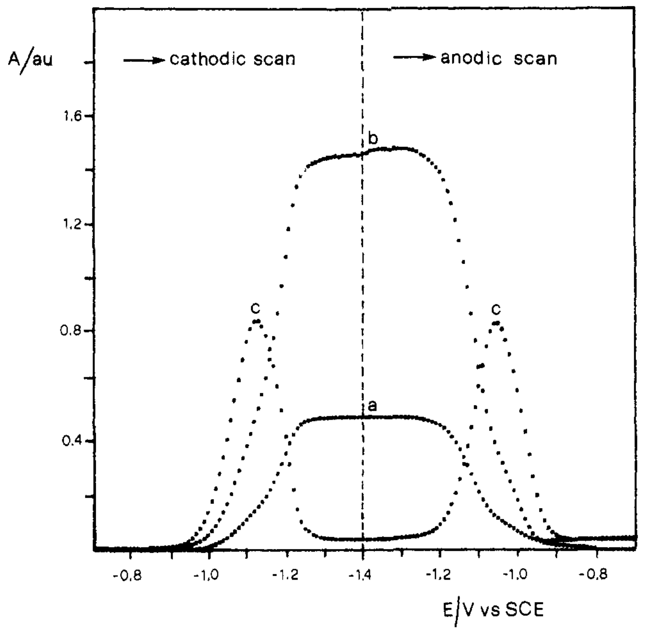

Figure 3. Plot of the absorbances at 424 (a), 632 (b), and 806 (c) nm as a function of the potential.

reversibility of the chemical processes involved. Analogous plots (not shown) of potentiostatic experiments at potentials corresponding to the rising portion of the less cathodic peak (A, Figure 1) show three S-shaped curves, which implies that the species responsible for the 806-nm peak does not undergo any chemical reaction and is stable over a limited potential range.

The whole of the voltammetric, bulk electrolysis and OTTLE data is consistent with the occurrence of two subsequent uncomplicated one-electron charge transfers.[19,20] The intermediate formally Co(II) (806-nm band) and the final formally Co(I) (424- and 632-nm bands) species are chemically stable, unlike all previously studied similar complexes. Cyclic voltammetric curves and absorbance–potential plots allow an approximate evaluation of $E^{r}_{1/2}$ (a good approximation of the standard potential[21]) for the Co(III)/Co(II) couple and a more precise estimation of this parameter for the Co(II)/Co(I) couple, referenced vs Fc, as follows:[22]

$$[\mathrm{LCo^{III}neo\text{-}Pent}]^+ + e^- \leftrightarrow \text{“}\mathrm{LCo^{II}neo\text{-}Pent}\text{”}$$

$$E^{r}_{1/2} \approx -1.39\ \mathrm{V\ at\ -17\ °C}$$

$$\text{“}\mathrm{LCo^{II}neo\text{-}Pent}\text{”} + e^- \leftrightarrow [\text{“}\mathrm{LCo^{I}neo\text{-}Pent}\text{”}]^-$$

$$E^{r}_{1/2} \approx -1.51\ \mathrm{V\ at\ -17\ °C}$$

where L includes ligands other than neopentyl, i.e., (DO)(DOH)pn and the possible axial water or solvent molecules. As suggested previously for much less well-behaved systems,[10,13] the neopentyl group may have migrated onto the equatorial ligand in the reduced species,[23] hence the quotes. Uncertainty over the location of the R group in such species has persisted for years,[13] and further study of the sterically hindered, well-behaved organocobalt species discovered here offers some promise for the resolution of this issue.

Acknowledgment. L.G.M. thanks the NIH (GM 29225) for support.

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[20] Ryan, M. D. *J. Electrochem. Soc.* **1978**, *125*, 547–555.

[21] Brown, E. R.; Sandifer, J. R. In *Physical Methods of Chemistry*, 2nd ed.; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley Interscience: New York, 1986; Vol. II, pp 273–432.

[22] Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461–466.

[23] Although our focus is not mechanism, the reversible character of the II/I couple and the quasi-reversible III/II couple suggest that the intramolecular transfer occurs in the III/II step.

