For the preparation of **9**, the borinate ester **7** (10 mmol) was dissolved in 15 mL of THF and treated with 3.33 mmol of $LiAlH_4$ in the presence of 1.56 mL (10 mmol) of 1-octene at 0 °C. The reaction mixture was stirred for 3 h at room temperature, and the aluminum salts were removed by a slow addition of 0.65 g of H_2SO_4 (6.66 mmol) and 0.5 mL of water at 0 °C. The reaction mixture was extracted with pentane (2 × 20 mL), the combined organic extracts were dried over anhydrous K_2CO_3, solvents were removed under vacuum, and the resulting **2** was subjected to the DCME reaction.[16] GC analysis using n-dodecane as an internal standard showed a 69% yield of 7-pentylpentadecan-7-ol. Approximately 5% of impurities could be detected.

In summary, the bromine atoms of alkyldibromoboranes serve as effective and easily replaceable blocking groups for stepwise hydroboration. They can be sequentially replaced via the hydridation reaction.[6] Subsequent stepwise hydroboration provides the mixed dialkylbromoboranes and trialkylboranes. This process represents the first general synthesis for such hitherto inaccessible derivatives via the stepwise hydridation–hydroboration processes. Both the mixed organoboranes as well as the sequential hydridation–hydroboration process possess great synthetic potential, some of which we are presently exploring.

Acknowledgment. We thank the National Institutes of Health for the financial support through Grant GM 10937-19.

Registry No. **1B** ($R^A = n\text{-}C_5H_{11}$, $R^B = n\text{-}C_6H_{13}$), 79329-70-7; **1B** ($R^A = n\text{-}C_6H_{13}$, $R^B = n\text{-}C_{12}H_{25}$), 79357-03-2; **2** ($R^A = n\text{-}C_6H_{13}$, $R^B = n\text{-}C_5H_{11}$, $R^C = n\text{-}C_8H_{17}$), 79329-09-2; **3B** ($R^A = n\text{-}C_6H_{13}$), 79329-71-8; **6B** ($R^A = n\text{-}C_5H_{11}$), 79357-04-3; **6B** ($R^A = n\text{-}C_6H_{13}$), 79357-05-4; **7** ($R^A = n\text{-}C_5H_{11}$, $R^B = n\text{-}C_6H_{13}$), 79329-10-5; **7** ($R^A = n\text{-}C_6H_{13}$, $R^B = n\text{-}C_{12}H_{25}$), 79329-11-6; **8** ($R^A = n\text{-}C_5H_{11}$, $R^B = n\text{-}C_6H_{13}$), 6064-27-3; **8** ($R^A = n\text{-}C_6H_{13}$, $R^B = n\text{-}C_{12}H_{25}$), 79329-12-7; **9** ($R^A = n\text{-}C_6H_{13}$, $R^B = n\text{-}C_5H_{11}$, $R^C = n\text{-}C_8H_{17}$), 79329-13-8; 1-pentene, 109-67-1; 1-hexene, 592-41-6; 1-dodecene, 112-41-4; 1-octene, 111-66-0.

Conversion of a Bridging Methylene Ligand to a Ketenylidene Moiety. Synthesis and Reactivity of $H_2Os_3(CO)_9(CCO)$

A. C. Sievert, D. S. Strickland, and J. R. Shapley*

Department of Chemistry and
Materials Research Laboratory
University of Illinois
Urbana, Illinois 61801

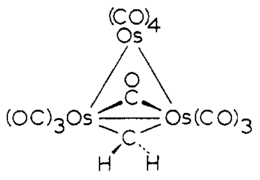
G. R. Steinmetz and G. L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

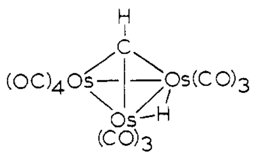
Received June 3, 1981

Summary: The product formed by thermally induced loss of carbon monoxide from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ is formulated as $H_2Os_3(CO)_9(\mu_3\text{-}1,2\text{-}\eta^2\text{-}CCO)$. The latter compound readily reacts with methanol to form the carbomethoxymethylidyne cluster, $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$.

