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Ester and amide functionalized alkylidyne triosmium clusters. Rearrangement to acyl-coordinated alkylidene complexes

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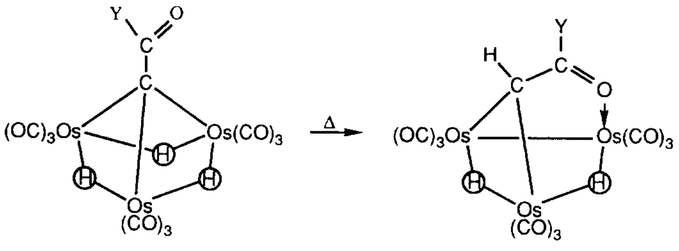
Abstract

Treatment of $H_3Os_3(CO)_9(\mu_3\text{-CBr})$ (**1**) with excess aluminum chloride in dichloromethane under an atmosphere of carbon monoxide, followed by quenching with methanol, provides $H_3Os_3(CO)_9(\mu_3\text{-CCO}_2Me)$ (**2**) (69%). Analogous reactions quenched with diethylamine or *N*-methylaniline give $H_3Os_3(CO)_9(\mu_3\text{-CC(O)NEt}_2)$ (**3**) (44%) or $H_3Os_3(CO)_9(\mu_3\text{-CC(O)NMePh})$ (**4**) (40%), respectively. The same products are obtained when $[H_3Os_3(CO)_9(CCO)^+]$ (generated in situ by protonating $H_2Os_3(CO)_9(CCO)$) is treated with excess methanol, diethylamine or *N*-methylaniline. Compound **2** is transesterified to the ethyl ester $H_3Os_3(CO)_9(\mu_3\text{-CCO}_2Et)$ (**5**), either when dissolved in concentrated sulfuric acid and quenched with ethanol or when heated in ethanol in the presence of a catalytic amount of sulfuric acid. Pyrolysis of the alkylidyne compounds **2** and **3** in hot toluene causes rearrangement to the alkylidene tautomers $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-CHC(O)OMe})$ (**6**) or $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-CHC(O)NEt}_2)$ (**7**) in high yield; the indicated structure for these compounds involves an alkylidene moiety spanning two osmium atoms with the acyl group bridging to the third osmium center. Under parallel conditions at 125 °C, the rearrangement requires 5.5 h for the ester (**2** → **6**) but only 10 min for the amide (**3** → **7**). The significance of this rate difference in consideration of mechanisms for the alkylidyne to alkylidene rearrangement is discussed.

Introduction

The development of reactions for the systematic functionalization of cluster compounds is an important goal in organometallic cluster chemistry [1,2]. Seyferth and coworkers [3] showed that treatment of halomethylidyne tricobalt clusters, e.g., $Co_3(CO)_9(\mu_3\text{-CBr})$, with excess aluminium chloride causes transformation into the "acylium" ion $[Co_3(CO)_9(CCO)^+]$, which could be trapped by alcohols and amines to form ester and amide derivatives. Keister and Horling [4] demonstrated an analogous transformation of $H_3Ru_3(CO)_9(\mu_3\text{-CBr})$ into $H_3Ru_3(CO)_9(\mu_3\text{-CCO}_2CH_3)$; this presumably proceeds via $[H_3ru_3(CO)_9(CCO)^+]$, which has been prepared by an alternative route and shown to give the methyl ester upon exposure to methanol [5]. In a preliminary communication [6] it was mentioned that the analogous triosmium compound $H_3Os_3(CO)_9(\mu_3\text{-CCO}_2CH_3)$ could be prepared directly from $[H_3Os_3(CO)_9(CCO)^+]$, itself generated from $H_2Os_3(CO)_9(CCO)$ [6,7],



(1)

Y = OCH_3, **2**
= $N(C_2H_5)_2$, **3**

Y = OCH_3, **6**
= $N(C_2H_5)_2$, **7**

or more conveniently by the aluminum chloride-mediated carbomethoxylation of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ [2]. We now report the details of these reactions involving the methyl ester compound together with related reactions leading to previously unreported ethyl ester and amide derivatives. We also describe the rearrangement of these acyl-functionalized alkylidyne compounds into acyl-coordinated alkylidene derivatives (see eqn. 1), a rearrangement that has no parallel in tricobalt cluster chemistry. Subsequent to the actual completion of our work [8], Keister, Churchill, and coworkers [9] reported the analogous rearrangement with $H_3Ru_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ and determined the structure of the alkylidene product. However, our specific observations on *both* ester and amide derivatives allow further comment on the probable mechanism of this rearrangement together with its relation to other rearrangements of triosmium alkylidyne compounds studied more recently [10,11].

