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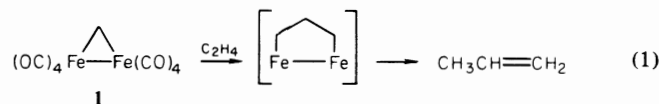
### Synthesis and Structure of Diosmacycloalkanes. Reversible Addition of Ethylene to a Methylene-Bridged Dimer

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Methylene-bridged dimers and their derivatives have been implicated in olefin metathesis,<sup>1</sup> acetylene polymerization,<sup>2</sup> and other important processes.<sup>3,4</sup> They also serve as models for the surface methylene groups that Pettit and co-workers have shown to be involved in the Fischer-Tropsch reaction<sup>5</sup> and in the hydrogenolysis of linear hydrocarbons.<sup>6</sup> Considerable interest has therefore been aroused by the report (also from Pettit's group<sup>7</sup>) that propene is formed from the reaction of  $(\mu\text{-CH}_2)\text{Fe}_2(\text{CO})_8$  (**1**) with ethylene, and by their proposal that the reaction (eq 1) involves a di-



ferracyclopentane intermediate. This hypothesis has stimulated efforts at the synthesis of dimetallacycloalkanes in general and has led to the successful preparation of  $((\mu\text{-CC'})\text{CH}_2\text{CH}_2\text{CH}_2)\text{-Co}_2(\text{CO})_2\text{Cp}_2$  (**2**) by Theopold and Bergman.<sup>8</sup> However, although propene is formed upon thermolysis of **2**, generation of the latter by the reaction of ethylene with the corresponding methylene-bridged dimer has not proven possible.<sup>9,10</sup> We now report the

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(3) For a complete bibliography see ref 1-7 in the following: Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.

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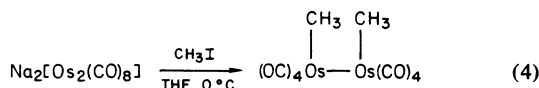
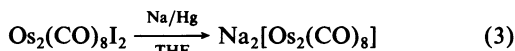
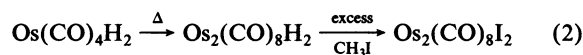
(6) Osterloh, W. T.; Cornell, M. E.; Pettit, R. *J. Am. Chem. Soc.* **1982**, *104*, 3759.

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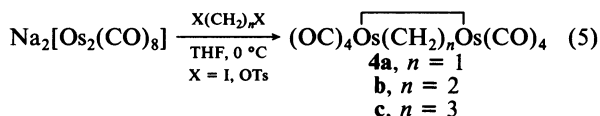
(8) Theopold, K. H.; Bergman, R. G. *Organometallics*, in press.

direct observation of 1,2-diosmacyclopentane formation by ethylene addition to the osmium analogue of **1** and the synthesis and structural characterization of the first 1,2-dimetallacyclobutane.

The dinuclear dihydride  $\text{Os}_2(\text{CO})_8\text{H}_2$ ,<sup>11</sup> which can be prepared in 24% yield by the controlled thermolysis of  $\text{cis-Os}(\text{CO})_4\text{H}_2$ ,<sup>12</sup> can be converted quantitatively to the known<sup>13</sup> dinuclear diiodide  $\text{Os}_2(\text{CO})_8\text{I}_2$  by treatment with methyl iodide (eq 2). Reduction



with sodium amalgam in THF (eq 3) gives a solution that apparently contains the dinuclear dianion  $[\text{Os}_2(\text{CO})_8]^{2-}$ .<sup>14-16</sup> Addition of an excess of methyl iodide to the dianion solution readily gives  $\text{Os}_2(\text{CO})_8(\text{CH}_3)_2$  (**3**);<sup>17</sup> addition of the dianion solution to 1–2 equiv of difunctional alkylating agents gives the 1,2-diosmacycloalkanes **4a–c** (eq 5). For the diosmacyclopentane **4c**<sup>18</sup>



