Communications

Electrophilic Acetylation and Alkylation of Arene-Coordinated Triosmium Clusters

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Summary: (Benzyne)triosmium clusters of the type $H_2Os_3(CO)_9Ar$ (Ar = C_6H_4 (**1**), C_9H_6 (**2**), C_4H_3N (**3**), and C_4H_2NMe (**4**)) undergo Friedel–Crafts acetylation and alkylation under mild conditions to produce the derivatives $H_2Os_3(CO)_9Ar'$ (**5–11**; Ar' = C_6H_3R, C_9H_5R, C_4H_2RN, and C_4HRNMe, where R = $COCH_3$ and Bu^t), displaying the nucleophilicity of the arene ligands despite the loss of electron density on coordination to the metal clusters. Most of the reaction products have been fully characterized by spectroscopic techniques.

Although the triosmium benzyne complex $H_2Os_3(CO)_9(C_6H_4)$ (1) and its analogues, e.g. $H_2Os_3(CO)_9(C_9H_6)$ (2), $H_2Os_3(CO)_9(C{-}CH{=}CH{-}CH{=}N)$ (3), and $H_2Os_3(CO)_9(C{=}C{-}CH{=}CH{-}NMe)$ (4), are well-known and easily prepared,[1-8] their chemistry has not been investigated in any detail. In the course of our recent work, we were interested in the reactivities of these cluster complexes toward the substitution on both the metal framework and the organic moiety. While the former will be reported elsewhere,[9] here we report the electrophilic substitution reactions of the organic moieties via Friedel–Crafts acetylation and alkylation.

On coordination to a metal cluster, the electron density of an arene is expected to decrease and the arene thereby to be deactivated toward the reaction with electrophiles. For example, in the face-capping benzene cluster $Os_3(CO)_9(C_6H_6)$, the coordinated benzene ligand easily undergoes reaction with nucleophiles, which is in contrast to the behavior of free benzene.[10] In complexes 1, 2, and 4, each organic moiety donates four electrons to the metal framework via two σ-bonds and one π-bond, while in complex 3, a slightly different bonding mode is present,[4] in which the carbon atom of the pyrrole ligand bridges two osmium atoms while the nitrogen atom donates two electrons to the third osmium atom. In spite of this loss of electron density on the arene ligands, these cluster complexes readily undergo acetylation reactions under Friedel–Crafts conditions, giving acylated products in moderate to good yields. In a typical reaction, 10 mg of the relevant cluster complex is dissolved in 5 mL of carbon disulfide, and the solution is added dropwise to a carbon disulfide solution of preformed aluminum chloride–acetyl chloride complex (20 mg of $AlCl_3$ and 0.7 mL of CH_3COCl in 5 mL of CS_2) at 0 °C over 30–45 min. The reaction mixture is then gradually warmed up to room temperature and stirred for ca. 0.5 h. The solvent is evacuated, and the residue is worked up by TLC on silica plates, with 50% CH_2Cl_2 in hexane as eluent. Apart from the unreacted starting material, the acylated cluster complexes $H_2Os_3(CO)_9(C_6H_3COCH_3)$ (5; 40–60%), $H_2Os_3(CO)_9(C_9H_5COCH_3)$ (6; 50–70%), $H_2Os_3(CO)_9[C{-}CH{=}C(COCH_3){-}CH{=}N]$ (7; ca. 25%), and $H_2Os_3(CO)_9[C{=}C{-}C(COCH_3){=}CH{-}NMe]$ (8; ca. 40%) are separated. When a similar strategy is applied in the reaction with *tert*-butyl chloride, complexes 1 and 2 give the substituted compounds $H_2Os_3(CO)_9(C_6H_3Bu^t)$ (9) and $H_2Os_3(CO)_9(C_9H_5Bu^t)$ (10) in reasonable yields (ca. 50% and 30%, respectively), while complex 3 only affords a very low yield of $H_2Os_3(CO)_9(C_4H_2Bu^tN)$ (11) and complex 4 gives no separable substituted product. Complexes 5–11 have been characterized by spectroscopic methods, and the relevant data are shown in Table I.