Experimental Section

General Procedures

Solvents used were reagent grade and were distilled under nitrogen from the following drying agents prior to use: tetrahydrofuran and toluene from sodium/benzophenone, dichloromethane from phosphorus pentoxide, methanol from magnesium methoxide, and ethanol from potassium carbonate. Diethylamine and *N*-methylaniline were distilled from barium oxide. Aluminum trichloride (Aldrich) was handled under nitrogen. Literature procedures were used for the preparation of $Os_3(CO)_{12}$ from OsO_4 (Alfa) [12], $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ from $H_3Os_3(CO)_9(\mu_3\text{-}COCH_3)$ [4], and $H_2Os_3(CO)_9(CCO)$ from $Os_3(CO)_{11}(CH_2)$ [6].

Preparative scale thin-layer chromatography (TLC) was carried out in air on Merck Silica Gel 60-GF254 (ca. 2 mm thickness). Multiple elution with petroleum ether was used to separate compounds with similar R_f values; increasing proportions of dichloromethane in petroleum ether were used to elute more slowly-moving components. Colorless bands were visualized using an ultraviolet lamp. Infrared spectra were recorded on a Perkin–Elmer model 281-B spectrophotometer and were calibrated with cyclohexane (2138.5 cm^{-1}) and polystyrene. Proton NMR spectra were obtained using a Varian EM-390 (90 MHz) instrument. Elemental analyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences. Electron impact mass spectra (70 eV) were obtained on a Varian-MAT CH-5 spectrophotometer by the staff of the Mass Spectrometry Laboratory.

Reactions of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ with $AlCl_3$ under carbon monoxide

(1) Methanol quench. In a nitrogen-purged glove bag $H_3Os_3(CO)_9(\mu_3\text{-CBr})$ (30.4 mg, 0.033 mmol), aluminum trichloride (95 mg, 0.71 mmol), and a magnetic stirring bar were placed in a three-neck, round-bottomed flask, which was then sealed with rubber stoppers. The flask was removed from the bag and dry dichloromethane (1 ml) was transferred to the flask by cannula, producing a cloudy orange solution. Gas inlet and outlet needles were then added for carbon monoxide and dichloromethane was added to a total volume of 30 ml. The solution was stirred under carbon monoxide for 30 min at room temperature, then methanol (1 ml) was added. This caused an immediate color change to green, then more slowly to light yellow. The solution was poured into 5% aqueous hydrochloric acid (50 ml). The organic layer was separated, and the aqueous phase was washed with several 10 ml portions of dichloromethane. The combined organic fractions were dried over magnesium sulfate, filtered, and evaporated to dryness. Purification of the product residue by TLC provided a pale yellow band of uncharacterized material followed by a colorless band of $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ (**2**), which moved only very slowly with petroleum ether. The product was extracted and then crystallized from dichloromethane/methanol (20.4 mg, 69%).

Anal. Calcd. for $H_3Os_3(CO)_9\mu_3\text{-}CCO_2CH_3$): C, 16.07; H, 0.67; Os, 63.63. Found: C, 16.30; H, 0.63; Os, 64.65%. ^1H NMR ($CDCl_3$): δ 3.83(s, 3H), −19.38(s, 3H). IR (C_6H_{12}): ν_{CO}, 2116(vw), 2089(vs), 2081(w, sh), 2030(s), 2025(vs), 2015(m), 1688(w) cm^{-1}. MS (^{192}Os): m/z 902 (M^+), and fragment ions.

Conducting the reaction in the same manner, but under a nitrogen atmosphere, provided starting material (6%) and at least five other minor products, but no **2**. Conducting the reaction as described above, but using only one equivalent of aluminum trichloride, yielded no net reaction; after quenching with methanol, only starting material was observed by ^1H NMR.

(2) Diethylamine quench. $H_3Os_3(CO)_9(\mu_3\text{-CBr})$ (36.8 mg, 0.040 mmol) and aluminium trichloride (~ 150 mg, 1.1 mmol) were allowed to react under a stream of carbon monoxide in dichloromethane in the manner described above. After 35 min the addition of diethylamine (0.5 ml) caused an immediate color change to light yellow. The organometallic products were extracted, and the product residue was purified by TLC (dichloromethane). The most slowly-moving band yielded colorless $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)N(C_2H_5)_2)$ (**3**) (16.6 mg, 44%). Smaller amounts of materials in three other bands were not isolated.

Anal. Calcd. for $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)N(C_2H_5)_2)$: C, 19.21; H, 1.40; N, 1.49. Found: C, 19.36; H, 1.53; N, 1.59%. ^1H NMR ($CDCl_3$): δ 3.70(q, 4H), 1.25(t, 6H, $^3J_{H-H}$ = 7.0 Hz), −19.02(s, 3H). IR (C_6H_{12}): ν_{CO}, 2113(w), 2085(vs), 2075(w, sh), 2033(m), 2026(vs), 2019(m, sh), 2012(s), 1582(vw) cm^{-1}. MS (^{192}Os): m/z 943 (M^+), and fragment ions.