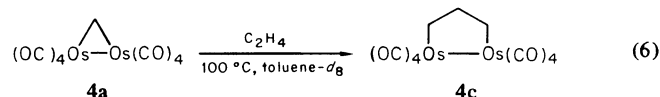
the use of 1,3-diiodopropane gave reasonable results, but for the smaller rings, **4a**<sup>19</sup> and **4b**,<sup>20</sup> the use of  $\text{CH}_2(\text{OTs})_2$ <sup>21-23</sup> and  $\text{TsOCH}_2\text{CH}_2\text{OTs}$  proved more satisfactory. Yields based on  $\text{Os}_2(\text{CO})_8\text{I}_2$  ranged from 10% (**4b**) to 35% (**4a**), although the

conversion from the dianion was probably higher.<sup>14</sup>

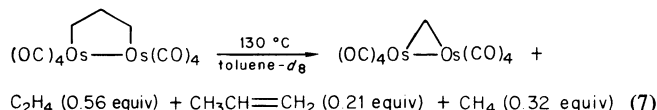
All three of the diosmacycloalkanes are air-stable, white, crystalline solids. The structure of the diosmacyclobutane **4b** has been confirmed by X-ray diffraction<sup>24</sup> and is shown in Figure 1. The molecule has approximate  $C_2$  symmetry. A  $27^\circ$  twist about the Os–Os bond keeps the  $\text{Os}(\text{CO})_4$  units out of the sterically unfavorable eclipsed configuration at the expense of bending the  $\text{Os}_2\text{C}_2$  ring and slightly compressing<sup>25</sup> ( $105^\circ$ ) the Os–C–C angles. The  $\mu$ -1,2-ethanediyl bridge contains a normal (1.53 (3) Å) carbon–carbon single bond. The two osmium–carbon bond lengths (2.22 (2) Å) equal the sum of the covalent radii calculated from the Os–Os and C–C bond lengths.<sup>26</sup> The fact that a single  $^1\text{H}$  NMR peak is observed down to  $-50^\circ\text{C}$  implies that the  $\text{Os}_2\text{C}_2$  ring in **4b** is quite flexible.

Although there have been previous reports of  $\mu$ -1,2-ethanediyl dimers without metal–metal bonds,<sup>4b,27</sup> **4b** is the first 1,2-dimetallacyclobutane. Bergman and co-workers obtained no such product from the reaction of  $\text{ICH}_2\text{CH}_2\text{I}$  with  $\text{Na}[\text{CpCo}(\text{CO})_2]$ ; even a stabilized derivative, from the diiodide of benzocyclobutadiene, was formed in only 16% yield and proved unstable at room temperature.<sup>8</sup>

The infrared spectrum<sup>28</sup> of the diosmacyclopropane **4a** shows the features characteristic<sup>29</sup> of a methylene bridge: antisymmetric C–H stretch at 2958 (vw), symmetric C–H stretch at 2933 (vw),  $\text{CH}_2$  wag at 943 (m), and  $\text{CH}_2$  rock at 780 (vw)  $\text{cm}^{-1}$ . **4a** can be converted to **4c** in good yield (85% by NMR) by treatment with 1.0 atm (8.4 equiv) of ethylene at  $100^\circ\text{C}$ ; the diosmacyclopentane can be isolated by TLC (silica gel/hexane). Reaction 6 is the first case of directly observable dimetallacyclopentane formation from an olefin and a methylene-bridged dimer containing two transition metals.<sup>30,31</sup>



Reaction 6 is reversible. When **4c** is heated to  $130^\circ\text{C}$  in toluene in a sealed tube, the formation of **4a**, along with other products, is observed (eq 7). (**4a** is unstable at  $130^\circ\text{C}$ , but NMR mon-



itoring of the reaction mixture shows that it reaches a maximum concentration of 10% of the initial concentration of **4c**.) The formation of propene from **4c** and the formation of **4c** from ethylene and **4a** offer direct evidence in support of the Pettit<sup>1b,7</sup> (eq 1) and Bergman<sup>9</sup> mechanisms for the formation of propene

(9) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489. Theopold, K. H.; Bergman, R. G. *Ibid.*, in press.

(10) Theopold and Bergman<sup>9</sup> suggest that the reaction requires a coordinatively unsaturated dicobaltacyclopentane and that the resulting coordinatively unsaturated dicobaltacyclopentane eliminates propene before it recoordinates the dissociated CO.

