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- (9) We will designate fragments as "native" if they were made from whole BSA and were not subjected to the reoxidation procedure.
- (10) Final concentrations of each fragment were ca. 10 μ M. Experiments in which a large molar excess of the complementary "native" fragment was used gave similar results.
- (11) In control experiments the unfolded, reduced fragments were reacted with iodoacetate to prevent subsequent refolding and reoxidation after the urea and mercaptoethanol were dialyzed out. As expected, these permanently unfolded fragments had absolutely no catalytic activity, when assayed against each other or with the corresponding complementary native fragments.
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- (13) Research Career Development Awardee of the National Institutes of Health, No. AI-00062-01.

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Decacarbonyltriosmium Complexes of Some Conjugated Dienes. The Crystal Structures of $\text{Os}_3(\text{CO})_{10}(s\text{-cis-C}_4\text{H}_6)$ and $\text{Os}_3(\text{CO})_{10}(s\text{-trans-C}_4\text{H}_6)$ ¹

Sir:

Examination of the coordination and mobility of ligands in metal cluster compounds provides detailed data that may be applicable to the less accessible problem of characterizing species chemisorbed on metal surfaces.² Metal cluster complexes of conjugated dienes are rare and have not been well-characterized structurally.³ We wish to report the preparation of a set of decacarbonyltriosmium complexes of conjugated dienes, some NMR evidence concerning the preferred modes of coordination, and the crystal structures of isomeric complexes of the *s-cis* and *s-trans* forms of 1,3-butadiene.

The unsaturated metal cluster compound $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was found to react readily with excess diene at room temperature in cyclohexane solution. Chromatographic separation provided the major cluster product, of formula $\text{Os}_3(\text{CO})_{10}(\text{diene})(\text{diene} = 1,3\text{-butadiene (1a)}, 2\text{-methyl-1,3-butadiene (2)}, 2,3\text{-dimethyl-1,3-butadiene (3)}, \textit{trans,trans-2,4-hexadiene (4)}, \text{and } 1,3\text{-cyclohexadiene (5)})$, as a stable yellow solid in each case.⁴ With 1,3-butadiene an additional compound (**1b**) of the same formula was isolated in low yield (vide infra). The mass spectrum of each compound includes a molecular ion and ions due to loss of up to ten carbonyl ligands.⁵

The ambient temperature ¹H NMR spectrum obtained for **1a** consists of three, well-separated multiplets (τ 4.74, 7.68, 9.51 in CDCl_3) assigned in order of increasing field to the *s*-vicinal protons (H_c , H_c') and to the geminal protons respectively *cis* (H_b , H_b') and *trans* (H_a , H_a') to H_c or H_c' . The coupling constants determined by iterative simulation ($J_{ab} = 2.89$,

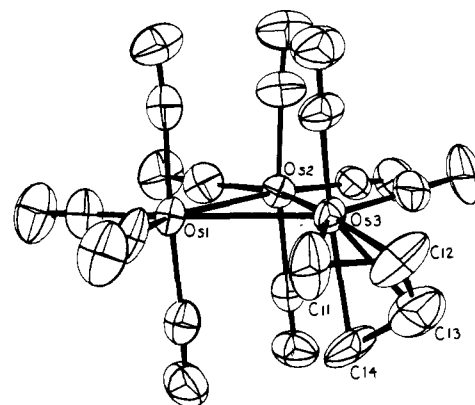


Figure 1. Molecular geometry of $\text{Os}_3(\text{CO})_{10}(s\text{-cis-C}_4\text{H}_6)$ (**1a**).

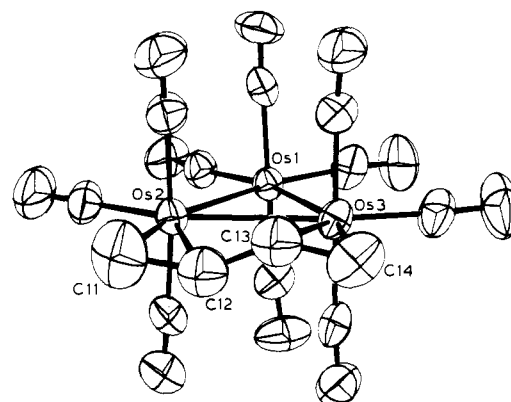


Figure 2. A view of the $\text{Os}_3(\text{CO})_{10}(s\text{-trans-C}_4\text{H}_6)$ (**1b**) molecule. Carbon atoms C(12) and C(13) are represented by isotropic thermal ellipsoids.

