Ligand Substitution Reactions in Metal Cluster Complexes. Evidence for Unusually Facile Metal–Metal Bond Cleavages in the Reactions of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ with $CNCF_3$ Including the Isolation and Structural Characterization of Intermediates

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Abstract: The reaction of $Os_3(CO)_{11}(NCMe)$ with an excess of $CNCF_3$ at 25 °C yielded two products $Os_3(CO)_{11}(\mu\text{-}CNCF_3)_2$ (**1**), 35%, and $Os_3(CO)_{10}(\mu\text{-}CNCF_3)_2$ (**2**), 4%. Compound **1** was converted to **2** in 87% yield at 80 °C. Both compounds **1** and **2** were characterized crystallographically. Compound **1** consists of an open triosmium cluster with $CNCF_3$ ligands bridging each of the two metal–metal bonds. Compound **2** consists of a closed triosmium cluster with two $CNCF_3$ ligands bridging the same edge of the cluster. Compound **2** was the principal product obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with an excess of $CNCF_3$; however, two additional products $Os_3(CO)_{10}(NCMe)(\mu\text{-}CNCF_3)_2$ (**3**), 17% yield, and $Os_3(CO)_9(NCMe)(\mu\text{-}CNCF_3)_2$ (**4**), 2% yield, were also obtained. Compound **3** is structurally analogous to **1** except for the presence of a NCMe ligand coordinated to the central osmium atom. Compound **4** is analogous to **2** except for the presence of a NCMe ligand coordinated to the unique metal atom. When heated to reflux in CH_2Cl_2, **3** was transformed into a mixture of **2** and **4**. Although they can be isolated, compounds **1** and **3** are also intermediates en route to **2** and **4**. Their characterization demonstrates the viability of previously proposed cluster-opening ligand addition steps as part of a mechanism of ligand substitution in the reactions of some metal cluster complexes. Crystal data: for **1**, space group = $Pca2_1$, a = 14.456 (2) Å, b = 11.077 (2) Å, c = 14.301 (4) Å, Z = 4, 1714 reflections, R = 0.029; for **2**, space group = $Pbcn$, a = 26.940 (6) Å, b = 11.361 (3) Å, c = 14.450 (2) Å, Z = 8, 1644 reflections, R = 0.034; for **3**, space group = $P\bar{1}$, a = 10.390 (3) Å, b = 15.416 (3) Å, c = 8.079 (1) Å, α = 99.16 (2)°, β = 104.61 (2)°, γ = 94.40 (2)°, Z = 2, 2475 reflections, R = 0.024; for **4**, space group = $P2_1/n$, a = 19.065 (4) Å, b = 13.080 (2) Å, c = 9.418 (2) Å, β = 90.12 (2)°, Z = 4, 2362 reflections, R = 0.036.

Introduction

The mechanisms of ligand addition and substitution are fundamental to understanding the reactivity of metal carbonyl cluster complexes.[1] Ligand substitution and fragmentation reactions of metal carbonyl cluster complexes have been shown to involve a two-term rate expression, eq 1, which has been interpreted in terms

$$k_{obs} = k_1 + k_2[L] \tag{1}$$

of dissociative and associative mechanisms, respectively.[1,2] A variety of structures having a cleaved metal–metal bond have been proposed to describe possible intermediates formed by the addition of a ligand to di- and trinuclear metal complexes.[1,2] The opening and closing of metal–metal bonds by the addition and elimination of nucleophiles have been *observed* for some high-nuclearity clusters and for selected small clusters that are stabilized by bridging ligands.[3] The trinuclear metal carbonyl cluster complexes of the iron subgroup, $M_3(CO)_{12}$ (M = Fe, Ru, Os), are the starting points for the study of a wide range of today's transition metal cluster complexes.[4] In this report, the reactions of the activated cluster complexes $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ with $CNCF_3$ are described. Two addition products, $Os_3(CO)_{11}(\mu\text{-}CNCF_3)_2$ (**1**) and $Os_3(CO)_{10}(NCMe)(\mu\text{-}CNCF_3)_2$ (**3**), and two substitution products, $Os_3(CO)_{10}(\mu\text{-}CNCF_3)_2$ (**2**) and $Os_3(CO)_9(NCMe)(\mu\text{-}CNCF_3)_2$ (**4**), have been obtained. It was shown that the substitution products **2** and **4** can be obtained from the addition products by ligand elimination and thus can be regarded as intermediates in an overall process of ligand substitution that involves metal–metal bond cleavage as a central feature.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored over 4-Å molecular sieves. CF_3NC was prepared by the previously reported procedure.[5] $Os_3(CO)_{11}NCMe$[6] and $Os_3(CO)_{10}(NCMe)_2$[7] were prepared by the published procedures. All other reagents were purchased from Aldrich and were used as received. All chromatographic separations were performed in air on TLC plates (0.25-mm silica gel 60 F_{254}). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. ^{19}F NMR spectra were taken at 188.3 MHz on a Bruker AM-200 spectrometer using $CFCl_3$ as a reference. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Os_3(CO)_{11}(NCMe)$ with CF_3NC. By use of a vacuum line system, approximately 20 mL of CH_2Cl_2 was condensed onto a 150.8-mg amount (0.164 mmol) of $Os_3(CO)_{11}(NCMe)$ in a 50-mL Schlenk tube. The vessel was then warmed to dissolve most of the triosmium compound. After recooling with liquid nitrogen, 0.82 mmol of $CNCF_3$ was condensed into the reaction flask. The mixture was warmed to 25 °C within 1 min