(3) N*-methylaniline quench.* $H_3Os_3(CO)_9(\mu_3\text{-CBr})$ (34.3 mg, 0.037 mmol) and aluminum trichloride (~ 150 mg, 1.1 mmol) were allowed to react under a stream of carbon monoxide in dichloromethane in the manner described above. After 35 min the addition of *N*-methylaniline (0.5 ml) caused an immediate color change to light yellow. The organometallic products were extracted, and the product residue was purified by TLC (dichloromethane). The most slowly-moving band yielded colorless $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)N(CH_3)C_6H_5)$ (**4**) (14.5 mg, 40%). Smaller amounts of material in four other bands were not characterized.

^{1}H NMR ($CDCl_3$): δ 7.33(m, 5H), 3.37(s, 3H), $-$19.19(s, 3H). IR (C_6H_{12}): ν_{CO}, 2113(w), 2086(vs), 2072(w, sh), 2030(m), 2025(s), 2018(vs), 2005(m), 1977(vw), 1582(vw) cm^{-1}. MS (electron impact, ^{192}Os): *m/z* 977 (M^+), and fragment ions.

Reaction of $H_3Os_3(CO)_9(\mu_3\text{-}COCH_3)$ with $AlCl_3$ under carbon monoxide. Methanol quench. To a flask containing $H_3Os_3(CO)_9(\mu_3\text{-}COCH_3)$ (50.5 mg, 0.058 mmol) was added aluminum trichloride (150 mg, 1.1 mmol) in a nitrogen-purged glove bag. Dry dichloromethane (3 ml) was transferred to the flask via cannula, producing a rust-orange colored solution. A gas inlet tube was then added and carbon monoxide bubbled through the solution and dichloromethane addition continued to a total volume of 50 ml. After stirring at room temperature for 45 min, addition of methanol caused immediate color changes to green then light yellow. The reaction was worked up as described in (1) above to give $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ (25.2 mg, 48%). The ^{1}H NMR spectrum of the reaction mixture prior to TLC showed the presence also of small amounts of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ (δ $-$19.58), $H_3Os_3(CO)_9$ (μ_3-CCl) (δ $-$18.99), and an unidentified species (δ $-$18.67).

Protonation of $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$. An NMR tube containing $H_2Os_3(CO)_9$ (μ_3-CCO) (18.5 mg, 0.021 mmol) was capped with a septum stopper, evacuated, and filled with nitrogen. Dry dichloromethane (0.3 ml) was added by cannula. The addition of $HBF_4 \cdot OEt_2$ (9.6 *M*, 2.6 μl, 0.025 mmol) at room temperature caused a fluffy white precipitate to form over the course of ~ 15 sec, leaving a light yellow solution. The ^{1}H NMR spectrum showed the single, weak, new hydride resonance of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$. After a small amount of dry ether was added to complete precipitation, the supernatant was removed. Then the white solid was washed with minimal dry ether and dried under vacuum. Excess ether appeared to deprotonate some of the $[H_3Os_3(CO)_9\text{-}(\mu_3\text{-}CCO)]^+$ (some yellow color returned); washing the solid with benzene yielded a sample with a better IR spectrum.

Anal. Calcd. for $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$: C, 13.87; H, 0.32. Found: C, 14.09; H, 0.44%. ^{1}H NMR (CH_2Cl_2): δ $-$19.35. IR (nujol mull prepared in an inert atmosphere box): ν_{CO} 2155(m), 2125(s), 2069(s, br), 2039(s, br) cm^{-1}. The bands for $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2H)$ [13] slowly grew in: 2082(vs), 2033(vs), 2024(s), 2015(s), 1998(s, br), 1634(m) cm^{-1}.

Reaction of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$ with methanol. $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$ was prepared as described above from $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ (23.4 mg, 0.027 mmol) and $HBF_4 \cdot OEt_2$ (9.6 *M*, 4 μl, 0.035 mmol). After addition of dichloromethane (0.5 ml), the addition of methanol (5 μl, 0.12 mmol) caused the solid to dissolved immediately. $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ was observed as the only product by ^{1}H NMR.

Protonation and reaction with methanol can also take place at low temperature. When $HBF_4 \cdot OEt_2$ (9.6 *M*, 58 μl, 0.56 mmol) was added to a dichloromethane solution of $H_2Os_3(CO)_9$ (μ_3-CCO) (15 mg, 0.017 mmol) under nitrogen in an NMR tube at $-$80 ° C, a white solid slowly formed. The ^{1}H NMR spectrum showed some unreacted starting material. With an addition 50 μl of acid (1.04 mmol total added), only the extremely weak hydride of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]^+BF_4^-$ was observed. The addition of methanol (110 μl, 2.7 mmol) at $-$80 ° C caused the solid to dissolve almost completely, and a single, broad hydride resonance appeared. Extraction into cold toluene at $-$78 ° C gave $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ as the only product.

