$$v(1) = k\frac{(K_{17})^2}{2K_{19}}K_{18}[\mathrm{Pt}][\mathrm{Si{-}H}]^2 \qquad (15)$$

Conclusion

The results of the kinetic study of the Pt-catalyzed hydrosilylation of allyl aryl ethers 1 and 2 provide expressions for the corresponding rate laws as functions of the concentration of silane and of the platinum salt. The unusual conditions of high dilution, which are probably essential to obtain the observed results, appear to be an interesting tool for mechanistic studies in coordination chemistry. The change in apparent order in platinum depending on the nature of the olefin was clearly unexpected but leads us to propose a mechanism involving a dinuclear homogeneous catalyst. Our interpretation contrasts with recent findings concerning the hydrosilylation of monoolefins. The nature of the reactants as well as the reaction conditions are so different that alternative pathways are not in opposition. With regard to the merit of the hydrosilylation of 2 for the preparation of monofunctional macrocycles, one can conclude that the reaction shows good selectivity at moderately high dilution. The control of the reaction in more diluted media will now be made much easier by the knowledge of rate laws and constants. Moreover, the proposed intermediates VI and VII have only one resorcylic derivative as a ligand; ester 2 can therefore be regarded as a suitable substrate to take advantage of the dilution principle.

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Single-Crystal Neutron Diffraction Study of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$, a Model for One Type of Chemisorbed Ethylene

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The molecular structure of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (1) has been determined by single-crystal neutron diffraction in order to establish the hybridization at the carbon atoms of the bridging ethylene. The final values for the lattice constants are a = 7.308 (2) Å, b = 13.448 (3) Å, c = 13.482 (4) Å, β = 101.25 (2)°, and V = 1299.5 (3) Å^3; the space group ($P2_1/c$) and value of Z (4) are known from an earlier X-ray study.[1] The results show that the ethylene carbons have almost completely rehybridized to sp^3. The C–C bond length in 1 (1.5225 (26) Å) is comparable to that in ethane and that of ethylene chemisorbed on Pt(111)—suggesting that the ethylene ligand in 1 is a good structural model for ethylene chemisorbed on Pt(111). The Os_2C_2 ring of 1 is distorted further away from planarity than the Os_4 ring of $Os_4(CO)_{16}$ or the C_4 ring of cyclobutane.

Introduction

The unique structural aspects of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (1) were apparent from the X-ray diffraction study carried out by some of us shortly after its preparation in 1982.[1] Whereas countless structures were known in which an ethylene ligand was coordinated to a single transition metal, 1 contained an ethylene which bridged two metals to form a four-membered ring. Just as conventional ethylene complexes suggested one way (Figure 1a) in which ethylene could be chemisorbed onto a metal surface, the diosmacyclobutane ring in 1 resembled the di-σ-bonded arrangement (Figure 1b) that had been proposed[2] as another way in which ethylene could be chemisorbed. The latter analogy has since found practical use: 1 has proven to be an excellent vibrational model for di-σ-bonded ethylene chemisorbed on Pt(111) at low temperatures.[3]

A few reports of dimetallacyclobutanes had appeared before ours on 1. In 1972 Carty, Palenik, and co-workers had reported a diiron adduct of maleic anhydride;[4a] in 1977 Green, Stone, and co-workers had reported a dipalladium adduct of C_2F_4;[4b] in 1981 Theopold and Bergman had reported an unstable dicobalt adduct of benzocyclobutadiene.[4c] However, only the first of these dimetallacyclobutanes had been characterized by X-ray crystallography, and none had contained ethylene itself. Soon after we prepared 1, studies in our laboratory, in the laboratory of Prof. Josef Takats at the University of Alberta,[5] and elsewhere[6] revealed that 1 was the parent compound for an extensive series of substituted diosmacyclobutanes (e.g., $(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2Me)Os_2(CO)_8$ (2)[5a,c,d] and $(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHC_6H_{13})Os_2(CO)_8$[6b]) and diosmacyclobutenes (e.g.,

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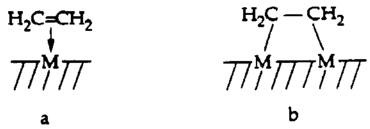

Figure 1. Ethylene chemisorbed as (a) a terminal ligand on a single metal atom and (b) a di-σ-bonded ligand bridging two metal atoms.