$J_{ac} = 8.58$, $J_{ac'} = -0.79$, $J_{bc} = 7.17$, $J_{bc'} = 1.02$, $J_{cc'} = 4.66$ Hz) compare closely with those of the tricarbonyliron complex of *s-cis*-butadiene.⁶ At low temperatures (-90°) each of the three multiplets splits into new signals (τ 3.90, 4.78, 5.17 (1:2:1); 7.32, 7.47, 7.90 (1:1:2); 9.16, 9.65 (2:2)), signifying the presence of two interconverting, almost equally populated conformers. One species is symmetrical, with respect to the two halves of the diene; the other is unsymmetrical. Ambient spectra for complexes **2**, **3**, and **5** are each also consistent with symmetrical coordination of the diene in the *s-cis* form.⁷ At -95° the spectrum of **5** is split, indicating that an unsymmetrical species is present; a symmetrical conformer is not observable. In contrast, the spectra of **2** and **3** are unchanged to -80 and -124° , respectively, suggesting that these compounds adopt only (or predominantly) a symmetrical structure.⁸

The solid-state structure of complex **1a** has been determined by x-ray diffraction. The complex crystallizes in space group $P2_1/n$ with a cell of refined dimensions $a = 8.051$ (2) \AA , $b = 14.778$ (3) \AA , $c = 15.356$ (2) \AA , and $\beta = 94.60^\circ$. Data were collected on a Syntex P₁ diffractometer using Mo $K\alpha$ radiation and corrected for absorption effects. The structure was solved by conventional Patterson and Fourier methods. Least-squares refinement of 2418 independent, observed reflections gave a conventional *R* factor of 0.036. A view of the molecular geometry is shown in Figure 1. The structure is derived from that of $\text{Os}_3(\text{CO})_{12}$ ⁹ with substitution of an axial and an equatorial carbonyl at Os(3) by the *s-cis*-butadiene ligand. Carbon atoms C(11) and C(12) are nearly in the Os_3 plane, but C(13) and C(14) are pulled away substantially from the axial site due to the small bite angle of the diene. The osmium-axial olefin bond ($\text{Os}(3)\text{-C}(13) = 2.24$ (2), $\text{Os}(3)\text{-C}(14) = 2.30$ (1) \AA) appears weaker than the osmium-equatorial olefin bond ($\text{Os}(3)\text{-C}(11) = 2.24$ (2), $\text{Os}(3)\text{-C}(12) = 2.20$ (1) \AA). The $\text{Os}(2)\text{-Os}(3)$ bond, *trans* to the equatorial olefin, is slightly longer (2.884

(3) Å) than the other Os–Os distances in the structure (2.861 (3) and 2.863 (3) Å), and the osmium–carbon distance to the carbonyl carbon approximately trans to C(14) is the shortest in the structure (1.88 (2) Å).

The unsymmetrical conformer observed in the NMR spectrum of **1a** may be identified with the solid-state configuration (Figure 1) and an analogous structure is assumed for **5**. A similar structure may be proposed for the symmetrical form of **1a** (and of **2** and **3**), except with the diene coordinated to the two equatorial positions at one osmium atom. Approximate line shape calculations for **1a** indicate that exchange of the axial and equatorial olefin sites in the unsymmetrical conformer can proceed independently of equilibration via the symmetrical (diequatorial) form. Further mechanistic details await the results of ^{13}C NMR studies.¹⁰

Complexes **1b** and **4** are readily distinguished from **1a**, **2**, **3**, and **5** by their infrared spectra¹¹ and analysis of their ^1H NMR spectra indicates coordination of the diene in its *s-trans* form. As for **1a**, three two-proton multiplets (τ 6.60, 7.74, 8.57 in CDCl_3) are seen for **1b**, but the *s*-vicinal protons (H_c , H_c') resonate at highest field and the protons (H_a , H_a') trans to the vicinal protons at lowest field. The coupling constants extracted from the iteratively simulated spectrum ($J_{ab} = 2.47$, $J_{ac} = 7.38$, $J_{ac'} = -0.65$, $J_{bc} = 11.13$, $J_{bc'} = -0.48$, $J_{cc'} = 11.37$ Hz) are generally comparable with those for uncomplexed *s-trans*-1,3-butadiene.¹² Particularly noteworthy is that the *s*-vicinal coupling constant ($J_{cc'}$) is significantly larger for **1b**, **4**,¹³ and free butadiene (11.4, 10.6, and 10.4 Hz, respectively) than for **1a**, **5**, and $\text{Fe}(\text{CO})_3(s\text{-cis-C}_4\text{H}_6)^{6a}$ (4.7, 3.7, and 4.8 Hz, respectively) and free cyclic *s-cis* dienes.^{6a,14} Coordination of both ends of an *s-trans* diene necessarily requires two metal centers and the alternative possibilities of diaxial or diequatorial coordination at adjacent osmium atoms can be envisioned. No splitting is seen in the NMR spectrum of **1b** to -76° and of the more soluble **4** to -127° , which supports the symmetrical, equatorially bridged structure. This assignment has been substantiated by a single-crystal x-ray diffraction study of **1b**.