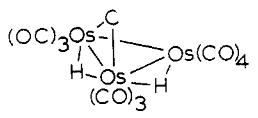
Recently a new triosmium methylene cluster, $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, was prepared by protonation of $[Os_3(CO)_{11}CHO]^-$ and was proposed to have structure I based on infrared and ^{13}C and ^1H NMR spectroscopy.[1]



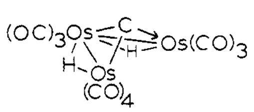
I



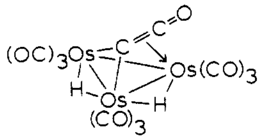
II



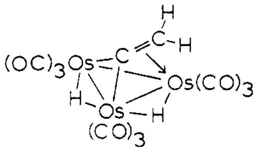
IIIa



IIIb



IV



V

The methylene cluster may also be obtained by treating $Os_3(CO)_{11}NCMe$ with CH_2N_2;[2] an X-ray crystallographic study of the trimethylsilyl derivative $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)$ is consistent with structure I.[2] From hydrogenation of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ in refluxing benzene, a yellow byproduct having the stoichiometry "$Os_3(CO)_{10}(CH_2)$" was observed.[1] The same compound (mass spectrum, m/z 870 M^+ (^{192}Os); IR (ν(CO), C_6H_{12}) 2121 mw, 2086 s, 2064 vs, 2055 vs, 2034 mw, 2006 ms, 1994 m, 1984 mw) is prepared in 84% yield by refluxing a nitrogen-purged toluene solution of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$.

Three formulations have been considered for "$Os_3(CO)_{10}(CH_2)$". The prospect of $HOs_3(CO)_{10}(\mu_3\text{-}CH)$ (II), analogous to the conversion of $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ into $H_3Os_3(CO)_9(\mu_3\text{-}CH)$,[3] is eliminated by the absence of a methylidyne ^1H NMR signal. A singlet hydride peak is seen at 25 °C (τ 29.73, CH_2Cl_2) and down to −80 °C. The $^{13}C\{^1H\}$ NMR spectrum of "$Os_3(CO)_{10}(^{13}CH_2)$" (90% ^{13}C enriched, from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}^{13}CH_2)^2$) shows a singlet at δ 8.6 ($CDCl_3$, 25 °C); off-resonance decoupling establishes that the labeled carbon is not hydrogen substituted (the τ 29.73 signal is now a doublet, $^2J(C\text{–}H) = 2.9$ Hz). A formula such as $H_2Os_3(CO)_{10}(C)$ seems unlikely, since compounds with either a divalent (IIIa) or a trivalent (IIIb) carbon atom are expected to be quite reactive and hence unstable. However, formulation of the yellow compound as a ketenylidene complex, $H_2Os_3(CO)_9(CCO)$ (IV), is consistent with all the available data. Thus, the IR spectrum (Nujol mull) shows a weak band at 1644 cm^{-1} which is assigned to ν(CCO) of the ketenylidene moiety. Furthermore, the ^{13}C NMR spectrum of a sample prepared from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ that was ca. 40% ^{13}C enriched at the carbonyls and 90% ^{13}C enriched at the methylene shows both the δ 8.6 singlet and a superimposed doublet ($^1J(C\text{–}C) = 86$ Hz) of ca. 40% total intensity. Simultaneously, a doublet with the same coupling constant, due to the ketenylidene carbonyl, appears at δ 160.3.

