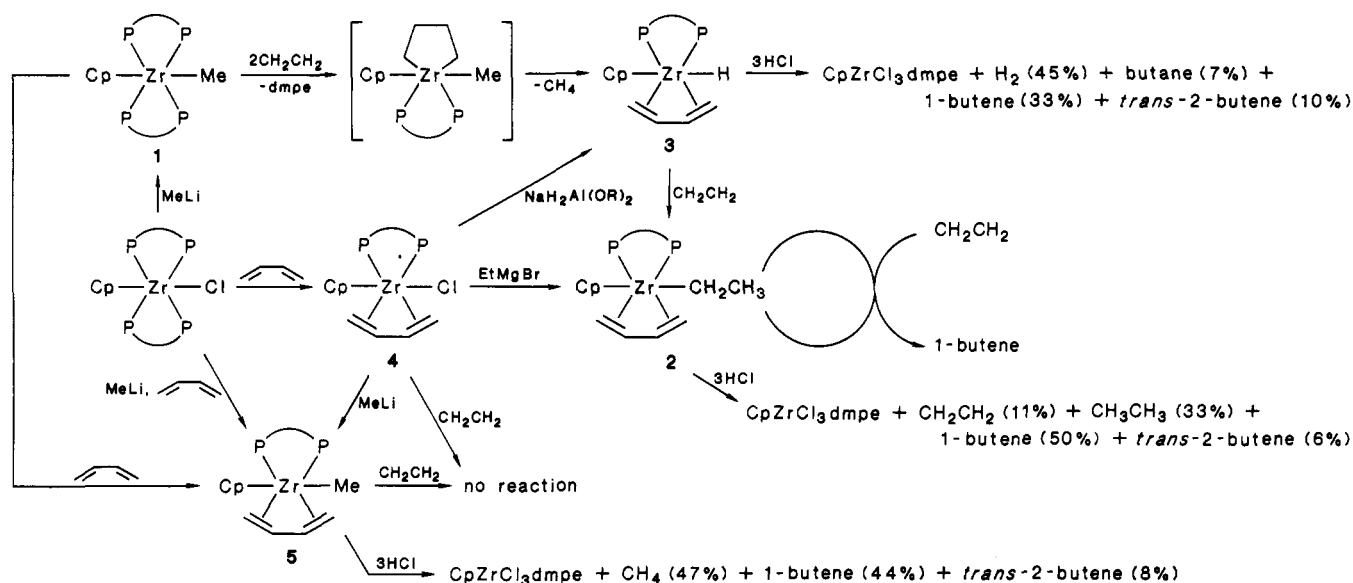


Scheme I



of any C₃ and C₅ products points out the inability of the Zr(II)-Me bond in the present case to undergo olefin insertion reactions. Furthermore this indicates that reductive coupling of ethylene is a possible pathway for the formation of the C₄ framework (Scheme I). In a following step, methane elimination together with hydrogen transfer to the metal center possibly leads to an intermediate butadiene-hydrido Zr species,¹⁴ which forms **2** via ethylene insertion reaction into the Zr-H bond (Scheme I). To verify this hypothesis, we have prepared in crystalline form the unprecedented CpZr(dmpe)(η⁴-butadiene)H^{13,15} (**3**) by reacting CpZr(dmpe)(η⁴-butadiene)Cl (**4**) with NaH₂Al(O-CH₂CH₂OCH₃)₂ (Red-Al) (Scheme I). As expected, **3** undergoes fast ethylene insertion into the Zr-H bond giving **2** in quantitative yield (Scheme I). The CH₄-elimination reaction seems a rather specific step in the reaction of **1** with light olefins and apparently not possible for conjugated olefins like butadiene.¹⁶ Reaction of **1** with butadiene led in fact to the formation of CpZr(dmpe)(η⁴-butadiene)Me (**5**) as bright orange crystals.¹³

In contrast to **5**, complex **2** is rather unstable and slowly decomposes in solution at room temperature. However, as shown in Scheme I, **2** acts as homogeneous catalyst for slow and selective mild condition dimerization of ethylene to 1-butene (ca. 3 turnovers/day at room temperature, atmospheric pressure). It is noteworthy that the isostructural¹⁷ Me (**5**) and Cl (**4**) derivatives do not display any reactivity with ethylene under the same reaction conditions. Furthermore the absence of C₆ and C₈ products, previously observed in the Zr- and Ti-promoted oligomerization of ethylene,¹⁸ suggests that the mechanism

in the present system is highly selective, a dominant role being probably played by the bulky dmpe.