Reaction of $[H_2Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$ with diethylamine. $[H_2Os_3(CO)_9\mu_3\text{-}CCO)][BF_4]$ was prepared as described above from $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ (17.6 mg, 0.020 mmol) and $HBF_4 \cdot OEt_2$ (9.6 *M*, 2.7 μl, 0.026 mmol), and then dichloromethane (0.5 ml) was added. The addition of diethylamine (2.1 μl, 0.020 mmol) caused the solid to dissolve immediately. The formation of $H_2Os_3(CO)_9(\mu_3\text{-}CC(O)N(C_2H_5)_2)$ was verified by ^1H NMR.

Reaction of $[H_2Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$ with N*-methylaniline.* $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$ was prepared as described above from $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ (24.1 mg, 0.028 mmol) and $HBF_4 \cdot OEt_2$ (9.6 *M*, 3.0 μl, 0.029 mmol), and dichloromethane (0.5 ml) was added. The addition *N*-methylaniline (10 μl, 0.092 mmol) caused the solid to dissolve immediately. The hydride resonances of $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)N(CH_3)C_6H_5)$ were observed in the ^1H NMR spectrum.

Reaction of $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ with H_2SO_4. Ethanol quench. An NMR tube containing $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ (21.4 mg, 0.024 mmol) was capped with a septum stopper and flushed with nitrogen through a syringe needle. Concentrated sulfuric acid (0.75 ml) was added via syringe, and the solid slowly dissolved to produce a tan solution. The ^1H NMR spectrum of this sample showed a single peak in the hydride region (ca. δ −19). The solution was poured into dry ethanol (10 ml), and dichloromethane (20 ml) was added. This mixture was added to distilled water (30 ml) and the organic layer was separated. After the aqueous phase was washed with several 10 ml portions of dichloromethane, the combined organic fractions were dried over magnesium sulfate, filtered, and evaporated to dryness. A single, slow-moving, colorless band was observed on a TLC plate, from which $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2C_2H_5)$ (**5**) (19.9 mg, 92%) was isolated.

Anal. Calcd. for $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2C_2H_5)$: C, 17.15; H, 0.89. Found: C, 17.40; H, 0.85%. ^1H NMR ($CDCl_3$): δ 4.31(q, 2H), 1.39(t, 3H, $^3J_{HH} = 6.9$ Hz), −19.35(s, 3H). IR (C_6H_{12}): ν_{CO}, 2115(vw), 2087(vs), 2079(w, sh), 2027(s, sh), 2022(vs), 2013(m), 1983(vw), 1684(w) cm^{-1}. MS (^{192}Os): *m/z* 916 (M^+) and fragment ions.

Acid-catalyzed reaction of $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ with ethanol. A solution of **2** (9.3 mg, 0.010 mmol) in ethanol (50 ml) was deaerated by saturation with nitrogen gas, then heated at reflux under an atmosphere of flowing nitrogen. After 0.5 hr the solvent was removed. The ^1H NMR spectrum of the residue showed only starting material.

The recovered **2** was placed back into ethanol (50 ml). Following deaeration, 5 drops 98% sulfuric acid was added, and the mixture was heated at reflux under nitrogen for 1 h. The volume was reduced under vacuum and dichloromethane (20 ml) added. The solution was poured into distilled water (30 ml), the organic layer separated, dried over magnesium sulfate, filtered, and evaporated to dryness. The ^1H NMR spectrum of the residue showed $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2C_2H_5)$ as the only product.

Pyrolysis of $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$. An NMR tube containing **2** (51.3 mg, 0.057 mmol) in dry toluene (0.5 ml) was sealed under 1 atm carbon monoxide. The tube was heated in an oil bath at 120–125°C. Periodically the tube was removed, cooled, and the ^1H NMR spectrum taken. After a total of 21 h heating, only $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}CHC(O)OCH_3$ (**6**) was observed. This light yellow compound was isolated in 78% yield (39.3 mg) after TLC.

Anal. Calcd. for $H_2Os_3(CO)_9(CHCO_2CH_3)$: C, 16.07; H, 0.67. Found: C, 16.35; H, 0.79%. ^1H NMR ($CDCl_3$): δ 3.94(d, 1H, $^3J_{H-H} = 1.2$ Hz), 3.53(s, 3H), −13.67(t, 1H), −15.13(d, 1H, $^2J_{H-H} = 1.6$ Hz). IR (C_6H_{12}): ν_{CO}, 2107(m), 2081(vs), 2053(vs), 2022(vs), 2009(s), 2001(vs), 1983(s), 1965(vw), 1952(vw), 1531(w) cm^{-1}. MS (^{192}Os): m/z 902 (M^+) and fragment ions.

Pyrolysis of $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)N(C_2H_5)_2$. An NMR tube containing **3** (6.6 mg, 0.007 mmol) in dry toluene (0.3 ml) was sealed under a atm carbon monoxide. No reaction was observed after 24 h at room temperature. Heating the tube at 125°C for 10 min resulted in complete conversion to $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}CHC(O)N(C_2H_5)_2)$ (**7**) by ^{1}H NMR. This compound was isolated in 77% yield (5.1 mg) after TLC.

