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Stepwise Reduction of CO to CH_4 on a Triosmium Cluster Face. Preparation and Characterization of $Os_3(CO)_{11}CH_2$

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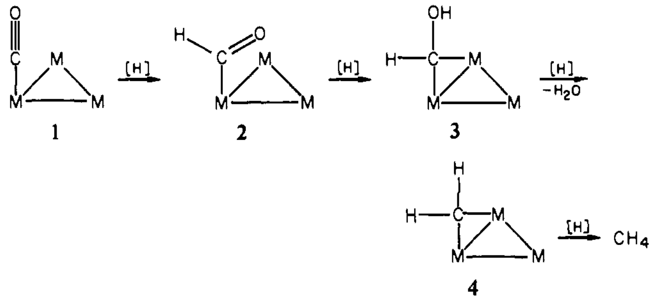
Numerous mechanistic schemes have been proposed for the metal-surface-catalyzed reduction of CO to yield hydrocarbons.[1-5] Many of these invoke formyl intermediates with reaction sequences similar to that outlined below for the hydrogenation of CO to CH_4.[1-3] We have been attempting to assess the feasibility of such transformations by using metal cluster complexes to model the proposed surface intermediates. Our initial focus has been on studies of the preparation and reactivity of formyl substituted clusters as models for **2**. Herein we describe the reaction of $[Os_3(CO)_{11}(CHO)]^-$ with acid which yields the new methylene cluster $Os_3(CO)_{11}CH_2$, a mimic for the surface intermediate **4**. The latter cluster when heated under an H_2 atmosphere evolves CH_4, and thus the stepwise reduction of CO to CH_4 on an Os_3 cluster face is demonstrated.



Treatment of $Os_3(CO)_{12}$ in tetrahydrofuran (THF) with K-[BH(O-*i*-Py)$_3$] at 0 °C gives an intense orange solution which shows an IR band at 1577 cm^{-1} and a singlet at δ 16.0 in its ^1H NMR spectrum. These spectral data indicate the presence of a formyl substituent and suggest the formation of $[Os_3(CO)_{11}(CHO)]^-$. Upon warmup to 25 °C, the solution turns dark orange and the IR band at 1577 cm^{-1} decreases in intensity as a new band at 1710 cm^{-1} grows in. This transformation is complete within ~2.5 h. At this point metathesis with $[(Ph_3P)_2N]Cl$ leads to the isolation of $[(Ph_3P)_2N][HOs_3(CO)_{11}]$,[6] which apparently derives from the formyl complex by the deinsertion reaction shown in eq 1. Similar results have been obtained by Pruett and co-workers[7]

$$Os_3(CO)_{12} + [BH(O\text{-}i\text{-}Pr)_3]^- \rightarrow [Os_3(CO)_{11}(CHO)]^- \xrightarrow[-CO]{} [HOs_3(CO)_{11}]^- \quad (1)$$

who treated THF solutions of $Os_3(CO)_{12}$ with Li[BHEt$_3$].

In an attempt to isolate a stable neutral product, excess 20% H_3PO_4 was added to the $[Os_3(CO)_{11}(CHO)]^-$ solution when this species' 1577 cm^{-1} IR band was at its maximum intensity (~45 min at 0 °C after addition of K[BH(O-*i*-Pr)$_3$]). The solution immediately turned dark red and workup by preparative scale liquid chromatography on silica with hexane eluant gave an orange-red, air-stable solid in typical yields of 20–30%. This material was identified as $Os_3(CO)_{11}CH_2$ by chemical analysis and by its spectral properties: mass spectrum, *m/e* 894 (parent), fragment ions corresponding to loss of 11 CO's and 2 H's; IR (hexane solution) 2116 w, 2063 s, 2031 s, 2010 m, 1995 m, 1920 vw, 1869 vw cm^{-1}.[8,9] Anal. Calcd: C, 15.92; H, 0.45. Found: C, 16.14; H, 0.23.

