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8. Spectral data for **6c**: NMR ($CDCl_3$) δ 1.4 (singlet, 3H) 1.48 (singlet, 3H) 1.7-2.5 (multiplet, 5H) 7.27 (singlet, 5H); IR (KBr) 3050 cm^{-1}, 1705, 1600; Mass (m/e) 91, 128, 129, 143, 158, 200; Anal Calcd. $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83,78; H, 7.72. Spectral data for **6d**: NMR ($CDCl_3$) δ 1.05 (doublet, 3H) 1.65 (doublet, 3H) 1.8-3.1 (multiplet, 5H) 7.0-7.5 (multiplet, 5H): IR (neat 3050, 1705, 1650, 1600; Mass (m/e) 77, 91, 115, 129, 143, 158, 200: Anal. Calcd. $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.61; H, 7.70.
9. The Reactions were quenched by naphthalene.
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Internal Hydride Assisted C-O Bond Scission of a μ_3-η^2-Coordinated Acyl and an Apparent Rotation of μ-Alkylidene Carbon in Molybdenum-Triosmium Cluster Compounds

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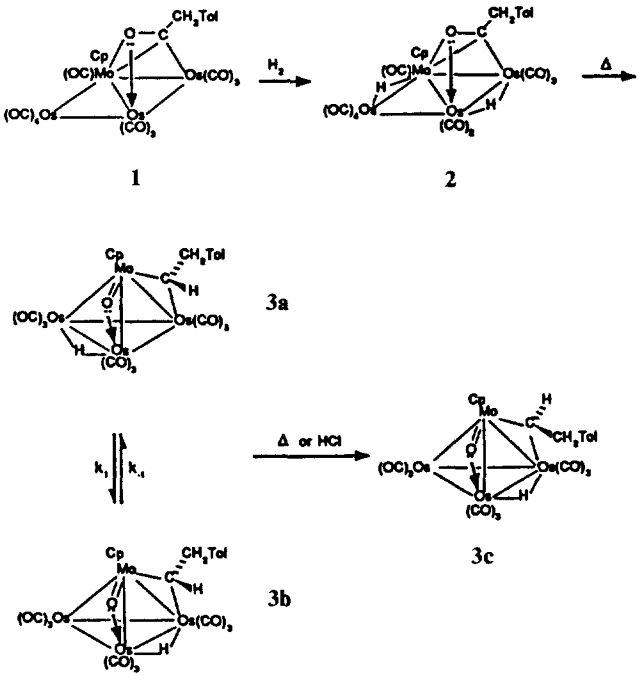
It has been suggested that the direct C-O bond scission in acyl species[1a] may play a significant role in hydrocarbon chain growth during Fischer-Tropsch synthesis. We have now extended our studies on the μ_3-η^2-acyl groups as potential surface intermediates to investigate the reactivity of acyl ligand on a molybdenum-triosmium mixed metal cluster framework. It has been reported that the tungsten-triosmium cluster compound $CpWOs_3(CO)_{11}[\mu_3$-η^2-$C(O)CH_2Tol](Cp=\eta^5$-C_5H_5, $Tol=p$-$C_6H_4Me)$ undergoes facile thermal μ_3-η^2-acyl C-O bond scission yielding the oxo-alkylidyne complex $CpWOs_3(CO)_9(\mu$-$O)(\mu_3$-$CCH_2Tol)$.[1] This oxo-alkylidyne complex has, in turn, been shown to undergo hydrogenation to provide a mixture of two isomers of the hydrido-oxo-alkylidene complex $CpWOs_3(CO)_9(\mu$-$H)(\mu$-$O)(\mu$-$CHCH_2Tol)$.[1a,2] We here report that an analogous molybdenum-triosmium acyl compound undergoes the acyl C-O bond scission assisted by internal hydride ligands and that an apparent rotation of μ-alkylidene carbon is directly observed on the molybdenum-triosmium cluster framework.



Scheme 1.

The triply-bridging acyl complex $CpMoOs_3(CO)_{11}[\mu_3$-η^2-$C(O)CH_2Tol](1)$[3] is isolated as the major product in 60% yield from a Stone reaction,[4] the reaction of $H_2Os_3(CO)_{10}$ with the molybdenum alkylidyne complex $Cp(CO)_2Mo(CTol)$ under mild conditions (5-20℃). Initial decarbonylation of compound **1** with $Me_3NO/MeCN$ followed by reaction with dihydrogen (50 psig, toluene, 80℃, 1 h) gives the dihydride complex $CpMoOs_3(CO)_{10}(\mu$-$H)_2[\mu_3$-η^2-$C(O)CH_2Tol](2)$[5] in a quantitative yield (Scheme 1). Thermolysis of compound **2** (toluene, 100 ℃, 1h) now induces scission of the acyl C-O bond to afford three isomeric hydrido-oxo-alkylidene complexes $CpMoOs_3(CO)_9(\mu$-$H)(\mu$-$O)(\mu$-$CHCH_2Tol)$ [**3a** and **3b** (59%) and **3c** (18 %)].[6] Complex **3c** is produced as well either by thermolysis of a mixture of **3a** and **3b** in toluene for a prolonged period (61%, 100℃, 19h) or by treatment with hydrochloric acid in acetone (72%, 56℃, 14h).