Anal. Calcd. for $H_2Os_3(CO)_9CHC(O)N(C_2H_5)_2$: C, 19.21; H, 1.40; N, 1.49. Found: C, 19.42; H, 1.59; N, 1.35%. ^{1}H NMR ($CDCl_3$): δ 4.38(d, 1H, $^3J_{H-H} = 1.5$ Hz), 3.37(q, 2H, $^3J_{H-H} = 7.0$ Hz), 3.13 (q, 2H, $^3J_{H-H} = 7.0$ Hz), 1.20 (t, 6H), -13.84(t, 1H, $J_{H-H} = 1.5$ Hz), -15.25(d, 1H, $^2J_{H-H} = 1.5$ Hz). IR (C_6H_{12}): ν_{CO}, 2100(m), 2074(vs), 2045(vs), 2017(vw), 2013(vs), 2003(s), 1995(vs), 1975(s), 1961(vw), 1948(vw), 1527(w) cm^{-1}. MS (^{192}Os): m/z 943 (M^+) and fragment ions.

A strictly analogous tube containing **2** was prepared and 5.5 h was required to effect conversion to **6** under exactly the same temperature conditions.

Protonation of $H_2Os_3(CO)_9(\mu\text{-}CHCO_2CH_3)$. An NMR tube containing **6** (20.0 mg, 0.022 mmol) in dichloromethane-d_2 (0.4 ml) was capped with a septum stopper and flushed with nitrogen. The addition of $HBF_4 \cdot OEt_2$ (9.6 M, 20 μl, 0.19 mmol) at 0°C caused the appearance of two new hydride resonances in a 1 : 2 pattern. $[H_3Os_3(CO)_9(\mu\text{-}CHCO_2CH_3)][BF_4]$ was precipitated as a white solid by the addition of ether; it was then washed with ether and dried under vacuum.

^{1}H NMR (CD_3CN): δ 4.04(s, br, 1H), 3.70(s, 3H), -14.47(s, br, 1H), -17.34(d, 2H, $^3J_{H-H} = 1.5$ Hz). IR (CH_2Cl_2): ν_{CO} 2151(m), 2125(s), 2110(vs), 2076(s), 2062(s), 2046(vs), 2016(m), 1996(m), 1977(w) cm^{-1}.

Pyrolysis of $HOs_3(CO)_{10}(CH_2CO_2CH_3)$. To $H_2Os_3(CO)_{10}$ (30.7 mg, 0.036 mmol) in $CDCl_3$ (0.5 ml) in an NMR tube was added ethereal methyl diazoacetate (1.0 equivalent). After 19 h at 25°C the ^{1}H NMR spectrum showed almost complete reaction to $HOs_3(CO)_{10}(CH_2CO_2CH_3)$ (δ -13.2, s, μ-H) [14]. The solution was transferred to a three-neck, round-bottomed flask, the volatiles removed, and deaerated toluene (100 ml) was added. The solution was heated at reflux with a nitrogen flush for 12.5 h. TLC provided a mixture of products; the third yellow band trailing purple $H_2Os_3(CO)_{10}$ yielded $H_2Os_3(CO)_9(CHCO_2CH_3)$ (5.6 mg, 17% yield based on $H_2Os_3(CO)_{10}$).

An attempt at photochemical conversion gave comparable results.

Results and discussion

Synthesis and characterization of ester and amide derivatives 2–4. When a dichloromethane solution of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ in the presence of a large excess of aluminum trichloride is treated with carbon monoxide for 30 min at room temperature, subsequent addition of methanol provides the methyl ester derivative $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ (**2**) in 60–70% yield after workup. Similarly, quenching the reaction with diethylamine or N-methylaniline produces the respective amides, $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)NRR')$ (**3**, R = R′ = Et; **4**, R = Ph, R′ = Me) in 40–50% yield. The ethyl ester derivative **5** is also formed under these conditions (IR). $H_3Os_3(CO)_9(\mu_3\text{-}CO_2CH_3)$ can also serve as the starting material for **2**, albeit in reduced yield (48%). Yields for the analogous reactions in the tricobalt system are notably higher [3]; however, the reported yield for $H_3Ru_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ is 38% [4].

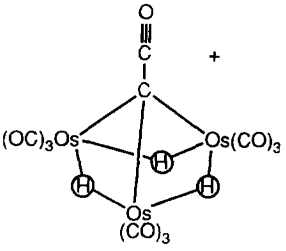
The ester- and amide-substituted alkylidene clusters are colorless compounds which elute slowly with dichloromethane on silica. The ^1H NMR spectrum of each shows single high-field resonances due to the equivalent hydride ligands and resonances appropriate for the organic moieties. The ester carbonyl stretch for **2** is observed at 1688 cm^{-1}, in close agreement with the value of 1685 cm^{-1} observed for the $H_3Ru_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ [4] and $Co_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ [15] clusters. The spectrum of each amide derivative shows a weak absorption at 1582 cm^{-1}, attributed to the carbonyl stretch of the amide moiety. These bands are reported to occur at 1575 and 1582 cm^{-1} for the tricobalt diethylamide [16] and methyl-phenylamide [17] methylidyne clusters, respectively.