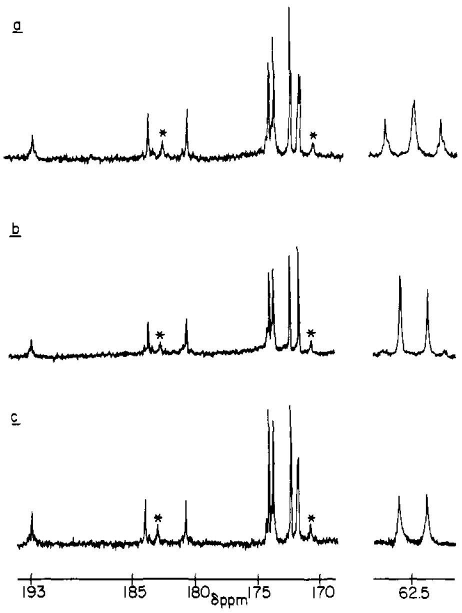


Figure 1. ^{13}C NMR spectra of $Os_3(CO)_{11}CH_2$ in CD_2Cl_2: (a) fully ^1H coupled, (b) $^{13}C\{^1H_a\}$, and (c) $^{13}C\{^1H_b\}$. $J_{^{13}C-H_a}$ = 144 Hz and $J_{^{13}C-H_b}$ = 147 Hz. Resonances at 171 and 183 ppm marked with an * are due to $Os_3(CO)_{12}$ impurity.

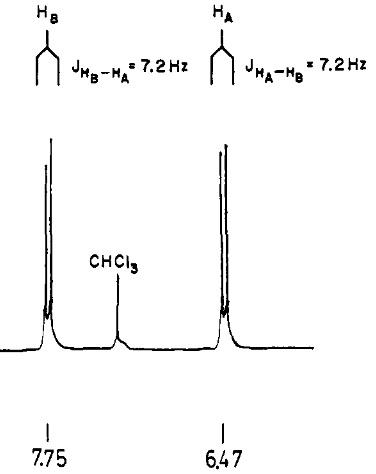
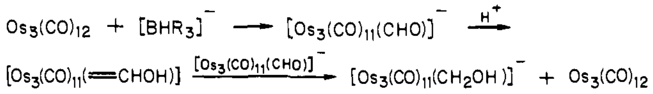


Figure 2. ^1H NMR spectrum of $Os_3(CO)_{11}CH_2$ in $CDCl_3$ solution.

Scheme I



$$Os_3(CO)_{12} + [BHR_3]^- \longrightarrow [Os_3(CO)_{11}(CHO)]^- \xrightarrow{H^+}$$

$$[Os_3(CO)_{11}({=}CHOH)] \xrightarrow{[Os_3(CO)_{11}(CHO)]^-} [Os_3(CO)_{11}(CH_2OH)]^- + Os_3(CO)_{12}$$

$$\downarrow H^+$$

$$H_2O + Os_3(CO)_{11}CH_2$$

A ^{13}C enriched sample of $Os_3(CO)_{11}CH_2$ was prepared by treating ^{13}CO enriched $Os_3(CO)_{12}$ with K[BH(*O*-*i*-Pr)$_3$] followed by H_3PO_4 acidification. The ^{13}C NMR spectrum of this material is shown in Figure 1a. The seven resonances in the 171–193-ppm

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(1) Huang, C. P.; Richardson, J. T. *J. Catal.* **1978**, *51*, 1.

(2) Pichler, H.; Schultz, H. *Chem. Ing. Tech.* **1970**, *42*, 1162.

(3) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

(4) Araki, M.; Ponec, V. *J. Catal.* **1976**, *44*, 439.

(5) van Barneveld, W. A. A.; Ponec, V. *J. Catal.* **1978**, *51*, 426.

(6) Addition of $[(Ph_3P)_2N]Cl$ followed by hexane to a THF solution of the $Os_3(CO)_{12}$/K[BH(O-*i*-Pr)$_3$] reaction mixture held at −30 °C gave $[(Ph_3P)_2N][HOs_3(CO)_{11}]$ as a microcrystalline yellow-orange powder in 72% yield. The compound was identified by comparison of its ^1H NMR and IR spectra to those reported by: Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1978**, 1358.

(7) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1979**, *182*, C57.

(8) $Os_3(CO)_{11}CH_2$ differs from the previously reported $H_2Os_3(CO)_{10}CH_2$ (Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225, corrected in *Ibid.* **1978**, *100*, 6544) by substitution of a carbonyl for two hydrides. For comparison, $H_2Os_3(CO)_{10}CH_2$ shows ^1H NMR resonances at δ 4.32, 5.12, 15.38, and 20.71.

