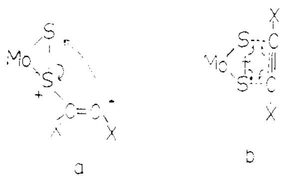


Figure 2. Proposed schemes for the addition of an acetylene to the $\overline{\text{Mo–S–S}}$ unit.

techniques has progressed to a conventional *R* value of 0.069.[8]

The structure of the dianion in I (Figure 1, Table I) shows three bidentate dithiolene (1,2-dicarbomethoxy-1,2-dithiolate) ligands coordinated to Mo(IV). The S_6 coordination polyhedron shows only small deviations from a trigonal prismatic geometry (D_{3h} symmetry). The three rectangular faces of the prism, S(1)S(2)S(3)S(4), S(3)S(4)S(5)S(6), and S(1)S(2)S(5)S(6), are nearly planar and are located 0.90, 0.91 and 0.92 Å from the Mo atom. The dihedral angles (δ) made by the S_6 polyhedron trigonal faces as described by Muetterties and Guggenberger[9] are 11.67, 15.36, and 19.70° at b_1 and 120.33, 119.84, and 119.88° at b_2 and range from 87.0 to 93.0° at the remaining edges of the polyhedron.[10] The mean value of the S–Mo–S interligand trans angles at 135° is quite close to the average value of 136 ± 1° found for the same angles in other trigonal prismatic complexes such as $Re[S_2C_2(C_6H_5)_2]_3$,[11] $V[S_2C_2(C_6H_5)_2]_3$,[12] $Mo(S_2C_2H_2)_3$,[13] $Mo(S_2C_6H_4)_3$,[14] and $[Nb(S_2C_6H_4)_3]^-$.[14] In the structure of the $[Mo(S_2C_2(CN)_2)_3]^{2-}$ complex[15] (the only other structurally characterized tris(dithiolene) Mo(IV) complex) the MoS_6 polyhedron (average Mo–S = 2.373 Å) is close to being midway between the octahedron and the trigonal prism. The apparent structural differences between the MoS_6 polyhedra in I and $[Mo(S_2C_2(CN)_2)_3]^{2-}$ very likely reflect differences in covalency in the Mo–L bond that stem from differences in the relative energies of the Mo(IV) d orbitals and the appropriate ligand orbitals.[14] On the basis of σ bonding, the trigonal prismatic coordination is favored over the octahedral one for highly covalent 4d and 5d transition-metal complexes containing metal ions in the d^0, d^1, and d^2 electronic configurations.[16] Not unlike other dithiolene complexes,[17] I undergoes two reversible one-electron oxidations[18] in CH_2Cl_2 at +0.02 and +0.48 V vs. SCE. The low oxidation potentials and the apparent stability of the oxidation products should allow for the covenient synthesis of the monoanionic and neutral derivatives of I.

The synthesis of I and in particular the generation of the dithiolene ligands[19] present an interesting problem from a mechanistic point of view. The formation of the 1,2-ethylene dithiolate ligand in I parallels the formation of the same ligand and its selenium analogue in reaction 1 (R = H, CH_3; E = S, Se). A

$$(C_5H_4R)_2TiE_5 + DMA \rightarrow (C_5H_4R)_2TiE_2C_2(CO_2CH_3)_2 \quad (1)$$

kinetic study of this reaction shows a second-order process with activation parameters of −19 cal/(mol K) for $\Delta S^{\ddagger}$ and 19 kcal/mol for $\Delta H^{\ddagger}$. An associative mechanism involving electrophilic attack on the E_5 ligand and a dipolar intermediate have been suggested for this reaction.[20] The large negative value for $\Delta S^{\ddagger}$, however, also is indicative of a highly ordered transition state and may be consistent with a cycloaddition reaction. The isolation of $(Ph_4P)_2[(S_4)Mo_2S_4(S_2)]$ from solutions of $(Et_4N)_2[(S_4)_2MoS]$ following the addition of Ph_4PCl suggests the presence of equilibria such as $[(S_4)_2MoS]^{2-} \rightleftarrows [(S_4)MoS(S_2)]^{2-} + S_2°$. In solutions of $[(S_4)_2MoS]^{2-}$ therefore, either MoS_2 or $Mo(S_4)$ units are possible reactive species toward DMA. By analogy to the $(C_5H_4R)_2TiE_5$/DMA system,[20] formation of the ethylene dithiolate ligand in I may proceed either by an associative mechanism involving a dipolar intermediate (Figure 2a) or by a Diels–Alder type (4 + 2) cycloaddition mechanism (Figure 2b). The interactions of other activated acetylenes and olefins with binary Mo–S complexes are currently under study in our laboratories.