The molecular configuration of **2** is shown in Figure 1.[7] The tetrametallic molecule contains a planar triangulated rhomboidal arrangement of metal atoms, with Mo and Os(2) atoms at the bridge-head positions. The present molecule has an μ_3-η^2-acyl group,[8] C(2)-O(1), associated with the triangular Os(1)-Os(2)-Mo face. The C(2)-O(1) bond length is

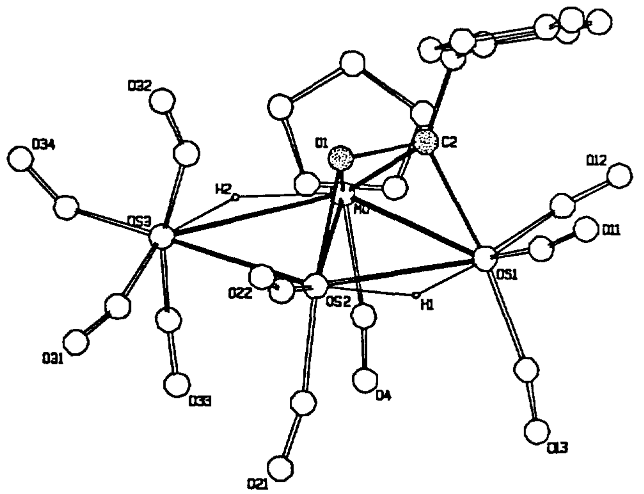


Figure 1. The molecular structure of $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**2-A**) molecule. Intermetallic distances are Os(1)-Os(2) = 2.862(3), Os(1)-Mo = 2.928(7), Os(2)-Os(3) = 2.799(5), Os(2)-Mo = 2.763(7), and Os(3)-Mo = 3.203(8) Å, Hydride ligands are shown in their predicted positions (see text).

1.371(18)Å. The two hydride ligands are inferred to occupy the Os(1)-Os(2) and Os(3)-Mo edges by consideration of metal-metal bond distances and metal-metal-ligand angles.[9]

The crystal structure of the tungsten analogue of **3a** has been previously determined.[2b] Compounds **3a** and **3b** are equilibrated in solution by a rapid hydride migration between edges of metal-metal bonds as shown to be the case in the analogous tungsten compound.[2a,10] The hydride migration rate between complex **3a** and **3b** was studied at 23℃ by ^{1}H-NNR spectroscopy. The two isomers are in equilibrium and the reaction follows first order kinetics: $K_{eq} = \mathbf{3a}/\mathbf{3b} = 1.20$, $k_{obs} = 5.97 \times 10^{-5}\ sec^{-1}$, $k_1 = 2.71 \times 10^{-5}\ sec^{-1}$ and $k_{-1} = 3.26 \times 10^{-5}\ sec^{-1}$. The third isomer of hydrido-oxo-alkylidene complex, **3c**, is produced either by thermolysis of a mixture of **3a** and **3b** or by treatment with hydrochloric acid. When the deuterated acid (DCl, acetone-d_6) was used, the hydrogen (100%) on the μ-alkylidene carbon and the hydride ligand (37%) in compound **3c** are labelled as deuterium in the ^{2}H-NMR spectrum. The result may indicate that the deuterium exchange occurs independently for the two sites.

The structural study of **3c** showed that metal framework adopted a pseudotetrahedral arrangement and that μ-oxo, μ-hydrido, and μ-alkylidene ligands bridged each edge of the Os(1)-Os(1)′-Mo triangular face (Figure 2).[11] The μ-oxo and μ-alkylidene groups, however, are disordered out of the crystallographic mirror plane which includes the Mo and Os(2) atoms and bisects the Os(1) and Os(1)′ bond, each occupying the opposite side of the plane with a half occupancy. As carbon atoms of the tolyl group [C(4)-C(8)] were located nearly on the mirror plane and their electron densities were overlapped with their own symmetry equivalents, they were treated as ordered in the refinement. The longest Os(1)-Os(1)′ edge is believed to be associated with the μ-hydride ligand.[9] The aryl moiety (CH_2Tol) is disposed towards the μ-oxo ligand, which clearly indicates an apparent rotation of the μ-alkylidene carbon.