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Table I. Crystallographic Data for Diffraction Studies

	1	**2**	**3**	**4**
empirical formula	$Os_3F_3O_{11}N_2C_{15}$	$Os_3F_3O_{10}N_2C_{14}$	$Os_3F_6O_{10}N_3C_{16}H_3$	$Os_3F_6O_9N32C_{15}H_3$
formula weight	1068.76	1040.75	1081.80	1053.79
crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
a (Å)	14.456 (2)	26.940 (6)	10.390 (3)	19.065 (4)
b (Å)	11.077 (2)	11.361 (3)	15.416 (3)	13.080 (2)
c (Å)	14.301 (4)	14.450 (2)	8.079 (1)	9.418 (2)
α (deg)			99.16 (2)	
β (deg)			104.61 (2)	90.12
γ (deg)			94.40 (2)	
V (Å^3)	2290 (1)	4423 (1)	1226.9 (5)	2348 (1)
space group	$Pca2_1$ (No. 29)	$Pbcn$ (No. 60)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Z	4	8	2	4
D_{calc} (g/cm^3)	3.10	3.13	2.97	2.98
μ(Mo Kα) (cm^{-1})	167.3	173.15	156.1	163.0
abs corr	empirical	empirical	empirical	analytical
temp (°C)	20	20	20	20
$2\theta_{max}$ (deg)	48.0	40.0	43.0	43.0
no. of obs ($I > 3\sigma(I)$)	1714	1644	2475	2363
no. of variables	333	306	355	322
residuals: R, R_w	0.029; 0.029	0.034; 0.038	0.024; 0.029	0.036, 0.041
goodness of fit	1.36	1.90	1.82	2.55
max shift in final cycle	0.00	0.01	0.08	0.45
largest peak in final diff map (e/Å^3)	1.42	1.19	0.62	1.09

and stirred for an additional 5 min. During this time, the color of the solution changed from yellow to orange. Finally, the Schlenk tube was flushed with nitrogen, and the solvent was evaporated under a stream of nitrogen. The residue was then washed with 30 mL of dichloromethane/pentane solution (2/1), giving 61 mg of $Os_3(CO)_{11}(\mu\text{-}CNCF_3)_2$ (**1**) as a yellow powder (35%). The washing was then evaporated to dryness, and the residue was isolated by TLC using a dichloromethane-/hexane 1/4 solvent mixture to yield 6.5 mg of violet $Os_3(CO)_{10}(\mu\text{-}CNCF_3)_2$ (**2**) (4%). Spectral data for **1**: IR (CH_2Cl_2) ν(CO) 2121 (s), 2073 (m), 2059 (vs), 2037 (m), 1996 (w), ν(CN) 1625 (m), 1588 (w) cm^{-1}; ^{19}F NMR (acetone-d_6, 239 K) δ = −59.71 (s, 3F), −59.95 (s, 3F). Anal. Calcd (found) for $Os_3C_{15}F_6N_2O_{11}$: C, 16.86 (16.85); N, 2.62 (3.26). Spectral data for **2**: IR (hexane) ν(CO) 2123 (w), 2079 (vs), 2050 (s), 2033 (s), 2006 (m), ν(CN) 1718 (w), 1696 (vw), 1661 (m) cm^{-1}; ^{19}F NMR (acetone-d_6, 297 K) δ = −59.28 (s, 6F). Anal. Calcd (found) for $Os_3C_{14}F_6N_2O_{10}$: C, 16.16 (15.93); N, 2.69 (2.87).

