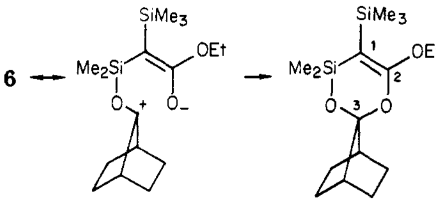
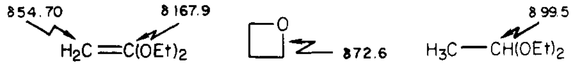


8

We assign the CMR absorptions at δ 58.9 and 164.7 (assumed carbonyl) to C_1 and C_2 of 8. Indeed, these values are remarkably close to those observed for dimethylketene acetal (9).[5] The ^{13}C NMR absorption at δ 113.8 we assign to C_3. The methylene carbons of oxetane[6] (10) are found at δ 72.6, while ketal carbons are usually around δ 100 (e.g., 1,1-diethoxyethane (11).[7] Lastly, one must contend with the IR band at 1560 cm^{-1} that is clearly too low to be an ester carbonyl. That this band is the olefinic stretching vibration in 8 is not immediately obvious since the C=C stretching frequency of enol ethers does not usually differ much from normal olefins.[8] However, it has long been known that silyl substitution produces dramatic bathochromic shifts of $\nu_{C=C}$ as can be dramatically seen for the olefinic sequence 12, 13, and 14.[9] Thus, a strong IR band at 1560 cm^{-1} is not unexpected for 8.



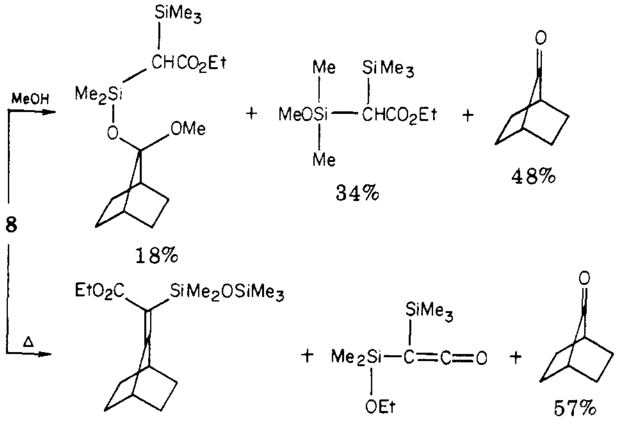
9, $\nu_{C=C}$ 1639 cm^{-1} 10 11

$H_2C{=}CH_2$
12, $\nu_{C=C}$ 1623 cm^{-1}

$Me_3SiCH{=}CH_2$
13, $\nu_{C=C}$ 1592 cm^{-1}

$(Me_3Si)_2C{=}CH_2$
14, $\nu_{C=C}$ 1569 cm^{-1}

Adduct 8 also provides an excellent rational for the reported observations[4] (surprising for 7) that both thermolysis and methanolysis of 7 regenerated norbornanone as the major product. While it is certainly possible that 7 is involved in formation of the minor thermolysis product 15, that explanation is not demanded.



15 (8%) (from 5)[10]

Registry No. 7, 83547-74-4; 8, 85185-51-9.

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Properties of the Pentacarbonyls of Ruthenium and Osmium

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Summary: The pentacarbonyls of ruthenium and osmium have been prepared by the action of high-pressure carbon monoxide on the corresponding solid trimetal dodecarbonyls at elevated temperatures. Physical data for the pentacarbonyls are reported along with some chemical properties of the osmium compound.

The pentacarbonyls of ruthenium and osmium have been known for several decades.[1,2] However, except for the work of Calderazzo and L'Eplattenier,[3] they have been little studied, presumably because of the difficulty involved in their preparation. We have developed a useful method for the routine synthesis of these important compounds in a pure form. This has allowed their spectral and physical characteristics to be accurately determined.