Recent work has shown facile reductive C-O bond scission of formyl or acyl ligands by direct thermolysis,[1] by external nucleophilic, or electrophilic reagents.[8a,12] The present study is unique in that the internal hydride ligands assist the C-O bond scission. This may result from that the two hydride ligands withdraw electron density from the cluster framework and increase the oxidation states and oxophilicity of metal centers. The position of carbonyl region infrared absorption bands of compound **2** is shifted to the higher frequency than that of compound **1**, reflecting the electronic effect due to the hydride ligands. Isomer **3c** may be favored by the large steric interaction between the cyclopentadienyl ligand and the aryl group in isomers **3a** and **3b**. Detailed mechanism concerning the μ-alkylidene carbon rotation in the present complexes remains speculative at the moment, although Shapley *et al.* proposed either bridge-terminal alkylidene movement[13] for $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$[14] or oxidative addition to form a dihydrido-alkylidyne species for $CpWOs_3(CO)_9(\mu\text{-}Cl)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$[10] in thermal reactions. A likely pathway, however, for the formation of **3c** by the acid can be proposed based on the deuterium labelling study. This involves deuteration of an alkylidene carbon-metal bond to form a cationic alkyl species followed by rotation around a carbon-metal single bond and deprotonation to give the deuterated compound. The mechanistic study of the isomerization in the μ-alkylidene complexes is the object of our further investigation.

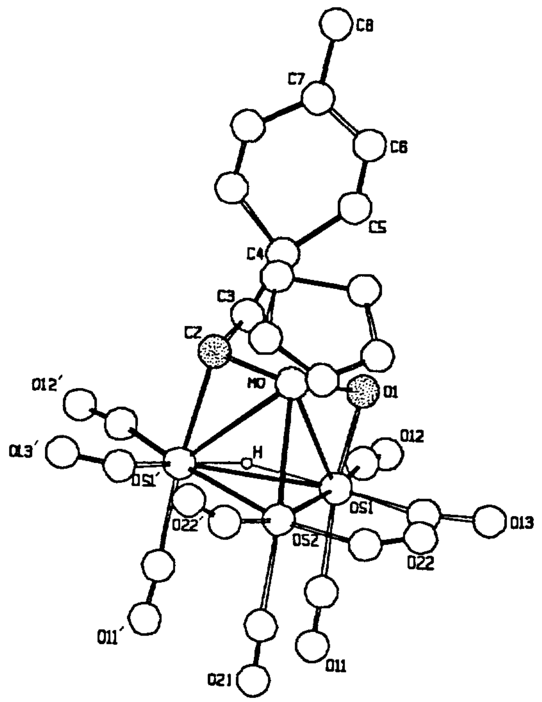


Figure 2. The molecular structure of $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**3c**) molecule. Selected bond lengths are Mo-Os(2) = 2.634(6), Mo-Os(1) = 2.846(3), Os(1)-Os(1)′ = 2.983(2) Os(1)-O(1) = 1.99(3), Mo-O(1) = 1.87(3), Os(1)-C(2) = 2.16(6), and Mo-C(2) = 1.88(5) Å. The hydride ligand is shown in the predicted position.