Thermolysis of 1. A benzene (15 mL) solution of **1** (36 mg, 0.0337 mmol) was heated to reflux for 5 min while the color changed from yellow to red. After the solution was cooled to room temperature, the solvent was evaporated to dryness, and the residue was chromatographed by TLC using a dichloromethane/hexane 1/4 solvent mixture to yield 30.4 mg of **2** (87%).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with CF_3NC. By use of a vacuum line system, approximately 25 mL of CH_2Cl_2 was condensed onto a 223-mg amount (0.233 mmol) of $Os_3(CO)_{10}(NCMe)_2$ in a 50-mL Schlenk tube. The vessel was warmed to dissolve most of the triosmium compound. After cooling with liquid nitrogen, 1.3 mmol of $CNCF_3$ was condensed into the reaction flask. The mixture was warmed to 25 °C within 1 min and stirred for an additional 5 min. During this time, the color of the solution changed from yellow to orange. Finally, the Schlenk tube was flushed with nitrogen, and the solvent was evaporated in a stream of nitrogen. The residue was separated by TLC using a dichloromethane-/hexane 1/1 solvent mixture to yield 108 mg of **2** (0.104 mmol, 45%), 5.0 mg of violet $Os_3(CO)_9(NCMe)(\mu\text{-}CNCF_3)_2$ (**4**) (0.0047 mmol, 2%), and 42.0 mg of orange $Os_3(CO)_{10}(NCMe)(\mu\text{-}CNCF_3)_2$ (**3**) (0.039 mmol, 17%) in the order of elution. Spectral data for **3**: IR (CH_2Cl_2) ν(CO) 2129 (w), 2110 (s), 2045 (vs), 2032 (s, sh), 2012 (m, br), 1971 (w), ν(CN) 1617 (m), 1588 (w) cm^{-1}; ^{19}F NMR (in CD_2Cl_2 at 293 K vs $CFCl_3$) δ = −60.1 (s, 3F), −61.4 (s, 3F); ^{1}H NMR (in CD_2Cl_2 at 293 K vs TMS) δ = 2.92 (s, 3H). Spectral data for **4**: IR (hexane) ν(CO) 2100 (w), 2065 (vs), 2057 (vs), 2029 (m), 2018 (s), 2001 (w), 1986 (w), ν(CN) 2215 (w), 1705 (w), 1692 (vw), 1636 (m) cm^{-1}; ^{19}F NMR (in CH_2Cl_2 at 293 K vs $CFCl_3$) δ = −58.5 (s, 3F), −59.1 (s, 3F); ^{1}H NMR (in CH_2Cl_2 at 293 K vs TMS) δ = 2.90 (s, 3H).

Thermolysis of 3. A solution of **3** (11.5 mg, 0.0106 mmol) in 10 mL of CH_2Cl_2 was heated to reflux for 40 min. During this time, the color changed from yellow to red. After removal of the solvent, the residue was separated by TLC using a dichloromethane/hexane 1/1 solvent mixture to yield 1.2 mg of **2** (0.0012 mmol, 11%), 2.6 mg of **4** (0.0025 mmol, 23%), and 4.8 mg of starting material **3** (42%).

Reaction of 2 with Me_3NO in NCMe. An acetonitrile solution (2 mL) of Me_3NO (3.05 mg, 0.041 mmol) was added dropwise to a solution containing 23.5 mg of **2** (0.0226 mmol), 10 mL of dichloromethane, and 5 mL of acetonitrile. The resulting solution was then stirred at room temperature for 20 min. After separation, 4.2 mg of **2** (18%) and 4.3 mg of **4** (0.0040 mmol, 18%), in addition to an unstable orange complex (about 10 mg), were obtained.

Reaction of 4 with Carbon Monoxide. A dichloromethane solution (20 mL) of **4** (12.4 mg, 0.012 mmol) was stirred under 1 atm of CO at room temperature for 5 h. After TLC separation, 5.5 mg of **2** (0.0050 mmol, 42%) was isolated.

Crystallographic Analyses. Crystals of each compound suitable for X-ray diffraction studies were obtained from solutions in mixtures of dichloromethane/hexane by cooling to 4 °C. All crystals used for intensity data collection were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atomic scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Lorentz/polarization (Lp) and absorption corrections were applied to the data for each structure. Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02(I_{net})^2)^2]^{1/2}/Lp$.