More work to clarify the mechanism of the catalytic cycle and attempts to characterize possible intermediates are included in our continuous studies on these systems.

Acknowledgment. This work has been supported by the University of Groningen and by a NATO travel grant (0402/87); we are also indebted to the generosity of Chemistry Department at Columbia University.

Registry No. **1**, 115227-32-2; **2**, 115227-33-3; **3**, 115227-34-4; **4**, 115227-38-8; **5**, 115227-35-5; CpZrCl(dmpe)₂, 114238-07-2; NaH₂Al(OCH₂CH₂OCH₃)₂, 22722-98-1; CpZr(dmpe)(η⁴-butadiene)(CH₂CH₂CH₃), 115227-36-6; CpZrCl₃dmpe, 115227-37-7; CH₄, 74-82-8; H₂, 1333-74-0; CH₃CH₃, 74-84-0; ethylene, 74-85-1; butadiene, 106-99-0; 1-butene, 106-98-9; propylene, 115-07-1; isobutene, 115-11-7; 2-butene, 107-01-7; 2,3-dimethyl-2-butene, 563-79-1; butane, 106-97-8; *trans*-2-butene, 624-64-6.

Supplementary Material Available: Spectroscopic and analytical data of complexes **2-5** and tables of crystal data, anisotropic thermal parameters, atomic coordinates, and bond lengths and angles (10 pages); a listing of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

The New Binary Carbonyl Os₄(CO)₁₄: An Example of Carbonyl Exchange on the Infrared Time Scale?

Victor J. Johnston, Frederick W. B. Einstein,* and Roland K. Pomeroy*

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

Received March 9, 1988

Summary: The new binary carbonyl Os₄(CO)₁₄ has been synthesized by the pyrolysis of Os₄(CO)₁₅. The structure of the compound shows an irregular tetrahedral Os₄ skeleton with 14, essentially terminal, carbonyl ligands. The spectroscopic properties of the cluster suggests it may be fluxional on the infrared time scale.

We have recently reported the synthesis and structure of Os₄(CO)₁₅¹ and Os₄(CO)₁₆,² the first tetranuclear binary

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(16) An analogous reaction has been found with propylene, while no reaction has been observed with isobutene, 2-butene, and 2,3-dimethyl-2-butene.

(17) The close similarity in the structures of CpZr(dmpe)(η⁴-butadiene)X (X = Et, Me, Cl) derivatives is deduced from the almost complete overlapping of the IR spectra.

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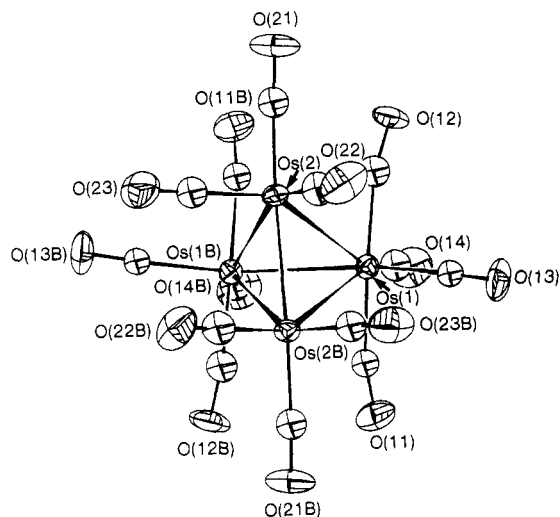


Figure 1. Molecular structure of $\text{Os}_4(\text{CO})_{14}$ (1).