Scheme I. Friedel–Crafts Reactions of Complexes 1–4

$$\underset{\mathbf{1}}{H_2Os_3(CO)_9(C_6H_4)} \xrightarrow[CS_2,\ 0\ °C \rightarrow \text{room temp}]{RCl/AlCl_3} H_2Os_3(CO)_9(C_6H_3R) \quad (1)$$

$$R = CH_3CO\ (\mathbf{5}),\ Bu^t\ (\mathbf{9})$$

$$\underset{\mathbf{2}}{H_2Os_3(CO)_9(C_9H_6)} \xrightarrow[CS_2,\ 0\ °C \rightarrow \text{room temp}]{RCl/AlCl_3} H_2Os_3(CO)_9(C_9H_5R) \quad (2)$$

$$R = CH_3CO\ (\mathbf{6}),\ Bu^t\ (\mathbf{10})$$

$$\underset{\mathbf{3}}{H_2Os_3(CO)_9(C_4H_3N)} \xrightarrow[CS_2,\ 0\ °C \rightarrow \text{room temp}]{RCl/AlCl_3} H_2Os_3(CO)_9(C_4H_2RN) \quad (3)$$

$$R = CH_3CO\ (\mathbf{7}),\ Bu^t\ (\mathbf{11})$$

$$\underset{\mathbf{4}}{H_2Os_3(CO)_9(C_4H_2NMe)} \xrightarrow[CS_2,\ 0\ °C \rightarrow \text{room temp}]{CH_3COCl/AlCl_3} \underset{\mathbf{8}}{H_2Os_3(CO)_9[C_4H(COCH_3)NMe]} \quad (4)$$

The infrared spectra of these acylated and alkylated clusters are very informative. In the IR spectra of complexes 5–8, the characteristic absorptions at 1693 cm^{-1} (5 and 6), 1683 cm^{-1} (7), and 1677 cm^{-1} (8) indicate unambiguously the presence of an acyl group. Moreover, as expected, most of the complexes (except complex 8) have the same IR pattern as their corresponding parent clusters, but the absorptions have shifted 1–5 wavenumbers higher (in the case of acylation) or 1–3 wavenumbers lower (in the case of alkylation). This implies that the electrophilic substitution on the arene does not cause any change in the symmetry of the molecule but a slight change in the electron density on the arene and also that on the cluster

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Table I. Spectroscopic Data for the Acylated and Alkylated Complexes

complex	MS, m/e[a]	IR ν_{CO}, cm^{-1} [b,c]	^{1}H NMR δ, ppm (J, Hz)[d]
$H_2Os_3(CO)_9(C_6H_3COCH_3)$ (**5**)	948	2111 m (2109), 2083 vs (2081), 2058 vs (2056), 2038 vs (2035), 2026 s (2024), 2012 vs (2009), 2004 s (2000), 1988 s (1985), 1957 vs (1954), 1693 w	8.43 dd (H_a, $J_{H_aH_b}$ = 1.7), 7.96 dd, (H_c, $J_{H_bH_c}$ = 8.5), 7.42 dd (H_b, $J_{H_aH_c}$ = 0.8), 2.51 s (COCH_3), −18.95 s (OsH)
$H_2Os_3(CO)_9(C_9H_5COCH_3)$ (**6**)	984	2110 m (2108), 2082 vs (2081), 2058 vs (2057), 2036 vs (2033), 2026 s (2025), 2013 vs (2011), 2003 s (2000), 1988 s (1986), 1957 vs (1956), 1693 w	7.99 d (H_a, $J_{H_aH_b}$ = 1.0), 7.93 dd (H_b, $J_{H_bH_c}$ = 8.0), 7.47 d (H_c), 3.94 AB quartet (H_d, $H_{d'}$), 2.59 s (COCH_3), −19.90 br s (OsH)
$H_2Os_3(CO)_9[C_4H_2(COCH_3)N]$ (**7**)	937	2112 m (2109), 2086 s (2083), 2058 vs (2055), 2033 s (2029), 2013 s (2009), 2005 s (2000), 1985 m (1982), 1683 w	7.90 s (H_b), 7.88 s (H_a), 2.38 s ($COCH_3$), −15.61 and −16.72 br s (OsH)
$H_2Os_3(CO)_9[C_4H(COCH_3)NMe]$ (**8**)	951	2114 m (2109), 2080 s (2077), 2056 vs (2052), 2042 w, 2027 s (2028), 2002 vs (2002, 1993), 1980 m, (1979), 1667 w	7.83 s (H_a), 3.60 s (NCH_3), 2.30 s (COCH_3), −18.98 s (OsH)
$H_2Os_3(CO)_9(C_6H_3Bu^t)$ (**9**)	962	2108 m, 2079 vs, 2054 s, 2034 vs, 2023 s, 2007 vs, 1998 s, 1983 s	7.86 d (H_c, $J_{H_aH_b}$ = 1.7), 7.80 d (H_a, $J_{H_bH_c}$ = 9.0), 6.92 dd (H_b), 1.26 s (Bu^t), −18.91 s (OsH)
$H_2Os_3(CO)_9(C_9H_5Bu^t)$ (**10**)	1000	2107 m, 2080 vs, 2056 vs, 2032 vs, 2024 s, 2010 vs, 1999 s, 1985 s	7.40 m, (H_a, H_b, H_c), 3.85 br d (H_d, $H_{d'}$), 1.33 s (Bu^t), −19.25 br s (OsH)
$H_2Os_3(CO)_9(C_4H_2Bu^tN)$ (**11**)	965	2107 w, 2081 s, 2053 vs, 2026 vs, 2008 s, 1998 m, 1980 mw, 1958 vw, br	[e]