(μ-η^1,η^1-CF_3CCCF_3)$Os_2(CO)_8$[5b–e] and (μ-η^1,η^1-HCCH)$Os_2(CO)_8$[5f]). X-ray determinations of the structures of 2,[5a,c,d] (μ-η^1,η^1-*cis*-$MeO_2CCHCHCO_2Me$)$Os_2(CO)_8$ (3),[5c,d] and (μ-η^1,η^1-*trans*-$MeO_2CCHCHCO_2Me$)$Os_2(CO)_8$ (4)[5c,d] showed their Os_2C_2 rings to be nonplanar, with Os–C–C–Os torsional angles of about 28°—establishing that the nonplanar Os_2C_2 ring we found in 1 was inherent in the diosmacyclobutane ring system and not the result of packing forces peculiar in 1.

While such basic structural features of 1 as the nonplanarity of its ring were apparent from the original X-ray diffraction study, crystals of 1 were highly susceptible to X-ray damage, even at low temperatures. This fact, along with the domination of the X-ray scattering from 1 by the two osmium atoms of this relatively small molecule, resulted in relatively imprecise carbon atom positions (C–C = 1.53 (3) Å) and no information on the hydrogen atom positions.[7] It has thus been difficult to compare the hybridization at the ring carbons in 1 with that in conventional ethylene complexes. DV–Xα calculations on 1 and the fact that $^1J(^{13}C–^{13}C)$ for these carbons is almost exactly equal to that in ethane imply sp^3 hybridization.[8]

More recently, our interest in the stereochemistry of ethylene exchange on 1 has required that we distinguish its cis dideuterio derivative from its trans one and has led us to analyze the nematic phase ^1H NMR spectra of 1.[9] The resulting dipolar coupling constants determine the geometry of the ethylene portion of 1 in solution[10] and require a solid-state structure of 1, in which the *hydrogen* nuclei have been located, for comparison.

We have therefore obtained a more detailed structure of 1 by neutron diffraction. Only a few conventional ethylene complexes, and no dimetallacyclobutanes, have previously been examined by that technique.[11]

Experimental Section

(μ-η^1,η^1-C_2H_4)$Os_2(CO)_8$ was prepared by a procedure based on that of Burke and Takats[5a,c,d] and that of Poë and Sekhar.[6b] The output of a high-pressure 450-W Hanovia lamp was passed through a saturated aqueous solution of $NaNO_2$ so that only light with $\lambda > 436$ nm remained. A suspension of 300 mg of $Os_3(CO)_{12}$ in 250 mL CH_2Cl_2 was irradiated overnight under 40 psi of ethylene in a Fischer-Porter apparatus. (The use of CH_2Cl_2 instead of benzene allowed the solvent to be removed on a rotary evaporator without significant loss of either 1 or the mononuclear $Os(CO)_4(C_2H_4)$ formed as a byproduct.) After removal of solvent the residue was taken up in pentane and the product 1 separated from $Os(CO)_4(C_2H_4)$ on a Chromatotron with pentane as eluant.

Seed crystals of 1 were grown overnight at −20 °C from 100–150-mg batches dissolved in 10–15 mL of pentane. Their size was increased by slow cooling to −40 °C followed by vacuum removal of some solvent. After several attempts this technique yielded single crystals suitable for neutron diffraction. The crystal used to collect most of the data used in this study measured 4.0 mm × 2.0 mm × 0.8 mm. A second crystal, used to collect a small portion of the data, measured 2.5 mm × 2.0 mm × 1.0 mm.

