)–Os(2)–Os(3)	50.9 (4)	C(6)–N–C(1)	107 (2)
C(3)–Os(2)–Os(1)	75.2 (5)	C(7)–N–C(1)	110 (2)
Os(3)–Os(2)–Os(1)	60.51 (3)	N–C(1)–Os(3)	109 (1)
C(32)–Os(3)–C(1)	82.8 (8)	N–C(2)–C(3)	112 (1)
C(32)–Os(3)–C(3)	90.3 (7)	C(4)–C(3)–C(2)	121 (2)
C(32)–Os(3)–Os(2)	63.4 (7)	C(4)–C(3)–Os(3)	119 (1)
C(32)–Os(3)–Os(1)	118.1 (7)	C(4)–C(3)–Os(2)	106 (1)
C(31)–Os(3)–C(1)	101.0 (8)	C(2)–C(3)–Os(3)	106 (1)
C(31)–Os(3)–C(3)	175.7 (8)	C(2)–C(3)–Os(2)	120 (1)
C(33)–Os(3)–C(1)	93.5 (8)	Os(3)–C(3)–Os(2)	76.8 (6)
C(33)–Os(3)–C(3)	94.4 (7)	O(2)–C(4)–C(3)	128 (2)
C(33)–Os(3)–Os(2)	123.1 (6)	O(2)–C(4)–O(1)	117 (2)
C(33)–Os(3)–Os(1)	67.5 (7)	C(3)–C(4)–O(1)	114 (2)
C(1)–Os(3)–C(3)	81.4 (7)	O–C–Os (av)	177 (2)
C(1)–Os(3)–Os(2)	119.3 (5)	O(32)–C(32)–Os(3)	162 (2)
C(1)–Os(3)–Os(1)	148.8 (5)	O(33)–C(33)–Os(3)	165 (2)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

was formed. A reasonable mechanism for the formation of 5 is shown in Scheme II. The first step involves a homolysis of the Os–N bond, the addition of HC_2CO_2Me, and insertion of the HC_2CO_2Me ligand into the metal–hydride bond to form a σ–π-coordinated alkenyl ligand, $C(CO_2Me)CH_2$ (see intermediate A). The insertion of alkynes into M–H bonds in clusters to yield σ–π-coordinated alkenyl ligands is a well-known reaction.[14] The conversion of η^2-CH_2NMe_2 ligands to η^1-CH_2NMe_2 ligands has been observed previously.[3] The formation of 5 is completed by the addition of the uncoordinated NMe_2 group to the CH_2 group of the alkenyl ligand, and the displacement of CO and coordination of the carbonyl ox-

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[14] (a) Orpen, A. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *Acta Crystallogr.* **1978**, *B34*, 2466. (b) Guy, J. J.; Reichert, B.E.; Sheldrick, G. M. *Acta Crystallogr.* **1976**, *B32*, 3319. (c) Sappa, E.; Tiripicchio, A.; Manotti Lanfredi, A. M. *J. Organomet. Chem.* **1983**, *249*, 391. (d) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295.

ygen atom of the carboxyl group. By analogy, it is known that tertiary phosphines will add to the CH_2 group of σ–π-coordinated alkenyl groups to form the zwitterionic ligands $R_3P^+CH_2C^-R$, in which the negatively charged carbon atom bridges two metal atoms.[15]

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Supplementary Material Available: Tables of positional parameters for hydrogen atoms and anisotropic thermal parameters for all three crystal structure analyses (10 pages); tables of structure factor amplitudes (55 pages). Ordering information is given on any current masthead page.

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Crystal Structure of $Fe_2Os(CO)_{12}$, a Structural Analogue of $Fe_3(CO)_{12}$ with No Required Site Symmetry and Only a ~12:1 "Star of David" Disorder Pattern: Example of an Acentric, but Close to Centric, Structure. Some Thoughts on the Solid-State Structure of $Fe_3(CO)_{12}$