Acknowledgment. This research was supported by NSF Grant CHE-8109065. X-ray equipment used in this research was obtained in part by the same grant and by the University of Iowa.

Supplementary Material Available: Structure factor tables for $(Ph_4P)_2[Mo(S_2C_2(COOCH_3)_2)_3]\cdot DMF\cdot C_6H_6$ (28 pages) and positional and thermal parameters for the Ph_4P^+ cations and the DMF and benzene molecules of solvation. Ordering information is given on any current masthead page.

---

[8] In the refinement process, isotropic temperature factors were assigned to all atoms. Assignment of anisotropic temperature factors to the anion results in 574 parameters and a rather small data to parameter ratio. Changing the rejection criterion to $F_o^2 \leq 2\sigma(F_o^2)$ increased the usable data to 3497; however, a larger *R* value (0.079) and larger estimated standard deviations were obtained. The crystallographic results reported herein have been obtained with $F_o^2 \geq 3\sigma(F_o^2)$ data and isotropic temperature factors.

[9] Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748–1756.

[10] The δ's for a trigonal prism are 0°, 0°, 0° at b_1, 120°, 120°, 120° at b_2, and 90° for the remaining six edges of the polyhedron. By comparison, δ's for the corresponding edges on an octahedron are all 70.5°.

[11] Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1966**, *5*, 411–416.

[12] (a) Eisenberg, R.; Stiefel, E. I.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 2874–2876. (b) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **1967**, *6*, 1844–1849.

[13] Smith, A. E.; Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1965**, *87*, 5798–5799.

[14] Bennett, M. J.; Cowie, M.; Martin, J. L.; Takats, J. *J. Am. Chem. Soc.* **1973**, *95*, 7504–7505.

[15] (a) Brown, G. F.; Stiefel, E. I. *Inorg. Chem.* **1973**, *12*, 2140–2147. (b) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295–369.

[16] Huisman, R.; DeJonge, R.; Haas, C.; Jellinek, F. *J. Solid State Chem.* **1971**, *3*, 56–66.

[17] McCleverty, J. *Prog. Inorg. Chem.* **1968**, *10*, 49–221.

[18] On a platinum electrode vs. SCE, solutions were 1×10^{-3} M in electroanalyte and 0.1 M in Bu_4NClO_4.

[19] The synthesis of a neutral, tris(diphenyl)dithiolene complex of molybdenum(VI), $Mo[S_2C_2(Ph)_2]_3$, has been accomplished previously (Schrauzer, G. N.; Mayweg, V. P. *Z. Naturforsch, B* **1964**, *19B*, 192–198) in the reaction between $Mo(CO)_6$, diphenylacetylene, and sulfur in benzene or toluene solution. This reaction may well involve Mo–S complexes that are generated in situ under the reaction conditions.

[20] Bolinger, M. C.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

Synthesis and Reactivity of a "Semi" Triply Bridging Methylidyne Complex. Crystal Structure of $HOs_3(CO)_{10}(CH)$

John R. Shapley,* Michelle E. Cree-Uchiyama, and
George M. St. George

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Melvyn Rowen Churchill* and Clifford Bueno

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received July 21, 1982

The methylidyne (CH) ligand—the simplest hydrocarbon ligand and a potential intermediate in the hydrogenolysis of carbon monoxide—is an object of current attention. Examples of methylidyne groups bound to one,[1] two,[2] three,[3] and four[4] transition-metal atoms have been reported recently. In this communication we report a new complex with a triply bridging methylidyne ligand, which in contrast with previous examples[3,5] is found

---

[1] $W(CH)Cl(PMe_3)_4$: Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.

