Communications to the Editor

Hydrogen-Mediated Photolysis of (η-C_5Me_5)Os$(CO)_2$H: Synthesis of (η-C_5Me_5)Os(CO)H_3 and Multiply Bonded Diosmium Compounds

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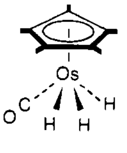
Sixteen-electron intermediates generated photochemically are highly reactive, complexing with donor ligands or undergoing oxidative-addition reactions with a variety of substrates.[1-3] While reaction of these intermediates with dihydrogen is well established,[4] it has rarely been applied to the synthesis of previously unknown metal hydrides. We report here on the transformations accomplished when solutions of metal carbonyl derivatives are irradiated in the ultraviolet while being purged with hydrogen, a process we term a hydrogen-mediated photolysis. In addition to providing a useful route to mononuclear di- or trihydride derivatives, the reaction affords an unexpected and valuable new pathway to multiply metal–metal-bonded compounds.

When (η-C_5Me_5)Os$(CO)_2$H (**1**)[5] is photolyzed[6] with continuous H_2 purge of the solution, the new compounds **2–4** are formed.[7-10]



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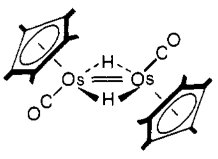

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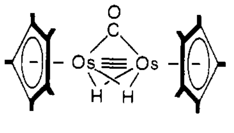

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All three products are present in at least IR-detectable amounts during the course of a 10-h irradiation, but time, concentration, and purge rate may be adjusted to optimize the yields of each.[11]

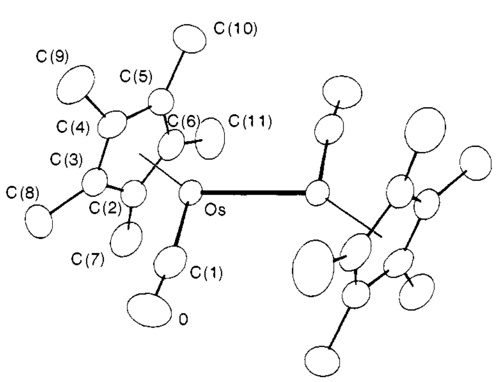

Figure 1. Structure of (η-C_5Me_5)$_2$Os$_2$(CO)$_2$(μ-H)$_2$ (**3**). Bridging hydrogens were not reliably located but are presumed to lie on opposite sides of the plane formed by the osmium atoms, the carbonyl carbons, and the ring centroids. The molecule is centrosymmetric. Selected bond lengths (Å) are as follows: Os–Os, 2.6773 (6); Os–C(1), 1.833 (9); C(1)–O, 1.18 (1); mean Os–ring carbon, 2.247. Selected bond angles (deg) are as follows: Os′–Os–C(1), 96.2 (3); Os′–Os–ring centroid, 138.4; C(1)–Os–ring centroid, 125.4; Os–C(1)–O, 173.3 (7).

The trihydride **2** is only the third mononuclear trihydride that is purely organometallic in the sense of having no phosphine or arsine ligands; the others are (η-C_5H_5)$_2$TaH_3[12] and (η-C_5H_5)$_2$NbH_3.[13] There is little doubt that **2** is formed by the reactions shown in eq 1 and 2. Equation 1 is effectively irreversible as CO is flushed from the system,[14] while eq 2 is expected

$$(\eta\text{-}C_5Me_5)Os(CO)_2H\ (\mathbf{1}) \xrightarrow{h\nu} [(\eta\text{-}C_5Me_5)Os(CO)H] + CO \qquad (1)$$

$$[(\eta\text{-}C_5Me_5)Os(CO)H] + H_2 \underset{h\nu}{\rightleftharpoons} (\eta\text{-}C_5Me_5)Os(CO)H_3\ (\mathbf{2}) \qquad (2)$$

to be reversible since H_2 elimination is a well-recognized photochemical reaction of metal polyhydrides.[1] The sharp NMR multiplets observed at −50 °C for the high-field protons of **2**[7] appear as very broad singlets at 25 °C, indicating that the molecule is fluxional. Dilute solutions of **2** are fairly stable, but in the pure state at room temperature, **2** forms **3** even in the dark (half-life ca. 15 h).