Generation and Reactivity of a Triosmium Carbon Radical. Hydrogen Abstraction, Arene Addition, and the Formation of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, a Dialkylidyne, Diketone Complex

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Summary: Photolyzing a mixture of $Re_2(CO)_{10}$ and $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ under CO (~2 atm) is a convenient method of generating the radical $H_3Os_3(CO)_9(\mu_3\text{-}C^\bullet)$. This species abstracts hydrogen from cyclohexane and toluene and adds to benzene. In deuteriated hydrocarbons $H_3Os_3(CO)_9(\mu_3\text{-}CD)$ is produced, but in cyclohexane-d_{12} a diketone complex, $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, also is formed.

Current interest focuses on the nature and reactivity of exposed carbon atoms in peripheral metal carbide clusters.[1-4] Observed reactivities have indicated that low-coordinate carbon atoms, especially μ_4-C, will be most reactive, perhaps best modeling carbon species on metal surfaces. To date no μ_3-C clusters have been isolated, although calculations suggest that such species may be accessible.[4] One class of μ_3-C clusters consists of the carbon radicals generated from stable μ_3-CX compounds. Such radicals have been proposed as intermediates in some reactions of $Co_3(CO)_9(\mu_3\text{-}CY)$ clusters[5] as well as in the reduction of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ by $(n\text{-}Bu)_3SnH$.[6] We wish to report a convenient method for the generation of the $H_3Os_3(CO)_9(\mu_3\text{-}C^\bullet)$ radical along with preliminary studies of its reactivity. We also report the formation and characterization of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, a novel dimeric diketone cluster.

Interconversion of triosmium methylidyne and halomethylidyne clusters proceeds cleanly and under mild conditions (eq 1),[7,8] using reagents precedented by organic alkyl radical reactions.[9] It is reasonable to propose that

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[1] Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.

[2] Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1.

[3] Wijeyesekera, S. D.; Hoffmann, R.; Wilker, C. N. *Organometallics* **1984**, *3*, 962.

[4] Kolis, J. W.; Basolo, F.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5626.

[5] Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

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

[7] (a) Keister, J. B.; Strickland, D. S.; Shapley, J. R. *Inorg. Synth.*, submitted for publication. (b) Strickland, D. S. Ph.D. Thesis, University of Illinois, 1983.

[8] Heating $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ at 45 °C in CO-saturated CCl_4 or $BrCCl_3$, with excess t-BuOCl, gives $H_3Os_3(CO)_9(\mu_3\text{-}CX)$ (X = Cl or Br), respectively, in ~90% yield after TLC on fluorescent silica (pentane). The reverse reaction is accomplished by heating $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ with excess $n\text{-}Bu_3SnH$ in heptane under CO at 60 °C (85%).

[9] (a) Kuivila, H. G. *Synthesis* **1970**, 499. (b) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047.

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$H_3Os_3(CO)_9(\mu_3\text{-}C^{\bullet})$ is generated in both of these transformations.

$$H_3Os_3(CO)_9(\mu_3\text{-}CH) \underset{n\text{-}Bu_3SnH,\ 60\ ^\circ C}{\overset{t\text{-}BuOCl,\ XCCl_3,\ 45\ ^\circ C}{\rightleftarrows}} H_3Os_3(CO)_9(\mu_3\text{-}CX) \quad (1)$$

$$X = Cl, Br$$

In order to examine the reactivity of the triosmium carbon radical in various solvents, we have utilized the halogen atom abstraction capabilities of the $^{\bullet}Re(CO)_5$ radical.[10] When a mixture of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ is photolyzed in a dry, deoxygenated hydrocarbon solvent such as cyclohexane, $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ is formed in high yield (>80%) along with the expected $Re(CO)_5Br$ (eq 2).[11] H abstraction is predominant also

$$H_3Os_3(CO)_9(\mu_3\text{-}CBr) + Re_2(CO)_{10} \xrightarrow[RH]{h\nu} H_3Os_3(CO)_9(\mu_3\text{-}CH) + Re(CO)_5Br \quad (2)$$

in toluene, but in benzene the ring-addition product $H_3Os_3(CO)_9(\mu_3\text{-}CC_6H_5)$[7b,12] becomes significant. In the latter reaction equivalent amounts of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ are observed also, but this is likely formed by H abstraction from the cyclohexadienyl radical intermediate rather than from benzene directly.[13]