[a] Based on ^{192}Os. [b] Recorded in hexane solution. [c] The absorptions of the corresponding parent clusters are listed in parentheses. [d] Recorded in CD_2Cl_2 solution on a WM 250-MHz spectrometer. [e] Yield of this complex is not enough to record an NMR spectrum.

as a whole. In the case of acylation, the presence of the electron-withdrawing group $COCH_3$ decreases the electron density on the arenes and the metal frameworks. Therefore, the back-donation from the metal atoms to the carbonyl ligands is weakened, which in turn results in stronger bonding between the carbon atom and the oxygen atom of a carbonyl. In the case of alkylation, since the *tert*-butyl group is weakly electron-donating, the result is just the opposite. The ^{1}H NMR data of these clusters give not only further confirmation of the occurrence of the substitution but also some information about the position of the substitution, as shown in Figure 1. The structures of clusters **8** and **9** have been confirmed by an X-ray crystallographic study, which will be reported later.

In the literature, there have been some reports on the Friedel–Crafts reactions of tricarbonyl(diene, triene, or tetraene)iron compounds,[11–13] and the yields of these reactions vary with the different systems. This reflects the different nucleophilicities of the relevant systems investigated. Such differences among the clusters **1**–**4** are also manifested by the yields of their Friedel–Crafts acylation reactions. In cluster **2**, $H_2Os_3(CO)_9(C_9H_6)$, the indyne ligand coordinates to the metal framework via the five-membered ring and the six-membered benzene ring remains intact. It is therefore expected to have the highest electron density and nucleophilicity. Indeed, the conversion from cluster **2** to the acylated species **6** could be up to 70%. At the other extreme, the pyrrole ligand in cluster **3**, $H_2Os_3(CO)_9(C_4H_3N)$, has a bonding mode different from the others in that a carbon atom bridges two osmium atoms and the nitrogen atom donates two electrons to the third Os atom, so the ligand has lost its aromaticity. Therefore, cluster **3** acts more like a diene species and its reactivity toward the electrophiles decreases.

Interestingly, the Friedel–Crafts reactions of these cluster complexes might provide a new scope for the organic synthesis. For example, uncomplexed indene is readily polymerized in the presence of aluminum chloride;[14] therefore, it is impossible for indene to undergo a Friedel–Crafts reaction under normal conditions. However, on coordination to a metal triangle in **2**, the π-bond