[2] $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$: Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.

[3] $[Cp_2Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]^+$: (a) Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7787. (b) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *Ibid.* **1981**, *103*, 63.

[4] $HFe_4(CO)_{12}(\mu_4\text{-}CH)$: (a) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541. (b) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1981**, *103*, 1485. (c) 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.

0002-7863/83/1505-0140$01.50/0

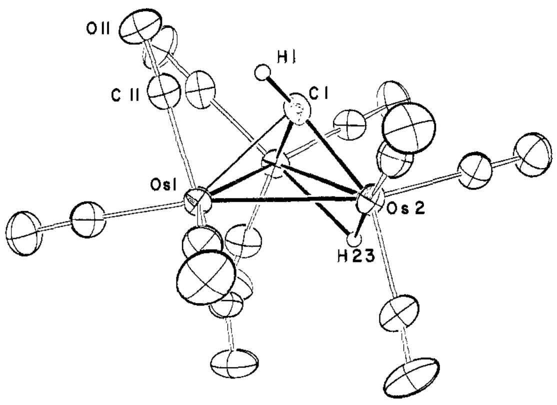


Figure 1. View of **3** showing the interaction of the methylidyne ligand with Os(1). Relative to a plane passing through Os(1), C(1), and the midpoint of Os(2)–Os(3), the C(1)–H(1) vector is bent toward the viewer and the Os(1)–C(11)–O(11) axis is bent away.

to interact much more strongly with two of the metal centers than with the third. The reactivity consequences of this "semi" triply bridging structure are described.

A two-step sequence (eq 1)[6] allows conversion of methoxymethylidyne compound **1**[7] into methylidyne compound **3**. The conversion can be followed conveniently by ^1H NMR. The hydride signal of **1** (δ −16.25) in CH_2Cl_2 is replaced by signals due to **2** (δ 8.85 (d, 1 H), −15.56 (d, 1 H, J = 2.4 Hz)) after addition of ca. 2 equiv of $LiBEt_3H$ (1 M in THF) at or below room temperature. Metathesis with R_4NBr (R = Me, Et) in aqueous THF (1:2) allows isolation of R_4N-**2** as slightly air-sensitive orange solids in ca. 70% yield.[8] Protonation of **2** is best carried out at low temperature (−60 °C, CD_2Cl_2, CF_3COOH), after which ^1H NMR signals due to methanol (δ 3.40) and **3** (δ 14.16 (d, 1 H), −18.13 (d, 1 H, J = 1.6 Hz)) appear. **3** is stable at room temperature and after crystallization from pentane is isolated as slightly air-sensitive bright yellow crystals (yield 70%).[10]

$$\underset{\mathbf{1}}{HOs_3(CO)_{10}(COMe)} \xrightarrow{H^-} \underset{\mathbf{2}}{[HOs_3(CO)_{10}(CHOMe)]^-} \xrightarrow{H^+} \underset{\mathbf{3}}{HOs_3(CO)_{10}(CH)} \quad (1)$$

The molecular structure of **3** is shown in Figure 1.[11,12] The hydrogen atoms in both the bridging hydride ligand and the bridging methylidyne ligand were located directly from the diffraction study. The CH ligand bridges Os(2) and Os(3) symmetrically, with Os(2)–C(1) = 2.003 (11) Å and Os(3)–C(1) = 2.011 (12) Å. These distances are approximately 0.10 Å shorter than the corresponding Os–CHR bond lengths in $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)$.[13] A key feature of **3** is that the CH ligand has a significant bonding interaction with the unique osmium atom. This is indicated by the short Os(1)–C(1) distance (2.353 (10) Å) and the acute dihedral angle between the Os(2)–C(1)–Os(3) plane and the Os_3 plane (69.7°). Taken together these parameters for **3** indicate a markedly stronger interaction between the alkylidyne carbon atom and the unique metal atom than that proposed for $HFe_3(CO)_{10}(COMe)$ [2.70 (1) Å, 91°][14] or seen in $HRu_3(CO)_{10}(COMe)$ [2.90 Å, 94.7°].[15] Furthermore, the displacement of C(1) from a position outside the Os_3 triangle to one above it perturbs the environments of Os(2) and Os(3) away from the closely octahedral geometries[16] displayed by typical $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}Y)$ complexes.[17] The CH bond is bent 24° out of the Os(2)–C(1)–Os(3) plane on the same side as Os(1); however, the Os(1)···H(1) distance is 2.36 (14) Å. The coordination of C(1) to Os(1) together with a close H(1)···C(11) contact (1.81 (14) Å) causes significant distortions in the intraligand angles of the $Os(CO)_4$ moiety.[12]

