derivatives. Silatetrahedrane is predicted to be very strained and may not yield isolable derivatives.

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Registry No. **1**, 88986-74-7; **2**, 76893-79-3; **3**, 76893-78-2; **4**, 109584-96-5; **5**, 109584-97-6; **6**, 109584-98-7; **7**, 109584-99-8; **8**, 109585-00-4; **9**, 109585-01-5; **10**, 109585-02-6; **11**, 109585-03-7; **12**, 109585-04-8; **13**, 109585-05-9; **14**, 109585-06-0; **15**, 109585-07-1; **16**, 109585-08-2; **17**, 109585-09-3; **18**, 109585-10-6.

Communications

Conversion of (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) to (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$): Interchange of Boron and Carbon Atom Positions

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Summary: The cluster (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) (I) reacts with BCl$_3$ to produce (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$) (II), a new example of a cluster vinylidene analogue. In the formation of II the boron and carbon atoms of the BCO unit exchange positions, going from μ_3-B to μ_3-C. An X-ray crystal structure determination reveals that the C–B bond vector differs by 15° from being normal to the plane of the metal atoms, unlike the markedly tilted bonds, B–C in the cluster vinylidene analogue (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-B-η^2-CH$_2$) and C–C in the cluster vinylidenes (CO)$_9$Co$_2$Ru(μ_3-C-η^2-CRH) (R = *t*-Bu, Ph).

The cluster (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO)[1] (I) reacts with BCl$_3$ to produce (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$) (II), a new example of a cluster vinylidene analogue which is noteworthy for two reasons: (1) in the formation of II the boron and carbon atoms of the BCO unit exchange positions, going from μ_3-B to μ_3-C; (2) the C–B bond vector differs by 15° from being normal to the plane of the metal atoms (Figure 1), unlike the markedly tilted bonds, B–C in the cluster vinylidene analogue (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-B-η^2-CH$_2$)[2] and C–C in cluster vinylidenes.[3,4]

Preparation of II is represented by reaction 1. The Cl$_3$B$_3$O$_3$ formed decomposes[5] to BCl$_3$ and B$_2$O$_3$ when excess BCl$_3$ is removed from the system. Chemical confirmation of the formation of an Os$_3$C cluster core was provided by quantitative hydrolysis of II to (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-CH) (III) and boric acid and also the conversion of II to III in glacial acetic acid.

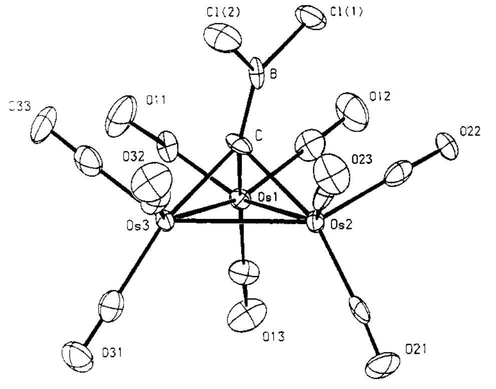
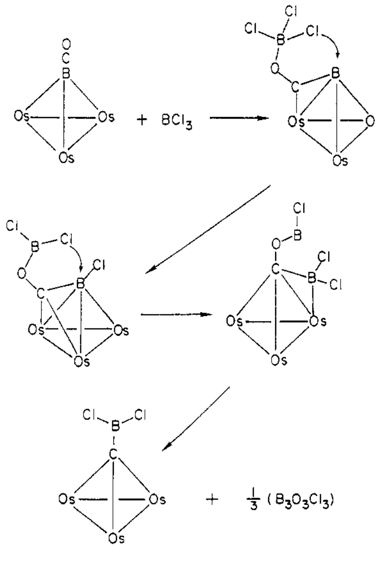


Figure 1. Structure of (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$). Selected distances (Å): Os(1)–Os(2) = 2.875 (1), Os(2)–Os(3) = 2.869 (1), Os(1)–Os(3) = 2.879 (1), Os(1)–C = 2.108 (13), Os(2)–C = 2.168 (14), Os(3)–C = 2.134 (13), C–B = 1.47 (2).

Scheme I



$$(\mu\text{-H})_3(\text{CO})_9\text{Os}_3(\mu_3\text{-BCO}) + \text{BCl}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} (\mu\text{-H})_3(\text{CO})_9\text{Os}_3(\mu_3\text{-CBCl}_2) + {}^1/_3(\text{Cl}_3\text{B}_3\text{O}_3) \quad (1)$$

$$\underset{\text{I}}{} \qquad \underset{\text{II}}{}$$

Movement of boron from a vertex site in μ_3-BCO to a terminal site in μ_3-CBCl$_2$ in the formation of II is believed

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to occur intramolecularly. No incorporation of boron into II from the BCl_3 reagent occurs. This was shown from a study of the reaction of $^{10}BCl_3$ with I. A ^{11}B NMR signal of normal intensity was observed for II while no ^{11}B NMR signals were produced for either $Cl_3B_3O_3$ or its decomposition products. On a much slower time scale than the preparative time scale, $^{10}BCl_3$ reacts with II to enrich II with the ^{10}B isotope.