(9) $Os_3(CO)_{11}CH_2$ has also been recently prepared by J. R. Shapley and co-workers by the addition of CH_2N_2 to $Os_3(CO)_{11}(CH_3CN)$. (J. R. Shapley, personal communication.)

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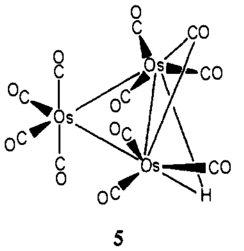
chemical shift region are assigned to the carbonyl ligands[10] and show an approximate intensity ratio of 1:1:1:2:2:2:2 in the fully decoupled spectrum.[11] This resonance pattern is similar to that reported[6] for $[HOs_3(CO)_{11}]^-$ whose structure is sketched in **5**. The structure **6** is thus indicated for $Os_3(CO)_{11}CH_2$. Consistent with the structure **6** is the presence of the weak IR band at 1869 cm^{-1} in the spectrum of $Os_3(CO)_{11}CH_2$ which can be assigned to the bridging carbonyl. The ^1H NMR spectrum of $Os_3(CO)_{11}CH_2$ (Figure 2) shows two equal intensity doublets at δ 6.47 and 7.75 which are due to the two inequivalent hydrogens of the methylene group, with $J_{H_a-H_b} = 7.2$ Hz. In the fully coupled ^{13}C NMR spectrum (Figure 1a) an apparent triplet is observed at 62.5 ppm with relative intensity 1 which can be assigned to the methylene carbon. However, the spectra shown in Figure 1b and 1c, in which the two methylene hydrogens are selectively decoupled, indicate that this pseudotriplet is due to a pair of partially overlapping doublets resulting from the coupling of the methylene carbon with the two inequivalent CH_2 protons.



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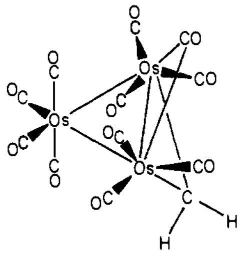

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Several experiments were conducted in an effort to elucidate the mechanism by which $Os_3(CO)_{11}CH_2$ forms. First, no $Os_3(CO)_{11}CH_2$ was produced when acidification was carried out before $[Os_3(CO)_{11}(CHO)]^-$ formed to a significant extent or after $[Os_3(CO)_{11}(CHO)]^-$ had thermally decomposed. Thus, $[Os_3(CO)_{11}(CHO)]^-$ must be the precursor to the $Os_3(CO)_{11}CH_2$ product. It was also observed that acidification of an $[Os_3(CO)_{11}(CHO)]^-$ solution with CF_3CO_2D gave $Os_3(CO)_{11}CH_2$, but no $Os_3(CO)_{11}CHD$ was detected. Conversely, H_3PO_4 protonation of $[Os_3(CO)_{11}(CDO)]^-$, prepared by reduction of $Os_3(CO)_{12}$ with $Li[BDEt_3]$, gave only $Os_3(CO)_{11}CD_2$. These deuterium labeling experiments clearly indicate that both methylene hydrogens derive from the borohydride reducing agent and that the function of the acid is to remove the carbonyl oxygen, presumably as H_2O. Finally, it was observed that addition of excess $K[BH(O\text{-}i\text{-}Pr)_3]$ did not lead to an increased $Os_3(CO)_{11}CH_2$ yield, implying that this species does not form as a result of a further reaction of $[Os_3(CO)_{11}(CHO)]^-$ with $[BH(O\text{-}i\text{-}Pr)_3]^-$.[12]

The reaction sequence that is most consistent with these various results is shown in Scheme I. Protonation presumably occurs at the formyl oxygen of $[Os_3(CO)_{11}(CHO)]^-$ to yield $Os_3(CO)_{11}(CHOH)$. Analogous formyl oxygen protonation has been shown to occur with $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHO)$ to yield $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHOH)]^+$.[13] Hydride transfer to the hydroxymethylene cluster from another $[Os_3(CO)_{11}(CHO)]^-$ would yield $[Os_3(CO)_{11}(CH_2OH)]^-$ and a corresponding amount of $Os_3(CO)_{12}$. An equivalent amount of $Os_3(CO)_{12}$ was isolated after acidification, consistent with this mechanistic proposal. Similar hydride transfer reactions have been observed by Gladysz[13] and Casey[14] and their co-workers. Continued protonation of $[Os_3(CO)_{11}(CH_2OH)]^-$ at the oxygen atom, followed by elimination of H_2O, would yield the observed $Os_3(CO)_{11}CH_2$ cluster. Note that according to this mechanism, both methylene hydrogens derive from the $[BHR_3]^-$ reducing agent, via the intermediacy of $[Os_3(CO)_{11}(CHO)]^-$, in accord with the experimental observations.