carbonyls of osmium. Here we describe the synthesis and structure of $\text{Os}_4(\text{CO})_{14}$, a stable tetranuclear cluster with 14, essentially terminal, carbonyl ligands. The molecules $\text{Os}_4(\text{CO})_n$ ($n = 14\text{--}16$) represent the first time that three binary carbonyls of the same metal have been prepared that differ in the number of CO ligands but have a constant number of metal atoms. Furthermore, tetrahedral clusters with 14 carbonyl substituents are exceedingly rare. It had been suggested on the basis of both steric³ and molecular orbital⁴ arguments that such clusters would probably not be stable. However, Shriver and co-workers subsequently showed with the synthesis of $[\text{Fe}_3\text{M}(\mu\text{-CO})_2(\text{CO})_{12}]^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) that these clusters were indeed capable of existence.⁵

Pyrolysis of $\text{Os}_4(\text{CO})_{15}$ ¹ in hexane at 80 °C affords $\text{Os}_4(\text{CO})_{14}$ (1) in 94% yield after 20 h.⁶ The structure⁷ of 1 (Figure 1) shows an irregular tetrahedral framework of metal atoms with a crystallographic twofold axis passing through the center of the Os(1)–Os(1B) and Os(2)–Os(2B) bonds. The Os–Os bond lengths are Os(1)–Os(1B) = 2.834 (1) Å, Os(1)–Os(2) = 2.892 (1) Å, Os(1)–Os(2B) = 2.810 (1) Å, Os(2)–Os(2B) = 2.763 (1) Å. Four of the carbonyl ligands are weakly semibridging; these involve a carbonyl attached to an osmium atom of an $\text{Os}(\text{CO})_4$ unit interacting with an osmium atom of an $\text{Os}(\text{CO})_3$ unit. The semibridging contacts are Os(2)–C(12) = 2.68 (2) Å and Os(2B)–C(11) = 2.66 (2) Å.

The tetrahedral core of the metal atoms is as expected from polyhedral skeletal electron pair theory.⁸ The var-

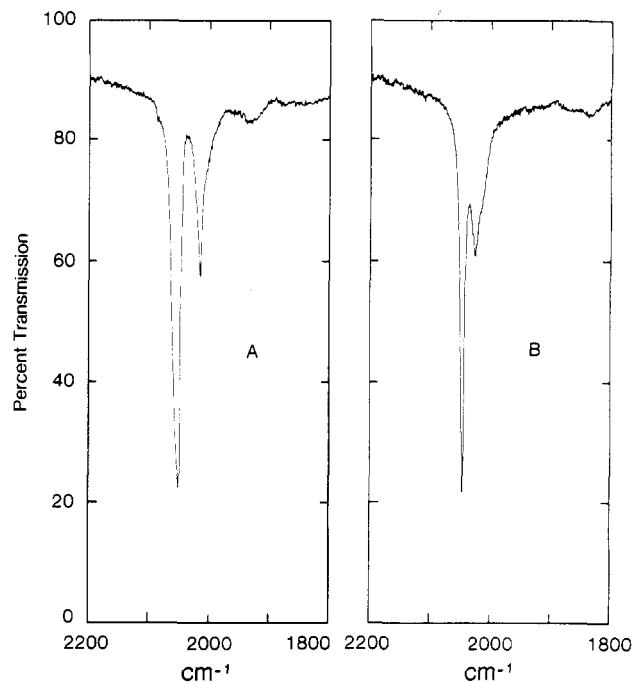
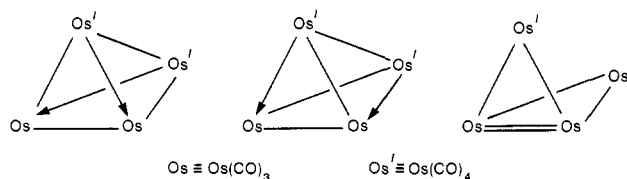


Figure 2. (A) Carbonyl stretching region of the infrared spectrum of 1 in hexane solution. (B) The spectrum of $\text{Fe}_3(\text{CO})_{12}$ under the same conditions (peak positions are 2047 and 2025 cm^{-1}).