The single-crystal neutron data were collected at the Manuel Lujan, Jr. Neutron Scattering Center of the Los Alamos National Laboratory (LANSCE) by using the LANSCE SCD instrument.[12] This instrument uses Laue geometry to collect the intensity data in a 25 cm × 25 cm ^3He-filled two-dimensional position-sensitive proportional counter placed 25 cm from the sample at $2\theta = 90°$. The instrument dimensions were determined by measuring diffraction data from a 3 mm diameter spherical Al_2O_3 single crystal ($a = 4.766$ Å, $c = 12.996$ Å). The spectral distribution of the source was measured by using the incoherent scattering from a 2 mm diameter bead of $V_{0.95}Nb_{0.05}$. All calculations were performed at LANSCE by using the General Structure Analysis System (GSAS).[13]

Diffraction data were collected by using a wavelength range of 0.5–5.5 Å. Due to the brittle nature of the crystals at low temperature, two crystals were required for the data collection. The crystals were glued to the end of a hollow aluminum rod and cooled with a Displex refrigerator to 12 K. The crystals fractured and fell off during data collection. The first crystal was remounted twice before it became too small to reuse. A total of 23 histograms, each containing about 450 reflections, were collected. The first crystal gave nine histograms from the first mounting and six from each of the other two mountings. Only two histograms were collected from the second crystal. The histograms were searched for diffraction maxima, and the lattice constants, the crystal orientation angles, and the crystal locations for all crystal settings were refined by using the locations of 1072 reflections that had peak intensities greater than 50 counts/pixel. The final values for the lattice constants are $a = 7.308$ (2) Å, $b = 13.448$ (3) Å, $c = 13.482$ (4) Å, $\beta = 101.25$ (2)°, and $V = 1299.5$ (3) Å^3. The space group ($P2_1/c$) and Z (4) were established by the earlier X-ray study.[1]

The intensity data were obtained by integration over a small region at each reflection position, using locations calculated from the lattice constants and crystal orientation and location parameters for each of the four crystal settings. The integration was limited to reflections with d spacings greater than 0.625 Å. These data were then corrected for the variation in incident beam intensity with neutron wavelength, geometric factors, and absorption (μ (cm^{-1}) = 0.24 + 0.35λ, maximum and minimum transmission were 0.945 and 0.698). Heavy-atom positions and thermal parameters from the X-ray refinement were used to establish an approximate scale factor and define the phases for an F_o map of the neutron scattering density. The four hydrogen atoms were easily located in this map and then entered into the refinement model.

Neutron absorption coefficients were obtained from Koster and Yelon[14] for the heavy elements and from Howard, Johnson, Schultz, and Stringer[15] for hydrogen. The function minimized was $w(F_o - F_c)^2$, with weights determined by $w = (2F_o/\sigma(F_o^2))^2$; $\sigma(F_o^2)$ was based on counting statistics. The neutron scattering lengths[14] used were $b_C = 0.665$, $b_O = 0.5805$, $b_H = -0.374$, and $b_{Os} = 1.09$. The final least-squares refinement included 243 variables, using 7517 reflections measured with $I/\sigma(I) > 1.0$; it yielded weighted and unweighted R factors of 0.073 and 0.107, with a

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[7] The position of the hydrogen atoms in the X-ray structures of 2 and 3 were determined,[5a,c] but the low precision associated with such X-ray results rendered confident conclusions regarding the hybridization at carbon difficult.

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Table I. Final Positional Parameters and Anisotropic Thermal Parameters (×100)[a] for $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$