^{13}C NMR data for **3** in solution[18] are fully consistent with the solid-state structure. At −100 °C the carbonyl signals form a

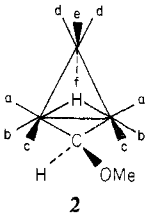
---

(5) Other μ_3-CH complexes: (a) $Co_3(CO)_9(\mu_3\text{-}CH)$: Bor, G.; Marko, L.; Marko, B. *Chem. Ber.* **1962**, *95*, 333. Ercoli, R.; Santambrogio, E.; Casagrande, G. T. *Chim Ind.* (*Milano*) **1962**, *44*, 1344. (b) $H_3Os_3(CO)_9(\mu_3\text{-}CH)$: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5226. Azam, K. A.; Deeming, A. J. *J. Mol. Catal.* **1977**, *3*, 207. (c) $H_3Ru_3(CO)_9(\mu_3\text{-}CH)$: Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304. For discussion of structural features of closely related compounds see: (d) Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966 and references therein.

(6) This sequence is modeled after the preparation of $(CO)_5W{=}CHPh$ from $(CO)_5W{=}C(OMe)Ph$: Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097.

(7) (a) Keister, J. B. *J. Chem. Soc., Chem. Commun.* **1979**, 214. (b) Gavens, Paul D.; Mays, M. J. *J. Organomet. Chem.* **1978**, *162*, 389.

(8) For Et_4N-**2** the OMe signal is seen (360 MHz) at δ 3.26 (s, 3 H) in addition to the cation resonances at δ 3.21 (q, 8 H) and 1.35 (t, 12 H, J = 7 Hz). Me_4N-**2**: Anal. Calcd for $C_{16}H_{17}NO_{11}Os_3$: C, 19.81; H, 1.77; N, 1.44. Found: C, 20.17; H, 1.81; N, 1.37. IR (KBr) ν_{CO} 2112 (w), 2072 (m), 2062 (m, sh), 2014 (vs), 1981 (vs), 1942 (s), 1931 (s) cm^{-1}. The ^{13}C NMR spectrum (90 MHz, CD_2Cl_2) of **2** (from ca. 50% ^{13}CO-enriched $Os_3(CO)_{12}$) shows the alkylidene carbon at δ 112.3 ($^1J_{CH}$ = 154 Hz); the carbonyl signals at −20 °C are at δ 187.9 (s, 0.5 C; d, 0.5 C, $^2J_{CC}$ = 34 Hz), 184.6 (s, 0.5 C; d, 0.5 C, $^2J_{CC}$ = 34 Hz), 182.0 (s, 1 C; d, 1 C, $^2J_{CC}$ = 13 Hz), 181.5 (d, 2 C, $^2J_{CH}$ = 10 Hz), 179.2 (s, 2 C), 174.5 (s, 2 C). These can be assigned to carbonyls e, f, a, b, d, and c, respectively, on the basis of large trans C–C and C–H couplings together with the observation that the δ 187.9 and 179.2 signals (e + d) are broad at 25 °C, due to 3-fold exchange. Structural models for **2** are the compounds $HOs_3(CO)_{10}(CHX)$, (X = CH_2PMe_2Ph,[9a] $CHNEt_2$[9b]).



2

(9) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141. (b) Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 848.