Compound **1** crystallized in the orthorhombic crystal system. The systematic absences observed during the collection of data were consistent with either of the space groups $Pbcm$ or $Pca2_1$. Efforts to solve the structure in the space group $Pbcm$ were unsuccessful. A solution with a high-quality refinement was obtained in the space group $Pca2_1$, thus confirming the correctness of this space group. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All the atoms were refined with anisotropic thermal parameters.

Compound **2** crystallized in the orthorhombic crystal system. The space group $Pbcn$ was identified uniquely on the basis of 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 the atoms were refined with anisotropic thermal parameters, except C(2) and N(1) of the $CNCF_3$ ligands, which produced negative values with anisotropic thermal parameters. These two atoms were thus refined isotropically.

Compound **3** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and

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

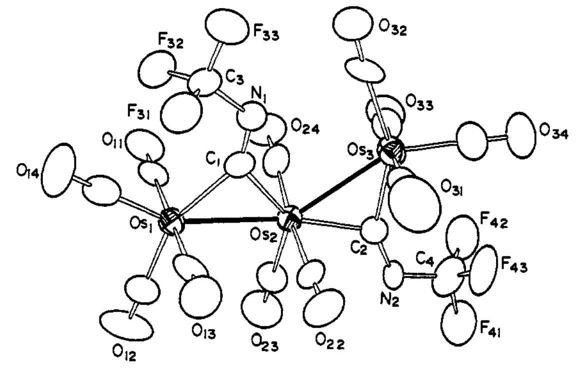

Figure 1. ORTEP diagram of $Os_3(CO)_{11}(\mu\text{-}CNCF_3)_2$ (**1**). Selected interatomic distances (Å) and angles (deg): Os(1)–Os(2) = 2.859 (1), Os(2)–Os(3) = 2.847 (1), Os(1)–C(1) = 2.07 (2), Os(2)–C(1) = 2.13 (2), Os(2)–C(2) = 2.10 (2), Os(3)–C(2) = 2.01 (2), C(1)–N(1) = 1.27 (2), C(2)–N(2) = 1.35 (2), Os(1)–Os(2)–Os(3) = 140.39 (4), C(1)–N(1)–C(3) = 120 (2), C(2)–N(2)–C(4) = 117 (2).

refinement of the structure. 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. The hydrogen atoms on the NCMe ligand were located and refined with independent isotropic thermal parameters.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. One CF_3 group, C(4), exhibited a 2-fold rotational disorder. A 50/50 disorder model employing independent isotropic thermal parameters for the fluorine atoms at each site was successfully refined. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the NCMe ligand were calculated by assuming idealized geometry and C–H = 0.95 Å. These were added to the structure factor calculations, but they were not refined.

Results and Discussion

Two products, $Os_3(CO)_{11}(\mu\text{-}CNCF_3)_2$ (**1**), 35% yield, and $Os_3(CO)_{10}(\mu\text{-}CNCF_3)_2$ (**2**), 4% yield, were obtained from the reaction of $Os_3(CO)_{11}(NCMe)$ with an excess of $CNCF_3$ in CH_2Cl_2 solvent at 25 °C. In an independent step, it was shown that compound **1** can be converted to **2** in a good yield (87%) simply by heating to 80 °C for 5 min. Both complexes were characterized by IR and ^{19}F NMR spectroscopy and by single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **1** is shown in Figure 1. The molecule was found to consist of an *open* triosmium cluster with a $CNCF_3$ ligand bridging each of the two metal–metal bonds. The Os–Os bond distances of 2.859 (1) and 2.847 (1) Å are slightly shorter than those in the closed cluster complex $Os_3(CO)_{12}$, 2.877 (3) Å.[9] The bridging $CNCF_3$ ligands are nonlinear, C–N–C = 120 (2) and 117 (2)°, as observed previously in the complexes $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CNCF_3)$,[10] $Fe_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CNCF_3)$,[11] and $[Cp^*Mo(CO)_2(\mu\text{-}CNCF_3)]_2$.[12] They are also structurally inequivalent. This inequivalence was confirmed in solution by ^{19}F NMR spectroscopy by the observation of two resonances of equal intensity at −34 °C at δ = −59.71 and −59.95 ppm. However, at higher temperatures, the resonances are broadened with a coalescence at 283 K, due to a dynamical averaging process. At 296 K, only a broad singlet is observed at δ = −60.2 ppm. The complex contains 50 valence electrons, and with two metal–metal bonds, each metal atom achieves an 18-electron configuration.