In toluene-d_8 ring addition becomes competitive with D abstraction, as expected for a significant primary kinetic isotope effect. No methylidyne ^1H NMR signal is observed for $H_3Os_3(CO)_9(\mu_3\text{-}CD)$ during the course of this reaction, providing evidence that hydrogen migration is not taking place in the radical intermediate (i.e., that the unpaired electron density is not delocalized onto the metals to an appreciable extent). However, ^1H NMR monitoring of a solution of $H_3Os_3(CO)_9(\mu_3\text{-}CD)$ in C_6D_6 has established that hydrogen scrambling between the metal and carbon sites can be observed after a few days at room temperature.[14] A spin saturation transfer study of this exchange process is described elsewhere.[15]

We expected cyclohexane-d_{12} to provide only $H_3Os_3(CO)_9(\mu_3\text{-}CD)$, but an additional, orange product precipitates from the reaction mixture. Spectroscopic data[16] are consistent with a symmetrical ketone or diketone structure incorporating two Os_3C units; the latter has been confirmed by a single-crystal X-ray diffraction study.[17] We note that bis(alkylidynetricobalt nonacarbonyl) clusters $[Co_3]C\text{–}X\text{–}C[Co_3]$ with various linking groups X, including the ketone with X = –C(O)–, have been characterized[18] but that the analogous diketone species has not been reported.

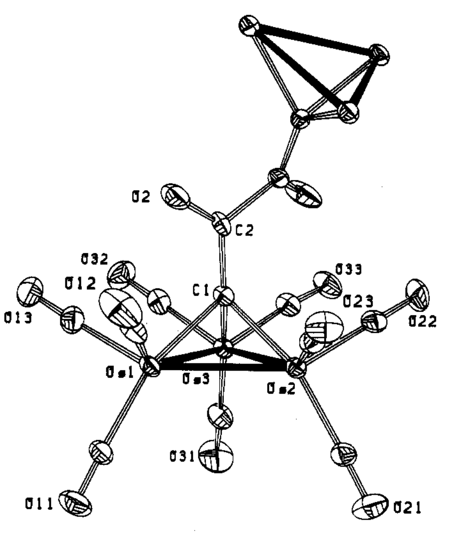

Figure 1. Molecular structure of $(H_3Os_3(CO)_9[\mu_3\text{-}C(CO)])_2$. The molecule rests on a crystallographic twofold axis. The carbonyl ligands are omitted in the top half for clarity; the bottom half shows the atom labels. Metal–metal distances are Os(1)–Os(2) = 2.892 (4), Os(1)–Os(3) = 2.883 (4), and Os(2)–Os(3) = 2.870 (4) Å. The average Os–C(1) distance is 2.12 (1) Å. The hydride ligands were not located.

The molecular structure of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$ is depicted in Figure 1. Notable aspects of the structure include the following observations: (1) Though the ketone group is directed toward the Os(1) center [dihedral ∠Os(1)–C(1)–C(2)–O(2) = 0.6 (17)°], there is apparently no direct interaction between the carbonyl oxygen atom and the metal center [Os(1)–O(2) = 3.38 (1) Å]. The C(1)–C(2) bond vector is nearly perpendicular to the Os_3 plane but is tilted slightly toward Os(1) [∠Os(1)–C(1)–C(2) = 123.6 (8)°; ∠Os(2)–C(1)–C(2) = 128.4 (8)°; ∠Os(3)–C(1)–C(2) = 132.7 (8)°], perhaps as a consequence of van der Waals contact between the ketone carbonyl oxygen and a metal carbonyl oxygen on the symmetry-related Os_3C unit [O(2)–O(33′) = 2.92 (1) Å]. (2) The distance between the cluster carbon atom and the ketone carbon atom [C(1)–C(2) = 1.46 (2) Å] is in the range expected for an acyl cluster.[18-20] (3) The bond lengths in the diketone moiety are reasonable [C(2)–O(2) = 1.21 (2) Å; C(2)–C(2′) = 1.56 (2) Å] and the dihedral angle between the two ketone C–O bond vectors is 147.9 (13)°.

The most important conclusion of the current work is that the triosmium carbon radical acts like a reactive organic alkyl free radical;[13,21] viz., hydrogen abstraction is

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[10] (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1974**, *96*, 2065. (b) Wrighton, M. S.; Bredesen, D. *J. Organomet. Chem.* **1973**, *50*, C35.

[11] These reactions were carried out in NMR tubes sealed under ~2 atm of CO, and their progress was monitored by ^1H NMR. The reactions were similar but less clean in the absence of CO. $HRe(CO)_5$ was not observed during the course of any of the reactions. Photolysis of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ in the absence of $Re_2(CO)_{10}$ led to no reaction.