A possible pathway (Scheme I) for formation of II could occur through initial adduct formation between BCl_3 and the oxygen of the unique carbonyl of I,[6] resulting in reduction of the CO bond order thereby inducing the carbon to move to a μ_2 site[8] with the resulting exposed vertex boron accepting a chlorine atom. This halogen transfer would result in further reduction of CO bond order which could cause the carbon to move to a μ_3 position. With transfer of a second chlorine atom to boron, the BCl_2 group would move to a μ_2 site, and with the elimination of ClBO it could then move to a terminal site on the μ_3-carbon. The reaction of BH_3 with I is believed to give an initial complex, $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}BCOBH_3)$. This reaction gives $(\mu\text{-}H_3)(CO)_9Os_3(\mu_3\text{-}B\text{-}\eta^2\text{-}CH_2)$ and $H_3B_3O_3$ with transfer of two H atoms of the coordinated BH_3 to the terminal carbon.[2]

For the synthesis of II, BCl_3 (0.132 mmol) was condensed into a CH_2Cl_2 solution (2 mL) of I (0.0605 g, 0.070 mmol). The solution was warmed to room temperature and stirred for 10 min. Volatiles were pumped from the reaction mixture, leaving behind a white residue consisting of a mixture of II and B_2O_3. Cluster II was extracted from this residue with CH_2Cl_2 which was then pumped away leaving a white solid, II, which was then washed with hexane. Yield of II: 95% (0.061 g, 0.067 mmol). Cluster II is stable under vacuum at room temperature but is very moisture-sensitive.

IR spectrum of II (ν_{CO}, CH_2Cl_2): 2020 (s (br)), 2089 (s) cm^{-1}. NMR spectra of II: ^1H NMR (CD_2Cl_2, 25 °C, δ-($Si(CH_3)_4$) 0.00) −19.43 (s) ppm; ^{11}B NMR (CD_2Cl_2, 25 °C, δ($BF_3{\cdot}OEt_2$) 0.00) 57.4 (s, br) ppm; ^{13}C NMR (CD_2Cl_2, 25 °C, δ($Si(^{13}CH_3)_4$) 0.00) 167.41 (3 C, s), 165.26 (6 C, d, J_{CH} = 11.3 Hz), 132.50 (1 C, s, br) ppm. Signals (3:6:1) of the carbon-13 NMR spectrum are consistent with the solid-state structure of II (Figure 1). Spin coupling (^{13}C–^1H) indicated in the signal of relative area 6 is consistent with hydrogen trans to carbon, implying the presence of Os–H–Os bridges.

The molecular structure of II (Figure 1)[10] has approximate C_s symmetry. The pseudo mirrow plane passes through B, C, Os(2), and the midpoint of the Os(1)–Os(3) bond. Positions of the hydrogen atoms, though not located, are implied as Os–H–Os bridges based on (1) Os–Os distances in the range observed for hydrogen-bridged osmium atoms[12,13] and (2) ^{13}C NMR spectrum discussed above. Structural parameters of the Os_3C core of the cluster (Figure 1) are consistent with those reported for other Os_3C units.[11,12] The B–C distance in II, 1.47 (2) Å, is comparable to the B–C distance in $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}BCO)$,[1] 1.469 (15) Å. These distances are significantly shorter than observed for a B—C single-bond distance, ca. 1.6 Å,[13,14] and can be attributed to some B=C character.

The μ_3-$CBCl_2$ unit of II is tilted only 15° from perpendicularity with respect to the Os_3 plane. The tilt angle is 60° for μ_3-BCH_2 in $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}B\text{-}\eta^2\text{-}CH_2)$,[2,15] while tilt angles of 43° and 40° are observed for μ_3-CCH_2 in $(CO)_9Co_2Ru(\mu_3\text{-}C\text{-}\eta^2\text{-}CRH)$ (R = *t*-Bu, Ph).[16]

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Registry No. I, 86727-98-2; II, 109801-61-8; BCl_3, 10294-34-5.

Supplementary Material Available: Listings of selected bond distances, selected bond angles, positional parameters, and anisotropic thermal parameters (5 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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[6] A Fenske–Hall calculation[7] indicates that this is the most negative oxygen atom in the molecule.

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[10] Crystal data for $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}CBCl_2)$ (0 °C): space group $P2_1/n$, a = 9.636 (5) Å, b = 13.810 (6) Å, c = 13.526 (6) Å, β = 93.52 (4)°, V = 1796.5 Å, ρ(calcd) = 3.402 g cm^{-3} for M_r 919.5, Z = 4, μ = 215.6 cm^{-1}, for Mo Kα. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/44 computer using the SDP (Structure Determination Package). The structure was solved by the direct method MULTAN 11/82 and difference Fourier syntheses. R_F = 0.045 and R_{wF} = 0.057 (227 parameters refined) for 2444 reflections ($I \geq 3.0\sigma(I)$) of 3152 unique reflections collected in the range of $4° \leq 2\theta \leq 50°$.

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[15] Two B–H–Os bridges in the structure probably force the μ_3-BCH_2 to an extreme tilt angle compared to the vinylidene complexes.

[16] Calculated from data in ref 4.

Transition-Metal Carbonyl Clusters as Novel Infrared Markers for Estradiol Receptor Site Detection

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Summary: The first use of transition-metal carbonyl cluster fragments, such as $Co_2(CO)_6$ and $Cp_2Mo_2(CO)_4$ (Cp = η^5-C_5H_5), as infrared biological markers for the in vitro detection of femtomole concentrations of estradiol receptor sites in lamb uterine cytosol is described.

Despite the tremendous advances in the chemistry of transition-metal carbonyl clusters over the past 10 years and their considerable potential in fields such as hetero- and homogeneous catalysis,[1,2] and possibly even super-

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