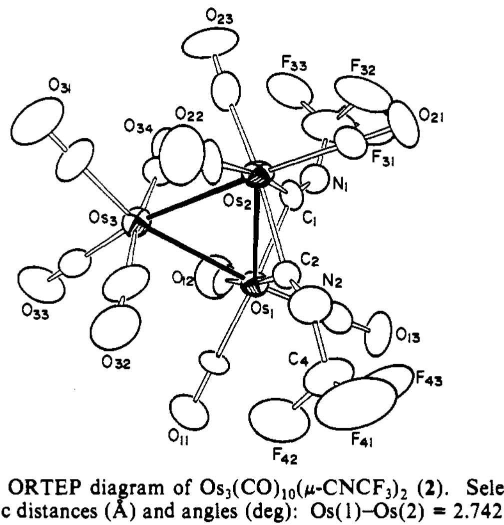

Figure 2. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}CNCF_3)_2$ (**2**). Selected interatomic distances (Å) and angles (deg): Os(1)–Os(2) = 2.742 (1), Os(1)–Os(3) = 2.850 (1), Os(2)–Os(3) = 2.850 (1), Os(1)–C(1) = 2.15 (2), Os(2)–C(1) = 2.11 (2), Os(1)–C(2) = 2.11 (2), Os(2)–C(2) = 2.15 (2), C(1)–N(1) = 1.24 (3), C(2)–N(2) = 1.22 (2), C(1)–N(1)–C(3) = 125 (2), C(2)–N(2)–C(4) = 126 (2).

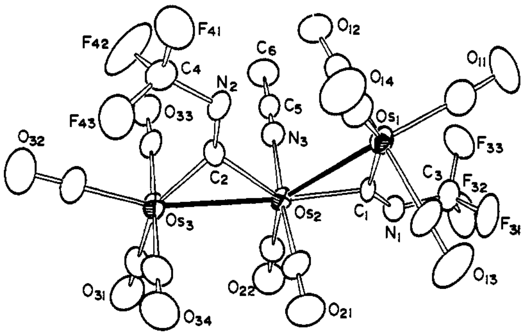

Figure 3. ORTEP diagram of $Os_3(CO)_{10}(NCMe)(\mu\text{-}CNCF_3)_2$ (**3**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Os(1)–Os(2) = 2.8233 (9), Os(2)–Os(3) = 2.863 (1), Os(1)–C(1) = 2.08 (1), Os(2)–C(1) = 2.06 (1), Os(2)–C(2) = 2.13 (1), Os(3)–C(2) = 2.06 (1), C(1)–N(1) = 1.27 (2), C(2)–N(2) = 1.27 (1), Os(1)–Os(2)–Os(3) = 137.06 (2), C(1)–N(1)–C(3) = 121.0 (9), C(2)–N(2)–C(4) = 120 (1).

An ORTEP drawing of the molecular structure of **2** is shown in Figure 2. The molecule consists of a closed triangular cluster of three osmium atoms with ten linear carbonyl ligands. There are two trifluoromethyl isocyanide ligands which bridge the same edge of the cluster. As expected, the ligand-bridged metal–metal bond distance, 2.742 (1) Å, is significantly shorter than the unbridged metal–metal bond distances, 2.850 (1) Å. The isocyanide ligands are again nonlinear, but the bend is not as large as for those in **1**, 125 (2) and 126 (2)°. In this structure, the isocyanide ligands are chemically equivalent, and they exhibit a single fluorine resonance, δ = −59.28 ppm, in the ^{19}F NMR spectrum. The presence of the two bridging ligands makes this structure analogous to those of $Fe_3(CO)_{10}(\mu\text{-}CO)_2$,[13] $Fe_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CNCF_3)$,[11] and $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CNCF_3)$.[10]

The principal product of the reaction of $Os_3(CO)_{10}(NCMe)_2$ with an excess of $CNCF_3$ was **2**, 45% yield, obtained by the substitution of the two labile NCMe ligands with $CNCF_3$ ligands. However, the two additional products $Os_3(CO)_{10}(NCMe)(\mu\text{-}CNCF_3)_2$ (**3**), 17% yield, and $Os_3(CO)_9(NCMe)(\mu\text{-}CNCF_3)_2$ (**4**), 2% yield, were also obtained. Compounds **3** and **4** were both characterized by IR and ^{19}F NMR spectroscopy and by single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **3** is shown in Figure 3. This complex is similar to that of **1** consisting of an *open* triosmium cluster with $CNCF_3$ ligands bridging each of the two metal–metal bonds. The only significant difference is the presence of a NCMe ligand in the place of a CO ligand on the central osmium Os(2). As in **1**,