atom	x	y	z	atom	x	y	z
Os(1)	0.10541 (15)	0.11413 (7)	0.30298 (8)	O(1)	0.36892 (31)	−0.05692 (13)	0.39530 (17)
Os(2)	0.32506 (15)	0.14997 (6)	0.15033 (8)	O(2)	−0.19571 (31)	−0.01046 (13)	0.16227 (16)
C(1)	0.26759 (26)	0.00254 (11)	0.35790 (13)	O(3)	−0.07326 (32)	0.12087 (16)	0.49087 (16)
C(2)	−0.08574 (26)	0.03506 (12)	0.21450 (14)	O(4)	−0.07826 (31)	0.31479 (13)	0.23138 (17)
C(3)	−0.00412 (26)	0.11712 (12)	0.42120 (14)	O(5)	0.27411 (33)	0.37791 (13)	0.15945 (17)
C(4)	−0.01103 (27)	0.23992 (11)	0.25478 (14)	O(6)	−0.00162 (31)	0.12733 (16)	−0.03320 (16)
C(5)	0.28918 (28)	0.29413 (11)	0.15758 (14)	O(7)	0.66063 (30)	0.18205 (15)	0.04963 (17)
C(6)	0.12032 (25)	0.13435 (12)	0.03378 (13)	O(8)	0.39486 (33)	−0.07688 (13)	0.16657 (17)
C(7)	0.53317 (25)	0.17030 (12)	0.08496 (14)	H(1)	0.4127 (6)	0.17297 (28)	0.44926 (28)
C(8)	0.36681 (26)	0.00619 (11)	0.16217 (13)	H(2)	0.6049 (6)	0.22987 (27)	0.30255 (32)
C(9)	0.50130 (26)	0.17123 (12)	0.30305 (14)	H(3)	0.3340 (6)	0.27607 (23)	0.37112 (31)
C(10)	0.36346 (27)	0.19540 (12)	0.37095 (13)	H(4)	0.5762 (6)	0.10191 (26)	0.32748 (32)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os(1)	0.53 (5)	0.41 (4)	0.50 (5)	0.04 (4)	0.20 (4)	0.06 (3)
Os(2)	0.63 (5)	0.47 (4)	0.44 (5)	−0.02 (4)	0.22 (4)	0.07 (3)
C(1)	0.87 (8)	0.63 (6)	0.99 (8)	−0.04 (7)	0.00 (7)	0.08 (6)
C(2)	0.82 (8)	0.72 (6)	0.94 (8)	−0.13 (7)	0.20 (7)	−0.07 (6)
C(3)	1.00 (8)	1.14 (6)	0.80 (8)	0.02 (8)	0.51 (7)	0.19 (6)
C(4)	1.00 (8)	0.70 (6)	0.88 (8)	0.17 (7)	0.24 (7)	0.17 (6)
C(5)	1.08 (9)	0.67 (6)	0.77 (8)	0.05 (7)	0.25 (7)	0.10 (6)
C(6)	0.83 (8)	1.07 (7)	0.54 (8)	0.08 (7)	0.10 (6)	−0.02 (6)
C(7)	0.83 (8)	1.16 (6)	0.77 (8)	0.07 (8)	0.40 (6)	0.04 (6)
C(8)	1.06 (8)	0.60 (6)	0.77 (8)	0.10 (7)	0.25 (7)	0.10 (6)
C(9)	0.87 (8)	0.95 (6)	0.69 (8)	−0.03 (8)	0.05 (6)	0.00 (6)
C(10)	1.06 (8)	0.91 (6)	0.58 (8)	−0.18 (7)	0.08 (7)	−0.14 (6)
O(1)	1.06 (10)	0.99 (8)	1.43 (10)	0.27 (9)	0.19 (8)	0.30 (7)
O(2)	1.18 (10)	1.00 (7)	1.06 (9)	−0.37 (9)	0.06 (8)	−0.30 (7)
O(3)	1.55 (11)	1.95 (9)	0.85 (10)	−0.04 (10)	0.70 (8)	−0.01 (8)
O(4)	1.14 (10)	0.75 (7)	1.63 (10)	0.43 (8)	0.49 (8)	0.22 (7)
O(5)	1.38 (11)	0.68 (7)	1.35 (10)	0.05 (9)	0.37 (8)	−0.04 (7)
O(6)	1.19 (10)	2.00 (9)	0.81 (9)	0.10 (10)	0.02 (8)	−0.20 (8)
O(7)	0.94 (9)	1.82 (9)	1.36 (10)	0.27 (10)	0.74 (8)	0.44 (8)
O(8)	1.41 (11)	0.61 (7)	1.63 (11)	0.05 (8)	0.45 (9)	−0.16 (7)
H(1)	2.77 (20)	2.82 (16)	0.81 (16)	−0.20 (19)	0.04 (15)	−0.01 (14)
H(2)	1.76 (19)	2.34 (16)	2.63 (22)	−0.53 (18)	0.34 (17)	−0.04 (16)
H(3)	2.52 (21)	1.31 (13)	2.37 (20)	0.12 (16)	0.43 (17)	−0.39 (14)
H(4)	2.14 (20)	2.31 (16)	2.28 (20)	0.23 (18)	0.44 (16)	−0.04 (15)

[a] The expression for the anisotropic thermal motion is $T = \exp\{-2\pi(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23})\}$.