When $Os_3(CO)_{11}CH_2$ was heated to 70–80 °C under an H_2 atmosphere, CH_4 was evolved in ~20% yield, as evidenced by mass spectral analysis of the gases above such solutions.[15] Only CH_2D_2 was produced when $Os_3(CO)_{11}CH_2$ was heated under a D_2 atmosphere. The only Os-containing products from these reactions which could be identified were small amounts of $Os_3(CO)_{12}$(<10%) and a trace amount of a material for which mass spectral evidence indicates the formulation $Os_3(CO)_{10}CH_2$. The mass spectrum of this latter compound shows a parent ion at m/e 866 and fragment ions corresponding to loss of 10 carbonyls and 2 hydrogens. This same material was isolated in an 80% yield following 70–80 °C thermolysis of $Os_3(CO)_{11}CH_2$ in benzene solution under N_2; $Os_3(CO)_{12}$ in a 20% yield was the only other product that could be detected from this reaction. When this material was heated to 70–80 °C under an H_2 atmosphere, it did not yield CH_4, and thus this species does not appear to be an intermediate in the CH_4 production. Although we do not know the structure of $Os_3(CO)_{10}CH_2$, the only resonance observed in its ^1H NMR spectrum in benzene-d_6 solution is a sharp singlet at δ −20.1 which implies one or more equivalent hydrides. No resonance which might be assigned to a μ^3-CH group was seen. Experiments directed toward more fully characterizing this latter compound are continuing.[16]

It is interesting that the results reported herein differ from those described by Pruett and co-workers.[7] These workers did acidify $[Os_3(CO)_{11}(CHO)]^-$ solutions with CF_3CO_2H and observed formation of 20–30% methanol, but no mention was made of the cluster products from their reactions or the manner in which the methanol was characterized. In our hands, CH_3OH was not observed by gas chromatographic techniques upon acidifiction with CF_3CO_2H, but $Os_3(CO)_{11}CH_2$ was produced in a yield similar to that obtained upon acidification with H_3PO_4. Also, no CH_3OH was detected when protonation was carried out with H_3PO_4.

In addition to demonstrating the stepwise reduction of CO to CH_4 on a cluster face, the results reported herein also show that reaction sequences similar to those established for monomeric formyl complexes can be carried over to cluster-based systems.[13,14] With regard to the mechanism of the surface-catalyzed reduction of CO, these results show that hydrogenation of surface-bound carbenes is a reasonable path for the production of hydrocarbons. Similar conclusions have been noted by others.[17]

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this research and Professor John Shapley for communication of unpublished results from related research being carried out in his laboratories. G.L.C. acknowledges the Alfred P. Sloan Foundation for a research fellowship and the Camille aand Henry Dreyfus Foundation for a Teacher–Scholar award.

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[10] (a) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 6775. (b) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

[11] ^{13}C NMR δ 193.4, 184.0, 180.9, 174.3, 173.9, 172.6, 171.9.

[12] The isolated yield of $Os_3(CO)_{11}CH_2$ actually decreased to 10% when a 6-fold excess of $K[BH(O\text{-}i\text{-}Pr)_3]$ was used compared to the 20% yield when a stoichiometric quantity of the borohydride was employed.

[13] (a) Wong, W.-K.; Tam, W.; Gladsyz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (b) Gladsyz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545.

[14] (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (b) Casey, C. P.; Andrews, M. A.; *McAlister*, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[15] Hydrogenation of mononuclear carbene complexes has been reported: Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 1651.

[16] Shapley and co-workers have also observed that pyrolysis of $Os_3(CO)_{11}CH_2$ leads to $Os_3(CO)_{10}CH_2$ (J. R. Shapley, personal communication).

[17] Summer, C. E.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

Improvement of Energy Conversion Efficiency by Specific Chemical Treatments of n-$MoSe_2$ and n-WSe_2 Photoanodes

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The apparent stability to photocorrosion reactions exhibited by the semiconducting transition-metal dichalcogenides which crystallize in layered structures has led to an increasing interest