Inert gas formalism applied to the dimer **3** requires a double bond between the osmium atoms, and its similarity to (μ-H)$_2$Re$_2$(CO)$_8$[15] is noteworthy. A single-crystal X-ray diffraction study has been carried out on **3** with the results shown in Figure 1.[16] The resemblance of the central Os(μ-H)$_2$Os portion of **3** to that in (μ-H)$_2$Os$_3$(CO)$_{10}$[17] is clear and is emphasized by the closely similar Os–Os distances (2.6773 (3) Å in **3** vs. 2.681 (1)

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(1) An up-to-date survey is available: Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; Chapters 2 and 7.

(2) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 3375.

(3) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc. A* **1971**, 1508. Wong, K. L. T.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694.

(4) (a) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054. (b) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221. (c) Foley, H. C.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7176. (d) Green, M. A.; Huffman, J. C.; Caulton, K. G. *Ibid.* **1981**, *103*, 695.

(5) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.*, in press.

(6) Hexane or cyclohexane solution, Hanovia 450-W medium-pressure mercury lamp through Pyrex glass at 20 °C, for periods of 1–10 h. Longer irradiations reduced the yields of all products.

(7) **2**: colorless solid, mp ca. 25 °C; IR (hexane) ν_{CO} 1968 cm^{-1} (s), ν_{OsH} 2079 cm^{-1} (w, br); ^{1}H NMR (CD$_2$Cl$_2$, −50 °C, 200 MHz) δ 2.26 (s, 15 H), −10.72 (t, J = 8.9 Hz, 1 H), −12.55 (d, J = 8.9 Hz, 2 H). Anal. Calcd for $C_{11}H_{18}OOs$: C, 37.06; H, 5.09. Found: C, 37.59; H, 5.52.

(8) **3**: dark red crystals, >175 °C dec; IR (hexane) ν_{CO} 1888 cm^{-1} (s); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 1.96 (s, 15 H), −18.60 (s, 1 H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ 11.7 (CH$_3$), 94.9 (η-C$_5$), 203.1 (CO). Anal. Calcd for $C_{22}H_{32}O_2Os_2$: C, 37.28; H, 4.55. Found: C, 37.11; H, 4.60.

(9) **4**: dark amber crystals, >160 °C dec; IR (hexane) ν_{CO} 1776 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 2.01 (s, 15 H), −13.25 (s, 1 H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ 10.9 (CH$_3$), 87.8 (η-C$_5$), 204.1 (CO). Anal. Calcd for $C_{21}H_{32}OOs_2$: C, 37.04; H, 4.74. Found: C, 37.29; H, 4.79.

(10) The mass spectra of compounds **2–4** (16 eV) showed the molecular ions, with more pronounced H loss in the case of **2** as expected for terminal vs. bridging hydrogen. IR spectra of **3** and **4** showed no evidence for terminal Os–H bands.

(11) Reactions were run to 50–60% conversion, and unreacted **1** was recovered and recycled; yields are on the basis of unrecovered **1**: for **2**, 2–4-h irradiation of **1** in hexane (ca. 1 mg mL^{-1}) at a high purge rate, 30% after two cycles; for **3**, 1–2-h irradiation of **1** in cyclohexane (5–10 mg mL^{-1}), moderate to high purge, 54% after four cycles; for **4**, 7–10-h irradiation of **1** in cyclohexane (ca. 5–10 mg mL^{-1}), 45% after one cycle.

(12) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854.

(13) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.

(14) A referee has pointed out that it is extremely difficult to purge released CO from solutions when there is no substrate available for the intermediate to react with and that by trapping the photogenerated species hydrogen may facilitate the efficient removal of CO. This possibility must be considered when reaction pathways are discussed.

(15) Bennett, M. J.; Graham, W. A. G.; Hoyano, J. K.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232.

(16) The structure determination was carried out by Dr. R. Ball of the Structure Determination Laboratory of this department. Crystal data for **3**: $C_{22}H_{32}O_2Os_2$, M = 708.90, monoclinic $P2_1/n$, a = 7.310 (1) Å, b = 15.327 (2) Å, c = 10.156 (2) Å, β = 107.16 (1)°, V = 1087 Å^3, z = 2, μ (Mo Kα) = 117.06 cm^{-1}. In the final cycle 118 parameters were refined by using 1697 observations having $I > 3.0\sigma(I)$. Final agreement factors were R = 0.024 and R_w = 0.034.

(17) Johnson, B. F. G.; Lewis, J.; Kilty, P. *J. Chem. Soc. A* **1968**, 2859.