Crystals of $\text{Os}_3(\text{CO})_{10}(s\text{-trans-C}_4\text{H}_6)$ obtained from chloroform solution form in space group $C2/c$ with a cell of dimensions $a = 30.638$ (6) Å, $b = 9.770$ (2) Å, $c = 13.285$ (3) Å, and $\beta = 112.82$ (2)°. Data collection and structure determination were performed as before. Refinement of 2473 independent, observed reflections resulted in an R factor of 0.036. A view of the molecule is presented in Figure 2. Isotropic thermal ellipsoids are shown for carbon atoms C(12) and C(13), which were observed to suffer from severe vibrational disorder. The *s-trans*-butadiene ligand bridges osmium atoms Os(2) and Os(3) with the olefin groups bound in equatorial positions. The Os(2)–Os(3) bond (2.932 (3) Å) is substantially longer than the other osmium–osmium bonds of the structure (2.856 (3) and 2.857 (3) Å).¹⁵

These results with complexes **1–5** demonstrate that conjugated dienes can coordinate to a triangular metal framework in several ways. An important factor determining the mode adopted must be interaction between diene substituents and adjacent carbonyl ligands, since the complexes of 1,3-butadiene, the unencumbered parent ligand, display the greatest structural variety. For further information on this point the preparation of complexes with a wider range of diene substituents is being pursued.

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- An equivalent amount of the corresponding monoolefin was also produced. The minor cluster products accompanying complexes **1–4** were identified as hydridoalkenyl compounds $\text{HOs}_3(\text{CO})_{10}(\text{CH}=\text{CRR}')$. See ref 1b and references therein.
- Ions derived from $\text{H}_2\text{Os}_3(\text{CO})_{10}$ are observed in the mass spectrum of **5**. These presumably result from decomposition of **5** to $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and benzene, as observed in cyclohexane solution at 80° . This process will be discussed further in a full paper.
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- Infrared evidence (ν_{CO} , C_6H_{12}) supports these conclusions in that the spectrum of **1a** (2114 m, 2066 s, 2064 s, 2033 s, 2029 s, 2025 s, 2011 s, 1999 vw, 1992 w sh, 1987 m, 1982 w sh, 1945 w, 1934 w cm^{-1}) contains too many bands for just one species. Rather it is the superposition of the two similar but distinct patterns observed for **2** or **3** and for **5** (2, 2114 m, 2065 s, 2033 s, 2028 s, 2010 s, 1997 w, 1986 m, 1980 w sh, 1932 w cm^{-1} ; **3**, 2113 m, 2064 s, 2032 s, 2027 s, 2009 s, 1997 w, 1985 m, 1975 w, 1927 w cm^{-1} ; **5**, 2111 m, 2062 s, 2032 s, 2022 s, 2009 s, 1992 w, 1985 m, 1976 w, 1939 w cm^{-1}).
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- A limiting low temperature spectrum of ^{13}CO -enriched **5** has been obtained at -108° (S. I. Richter, M. Tachikawa, and J. R. Shapley, unpublished results). The pattern observed (2:1:1:1:1:1:1:1, to increasing field) is consistent with the assigned structure, assuming one accidentally degenerate pair of signals.
- $\text{Ir}(\nu_{\text{CO}}$, C_6H_{12}): **1b**, 2109 m, 2063 m, 2047 s, 2019 vs, 1994 s, 1975 m, 1942 vw cm^{-1} ; **4**, 2107 m, 2061 m, 2045 s, 2041 s, 2017 vs, 1993 s, 1974 m, 1940 vw cm^{-1} .
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- Similar elongation of a metal–metal bond associated with a bridging *s-trans*-butadiene ligand was observed for $\text{Mn}_2(\text{CO})_8(s\text{-trans-C}_4\text{H}_6)$: H. E. Sasse and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, **392**, 167 (1972). Further discussion and comparison of the structural features of complexes **1a** and **1b** will be presented in a full paper.

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A Novel Catalytic Property of Magnesium Oxide for Hydrogenation of 1,3-Butadiene

Sir:

We wish to report a novel catalytic property of MgO which was obtained by evacuating $\text{Mg}(\text{OH})_2$ at an unusually high temperature, 1100°C . Although the catalyst did not show any activity for $\text{H}_2\text{-D}_2$ equilibration, it was active and highly selective for the hydrogenation of 1,3-butadiene to *cis*-2-butene,

Table I. Isotopic Distribution of Products in the Deuteriogenation of 1,3-Butadiene over MgO at 0°C

| Product | % each product | % of each isotopic species | | | |
|------------------------|----------------|----------------------------|-------|-------|------------------|
| | | d_0 | d_1 | d_2 | $d_3\text{-}d_8$ |
| 1,3-Butadiene | 59.0 | 100.0 | 0 | 0 | 0 |
| 1-Butene | 2.9 | 0.7 | 2.1 | 97.2 | 0 |
| <i>trans</i> -2-Butene | 6.4 | 2.5 | 1.4 | 96.1 | 0 |
| <i>cis</i> -2-Butene | 31.7 | 0.4 | 1.2 | 98.4 | 0 |