(10) **3**: Anal. Calcd for $C_{11}H_2O_{10}Os_3$: C, 15.28; H, 0.23; Os, 65.99. Found: C, 15.43; H, ~0; Os, 65.50. Mass spectrum m/z 870 (M^+, ^{192}Os); IR (C_6H_{12}) ν_{CO} 2110 (s), 2068 (vs), 2066 (vs), 2030 (sh), 2023 (vs), 2012 (s), 2002 (m).

(11) Diffraction data (Mo Kα) for **3** were collected with a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved with the (SUNY-Buffalo-modified) Syntex XTL system. **3**: space group $P\bar{1}$, a = 9.404 (2) Å, b = 9.300 (2) Å, c = 11.002 (3) Å, α = 94.76 (2)°, β = 94.44 (2)°, γ = 118.49 (2)°, V = 835.2 (4) Å^3, ρ(calcd) = 3.44 g·cm^{-3} for mol wt = 864.7 and $Z = 2$. R_F = 3.5% and R_{wF} = 4.3% for all 2949 reflections with $4° < 2\theta < 50°$.

(12) A complete listing of bond distances and angles are provided as supplementary material. For convenience the following details are reproduced here. The metal–metal distances are Os(1)–Os(2) = 2.842 (1) Å, Os(1)–Os(3) = 2.845 (1) Å, and Os(2)–Os(3) = 2.910 (1) Å. Distances and angles involving the hydride ligand are Os(2)–H(23) = 1.79 (8) Å, Os(3)–H(23) = 2.00 (8) Å, Os(2)–H(23)–Os(3) = 100.2 (35)°. Atoms H(23), Os(2), Os(3), and C(1) are close to coplanar (the dihedral angle between the Os(2)–Os(3)–H(23) and Os(2)–Os(3)–C(1) planes is 6.8°). Intraligand angles involving Os(1) and C(11) are C(11)–Os(1)–Os(2) = 105.19 (34)°, C(11)–Os(1)–Os(3) = 99.86 (34)°, C(11)–Os(1)–C(12) = 94.02 (53)°, C(11)–Os(1)–C(13) = 87.80 (52)°, and C(11)–Os(1)–C(14) = 172.67 (49)°.

(13) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975.

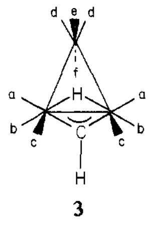
(14) Shriver, D. F.; Lehman, D.; Strope, D. *J. Am. Chem. Soc.* **1976**, *97*, 1594.

(15) Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Süss, G. *J. Organomet. Chem.* **1979**, *173*, 187.

(16) Ignoring the Os(2)–Os(3) bond; see: Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1981**, *103*, 1216.

(17) Churchill, M. R.; Wasserman, H. *Inorg. Chem.* **1981**, *20*, 2905 (and references given in Table VII).

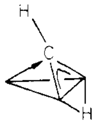
(18) At −100 °C the signals observed (90 MHz, 3:1 CD_2Cl_2:C_7D_8) are δ 176.7 (s, br, 1 C), 173.4 (s, br, 2 C), 171.8 (s, br, 2 C), 171.1 (d, 2 C, $^2J_{CH}$ = 10 Hz), 169.0 (s, 2 C), 168.0 (s, br, 1 C). These signals are assigned to carbonyls e, a, d, b, c, and f on the basis of trans C–H and C–C couplings together with their variable-temperature behavior. Under optimum resolution the peak at δ 173.4 (a) is seen to be a singlet overlapping a shorter doublet due to coupling (50%) with the methylidyne carbon. The latter resonates at δ 219.



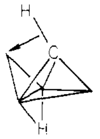
3

1:2:2:2:2:1 pattern. The unusual position of one of the axial carbon resonances, namely, to higher field than any of the other signals, is attributed to the distortion caused by steric interaction between this carbon (C(11)) and the bridging CH group. At higher temperatures the two axial carbonyl resonances broaden (at slightly different rates) and then coalesce (ca. -60 °C) with one of the remaining signals. These changes are due to localized 3-fold exchanges at the $Os(CO)_4$ center, as has been observed for **1**.[7b] The significantly lower activation energy for **3** ($\Delta G^{\ddagger}$ = ca. 9 kcal/mol) compared to **1** ($\Delta G^{\ddagger}$ = ca. 17 kcal/mol) can again be attributed to the distortions in **3**, in particular to the pseudo-seven-coordinate geometry around Os(1).