The electron impact mass spectrum of $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ shows the molecular ion together with ions which correspond to fragments that have lost several carbonyl and hydride ligands. A series of ions is also observed in which elimination of methanol has occurred. Analogous fragmentation pathways are seen for **3**–**5** as well; in particular, for $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)N(C_6H_5)CH_3)$, the strongest series of ions is initiated by elimination of *N*-methylaniline. These unusual fragmentations for esters and amides [18] presumably reflect the unusual stability associated with the "ketene" fragment, in this case $H_3Os_3(CO)_9(CCO)^+$.

The reaction of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ with aluminium trichloride was performed under several conditions, quenching with methanol, in order to gain some insight into the formation of **2**. Two requirements appear to be an excess of the Lewis acid reagent and the presence of external carbon monoxide. When the reaction was carried out with one equivalent of aluminum trichloride, only unreacted $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ was obtained. When the reaction was performed under nitrogen, with an excess of aluminum trichloride, no $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2CH_3)$ was produced and very little of the starting material was recovered. The highest yields of the acyl derivatives were obtained when the bromomethylidyne cluster and the aluminum trichloride were allowed to mix in dichloromethane prior to introduction of carbon monoxide. For the analogous reaction in the cobalt system, Seyferth and coworkers [3] have proposed a dual role for aluminum trichloride, namely, to cause the halogen substituent to ionize as well as to induce migration of a carbonyl ligand to the incipient carbocation center. Our observation of a requirement for external carbon monoxide, which contrasts with both the tricobalt and triruthenium [4] systems, presumably reflects the greater osmium–carbonyl bond strength. In related work involving $AgSbF_6$ as the ionizing reagent, evidence for direct trapping of ^{13}CO at the carbocation center has been obtained [19].

Formation and reactivity of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]^+$. $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ can be protonated by one equivalent of $HBF_4 \cdot OEt_2$ at room temperature. White $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)][BF_4]$, which displays a single hydride resonance at δ -19.35, slightly downfield from the neutral compound, is largely precipitated from concentrated dichloromethane solutions. That the site of protonation is a metal center rather than the carbonyl oxygen atom is indicated by the bleaching of the color from yellow to white and by the simplicity of the infrared spectrum in the carbonyl region (Nujol mull): 2155(m), 2125(s), 2069(s, br), 2039(s, br) cm^{-1}. High symmetry is indicated, so the $[H_3Os_3(CO)_9(CCO)]^+$ molecule probably has an upright structure, **8**, much as has been shown to be the case for $H_2Os_3(CO)_9(\mu_3\text{-}$

CCO) [7]. The high stability of the acylium ion must result from the ability of the cluster to partially delocalize the positive charge. The infrared absorptions of the metal carbonyl ligands are shifted to higher energy than those in $H_2Os_3(CO)_9(\mu_3$-CCO), so a significant amount of the positive charge does reside on the metals. However, nucleophiles readily attack at the β-carbon atom of the cation, presumably due to the reduced amount of electron density available to be transferred into the carbonyl π^* orbitals from the Os_3C cluster unit. For this reason the cation is very moisture-sensitive; in the nujol mull of $[H_3Os_3(CO)_9(\mu_3$-CCO)]$[BF_4]$, the infrared absorptions of the carboxylic acid methylidyne cluster grow in over the course of running through several spectra. $H_3Os_3(CO)_9(\mu_3$-$CCO_2H)$ [13] can be isolated in high yield by addition of water to a dichloromethane suspension of the acylium cation.



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The addition of methanol to $[H_3Os_3(CO)_9(\mu_3$-CCO)]$[BF_4]$ causes its immediate conversion to $H_3Os_3(CO)_9(\mu_3$-$CCO_2CH_3)$ (**2**). Diethylamine reacts in a similar fashion to give $H_3Os_3(CO)_9(\mu_3$-$CC(O)N(C_2H_5)_2)$ (**3**). This is consistent with the reactivity of the intermediate formed upon interaction of $H_3Os_3(CO)_9(\mu_3$-CBr) with aluminum trichloride, under carbon monoxide, with diethylamine. Addition of *N*-methylaniline to $[H_3Os_3(CO)(\mu_3$-CCO)]$[BF_4]$ similarly produces $H_3Os_3(CO)_9(\mu_3$-$CC(O)N(CH_3)C_6H_5)$ (**4**). Thus, the triosmium acylium cation reacts with these nucleophiles much as does $[Co_3(CO)_9CCO][PF_6]$ [1].