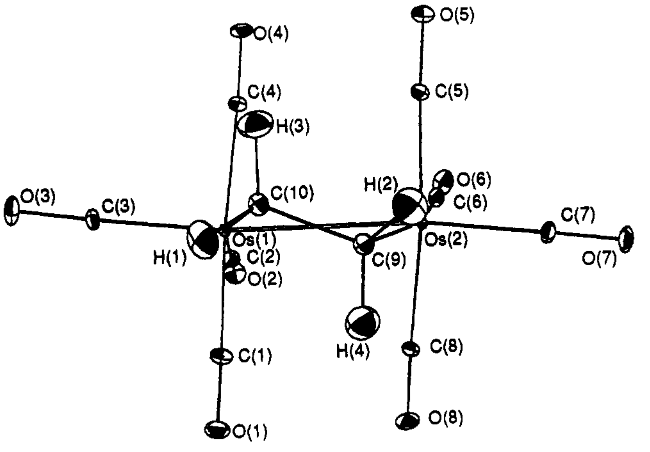

Figure 2. Thermal ellipsoid plot (50% probability) of the structure of 1.

reduced $\chi^2 = 6.85$. The variable list included 23 scale factors, one for each histogram, four type II[16] extinction parameters, one for each crystal mounting, and 216 atomic parameters (all atoms with anisotropic thermal parameters). The maximum extinction applied to a reflection was 0.56. The final atomic positions and thermal parameters are given in Table I.

Description of the Structure and Discussion

The molecular structure of 1, as determined in this neutron diffraction study, is shown in Figure 2, and selected bond distances and angles are listed in Table II. The carbonyl Os–C distances trans to the Os–Os bond (the average of Os(1)–C(3) and Os(2)–C(7) is 1.919 [1] Å[17]) are

Table II. Selected Bond Distances and Angles in $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (1)

atoms	distance, Å	atoms	angle, deg
Os(1)–Os(2)	2.8867 (16)	Os(2)–Os(1)–C(1)	91.01 (7)
Os(1)–C(1)	1.9654 (20)	Os(2)–Os(1)–C(2)	94.93 (7)
Os(1)–C(2)	1.9635 (21)	Os(2)–Os(1)–C(3)	165.69 (7)
Os(1)–C(3)	1.9184 (20)	Os(2)–Os(1)–C(4)	83.38 (7)
Os(1)–C(4)	1.9473 (19)	Os(2)–Os(1)–C(10)	70.48 (6)
Os(1)–C(10)	2.2172 (22)	C(1)–Os(1)–C(2)	96.93 (8)
Os(2)–C(5)	1.9612 (18)	C(1)–Os(1)–C(3)	91.25 (8)
Os(2)–C(6)	1.9582 (22)	C(1)–Os(1)–C(4)	168.86 (9)
Os(2)–C(7)	1.9202 (20)	C(1)–Os(1)–C(10)	79.57 (8)
Os(2)–C(8)	1.9592 (18)	C(2)–Os(1)–C(3)	98.82 (9)
Os(2)–C(9)	2.2239 (22)	C(2)–Os(1)–C(4)	93.15 (9)
C(1)–O(1)	1.1385 (25)	C(2)–Os(1)–C(10)	164.80 (9)
C(2)–O(2)	1.1382 (27)	C(3)–Os(1)–C(4)	91.89 (8)
C(3)–O(3)	1.1512 (26)	C(3)–Os(1)–C(10)	96.05 (9)
C(4)–O(4)	1.1377 (24)	C(4)–Os(1)–C(10)	89.47 (8)
C(5)–O(5)	1.1328 (24)	Os(1)–Os(2)–C(9)	70.34 (6)
C(6)–O(6)	1.1422 (28)	Os(1)–C(1)–O(1)	174.52 (17)
C(7)–O(7)	1.1369 (26)	Os(1)–C(2)–O(2)	179.21 (17)
C(8)–O(8)	1.1352 (23)	Os(1)–C(3)–O(3)	178.11 (18)
C(9)–C(10)	1.5225 (26)	Os(1)–C(4)–O(4)	176.68 (19)
C(9)–H(2)	1.094 (4)	Os(2)–C(9)–C(10)	104.62 (13)
C(9)–H(4)	1.099 (4)	C(10)–C(9)–H(2)	112.95 (27)
C(10)–H(1)	1.089 (4)	C(10)–C(9)–H(4)	110.50 (25)
C(10)–H(3)	1.106 (4)	H(2)–C(9)–H(4)	108.0 (4)
		Os(1)–C(10)–C(9)	104.81 (11)
		C(9)–C(10)–H(1)	113.05 (27)
		C(9)–C(10)–H(3)	111.25 (25)
		H(1)–C(10)–H(3)	107.3 (3)