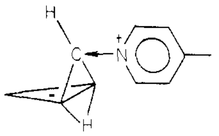
Although in **3** both H(1) and C(1) are close to Os(1), the interaction of the methylidyne group with this atom is fundamentally different from that found in the compound $HFe_4(CO)_{12}(\mu_4\text{-}CH)$.[4] In this latter compound the C–H bond acts as a two-electron *donor* to the adjacent unsaturated iron atom (see **4**). This is evidenced spectroscopically by a shift in the C–H ^1H NMR resonance to high field (δ -1.31) and a diminished C–H coupling constant (103 Hz).[4a] The three-center C–H–Fe bond also is acidic, since upon removal of the hydrogen atom as a proton, the electron pair remaining forms a two-center C–Fe bond.[4] However, for the CH group in **3** the ^1H NMR signal occurs at low field (δ 14.2), the coupling constant is relatively high (166 Hz, and there is no evidence of acidity (vide infra). Thus, the bonding in **3** can be regarded as two-electron donation from the formally saturated (18 electron) $Os(CO)_4$ center[19] to the nominally sp^2-hybridized carbon atom of the bridging CH moiety. In alkoxy- and aminoalkylidyne compounds related to **1**, there is crystallographic and spectroscopic evidence for π bonding between the hetero atom and the alkylidyne carbon atom.[7b,15,21] Such a resonance interaction is not available in **3**, and stabilization is achieved instead by an electrophilic interaction with the third metal atom.[22]



3



4



5

The facile reactions of **3** with various nucleophiles provide further evidence for the electrophilic nature of the methylidyne ligand. Addition of 4-methylpyridine (1 equiv) to **3** at -60 °C immediately forms the pyridinium derivative **5**.[23] The structure of **5** is evidently analogous to that of **2**; frontside attack by the base on the CH ligand displaces the Os → C donation from the backside. A similar reaction of **3** with $LiBEt_3H$ generates $[HOs_3(CO)_{10}(CH_2)]^-$ (**6**).[24] Protonation of **5** regenerates **3**, implying that the proton is added at the nitrogen atom, but protonation of **6** occurs at the Os–C bond to generate $HOs_3(CO)_{10}(CH_3)$[25] (**7**; eq 2). The conversion of **3** to **7** represents the overall hydrogenation of CH to CH_3, which, however, cannot be effected directly with H_2 due to the facile thermal rearrangement of **3** to $H_2Os_3(CO)_9(CCO)$.[26] Finally, treatment of **3** with $RHC^-{-}N_2^+$ (R = H, $SiMe_3$) leads to $HOs_3(CO)_{10}(CH{=}CHR)$ (R = H,[27] $SiMe_3$[13]) in high yield (>90% by NMR) presumably via nucleophilic attack followed by N_2 loss. Related coupling reactions with other carbon nucleophiles are being investigated.[28]

$$\underset{\mathbf{3}}{HOs_3(CO)_{10}(CH)} \xrightarrow{H^-} \underset{\mathbf{6}}{[HOs_3(CO)_{10}(CH_2)]^-} \xrightarrow{H^+} \underset{\mathbf{7}}{HOs_3(CO)_{10}(CH_3)} \quad (2)$$

Acknowledgment. This research was supported at the University of Illinois by NSF Grant CHE 81-00140 (J.R.S.) and at SUNY-Buffalo by NSF Grant CHE 80-23448 (M.R.C.). Acknowledgment also is made for the use of instrumentation in the Regional NMR Center at the University of Illinois (NSF Grant CHE 79-16100).

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

---

(19) Donation from an $Os(CO)_4$ group is seen also in the compound $HOs_3(CO)_{10}(CF_3CCHCF_3)$: Laing, M.; Sommerville, P.; Dawoodi, Z.; Mays, M. J.; Wheatley, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1035.