iation in the metal bond lengths cannot, however, be rationalized by the theory in its present state. In each of the resonance structures shown for 1 in the scheme



the osmium atoms have an 18-electron count. Although this is a simple view of the molecule, it accounts for the variation in bond lengths in 1 and that the Os(1)–Os(1B) bond is the shortest metal–metal bond. Furthermore, those bonds that are partially dative are those which are semibridged by carbonyl ligands. This is expected to offset the polar character of these bonds.⁹ A similar Os_4 framework was found for $\text{Os}_4(\text{CO})_{13}(\text{PMe}_3)$.¹⁰

The carbonyl stretching region of the infrared spectrum of 1 in hexane consists of two broad absorptions¹¹ plus a third even broader absorption that is barely detectable above the base line (Figure 2).¹² The ¹³C NMR spectrum of 1 (¹³CO-enriched) in $\text{CHFCl}_2/\text{CD}_2\text{Cl}_2$ consists of a sharp singlet even at -130 °C. This behavior is reminiscent of that of $\text{Fe}_3(\text{CO})_{12}$ which exhibits a singlet in the ¹³C NMR

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(6) The reported yield is of the crude product; it did, however, contain a trace impurity believed to be $\text{Os}_4\text{H}_4(\text{CO})_{12}$. The analytical sample and the sample used for the spectrum shown in Figure 2 were obtained after two recrystallizations from CH_2Cl_2 –hexane. Anal. Calcd for $\text{C}_{14}\text{O}_{14}\text{Os}_4$: C, 14.58; H, 0.0. Found: C, 14.88; H, 0.0. IR (hexane): $\nu(\text{CO})$ 2058 (s), 2018 (m), 1938 (vw, br) cm^{-1} . ¹³C NMR ($\text{CHFCl}_2/\text{CD}_2\text{Cl}_2$, 6/1, 0 °C): δ 177.1. MS: m/e 1154 (M^+).

(7) X-ray diffraction data for $\text{Os}_4(\text{CO})_{14}$: $M_r = 1152.8$; monoclinic; space group $\text{C}2/c$; $a = 13.275$ (2) Å, $b = 13.033$ (1) Å, $c = 11.593$ (1) Å, $\beta = 90.435$ (9)°; $V = 2000.5$ Å³; $Z = 4$, $D_{\text{calcd}} = 3.818$ g cm^{-3} (an empirical absorption correction was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo $\text{K}\alpha$, graphite monochromator ($\lambda(\text{K}\alpha_1) = 0.70930$ Å); scan range = $0^\circ \leq 2\theta \leq 50^\circ$; reflections = 1301 with $I_o \geq 2.5\sigma(I_o)$; $R_F = 0.033$, $R_w = 0.040$; no. of variables = 109.

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(11) The peak width at half-height of the absorption at 2058 cm^{-1} is 14.5 cm^{-1} . By comparison, for the most intense absorption of $\text{Os}_3(\text{CO})_{12}$ (at 2068 cm^{-1}) under the same conditions it is 5 cm^{-1} .

(12) Twelve infrared-active carbonyl stretches are predicted for 1 with C_{2v} symmetry and all CO ligands terminal. For the more symmetric form with two carbonyls bridging opposite edges of a regular tetrahedron (i.e., D_{2d} $\text{Os}_4(\mu\text{-CO})_2(\text{CO})_{12}$) five infrared-active absorptions are expected in the terminal CO region.

spectrum to $-150\text{ }^{\circ}\text{C}$.¹⁴ The infrared spectra of the two compounds are remarkably similar in the carbonyl stretching region (Figure 2). Cotton and Hunter¹⁴ have proposed that $\text{Fe}_3(\text{CO})_{12}$ adopts a continuum of different structures in solution and this is responsible for the broadness of the infrared absorptions (this interpretation has, however, recently been questioned¹⁵). Similar arguments could be used to rationalize the broad bands in the spectrum of 1.