[12] (a) Shore, S. G.; Jan, D.-Y.; Hsu, W.-L.; Kennedy, S.; Huffman, J. C.; Wong, T.-C. L.; Marshall, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 392. (b) Yeh, W.-Y.; Shapley, J. R.; Li, Y.-J.; Churchill, M. R. *Organometallics* **1985**, *4*, 767.

[13] Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry*; Cambridge University Press: Cambridge, 1974; Chapter 11.

[14] The equilibrium product mixture obtained favors deuterium in the carbon site as expected from zero-point energy considerations. Compare $HOs_3(CO)_{10}CHD_2$: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

[15] VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077.

[16] Anal. Calcd for $[H_3Os_3(CO)_9CCO]_2\cdot CH_2Cl_2$: C, 15.21; Os, 62.83. Found: C, 15.68; Os, 62.65. Yield: 15%. MS (electron impact, field desorption, or fast atom bombardment, ^{192}Os): m/z 871, $[H_3Os_3(CO)_9CCO^+]$. IR (cyclohexane): ν_{CO} 2092 (s), 2034 (w, sh), 2028 (w, sh), 2018 (s), 1615 (w) cm^{-1}. IR (KBr): ν_{CO} 2073 (s), 1986 (s), 1613 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ –19.25.

[17] $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2(CH_2Cl_2$ solvate) crystallizes in the centrosymmetric monoclinic space group $C2/c$ with a = 14.224 (4) Å, b = 12.740 (3) Å, c = 19.805 (6) Å, β = 99.25 (2)°, V = 3542 (2) Å^3, and ρ(calcd) = 3.406 g cm^{-3} for Z = 4. Diffraction data (Mo Kα, 2θ = 3.0–55.0°) were collected on a Syntex P2$_1$ diffractometer and were corrected numerically for absorption. The structure was solved by a combination of direct methods (MULTAN 80) and difference-Fourier techniques and was refined via full-matrix least squares (SHELX 76) to R_F = 3.3% and R_{wF} = 4.3% for 233 parameters (including an empirical parameter for extinction) against those 2495 reflections with $I > 3\sigma(I)$. Anisotropic thermal parameters were used for all non-hydrogen atoms. The crystal for this study gradually became cloudy, with no change in color, during the course of the structure determination. This was presumably due to loss of CH_2Cl_2 solvate molecules. Correction for decay was made as a linear function of the behavior of standard intensities measured at regular intervals and applied in an isotropic manner; total decay was <10%.

[18] Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73.

[19] Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1381.

[20] Allegra, G.; Valle, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr.* **1969**, *B25*, 107.

[21] Pryor, W. A. *Free Radicals*; McGraw-Hill: 1966.

rapid and pervasive and addition to benzene occurs readily. Neither delocalization of the unpaired spin nor steric shielding of the radical center "stabilize" the $Os_3C^{\bullet}$ radical as they do in less reactive, persistent radicals such as the $Ph_3C^{\bullet}$ radical. Isolation of the dialkylidyne diketone complex implies that CO addition to the carbon center in the $Os_3C^{\bullet}$ intermediate to form an acyl radical competes with deuterium abstraction from solvent; the diketone apparently is formed by coupling of two of these acyl radicals.[22] Further studies concerning the reactivity of $H_3Os_3(CO)_9(\mu_3\text{-}C^{\bullet})$ and $H_3Os_3(CO)_9(\mu_3\text{-}C\dot{C}O)$ are in progress.

Acknowledgment. This research was supported by National Science Foundation Grants CHE 81-00140 and CHE 84-07233. We acknowledge Dr. Karin Karel for some initial observations on the radical reactivity of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$.

Supplementary Material Available: Tables of final positional parameters, anisotropic thermal parameters, and selected distances and angles (9 pages); a listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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[22] Goldberg, K. I.; Bergman, R. G. *Organometallics* **1987**, *6*, 430.