---

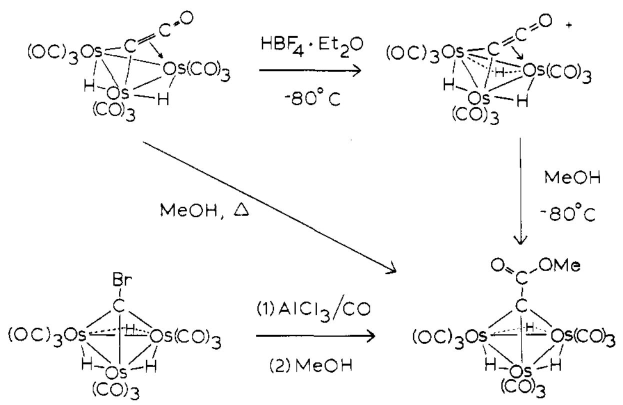
[1] Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278.

[2] Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.*, in press.

[3] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

0276-7333/82/2301-0214$01.25/0

Scheme I



Under the same conditions ($CDCl_3$, 25 °C) the osmium carbonyl carbons appear as broad resonances at δ 165.8 and 175.6 (ratio 2:1). However, at a lower temperature a 2:2:1:2:2 pattern is observed (−60 °C, CD_2Cl_2, δ 179.6, 173.0, 169.9, 168.0, 158.3). If the hydride ligands in $H_2Os_3(CO)_9(CCO)$ are placed unsymmetrically as shown in IV, which is proposed in analogy with the arrangement established for $H_2Os_3(CO)_9(CCH_2)$ (V),[4] then the low-temperature ^1H and ^{13}C NMR data require rapid hydride equilibration. Alternatively, the actual hydride positions in $H_2Os_3(CO)_9(CCO)$ may be equivalent.

The reactivity of $H_2Os_3(CO)_9(CCO)$ is consistent with its formulation (see Scheme I). Heating the ketenylidene complex in methanol affords the carbomethoxymethylidyne cluster, $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$. The same alkylidyne cluster may be prepared from $H_2Os_3(CO)_9(CCO)$ by an alternative procedure. Treatment of a CH_2Cl_2 solution of $H_2Os_3(CO)_9(CCO)$ with $HBF_4·OEt_2$ at −80 °C gives an off-white precipitate (presumably $[H_3Os_3(CO)_9(CCO)]^+$ or $[H_2Os_3(CO)_9(CCOH)]^+$) which reacts with methanol at −80 °C to afford $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$ (mass spectrum, *m/z* 902 M$^+$ (^{192}Os); ^1H NMR ($CDCl_3$, 35 °C) τ 6.17 (s, 3 H), 29.38 (s, 3 H); IR (ν(CO), C_6H_{12}) 2116 vw, 2089 vs, 2081 w, sh, 2030 ms, 2025 vs, 2015 mw, 1688 vw) in high yield. $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$ can also be prepared by treating $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$[5] with $AlCl_3$ in CH_2Cl_2 under CO followed by addition of methanol. An analogous procedure was used by Seyferth to prepare $Co_3(CO)_9(\mu_3\text{-}CCO_2Me)$[6] and by Keister to prepare $H_3Ru_3(CO)_9(\mu_3\text{-}CCO_2Me)$.[5]

The sequence of C–H bond cleavage and C–C bond formation in the conversion of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ to $H_2Os_3(CO)_9(CCO)$ is not yet clear. Possible intermediates include IIIa or IIIb, II, or a complex of ketene. Transfer of an alkylidene ligand to coordinated CO is known in mononuclear transition-metal chemistry.[7] Transfer of CO to alkylidyne ligands has also been observed.[8] The migration of coordinated CO to a carbon center has been proposed to account for the formation of $[Co_3(CO)_9CCO]^+$ from $Co_3(CO)_9(\mu_3\text{-}CCl)$ and $AlCl_3$[6] and for the formation of $[Fe_4(CO)_{12}(\mu_4\text{-}CCO_2Me)]^-$ from the oxidation of $[Fe_6C(CO)_{16}]^{2+}$ by tropylium bromide in methanol.[9,10]

Acknowledgment. This research has been supported at the University of Illinois by National Science Foundation Grants DMR 80-20250 and CHE 81-00140. Support of this research at The Pennsylvania State University has been provided by the Department of Energy, Office of Basic Energy Sciences. J.R.S. and G.L.G. acknowledge the Alfred P. Sloan Foundation for research fellowships and the Camille and Henry Dreyfus Foundation for Teacher–Scholar awards.