Transesterification of $H_3Os_3(CO)(\mu_3$-$CCO_2CCH_3)$. Compound **2** dissolves in concentrated sulfuric acid to produce a pale brown solution. Pouring this solution into ethanol forms $H_3Os_3(CO)_9(\mu_3$-$CCO_2C_2H_5)$ (**5**), which is isolated in greater than 90% yield following dichloromethane extraction and TLC. The isolation of $[Co_3(CO)_9CCO][PF_6]$ from the reaction of $Co_3(CO)_9(\mu_3$-$CCO_2CH_3)$ with HPF_6 [16] and the isolation of stable $[H_3Os_3(CO)_9(\mu_3$-CCO)]$[BF_4]$ argue for the formation of the latter ion when $H_3Os_3(CO)_9(\mu_3$-$CCO_2CH_3)$ is dissolved in the strong acid medium. We observe only one signal in the hydride region of the ^1H NMR spectrum, but we cannot prove that this is due to the carbonylmethylidyne cation.

The transesterification also proceeds in dilute solution but requires acid catalysis. Thus, no reaction is observed after heating $H_3Os_3(CO)_9(\mu_3$-$CCO_2CH_3)$ in neat ethanol at reflux for 0.5 h, but the ^1H NMR spectrum shows the carboethoxy-methylidyne cluster as the only product after heating in the presence of a small amount of sulfuric acid. This behavior of **2**, contrasts with that of $Co_3(CO)_9(\mu_3$-$CCO_2CH_3)$, hydrolysis of which could not be effected using modest amounts of mineral acids [17].

Alkylidyne to alkylidene rearrangement. Heating a toluene solution of **2** or **3** causes conversion to $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}CHC(O)OCH_3)$ (**6**) or $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}CHC(O)N(C_2H_5)_2)$ (**7**), respectively (see eqn. (1)). Spectra data for the pale yellow compounds **6** and **7** establish their formulation as dihydrido-alkylidene clusters stabilized by acyl oxygen coordination The metal carbonyl (ν_{CO}) infrared spectra of **6** and **7** show closely similar patterns, with that for **7** shifted uniformly to lower energy. The coordinated acyl IR band appears at 1531 cm^{-1} for **6** and at 1527 cm^{-1} for **7**. The ^1H NMR spectra exhibit alkylidene α-CH resonances at δ 3.94 (**6**) and δ 4.38 (**7**) and two inequivalent hydride ligands are indicated. These spectral characteristics are comparable with those reported by Deeming and coworkers for a group of related triosmium compounds, one of which has been structurally characterized [20,21]. Also, Keister, Churchill, and coworkers [9] have established the structure of $H_2Ru_3(CO)_9(\mu_3,\eta^2\text{-}CHC(O)OCH_3)$, the triruthenium analog of **6**.

Further details of stereochemistry can be extracted from the ^1H NMR spectra of **6** and **7**. In each case the alkylidene α-CH is coupled to one of the hydride ligands ($J \approx 1.2$ Hz for **6**), which is also coupled to the second hydride ($J \approx 1.6$ Hz for **6**). Thus, the lower-field hydride signal, which appears as a triplet, is assigned to the hydride ligand bridging the same edge of the metal triangle as the α-CH moiety, whereas the higher-field signal, a doublet, is assigned to the hydride ligand bridging the adjacent edge. This assignment is supported by the spectrum of the complex derived from protonation of **6** on the remaining Os–Os bond; now the higher-field hydride signal corresponds to 2H, and it is clearly coupled to the lower-field 1H hydride signal. Finally, for the ethyl groups in **7**, two signals for the methylene protons are observed but only one methyl signal is resolved. If there were "fast" hydride ligand mobility from a bridged to the unbridged edge, thereby creating an effective plane of symmetry through the nitrogen atom, the methyl groups would be enantiotopic, having only one signal, and the methylene groups would be divided into two diastereotopic pairs, having potentially two signals. Such a hydrogen migration process has been detected for the triruthenium analog of **6** [9], but it is expected to have a significantly higher energy barrier for the triosmium compounds [10]. Thus, we prefer an alternative explanation for the signals seen for **7**, namely, that there is just partial resolution of the four methylene and two methyl signals potentially observable for the asymmetric, "static" structure.