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3. Compound **1**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.2-7.14 (m, 4H), 5.30 (s, 5H), 3.54-3.44 (m, 2H), 2.36 (s, 3H); IR (CCl_4) ν (CO) 2095 (m) 2064 (s), 2032 (sh), 2022 (s), 2011 (s), 1978 (m) cm^{-1}; MS (70eV, ^{98}Mo, ^{192}Os) *m/z* 1180 (M^+).
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5. Compound **2**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.19-7.12 (m, 4H), 5.33 (s, 5H), 3.74-3.56 (m, 2H), 2.35 (s, 3H), −12.2 (s, 1H), −17.6 (s, 1H); ^{13}C-NMR (75 MHz, CD_2Cl_2, −10 ℃) δ 224.7, 187.2, 185.1, 180.2, 177.4, 176.1, 175.9 (d, $^2J_{CH}=11.8$ Hz), 174.5, 173.4 (acyl), 168.9 (d, $^2J_{CH}=7.3$ Hz), 168.0; IR (CCl_4) ν (CO) 2119 (m), 2076 (s), 2059 (vw), 2045 (s), 2033 (sh), 2024 (m), 2012 (vs), 2000 (sh), 1981 (m), 1946 (m) cm^{-1}.
6. Compound **3a**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17-7.27 (m, 4H), 6.67 (dd, 1H, J=8.6 Hz, J=6.4 Hz), 5.90 (s, 5H), 4.01 (dd, 1H, J=14.4 Hz, J=6.4 Hz), 3.52 (dd, 1H, J=14.4 Hz, J=8.6 Hz), 2.39 (s, 3H), −16.6 (s, 1H); MS (70eV, ^{98}Mo, ^{192}Os) *m/z* 1126 (M^+). Compound **3b**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.14-7.27 (m, 4H), 5.89 (s, 5H), 5.70 (dd, 1H, J=8.7 Hz, J=6.4 Hz), 3.71 (dd, 1H, J=14.5 Hz, J=6.4 Hz), 3.37 (dd, 1H, J=14.5 Hz, J=8.7 Hz), 2.38 (s, 3H), −19.2 (s, 1H). Compound **3c**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.14-7.23 (m, 4H), 6.59 (dd, 1H, J=11.4 Hz, J=5.9 Hz), 5.38 (s, 5H), 4.74 (dd, 1H, J=12.2 Hz, J=5.9 Hz), 2.52 (dd, 1H, J=12.2 Hz, J=11.4 Hz), 2.40 (s, 3H), −18.6 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, −10℃) δ 189.0, 185.2, 185.1, 182.4, 176.1, 175.2, 170.2, 169.7 (d, $^2J_{CH}=13.1$ Hz), 168.3 (d, $^2J_{CH}=9.8$ Hz), 140.5 (d, $^1J_{CH}=140.6$ Hz, alkylidene carbon); IR (C_6H_{12}) ν (CO) 2086 (s), 2060 (vs), 2028 (vs), 2012 (s), 2000 (m), 1990 (w), 1955 (w), 1941 (m) cm^{-1}; MS (70 eV, ^{98}Mo, ^{192}Os) *m/z* 1126 (M^+). Satisfactory microanalyses (C, H) have been obtained for all new compounds.
7. Crystal data for **2**: $C_{24}H_{16}O_{11}Os_3Mo$; $M=1146.9$; orthorhombic; space group $Pna2_1$; $a=12.966(9)$ Å, $b=11.256(3)$ Å, $c=38.505(10)$ Å; $V=5620(7)$ Å^3; ρ (calcd)=2.71g cm^{-3}; $Z=8$; μ=(Mo Kα)=140 cm^{-1}. Diffraction data were collected with a CAD4 diffractometer. The structure was solved by a combination of direct method and difference Fourier technique. Two crystallographically independent molecules (**2-A** and **2-B**) were refined in alternating full matrix least-squares cycles (anisotropic thermal parameters for metal atoms and hydrogen atoms not included in the structure factor calculations). As the poor diffraction quality did not permit a well-tempered refinement, a restrained refinement procedure was employed as follows: Os-C (carbonyl)=(1.94± 0.01) Å, C-O (carbonyl)=(1.15± 0.01) Å. Furthermore, the phenyl and cyclopentadienyl rings were approximated to regular polygons with C-C= 1.39 and 1.42 Å, respectively. This refinement scheme led to convergence with $R_F=9.7\%$ and $R_{wF}=9.9\%$ for 2530 data ($F\geqq 3\sigma_F$).
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11. Crystal data for **3c**: $C_{23}H_{16}O_{10}Mo$; $M=1118.9$; orthorhombic; space group $Pmn2_1$; $a=12.438(7)$, $b=8.797(2)$, $c=11.846(4)$; $V=1296(1)$ Å^3; ρ (calcd)=2.87 g cm^{-3}; $Z=2$; μ(Mo Kα)=152 cm^{-1}. Diffraction data were collected and treated as described for **2**. Full matrix least-squares refinement with the disordered model (anisotropic thermal parameters for the metal atoms) led to convergence with $R_F=5.6\%$ and $R_{wF}=5.5\%$ for 999 data ($I\geqq\sigma_I$).
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The Hydrometallation of Vinylcyclopropane by the Rh-H Gernerated from C-H Bond Activation

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C-H bond activation is one of the recent interests in organometallic chemistry[1]. Although the C-H bond of aldehyde can be easily cleaved by transition metals, subsequent decarbonylation of the acylmetal hydride and reductive-elimination of the resulting alkylmetal hydride gives alkane[2]. This decarbonylation can be prevented by cyclometallation, since a five-membered ring is the right size for a stable metallacycle complex[3]. The C-H bond activation of 8-quinolinecarboxaldehyde (**1**), a good cyclometallation substrate, by Wilkinson's complex (**2**) gives a stable acylrhodium(III) hydride (**3**) (Scheme 1)[4]. This report describes the hydrometallation of the acylrhodium(III) hydride **3** into vinylcyclopropanes and subsequent ring-cleavage of the cyclopropyl group of the hydrometallated intermediate complexes.

Compound **1** was allowed to react with a solution of **2** in THF at room temperature for 15 min. The white precipitate was isolated in 95% yield with addition of pentane to the resulting reaction mixture and characterized as a stable acyl rhodium(III) hydride **3**, the coordinatively saturated complex[4]. Addition of one equivalent of $AgBF_4$ into the complex **3** in THF generated a vacant coordination site like **4**,