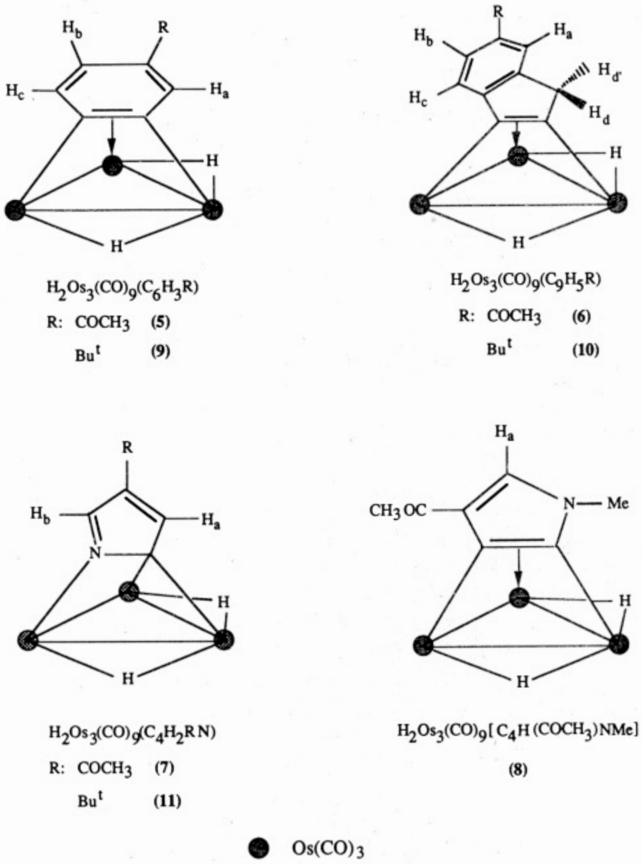

Figure 1. Proposed structures for clusters **5**–**11**.

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of the five-membered ring is bonded to a metal atom; thus, the ligand loses the ability to polymerize, which in turn makes the Friedel–Crafts reaction possible. Moreover, in each case of the reactions of complexes 1–4, only one substituted complex is isolated, which might imply the high selectivity of the reaction. Further investigation of the reactivity of the acylated cluster complexes is in progress in order to find out the possibility of synthetic utility of the acylation reactions of these clusters.

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Registry No. 1, 38979-81-6; 2, 67265-50-3; 3, 109464-89-3; 4, 85159-47-3; 5, 123358-57-6; 6, 123358-58-7; 7, 123358-59-8; 8, 123358-60-1; 9, 123358-61-2; 10, 123358-62-3; 11, 123380-76-7.

Reactivity of Coordinated Carbon Dioxide: Reactions of $(C_5H_5)_2Mo(\eta^2-CO_2)$ with Electrophiles

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Summary: The title complex **1** reacts with a variety of electrophilic reagents to afford products derived from O-centered electrophilic attack on coordinated CO_2. In the case of Me_3SiCl, ${}^tBuMe_2SiCl$, and HCl complete oxygen transfer occurs, producing $[(C_5H_5)_2Mo(CO)Cl]Cl$ (**2a**) and $R_3SiOSiR_3$ or H_2O. The reaction of **1** with $Me_3SiOSO_2CF_3$ in THF affords the unusual dicationic complex $[(C_5H_5)_2Mo(CO)(THF)](OSO_2CF_3)_2$ (**3**), whose structure has been established by X-ray diffraction.

The prospects for useful transition-metal-mediated reactions of carbon dioxide have stimulated widespread interest in the coordination chemistry of this typically unreactive molecule.[2] Although a number of discrete metal–CO_2 complexes have been characterized,[3] the reactivity of coordinated carbon dioxide, particularly in η^2 complexes, remains virtually unknown.[4] For a few η^1 complexes reductive disproportionation and O-centered electrophilic attack have been observed.[5,6] Following our recent discovery of the first photoinduced reaction of coordinated CO_2 in $(C_5H_5)_2Mo(\eta^2-CO_2)$ (1),[7] we present here our findings on the *dark* reactions of this η^2 complex with several electrophilic and oxophilic reagents, which result in reduction of coordinated CO_2 via O-transfer to the attacking reagent.

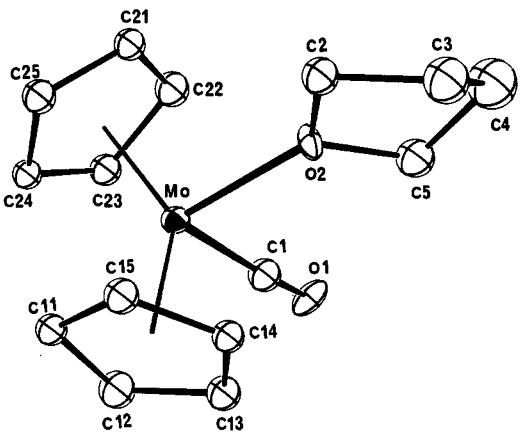
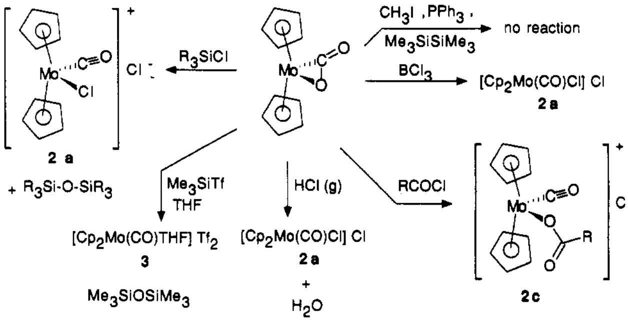