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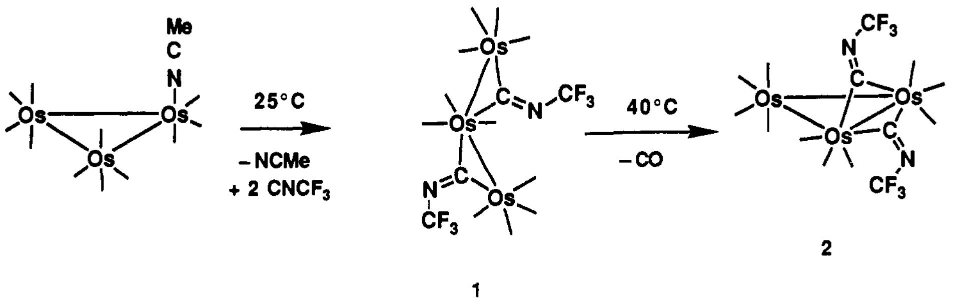
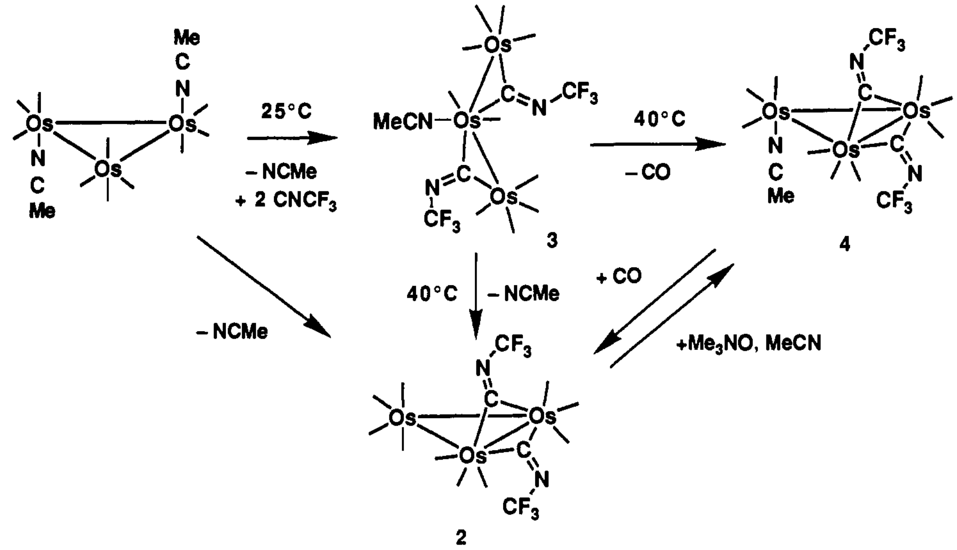
Scheme I



Scheme II



the $CNCF_3$ ligands are inequivalent, and at 293 K, the ^{19}F NMR spectrum shows two singlets at $\delta = -60.1$ and -61.4 ppm which are slightly broadened by an exchange process which is probably similar to that which also occurs in **1**.

An ORTEP drawing of the molecular structure of **4** is shown in Figure 4. This complex is similar to that of **2**, consisting of a closed triosmium cluster with $CNCF_3$ ligands bridging the same metal–metal bond. The only significant difference between **4** and **2** is the presence of a NCMe ligand in an axial coordination site on the osmium atom Os(2). Due to the presence of the NCMe ligand, the bridging $CNCF_3$ ligands are inequivalent, and accordingly, two singlets were observed at $\delta = -58.5$ and -59.1 ppm in the ^{19}F NMR spectrum at 293 K. Compound **4** can also be obtained (18% yield) by treatment of **2** with Me_3NO in NCMe at 25 °C. The reaction of **4** with CO at 1 atm and 25 °C gave **2** in 42% yield after 5 h.