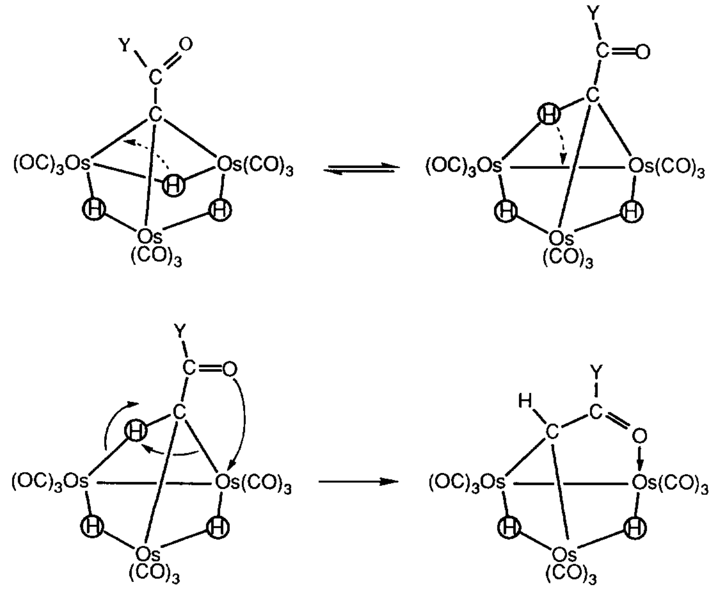
The reactions forming **6** and **7** are extremely clean (by ^1H NMR) when carried out under an atmosphere of carbon monoxide. In the absence of external carbon monoxide the yields are diminished somewhat, but the rates of conversion are not obviously affected. For a direct comparison under parallel conditions, two NMR tubes, containing identical concentrations of **2** or **3** in toluene and sealed under an atmosphere of carbon monoxide, were placed in an oil bath at 125 °C. The rearrangement **3** $\rightarrow$ **7** was complete in 10 minutes whereas **2** $\rightarrow$ **6** took 5.5 hours. Assuming first-order behavior and that the respective half-lives have the corresponding ratio of 1 : 33, this corresponds to a difference in $\Delta G^{\ddagger}_{398}$ of roughly 3 kcal/mole (ca. 27 (**3** $\rightarrow$ **7**) and 30 kcal/mole (**2** $\rightarrow$ **6**), respectively).

Mechanistic considerations. The alkylidyne to alkylidene rearrangement raises several interesting mechanistic questions. However, our current results coupled with results from other recent studies leads to a relatively detailed picture of this rearrangement. If the first stage were simply reductive elimination to form an α C–H bond, then the stereochemistry of the unsaturated species $H_2Os_3(CO)_9(CH$-

CO_2Me) would be wrong in that the ester carbonyl would be pointing away from the site to which it needs to coordinate. Of course, the alkylidene might "turn around" via bridge–terminal migration steps, but such an unsaturated species should be trapped by exogeneous CO to give $H_2Os_3(CO)_{10}(\mu\text{-}CHCO_2Me)$. This is the alkylidene tautomer of the alkyl complex $HOs_3(CO)_{10}(CH_2CO_2Me)$, which is available from the reaction of $H_2Os_3(CO)_{10}$ with N_2CHCO_2Me [14]. Furthermore, the deuterium scrambling observed in the product from $D_2Os_3(CO)_{10} + N_2CHCO_2Me$ suggests that the alkyl and alkylidene forms are interconvertible [22]. Pyrolysis of the alkyl does give $H_2Os_3(CO)_9(\mu_2,\eta^2\text{-}CHCO_2Me)$, but the yield is very low and the formation of numerous other products, including $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$, attests to its complexity. Thus, it does not appear that an unsaturated from of $H_2Os_3(CO)_9(CHCO_2Me)$ is involved in the rearrangement for the triosmium system, and the analogous intermediate very likely can be eliminated from consideration for the triruthenium system [9] as well.

A key development in our thinking was the observation that $H_3Os_3(CO)_9(\mu_3\text{-}CD)$ undergoes intramolecular H/D exchange [8]. This was later studied quantitatively for $H_3M_3(CO)_9(\mu_3\text{-}CH)$ (M = Os, Ru) by saturation transfer ^1H NMR [10]. A mechanism was proposed that involved the reversible formation of an intermediate methylene complex with one agostic C ··· H ··· Os bond pair. In this way no unsaturated species is formed. Direct evidence for such an equilibrium in triiron chemistry has been provided in thoroughgoing studies by Fehlner and coworkers [23]. Furthermore, Fehlner's more recent work has shown a direct equilibrium between benzylidyne (PhC) and benzylidene (PhCH) forms in a $FeCo_2$ mixed-metal system [24].

Applying these ideas to the present acyl derivative case leads to a mechanistic proposal (see Scheme 1) in which the key steps are: (1) a reversible migration of



Scheme 1.

hydrogen from bridging an Os–Os bond to bridging a C–Os bond, and (2) attack of the acyl oxygen at one of the other two metal centers concomitant with a smooth flow of electron pairs to form the observed product. The rate determining step is therefore step 2; however, the overall rate will involve both the equilibrium constant for step 1 and the specific rate constant for step 2 (assumed irreversible). It is unlikely that changing the acyl group from an ester to an amide would have a strong effect on the initial equilibrium involving hydrogen transfer, i.e., step 1. On the other hand, the more basic carbonyl in the amide would be a better nucleophile in step 2, consistent with the observed rate acceleration.

This general mechanism also suffices to explain the observation of H/D exchange in $H_3Os_3(CO)_9(\mu_3\text{-}CC_6D_5)$ [11]. In this case the initial Os–H–Os to Os–H–C rearrangement is followed by attack of a phenyl ortho–CD bond pair on the cluster and then complete oxidative addition to give an Os–C sigma bond. Reversal of this process gives a phenyl ortho–CH bond and leaves the deuterium atom bridging on the metal framework. Similar ideas have also been utilized in a recently published mechanistic analysis of hydrocarbon reductive elimination from triruthenium alkylidyne complexes [25].

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