It is conceivable that the CO exchange in 1 is so fast so as to cause the broadening of the absorptions in the infrared spectrum of the compound. The range in the chemical shifts of the ^{13}C NMR resonances of chemically different carbonyls in rigid osmium clusters is usually at least 10 ppm or $\sim 1000\text{ Hz}$ at an operating frequency of 100.6 Hz. (For example, the chemical shift separation between the resonances of the axial and equatorial CO ligands in $\text{Os}_3(\text{CO})_{12}$ is 11.9 ppm.¹⁶) For two sites undergoing fast exchange, the rate constant required to observe a detectable broadening (of 0.5 Hz) due to exchange is given by $\pi(\Delta\nu)^2$, where $\Delta\nu$ is the chemical shift difference between the two signals when the molecule is rigid.¹⁷ The sharp singlet in the solution ^{13}C NMR spectrum of 1 at $-130\text{ }^{\circ}\text{C}$ therefore suggests that the carbonyls in the compound are undergoing exchange with a rate constant of at least $3 \times 10^6\text{ s}^{-1}$ at this temperature.¹⁸ If it is further assumed that the rate doubles with every ten degree rise in temperature, then a minimum rate of $\sim 2 \times 10^{11}\text{ s}^{-1}$ is estimated for the CO exchange in 1 at $30\text{ }^{\circ}\text{C}$. This is a rate approaching that necessary to cause detectable broadening of infrared absorptions.²⁰ From the uncertainty principle, a rate necessary to cause a broadening of 5 cm^{-1} and thus coalesce two infrared peaks separated by this frequency is approximately $9.4 \times 10^{11}\text{ s}^{-1}$. Dynamic rearrangement observable on the infrared time scale has recently been reported for some $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complexes.²²

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University for financial support. We also thank Professor W. A. G. Graham (University of Alberta) for valuable discussions.

Registry No. 1, 115227-28-6; $\text{Os}_4(\text{CO})_{16}$, 110698-51-6.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles for 1 along with details of the data collection and refinement of the structure (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any masthead page.

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Laser Photolysis of Aryl-Substituted Digermanes. Generation of Germyl Radicals and Germylenes

Kunio Mochida* and Masanobu Wakasa

Department of Chemistry, Faculty of Science
Gakushuin University
1-5-1 Mejiro, Tokyo 171, Japan

Yasuhiro Nakadaira

The University of Electro-Communications
1-5-1 Chofugaoka, Chofu, Tokyo 182, Japan

Yoshio Sakaguchi and Hisaharu Hayashi*

The Institute of Physical and Chemical Research
Wako, Saitama 351-01, Japan

Received March 16, 1988

Summary: Laser flash photolysis of the phenyl-substituted digermanes $(\text{Ph}_n\text{Me}_{3-n}\text{Ge})_2$ results in Ge-Ge bond homolysis to give germyl radicals and probably a germylene.

The photochemistry of organosilicon compounds having a $\sigma(\text{Si-Si})-\pi(\text{C-C})$ conjugated system has been the subject of considerable interest in recent years.¹ However, there have been few reports on photochemical studies of the germanium analogue.² We describe herein the first laser photolysis studies on the aryl-substituted digermanes $(\text{Ph}_n\text{Me}_{3-n}\text{Ge})_2$ (1-3, $n = 1-3$, respectively). Photolysis of the phenylated digermanes causes germanium-germanium bond homolysis which leads to the formation of a germyl radical and probably a germylene.

Laser flash photolysis³ ($\lambda = 266\text{ nm}$, pulse width 5 ns, power 10 mJ/pulse) of 1-3 (10^{-3} M) in THF at 293 K gave two well-separated transient absorption bands as shown in Figure 1. Careful examination of the transient peak at shorter wavelength shows that this is composed of the two components (half-life in THF and hydrocarbon media, $t_{1/2} < 5\text{ }\mu\text{s}$ and $t_{1/2} > 20\text{ }\mu\text{s}$, respectively). The former is reasonably assigned to that of the aryl-substituted germyl radical $\text{Ph}_n\text{Me}_{3-n}\text{Ge}^{\cdot}$ ($n = 1-3$) from comparison of spectral characteristics with those of the germyl radical reported.⁴⁻⁶ The experimentally determined decay constants of these transient species are summarized in Table I and are dependent on the concentrations of the employed phenylated digermanes. This is reasonably attributed to the addition of the generated germyl radical to the aromatic ring on the germanium.^{7,8} The assignment of the shorter lived tran-

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