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(14) We have not yet isolated a salt of the dianion. The IR of the THF solution after reduction ( $\nu_{\text{CO}}$  1978 (vs), 1949 (s), 1878 (s), 1834 (m)  $\text{cm}^{-1}$ ) contains bands similar to those<sup>15</sup> of  $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$  in THF; the absence of bridging carbonyls suggests that  $\text{Na}_2[\text{Os}_2(\text{CO})_8]$  has a nonbridged structure like that of  $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$ .<sup>16</sup> However, the additional band in the IR spectrum of the  $\text{Os}_2(\text{CO})_8\text{I}_2$  reduction solution suggests that something besides  $[\text{Os}_2(\text{CO})_8]^{2-}$  may also be present. The addition of 2 equiv of  $\text{CF}_3\text{CO}_2\text{H}$  converts the IR spectrum of the reduction solution principally to that of  $\text{Os}_2(\text{CO})_8\text{H}_2$ .<sup>11,12</sup>

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(17) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

(18)  $^1\text{H}$  NMR (benzene- $d_6$ )  $\delta$  3.12 (2 H), 1.10 (4 H); IR (hexane) 2122 (vw), 2079 (m), 2042 (m), 2034 (vs), 2022 (m), 2014 (m), 1996 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{11}\text{H}_8\text{Os}_2$ : C, 20.43; H, 0.93. Found: C, 20.80; H, 1.01. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(19) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

(20) Chin, H. B.; Smith, M. B.; Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 5285.

(21)  $^1\text{H}$  NMR (benzene- $d_6$ )  $\delta$  3.12 (2 H), 1.10 (4 H); IR (hexane) 2122 (vw), 2079 (m), 2042 (m), 2034 (vs), 2022 (m), 2014 (m), 1996 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{11}\text{H}_8\text{Os}_2$ : C, 20.43; H, 0.93. Found: C, 20.80; H, 1.01. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(22) The fact that these reactions succeed suggests that the synthesis of dimetallacyclopentanes from dinuclear dianions is best accomplished by successive  $\text{S}_{\text{N}}2$  reactions (two-electron processes) under conditions where one-electron transfers are minimized. We are aware of only one, unsuccessful, previous attempt<sup>23</sup> at the synthesis of methylene-bridged dimers from  $\text{CH}_2^-(\text{OTs})_2$ .

(23) Berke, H.; Weiler, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 150.

(24) **4b**:  $a = 7.355$  (1) Å,  $b = 13.522$  (2) Å,  $c = 13.544$  (2) Å,  $\beta = 101.01$  (1) $^\circ$  at  $-140^\circ\text{C}$ ; space group  $P2_1/c$ , with  $Z = 4$ . Of 2651 reflections measured, 2018 were taken as observed ( $I > 2.5\sigma(I)$ ). Least-squares refinement (empirical absorption correction, 181 parameters) to convergence gave  $R = 0.062$ ,  $R_w = 0.080$ , and  $\text{GOF} = 1.44$ .

(25) A planar  $\text{Os}_2\text{C}_2$  ring with the observed bond lengths would have an approximate tetrahedral ( $108^\circ$ ) angle at carbon.

(26) The sum of covalent radii for an Os–C single bond has been given elsewhere as 2.211 Å: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291.

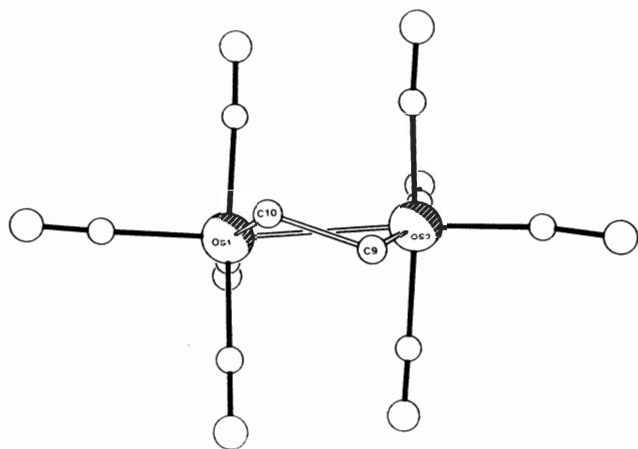
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(29) Oxtun, I. A.; Powell, D. B.; Sheppard, N.; Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1982**, 719.