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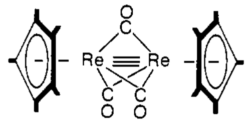
Å in $H_2Os_3(CO)_{10}$[18]). Both $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ undergo interesting reactions involving the $M(\mu\text{-}H)_2M$ core,[19] and we anticipate that **3** will be reactive as well. In preliminary investigations, we have found that **3** reacts slowly with CO (30 psig) to form **1**,[20] while reaction with CH_2N_2 results in addition of CH_2 to the molecule.

The third product of irradiation of **1** with H_2 purge is the dinuclear 30-electron complex **4**, which on the 18-electron formalism would contain an osmium–osmium triple bond.[22] It is isoelectronic with the recently described $Re(\mu\text{-}CO)_3Re$ complex **5**[23] and may be compared with the dinuclear rhodium complex $L_2Rh(\mu\text{-}H)_2(\mu\text{-}CO)RhL_2$ ($L = P(O\text{-}i\text{-}C_3H_7)_3$) characterized, although not isolated, from reaction of CO with the catalyst precursor $[L_2Rh(\mu\text{-}H)]_2$.[24] Reactions of **4** will likewise be of interest; preliminary investigations show that it reacts readily with CO to form **1** and **3**.



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Details of the processes that give rise to **3** and **4** are not clear, but eq 3–5 may be involved. Equation 5 has been demonstrated

$$2[(\eta\text{-}C_5Me_5)Os(CO)H] \rightarrow (\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2\ (\mathbf{3}) \tag{3}$$

$$[(\eta\text{-}C_5Me_5)Os(CO)H] + \mathbf{2} \rightarrow (\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2\ (\mathbf{3}) + H_2 \tag{4}$$

$$(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2\ (\mathbf{3}) \xrightarrow{h\nu} (\eta\text{-}C_5Me_5)_2Os_2(\mu\text{-}CO)(\mu\text{-}H)_2\ (\mathbf{4}) + CO \tag{5}$$

by irradiation of solutions of pure **3** (N_2 or H_2 purge) whereby **4** forms as the only product accompanied by some decomposition. Furthermore, irradiation of **2** (N_2 atmosphere) affords **3** in good yield. The question remains as to the path leading to **3**, whether straight dimerization (eq 3) or another process such as dinuclear hydrogen elimination[25] as suggested in eq 4. On this point, a key observation is that irradiation of **1** under identical conditions except for substitution of an N_2 for H_2 purge gave only low conversion to **3** and **4** (and no **2**). Thus, dimerization of the 16-electron intermediate (eq 3) may constitute only a minor pathway, with the role of hydrogen to provide a second pathway via **2**.[26] Further study of the mechanism is in progress.[14]

We also have found that photolysis[6] of $(\eta\text{-}C_5H_5)Re(CO)_3$ with hydrogen purge provides a more convenient route to $(\eta\text{-}C_5H_5)Re(CO)_2H_2$, a compound recently prepared through a hydridosilylrhenium intermediate.[27] A similar hydrogen-purge photolysis[6] of $(\eta\text{-}C_5Me_5)Re(CO)_3$ gave the new pentamethyl analogue $(\eta\text{-}C_5Me_5)Re(CO)_2H_2$ (**6**).[28] Additionally, hydrogen-mediated photolysis of $(\eta\text{-}C_5Me_5)Re(CO)_3$ using only a water-cooled quartz jacket (no Pyrex filtration) afforded **5** in better yield (under optimized conditions) than did the reported method.[23]

The results summarized above demonstrate the synthetic utility of dihydrogen addition to 16-electron intermediates generated by loss of a carbonyl ligand through ultraviolet irradiation. The hydrogen-mediated photolysis reaction has also led to interesting carbonyl- or hydrido-bridged dimers having formal double and triple bonds. We are currently investigating the reactivity of these dimers and attempting to extend the general reaction to metals other than rhenium and osmium.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

Registry No. 1, 81554-96-3; **2**, 81753-10-8; **3**, 81740-97-8; **4**, 81740-98-9; **5**, 81740-99-0; 6, 81741-00-6; $(\eta\text{-}C_5Me_5)Re(CO)_3$, 12130-88-0.