Compound **1** was formed by the displacement of the labile NCMe ligand of $Os_3(CO)_{11}(NCMe)$ and the addition of two molecules of $CNCF_3$; see Scheme I. At present, we have no evidence concerning the sequence of the two steps. However, it was shown that **1** can be converted to **2**. It was also demonstrated that **4** can be obtained from **3**. When compound **3** was refluxed in CH_2Cl_2 solvent for 40 min, it was transformed partially into **2** (11%) and **4** (23%) by the loss of NCMe and CO ligands, respectively; see Scheme II. However, the slowness of this transformation suggests that the bulk of the **2** formed in the original reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CNCF_3$ was not formed via **3** as an intermediate but was most likely formed by a direct substitution of the two NCMe ligands. The surprising formation of compound **3** in the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CNCF_3$ indicates that there is also a mechanism of ligand addition involving the cleavage of a metal–metal bond that is sufficiently low in energy that it competes with the rate of simple displacement of the NCMe ligands to yield **2**. Since **4** is formed in very small amounts in the original reaction, it is probable that all of **4** is formed via **3**. Thus, both open cluster complexes could be viewed as intermediates of a ligand substitution mechanism that proceeds by a ligand addition step involving the cleavage of a metal–metal bond.[1,2] It is quite surprising that the activation energy for the bond cleavage mechanism that yields **3** is so low in energy that it competes effectively with a mechanism of simple substitution of the NCMe ligands that yields **2** directly.[14] The latter mechanism probably does not involve a metal–metal bond cleavage step.

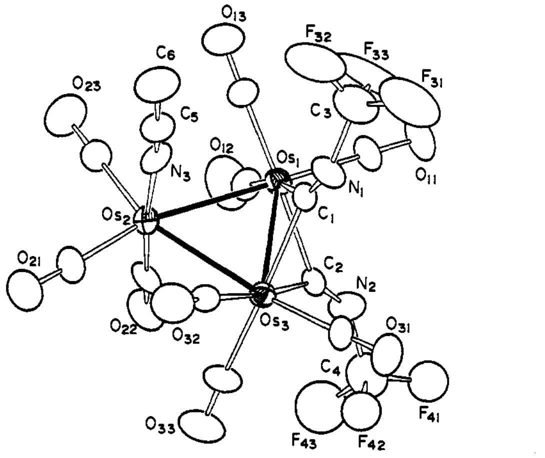


Figure 4. ORTEP diagram of $Os_3(CO)_9(NCMe)(\mu\text{-}CNCF_3)_2$ (**4**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Os(1)–Os(2) = 2.736 (1), Os(1)–Os(3) = 2.7379 (9), Os(2)–Os(3) = 2.8329 (9), Os(1)–C(1) = 2.08 (2), Os(3)–C(1) = 2.13 (2), Os(1)–C(2) = 2.12 (2), Os(3)–C(2) = 2.09 (2), C(1)–N(1) = 1.25 (2), C(2)–N(2) = 1.21 (2), C(1)–N(1)–C(3) = 120 (1), C(2)–N(2)–C(4) = 124 (2).

Brodie et al. have recently proposed a ligand-bridged structure

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[14] Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* 1977, *124*, C19.

for intermediates traversed in the ligand substitution processes by a cluster-opening ligand addition mechanism that is amazingly similar to those observed for **1** and **3**.[1a] We feel that the isolation and characterization of **1** and **3** provide strong support for the viability and importance of such bond cleavage mechanisms for ligand substitution processes in metal cluster complexes.

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Supplementary Material Available: For all four of the structural analyses, tables of hydrogen atom positional parameters and anisotropic thermal parameters (27 pages); listings of structure factor amplitudes (58 pages). Ordering information is given on any current masthead page.

Rearrangement of a Propargyl Vinyl Rhenium Complex to a Rhenium Allenyl Vinyl Ketone Complex