(30) The synthesis of titanacyclobutanes from olefins and  $\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{AlMe}_2$  has recently been reported.<sup>31</sup>

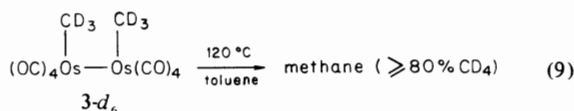
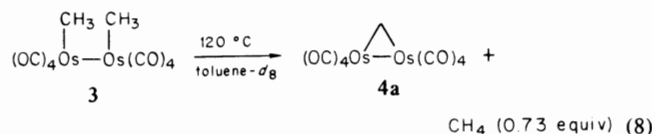
(31) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358.



**Figure 1.** Molecular structure of  $((\mu\text{-CC}')\text{CH}_2\text{CH}_2)\text{Os}_2(\text{CO})_8$  (**4b**). Distances (Å): Os(1)–Os(2), 2.883 (1); Os(1)–C(10), 2.22 (2); Os(2)–C(9), 2.22 (2); C(9)–C(10), 1.53 (3). Angles (deg): Os(1)–Os(2)–C(9), 70.1 (6); Os(2)–C(9)–C(10), 105.7 (13); C(9)–C(10)–Os(1), 103.8 (12); C(10)–Os(1)–Os(2), 71.1 (5).

from ethylene and methylene-bridged dimers.

The diosmacyclopropane **4a** is also formed upon thermolysis of the dimethyl analog **3** with elimination of methane. As shown by the labeling experiments (eq 8 and 9) solvent attack is not



involved. (Again **4a** is unstable under the reaction conditions, but NMR shows that it reaches a maximum concentration of 40% of the initial concentration of **3**.) Similar reactions presumably explain the several reported cases<sup>32</sup> where methylene-bridged dimers are formed under conditions that would have been expected to generate dimethyl complexes. An investigation into the mechanism of methane elimination from **3** is in progress.

**Acknowledgment.** This work was supported by NSF Grants CHE-7920373 and CHE-8207597. The Nicolet R3m/E diffractometer and computer system were purchased with funds provided by NSF Grant CHE-8103011. We are grateful to Johnson Matthey, Inc., for a generous loan of  $\text{OsO}_4$ , to Professor J. K. Stille and K. E. Warner for helpful discussions, and to Professor R. G. Bergman for preprints of ref 8 and 9.

**Registry No.** **3**, 82666-17-9; **4a**, 83705-04-8; **4b**, 83705-05-9; **4c**, 83705-06-0;  $\text{Na}_2[\text{Os}_2(\text{CO})_8]$ , 83705-03-7;  $\text{CH}_2(\text{OTs})_2$ , 24124-59-2;  $\text{TsOCH}_2\text{CH}_2\text{OTs}$ , 6315-52-2;  $\text{I}(\text{CH}_2)_3\text{I}$ , 627-31-6;  $\text{C}_2\text{H}_4$ , 74-85-1; Os, 7440-04-2.

**Supplementary Material Available:** Listing of atomic coordinates and thermal parameters for  $((\mu\text{-CC}')\text{CH}_2\text{CH}_2)\text{Os}_2(\text{CO})_8$  (1 page). Ordering information is given on any current masthead page.

(32) (a) Hursthouse, M. B.; Jones, R. A.; Abdul Malik, K. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. (b) Muetterties, E. L., unpublished work, ACS Symposium on Binucl. Met. Compd., New Orleans, LA, as quoted in ref 185 of ref 4b. (c) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1318. (d) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809. (e) Vazquez de Miguel, A.; Isobe, K.; Taylor, B. F.; Nutton, A.; Maitlis, P. M. *Ibid.* **1982**, 758. (f) Müller, J.; Passon, B.; Pickardt, J. *J. Organomet. Chem.* **1982**, *228*, C51.