Pure $Ru(CO)_5$ was formed nearly quantitatively by the reaction of solid $Ru_3(CO)_{12}$ with CO (ca. 200 atm) at 160 °C.[4] When freshly prepared, $Ru(CO)_5$ was a colorless liquid at room temperature (mp −17 to −16 °C) which rapidly developed a yellow-orange coloration due to the formation of $Ru_3(CO)_{12}$. It was extremely sensitive to heat and light and had to be handled in the dark to prevent decomposition. Pure $Os(CO)_5$ was formed (in ca. 60% yield) from the corresponding reaction of $Os_3(CO)_{12}$ and CO (200 atm) only at much higher temperatures (280–290 °C).[5] The much more forcing conditions required are consistent with the view that the osmium–osmium bonds are stronger than ruthenium–ruthenium bonds.[7] As isolated, $Os(CO)_5$ formed large, colorless to pale yellow crystals that melted at 2–2.5 °C to give a mobile yellow liquid. It was far more robust than its ruthenium congener and only formed $Os_3(CO)_{12}$ at a significant rate at 80 °C or above (in solution under normal laboratory lighting). It may be stored indefinitely at −15 °C without any special precautions.

If the reactions were carried out in hexane, solutions of the pentacarbonyls were produced. However, the conditions used to prepare $Os(CO)_5$ were sufficiently extreme to cause the formation of some hexenes by dehydrogenation of the solvent. (Control experiments have shown that

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(1) Manchot, W.; Manchot, W. J. *Z. Anorg. Allg. Chem.* **1936**, *226*, 385.

(2) Heiber, W.; Stallmann, H. *Z. Elektrochem.* **1943**, *49*, 288.

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(4) The trimetal dodecacarbonyl, $M_3(CO)_{12}$ (1.0–2.0 g), was placed in a high-pressure autoclave (500 mL) and the vessel pressurized with CO (ca. 200 atm). It was sealed and heated (M = Ru, 160 °C; M = Os, 280 °C) for 48 h after which the autoclave was cooled to −78 °C and the gas vented. The autoclave was connected to a vacuum line, and, as the autoclave warmed to room temperature, the $M(CO)_5$ product was vacuum distilled ($<5 \times 10^{-3}$ mmHg) into a trap cooled to −196 °C (M = Ru, quantitative yield; M = Os, yield ca. 60%). The ruthenium compound was collected with the strict exclusion of light.

(5) This method of preparation is reminiscent of the original synthesis of $Os(CO)_5$[2]: treatment of OsO_4 with CO (200–300 atm) at 150–300 °C. Dodecacarbonyltriosmium is usually prepared from OsO_4 and CO under milder conditions (100 atm, 150 °C).[6]

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

(7) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; 4th ed.; Wiley: New York, 1980; p 1082.

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Table I. Physical and Spectroscopic Properties of the Pentacarbonyls

	mp, °C	ν(CO),[a] cm^{-1}	^{13}C NMR,[b] ppm
$Fe(CO)_5$	−20.5[c]	2022.5 2000.5	210.6
$Ru(CO)_5$	−17 to −16	2036.5 2001.5	200.4
$Os(CO)_5$[d]	2 to 2.5	2035.0 1993.0	182.6

[a] Hexane solution. [b] Recorded at 100.6 MHz, $CDCl_3$ solution at −40 °C. [c] Wender, I.; Pino, P., Eds. "Organic Syntheses via Metal Carbonyls"; Wiley: New York, 1968; p 39. [d] Calcd: C, 18.17, H, 0.0. Found: C, 18.37; H, 0.0.

this dehydrogenation was independent of the presence of osmium carbonyls.) A very minor byproduct using this method was $Os(CO)_4H_2$ presumably formed by the reaction of $Os(CO)_5$ with the hydrogen liberated from the solvent.[8] In most cases, the presence of the hexenes does not interfere with the chemistry of $Os(CO)_5$ although it was not possible to prepare $Os_2(CO)_9$[9] from such solutions since the low-temperature photolysis yielded the olefin complex $Os(CO)_4(\eta^2$-hexene).