Registry No. I, 77208-32-3; IV, 78697-97-9; $[Os_3(CO)_{11}CHO]^-$, 73788-03-1; $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$, 78697-98-0; $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$, 73746-96-0.

---

[4] Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.

[5] Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19* 2304.

[6] Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758.

[7] Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133.

[8] Kreissel, F. R.; Uedelhoven, W.; Erber, K. *Angew. Chem., Intl. Ed. Engl.* **1978**, *17*, 859.

[9] Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417.

[10] **Note added in proof:** A compound formulated as $Fe_3(CO)_{10}(CCO)$ has recently been reported (Davis, J. H.; Beno, M. A.; Williams, J. M.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668).

Preparation of Dianionic Carbonyl Complexes of Molybdenum and Tungsten

John M. Maher, Richard P. Beatty, and N. John Cooper*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received June 23, 1981

Summary: Reduction of $[M(CO)_5(NMe_3)]$ (M = Cr, Mo, W) in THF with alkali naphthalides gives high purity solutions of the corresponding $[M(CO)_5]^{2-}$ dianions. Stable crystalline salts of the $[M(CO)_5]^{2-}$ dianions (M = Mo, W) were prepared by complexing the sodium counterions with a cryptand. Reduction of $[W(CO)_4(NH_3)\{P(i\text{-}Pr)_3\}]$ with sodium naphthalide gives $[W(CO)_4\{P(i\text{-}Pr)_3\}]^{2-}$, as demonstrated by reaction with Ph_3SnCl and counterion exchange to give $[NEt_4][W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$.

The development of the chemistry of the pentacarbonyl dianions of molybdenum and tungsten has been severely restricted by the lack of a convenient preparation of solutions of the complexes in an innocuous solvent such as an ether.[1] We wish to report new syntheses of these dianions using an alkali naphthalide as the reductant[8] which provide direct excess to high purity solutions of the

---

[1] As noted by others,[2] Behrens' procedures are technically difficult and only suitable for preparing small quantities of the dianions[3,4] or give samples contaminated with other salts.[5] The cesium salts $Cs_2[M(CO)_5]$ (M = Cr, Mo, W), prepared by Cs/Hg reduction of the corresponding hexacarbonyls, are insoluble in ethereal solvents and are usually contaminated with Hg.[6] In our hands, the reduction of $[W(CO)_6]$ with Na/Ng in dimethoxyethane[7] invariably resulted in mixtures of $Na_2[W_2(CO)_{10}]$ and $Na_2[W(CO)_5]$, an observation which is consistent with the published spectra of such reactions and with the rather low yields reported for some of the reactions carried out by using material prepared in this way.[7] Only reduction of the hexacarbonyls with Na in hexamethylphosphoramide[2] gives pure samples of the dianions in a convenient reaction, but the reactivity and high boiling point of this solvent considerably restrict the utility of this approach.[6]

[2] Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7825.

[3] Behrens, H.; Haag, W. *Chem. Ber.* **1961**, *94*, 312.

[4] Behrens, H.; Vogl, J. *Chem. Ber.* **1963**, *96*, 2220.

[5] Behrens, H.; Weber, R. *Z. Anorg. Allg. Chem.* **1957**, *291*, 122.

[6] Ellis, J.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

[7] Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357.

[8] $NaC_{10}H_8$ has been used previously to prepare metal carbonyl anions: Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.

0276-7333/82/2301-0215$01.25/0 © 1982 American Chemical Society