(20) If in **3** the bridging hydrogen is removed as a proton and the $Os(CO)_3$ groups are replaced by isolobal CH^+ moieties, the species generated is $(CO)_4Os(C_3H_3)^+$, an 18-electron complex of the cyclopropenium ion.

(21) For aminoalkylidyne complexes $HRu_3(CO)_{10}(CNMe_2)$ and $HOs_3(CO)_{10}(CNH\text{-}t\text{-}Bu)$ see respectively: (a) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843. (b) Adams, R. D.; Golembeski, N. M. *Ibid.* **1979**, *18*, 2255.

(22) We thank a referee for suggesting that this point be mentioned explicitly.

(23) **5**: ^1H NMR (CD_2Cl_2) δ 8.48 (d, 2 H, *J* = 5.9 Hz), 7.84 (d, 1 H, *J* = 3 Hz), 7.28 (d, 2 H, *J* = 5.9 Hz), 2.27 (s, 3 H), -16.00 (d, 1 H, *J* = 3 Hz); IR (CH_2Cl_2) ν_{CO} 2110 (w), 2088 (m), 2066 (s, br), 2040 (vs), 2030 (s), 2022 (sh), 2002 (s, br), 1957 (m, br). The compound is stable at 25 °C (isolated yield 78%).

(24) Et_4N-**6**: ^1H NMR (CD_2Cl_2) δ 5.23 (dd, 1 H_a, J_{ab} = 5 Hz, J_{ac} = 3 Hz), 4.26 (d, 1 H_b), -17.00 (d, 1 H_c) in addition to Et_4N^+ signals.

(25) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. None of the tautomeric methylene compound, which would result from Os–Os bond protonation, was observed under these conditions (-40 °C).

(26) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185.

(27) (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614. (b) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29.

(28) After submission of this work a paper by Casey and Fagan appeared [Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950] that described the 1,2-addition reaction of $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$ with olefins, e.g., ethylene. We find that reaction of **3** with ethylene is not competitive with its intramolecular rearrangement to $H_2Os_3(CO)_9(CCO)$.[26]

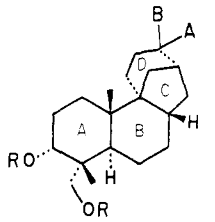
Biogenetic-Type Total Synthesis of (±)-Aphidicolin

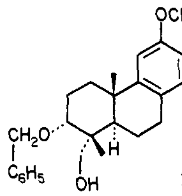
Eugene E. van Tamelen,* Steven R. Zawacky,
Ronald K. Russell, and James G. Carlson

Department of Chemistry, Stanford University
Stanford, California 94305

Received September 17, 1982

Aphidicolin, a potent antiviral agent and an accepted tool for the study of DNA replication,[1,2] possesses a complex diterpenoid structure (**1**)[2] unique in the biosynthesis[2,3] and nonenzymic total synthesis areas.[4,5] Herein we report a concise aphidicolin total





2

1 R = H; A = αCH_2OH; B = βOH
15 R, R = $C(CH_3)_2$; A = H; B = OH
16 R, R = $C(CH_3)_2$; A, B = O

---

(1) Bucknall, R. A.; Moores, H.; Simms, R.; Hesp, B. *Antimicrob. Agents Chemother.* **1973**, *4*, 294.

(2) Dalziel, W.; Hesp, B.; Stevenson, K. M.; Jarvis, J. A. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2841.

(3) Adams, M. R.; Bu lock, J. D. *J. Chem. Soc., Chem. Commun.* **1975**, 389.

(4) For the first syntheses of (±)-17-noraphidicolin-16-one, see: (a) McMurry, J. E.; Andrus, A.; Ksander, G. M.; Musser, G. H.; Johnson, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 1330. (b) Trost, B. M.; Nishimura, Y.; Yamamoto, K. *Ibid.* **1979**, *101*, 1328. For the reconstitution of aphidicolin from optically active 17-noraphidicolin-16-one gotten by degradation of the natural product, see ref 2.

0002-7863/83/1505-0142$01.50/0