The ^{13}C NMR spectrum of each pentacarbonyl recorded in $CDCl_3$ at −40 °C showed a singlet. For $Os(CO)_5$, the singlet remained sharp at −110 °C ($CFCl_2H$ solution), indicating, as expected,[10] rapid exchange between axial and equatorial ligands. The ^{13}C chemical shifts along with other physical data for the compounds are collected in Table I.

The mass spectrum showed a parent ion with the expected isotopic distribution for each case. Successive loss of five carbonyl groups from the parent ion, and the carbide-containing ions $[OsC(CO)]^+$ and $[MC]^+$ (M = Ru, Os), was also clearly observed. No higher molecular weight ions of significant abundance were detected.

The chemistry of $Os(CO)_5$ is currently under investigation.[11] As expected it undergoes the oxidative elimination reaction with a variety of substrates. In some cases ionic intermediates have been isolated. For example, from the reaction with Cl_2 in solution at −78 °C a white compound was isolated (in quantitative yield) that had properties[12] consistent with the formulation $[Os(CO)_5(Cl)][Cl]$.[13] The compound was stable at room temperature unlike similar iron derivatives;[14] when a suspension of it was refluxed in hexane, the known[15] dimer $[Os(CO)_3Cl_2]_2$ was produced.

The olefin complex $Os(CO)_4(\eta^2$-dimethyl fumarate) has also been synthesized, from the UV irradiation of a solution of $Os(CO)_5$ and dimethyl fumarate under a CO atmosphere.[16] The two signals observed in the ^{13}C NMR spectrum of the compound (in $CDCl_3$) that are assigned to the carbonyl ligands were sharp at room temperature. When the solution was warmed, the peaks broadened, but even at 105 °C (toluene-d_8 solution, 100.6 MHz operating frequency) they still had not quite collapsed. By assuming a collapse temperature of 115 °C, a barrier to rearrangement, $\Delta G^{\ddagger}_{388}$, of 18.8 kcal mol^{-1} may be estimated. This barrier is higher than that found for $Ru(CO)_4(\eta^2$-diethyl fumarate) ($\Delta G^{\ddagger}_{298}$ = 15.4 kcal mol^{-1}) which in turn is higher than that in $Fe(CO)_4(\eta^2$-diethyl fumarate) ($\Delta G^{\ddagger}_{298}$ = 12.8 kcal mol^{-1}).[17]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. $[Os(CO)_5(Cl)][Cl]$, 85097-37-6; $Os(CO)_4B$ (B = η^2-dimethyl fumarate), 85097-38-7; $Ru(CO)_5$, 16406-48-7; $Os(CO)_5$, 16406-49-8; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; CO, 630-08-0.

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(11) A crystal structure determination of $Os(CO)_5$ by X-ray diffraction techniques will be attempted in the near future.

(12) Calcd for $OsC_5O_5Cl_2$: C, 15.11, H, 0.0. Found: C, 14.96; H, 0.0 Insoluble in hexane, sparingly soluble in CH_2Cl_2. IR (CH_2Cl_2): ν(CO) 2175 (w), 2104 (vs), 2084 (m), 2075 (sh), 2055 (s) cm^{-1}.

(13) The compound is not the known[8] *cis*-$Os(CO)_4Cl_2$ that we have prepared from the reaction of $Os(CO)_5$ with CCl_4.

(14) Noack, K. *J. Organomet. Chem.* **1968**, *13*, 411.

(15) Bruce, M. I.; Cooke, M.; Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1969**, 897.

(16) Calcd for $OsC_{10}H_8O_8$: C, 26.91; H, 1.81. Found: C, 27.01; H, 1.81. IR (hexane): ν(CO) 2136.5 (w), 2062.5 (s), 2045 (m), 2008.5 (s) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 25.3 (=C<), 51.9 ($-CH_3$), 172.2, 173.2 (−CO), 176.8 (−C(O)−). MS: m/e 446 w (P^+), 418 s [$(P - CO)^+$].

(17) Kruczynski, L.; Martin, J. L.; Takats, J. *J. Organomet. Chem.* **1974**, *80*, C9.