Supplementary Material Available: Detailed results of the X-ray crystal structure of $(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2$, tables of experimental details, positional and thermal parameters, general temperature factor expressions (*U*, *B*), bond distances, and bond angles, and the structure of $(\eta\text{-}C_5Me_5)_2Os_2(CO)_2(\mu\text{-}H)_2$ (8 pages). Ordering information is given on any current masthead page.

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(18) (a) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697. (b) Broach, R. W.; Williams, J. W. *Ibid.* **1979**, *18*, 314. (c) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297.

(19) (a) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (b) Calvert, R. B.; Shapley, J. R. *Ibid.* **1977**, *99*, 5225. (c) Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *Ibid.* **1980**, *102*, 6156. (d) Adams, R. D.; Dawoodi, A. *Ibid.* **1981**, *103*, 6510. (e) Adams, R. D.; Katahira, D. A.; Yang, L. W. *J. Organomet. Chem.* **1981**, *219*, 85. (f) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *219*, 103. (g) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318.

(20) It appears that **3** forms mononuclear products more readily than $H_2Os_3(CO)_{10}$,[19a] perhaps because it lacks the bridging $\mu\text{-}Os(CO)_4$ group of the latter. A derivative of $H_2Re_2(CO)_8$ bridged by $Ph_2PCH_2PPh_2$ is also less susceptible to fragmentation than the parent compound.[21]

(21) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171.

(22) Completion of the X-ray structure of **4** has been delayed by a disorder problem, but a preliminary value for the Os–Os distance is 2.441 Å (R. Ball, personal communication). This compound involves Os(II), and the bond length is longer than values reported recently (2.344 (2) and 2.357 (1) Å) for an Os(III)–Os(III) triple bond: Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437.

(23) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

(24) Burch, R. R.; Muetterties, E. L.; Schultz, A. J.; Gebert, E. G.; Williams, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5517.

(25) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

(26) A two-pathway dimerization mechanism, with one pathway facilitated by H_2, has also been proposed for dimerization of $H_5Re(PMe_2Ph)_2$.[4d]

(27) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783.

(28) **6**: colorless crystals, mp 75–76 °C; IR (hexane, ν_{CO}) 2008 (ms), 1938 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.24 (s, 15 H), −9.63 (s, 2 H). Anal. Calcd for $C_{12}H_{17}O_2Re$: C, 37.98; H, 4.52. Found: C, 38.00; H, 4.42.

Oxidative Addition of the Carbon–Hydrogen Bonds of Neopentane and Cyclohexane to a Photochemically Generated Iridium(I) Complex

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We report the stoichiometric oxidative additon of carbon–hydrogen bonds of alkanes to a photochemically generated iridium complex.[1] The results demonstrate clearly that in the proper circumstances, such a reaction of totally unactivated sp^3 C–H bonds is both energetically and kinetically favorable.

Irradiation[2a] of a solution of $(\eta\text{-}C_5Me_5)Ir(CO)_2$[2b] (**1**) in neopentane (2,2-dimethylpropane) at room temperature proceeded according to eq 1, with formation of the new hydridoneopentyl-

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(1) Shortly after the submission of this communication, we learned that similar results had been reported for a closely related iridium system: Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; *Chem. Eng. News.* **1982**, *60*, 59. These workers photolyzed $(\eta\text{-}C_5Me_5)Ir(PMe_3)H_2$ and found that C–H bonds of neopentane and cyclohexane added readily to the presumed intermediate $[(\eta\text{-}C_5Me_5)Ir(PMe_3)]$, forming Me_3P derivatives of **2** and **4**. The more electron-rich Me_3P species should have an even greater tendency than the carbonyl to undergo oxidative-addition reactions, although the behavior seems roughly similar in the reactions so far examined. Differences in selectivities might be expected, and distinctions may arise in secondary reactions of the phosphine and carbonyliridium(III) complexes.

(2) (a) In this and other irradiations, degassed solutions in closed quartz tubes were placed approximately 5 cm from a Hanovia 450-W medium-pressure mercury lamp fitted with a cylindrical Pyrex filter and a water-cooled quartz jacket. In this experiment the solution contained 10 mg of **1**/g of neopentane. At the end of the 5 h of irradiation, neopentane was removed in vacuum and hexane was added. The IR spectrum of the products in hexane showed no carbonyl stretching bands other than those of **1** and **2**. (b) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. The IR spectrum of **1** in hexane exhibits ν_{CO} at 2020 (s), 1953 (s) cm^{-1}, and the ^1H NMR a singlet at δ 1.73 in C_6D_6.

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