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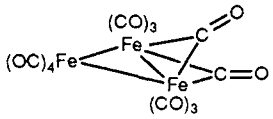
The heteroatomic trinuclear cluster $Fe_2Os(CO)_{12}$ crystallizes in the noncentrosymmetric monoclinic space group *Pn* (variation of *Pc*; C_s^2; No. 7) with $a = 8.377$ (2) Å, $b = 22.715$ (8) Å, $c = 8.953$ (2) Å, $\beta = 96.510$ (18)°, $V = 1692.6$ (8) Å^3, and $Z = 4$. The molecular packing is close to, but not exactly, that required for space group $P2_1/n$ (cf. $Fe_3(CO)_{12}$, $P2_1/n$, $a = 8.359$ (2) Å, $b = 11.309$ (2) Å, $c = 8.862$ (2) Å, $\beta = 97.00$ (2)°, $V = 831.5$ (3) Å^3, and $Z = 2$, i.e., similar except that, in the $Fe_2Os(CO)_{12}$ structure, 2_1 and *i* operations are absent and *b* is doubled). Diffraction data for $\pm h,+k,\pm l$ were collected for $2\theta = 4.5$–$50.0°$ with Mo Kα radiation. The structure was solved by Patterson and difference-Fourier methods, and refinement converged with $R_F = 4.9\%$, $R_{wF} = 4.8\%$, and GOF = 1.772 for all 5993 point-group-unique reflections ($R_F = 4.0\%$, $R_{wF} = 4.6\%$ for those 5220 data with $|F_o| > 6\sigma(|F_o|)$). There are two crystallographically distinct $Fe_2Os(CO)_{12}$ molecules in the unit cell. Each suffers an approximately 12:1 "star of David" disorder of the metal atoms. The major components are unambiguously defined and contain an $Os(CO)_4$ system linked to two $Fe(CO)_3$ units, which, in turn, are bridged by two asymmetrically bridging carbonyl ligands—i.e., a connectivity similar to that in $Fe_3(CO)_{12}$. Bond lengths of note (in Å) are as follows: molecule A, Os(A)–Fe(1A) = 2.735 (2), Os(A)–Fe(2A) = 2.740 (3), Fe(1A)–Fe(2A) = 2.589 (4), Fe(1A)–C(BR1A) = 2.245 (16), Fe(2A)–C(BR1A) = 1.939 (16), Fe(1A)–C(BR2A) = 1.918 (17), Fe(2A)–C(BR2A) = 2.224 (16); molecule B, Os(B)–Fe(1B) = 2.745 (3), Os(B)–Fe(2B) = 2.746 (3), Fe(1B)–Fe(2B) = 2.594 (4), Fe(1B)–C(BR1B) = 2.084 (20), Fe(2B)–C(BR1B) = 2.047 (19), Fe(1B)–C(BR2B) = 1.937 (17), Fe(2B)–C(BR2B) = 2.123 (17).

Introduction

The saga of the structural characterization of triiron dodecacarbonyl, $Fe_3(CO)_{12}$, has been vividly recounted by Wei and Dahl.[1] Further refinement of the crystal structure was later carried out by Cotton and Troup.[2] It is established that *in the macroscopic solid state* the molecule has structure 1 and that the molecules are statistically disordered about sites of $\bar{1}$ (C_i) symmetry in space group $P2_1/n$.



1

The heteronuclear species $Fe_2Os(CO)_{12}$ has been synthesized from $Fe_2(CO)_9$ and $H_2Os(CO)_4$.[3] The substitutional reactivity of this material has recently been studied by Shojaie and Atwood.[4] As a prelude to investigating some products of substitution, we have carried out a single-crystal X-ray diffraction study on the parent compound, $Fe_2Os(CO)_{12}$. Our results, reported below, may also have relevance toward understanding the crystal structure of $Fe_3(CO)_{12}$.

Experimental Section

Collection of X-ray Diffraction Data for $Fe_2Os(CO)_{12}$. Crystals were provided by Shojaie and Atwood.[4] A black crystal with approximate dimensions 0.30 × 0.30 × 0.33 mm was inserted into a glass capillary with its extended direction parallel to the wall of the capillary. It was then mounted in a eucentric goniometer and accurately aligned and centered on a Syntex $P2_1$ automated four-circle diffractometer. All further setup operations (i.e. determination of the crystal's unit cell parameters and orientation matrix) and collection of the intensity data were performed as described previously.[5] Details appear in Table I. The

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