Figure 1. ORTEP diagram for the cation of $[(\eta^5-C_5H_5)_2Mo(CO)(C_4H_8O)](CF_3SO_3)_2$ (**3**). Selected bond lengths (Å) and angles (deg): Mo–Cp(1) = 1.99 (2), Mo–Cp(2) = 1.98 (2), Mo–O(2) = 2.14 (1), Mo–C(1) = 2.03 (2), C(1)–O(1) = 1.17 (2); Cp(1)–Mo–Cp(2) = 137.2 (8), O(2)–Mo–C(1) = 89.3 (7).

Scheme I



Treatment of a THF solution of 1 with 2 equiv of Me_3SiCl at −78 °C results in the immediate precipitation of a pale orange solid identified as $[(C_5H_5)_2Mo(CO)Cl]Cl$ (**2a**, 97%[8]) on the basis of its spectroscopic properties[9] (Scheme I). Analysis of the reaction solution by ^1H NMR and GC/MS methods revealed the presence of an approximately equal amount of $Me_3SiOSiMe_3$.[10] The reaction between 1 and ${}^tBuMe_2SiCl$ proceeded analogously, albeit more slowly, also giving **2a** (92%) and ${}^tBuMe_2SiOSiMe_2Bu^t$.[11] Complex 1 also reacts rapidly with 2 equiv of $Me_3SiOSO_2CF_3$ in THF at −78 °C to quantitatively afford the cationic carbonyl complex **3** (ν_{CO} 2060 cm^{-1}) and $Me_3SiOSiMe_3$. Since spectroscopic and analytical data[12] for **3** did not allow an unambiguous structural

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[1] Address inquiries regarding X-ray diffraction results to this author.

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[8] IR (KBr): 2040 cm^{-1}. ^1H NMR (DMSO-d_6): δ 6.39. MS (FAB): *m/e* 291 ($Cp_2{}^{98}MoCOCl^+$), 263 ($Cp_2{}^{98}MoCl^+$), 256 ($Cp_2{}^{98}MoCO^+$). The IR and NMR data coincide with those of $\{Cp_2Mo(CO)Cl\}AlCl_4$.[9]

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[10] MS (EI, 12 eV) of $(CH_3)_3SiOSi(CH_3)_3$: *m/e* 147 ($M^+ - CH_3$, 100), 73 ($Si(CH_3)_3{}^+$, 2). The ratio of *m/e* 147/148/149 peaks (100:17:8) was identical with that for authentic $(CH_3)_3SiOSi(CH_3)_3$.

[11] MS (EI, 12 eV) of $(CH_3)_3CSi(CH_3)_2OSi(CH_3)_2C(CH_3)_3$: *m/e* 246 ($M^+$, 1), 231 ($M^+ - CH_3$, 1), 189 ($M^+ - C(CH_3)_2$, 20), 147 ($M^+ - 2C(CH_3)_2$, 100).

[12] Analytical and spectroscopic data for **3** are as follows. IR (KBr): 2060 cm^{-1}. ^1H NMR (acetone-d_6): δ 6.96 (s, C_5H_5, 10 H), 4.01 (apparent t, J = 6.6 Hz, 4 H), 1.98 (m, 4 H). ^{19}F NMR (acetone-d_6): δ −89.6 (vs, CF_3CO_2H). MS (FAB): *m/e* 405 ($Cp_2{}^{98}Mo(CO)OSO_2CF_3{}^+$), 377 ($Cp_2{}^{98}MoOSO_2CF_3{}^+$), 328 ($Cp_2{}^{98}MoCO(C_4H_8O)$), 256 ($Cp_2{}^{98}MoCO^+$). Anal. Calcd for $[(C_5H_5)_2Mo(CO)(C_4H_8O)](CF_3SO_2)_2$: C, 32.7; H, 2.9; F, 18.3. Found: C, 33.2; H, 2.9; F, 20.2.

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