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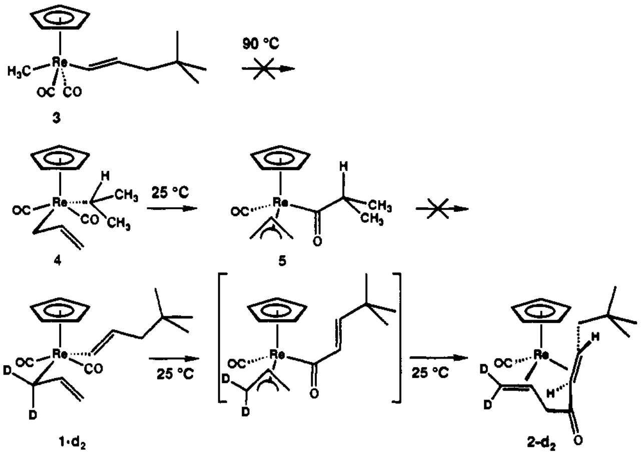
Abstract: An η^1- to η^3-propargyl rearrangement promotes vinyl migration to CO in *trans*-$C_5H_5(CO)_2Re(CH_2C{\equiv}CH)$-$((E)$-$CH{=}CHCH_2CMe_3)$ (**7**) which eventually leads to the formation of allenyl vinyl ketone complex $C_5H_5(CO)Re$-$(\eta^2,\eta^2$-$H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**8**). This allenyl vinyl ketone complex **8** undergoes additional transformations at room temperature leading to the diastereomeric allenyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2$-$H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**9**) by complexation of rhenium to the opposite face of the vinyl group and to the π-allyl σ-vinyl rhenium complex $C_5H_5(CO)Re[\eta^3$(*exo,syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**10**) by a net [1,5] hydrogen migration. Upon heating at 105 °C, allenyl vinyl ketone complex **9** rearranged to the isomeric π-allyl σ-vinyl rhenium complex $C_5H_5(CO)Re[\eta^3$(*endo,-syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**). When the first formed π-allyl σ-vinyl rhenium complex **10** was heated at 105 °C, it first rearranged to allenyl vinyl ketone complex **9** and then to the more stable π-allyl σ-vinyl rhenium complex **11**. Two different mechanisms can account for the interconversion of allenyl vinyl ketone complexes with π-allyl σ-vinyl rhenium complexes. One involves a [1,5] sigmatropic hydrogen shift over the unsaturated organic fragment and the second involves transfer of hydrogen via a rhenium hydride intermediate.

Introduction

We recently reported the unusually facile rearrangement of the allyl vinyl rhenium complex $C_5H_5(CO)_2Re(CH_2CH{=}CH_2)$-$((E)$-$CH{=}CHCH_2CMe_3)$ (**1**) to the allyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2$-$H_2C{=}CHCH_2COCH{=}CHCH_2CMe_3)$ (**2**).[1,2] In contrast, the methyl vinyl rhenium complex *trans*-C_5H_5-$(CO)_2Re(CH_3)((E)$-$CH{=}CHCH_2CMe_3)$ (**3**) was stable for hours at 90 °C. A key to understanding the mechanism of formation of **2** was the observation that the isopropyl allyl rhenium complex *trans*-$C_5H_5(CO)_2Re(CH_2CH{=}CH_2)(CHMe_2)$ (**4**) rearranged to the stable η^3-allyl acyl complex $C_5H_5(CO)Re$(*exo*-η^3-$CH_2CHCH_2)(COCHMe_2)$ (**5**), which did not undergo reductive elimination to give a ketone. A second important observation came from a deuterium labeling study which showed that C_5H_5-$(CO)_2Re(CD_2CH{=}CH_2)((E)$-$CH{=}CHCH_2CMe_3)$ (**1**-*d*) with deuterium label on the sp^3 allyl carbon rearranged to C_5H_5-$(CO)Re(\eta^2,\eta^2$-$D_2C{=}CHCH_2COCH{=}CHCH_2CMe_3)$ (**2**-*d*) which had deuterium on the sp^2 allyl carbon. The net result of the conversion of **1** to **2** is the coupling of the allyl and vinyl groups to CO with coordination of both carbon–carbon double bonds to rhenium. Allyl vinyl ketone complex **2** has an interesting geometry in which the alkene ligands are "crossed". The double bond of the allyl ligand is roughly parallel to the plane of the cyclopentadienyl ligand, while the vinyl ligand coordinates roughly perpendicular to that plane.[3]

Scheme I



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[1] Casey, C. P.; Vosejpka, P. C.; Gavney, J. A., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4083.

[2] The rhenium allyl vinyl ketone complex **2** contains three stereogenic centers: the rhenium, the enantioface of the allyl ligand, and the enantioface of the enone ligand. The kinetically formed isomer is the *RRR* (*SSS*) diastereomer. The rhenium allyl vinyl ketone complex **6** is the *RSS* (*SRR*) diastereomer, which corresponds to bonding of the rhenium atom to the opposite enantiofaces of the alkene ligands from **2**.

[3] The angle between the plane defined by the Cp centroid, Re, and the alkene centroid and the plane defined by Re and the two carbons of the alkene is 90° for a "parallel" conformation and 0° for a "perpendicular" conformation. (In the "parallel" conformation the alkene C=C bond is parallel to the plane of the Cp ring.)

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