Book Reviews

Inorganic Reactions and Methods. Vol. 11. The Formation of Bonds to C, Si, Ge, Sn, Pb (Part 3). J. J. Zuckerman, Editor. VCH Publishers, Weinheim. 1988. xxii + 594 pages. $150.00

Two volumes of this series have been reviewed in this journal already, but it may be useful to repeat that it is the purpose of this series to treat all possible types of bonds between all elements of the periodic table, i.e., all reaction types leading to their formation. In the volumes that have appeared so far, this has been done in a well-conceived and well-organized way, and, as a result, these volumes will be a valuable literature resource for the synthetic chemist. An introductory section on "How to Use this Book" and a "Preface to the Series" (repeated in each volume) serve well to introduce the reader to the organization of the books of this series. A fair portion of each volume is taken up with useful author, compound, and subject indexes (222 out of the 594 pages in the present volume).

The volume being reviewed here covers the formation of bonds to elements of group IVB (C, Si, Ge, Sn, Pb) by elements of groups IA (Li, Na, K, Rb, Cs), IB (Cu, Ag, Au), and IIB (Zn, Cd, Hg). This involves a good bit of preparative main-group organometallic chemistry: organolithium, -sodium, and -potassium compounds; organocopper, organozinc, and organomercury compounds; silyl, germyl, stannyl, and plumbyl alkali-metal and mercury compounds. The authors (J. Y. Corey, F. Glockling, K. Grätz, F. Huber, E. Grovenstein, Jr., M. E. Newcomb, A. K. Sawyer, E. K. Storms, K.-H. Thiele, and G. van Koten) have done their job very well, and all sections give a thorough and complete picture of the synthetic transformations which they discuss.

The information concerning the various reaction types that serve to form the bond in question is presented by means of text and tables of examples and with liberal use of equations. Detailed experimental procedures are not provided, but these can be found in the many references which are cited. Special conditions and hazards and safety precautions usually are mentioned.

All topics are covered well by their authors. The most generally useful sections will be those devoted to the synthesis of the C–Li bond, i.e., to the preparation of organolithium reagents. M. E. Newcomb has provided an excellent survey of this topic with very useful tables that bring many examples, with good discussions of the various procedures and with a great many references to the original literature.

We hope that the untimely death of Professor J. J. Zuckerman, the editor of "Inorganic Reactions and Methods", in December 1987, will not jeopardize this series. Professor Zuckerman, who was well-known for his original contributions to organotin chemistry and for his many well-received contributions to the review and monograph literature dealing with structure, bonding, and spectroscopy of group IVB element compounds, undertook the arduous job of organizing this 17-volume handbook of chemical bond synthesis some years ago. Interactions with an 11-member editorial advisory board, 26 editorial consultants, and a very large number of authors finally bore fruit, and four volumes of the 17 planned have appeared, two last year and two so far this year. It is hoped that the series, which has started off so well under Professor Zuckerman's enthusiastic and very effective direction, will be completed. When complete, it will be a fine monument to the memory of Professor Zuckerman.

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Inorganic Reactions and Methods. Vol. 2. The Formation of the Bond to Hydrogen (Part 2). J. J. Zuckerman, Editor. VCH Publishers, Weinheim. 1987. xxvi + 476 pages. $150.00

Volume 11 of this series is reviewed above, and the general information and comments in that review need not be repeated here. In the present volume are covered the methods of forming bonds to hydrogen by elements of periodic groups VB (N, P, As, Sb, Bi), IVB (C, Si, Ge, Sn, Pb), IIIB (B, Al, Ga, In, Tl), IA (Li, Na, K, Rb, Cs, Fr), IIA (Be, Mg, Ca, Sr, Ba, Ra), IB (Cu, Ag, Au), and IIB (Zn, Cd, Hg) and the transition and inner-transition metals.

The authors (N. Bartlett, L. Barton, F. Glockling, A. P. Hagen, A. Herold, G. G. Libowitz, T. J. Lynch, A. J. Maeland, J. F. Mareche, A. D. Norman, J. R. Norton, and J. Topich) cover their topics thoroughly and well, and, as a result, the book will be a useful one to have on the library shelves.

The major fault with this book and the one reviewed above, and very likely, with the whole series, is that one finds cited very few literature references with dates later than 1982. The fields of inorganic and organometallic synthesis have been moving ahead at a brisk pace, and it is unfortunate that these books are not more up-to-date. However, it should be appreciated that when such a large number of authors is involved—24 just for the two volumes reviewed here—delays longer than those usual for an edited multiauthor book are inevitable. If one accepts that this series provides a literature base for the total field of preparative inorganic/organometallic chemistry up to the end of 1982, then it is clear that this series if a very valuable literature resource. The later literature on specific topics can be easily covered by using the various available data bases.

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