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shorter than the other carbonyl Os-C distances, which average 1.959 [6] Å.[17] The Os-Os bond in 1 is thus a sufficiently powerful σ donor to increase d_π donation to, and the Os-C bond order of, the carbonyl trans to it; the Os-C σ bond is not. A similar difference has been noticed between the axial (i.e., trans to the metal-metal bond) and equatorial carbonyl M-C bond lengths in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.[18]

The length of the Os-Os bond in 1, 2.8867 (16) Å, is close to the standard value for an Os-Os single bond, the average Os-Os distance in $Os_3(CO)_{12}$ (2.877 [3] Å).[17,19] However, as $Os(CO)_4$ and CH_2 have similar frontier orbitals and are said to be "isolobal",[20] it is instructive to compare the Os-Os bonds in 1 with those in $Os_4(CO)_{16}$. The latter, which average 2.99 [1] Å,[17,21] are considerably longer, reflecting the repulsive interactions that arise when all four ring positions are occupied by $Os(CO)_4$ groups.

The neutron results permit a more precise description of the nonplanarity of the Os_2C_2 ring of 1 than was possible from our earlier X-ray results. At 32.5°, the Os-C-C-Os torsional angle of 1 is comparable to those found in substituted diosmacyclobutanes by relatively precise X-ray structure determinations (29.7° in 2,[5c] 24.0° in 3,[5c] and 29.9° in 4[5c]).

It is instructive to compare the nonplanarity of the Os_2C_2 ring in 1 with that of $Os_4(CO)_{16}$[21] and that of cyclobutane.[22] The most popular measure of nonplanarity in a four-membered ring is the dihedral angle about which the ring is folded; this angle is 21.1° in $Os_4(CO)_{16}$, 27.9° in cyclobutane, and 32.9° in 1.[23] The eclipsed interactions that oppose planarity are thus stronger in the mixed (Os_2C_2) ring of 1 than in the corresponding Os_4 or C_4 case.

The twist away from planarity of the Os_2C_2 ring in 1 preserves the planar coordination of two carbonyl ligands and two σ bonds around each osmium. Thus C(6), C(7), C(9), and Os(1) remain virtually coplanar about Os(2), and C(2), C(3), C(10), and Os(2) remain virtually coplanar about Os(1). The twist also keeps the hydrogens of each CH_2 equidistant from the Os to which it is attached; e.g., the Os(1)-H(1) distance, 2.798 (4) Å, is essentially the same as the Os(1)-H(3) distance, 2.789 (4) Å.

Symmetry of 1. The molecules of 1 have no crystallographic site symmetry, and the four C-H bonds of their ethylene fragments are thus crystallographically independent. However, the molecules of 1 have approximate C_2 symmetry. The four C-H bonds of 1 can thus be grouped into a pair of essentially equivalent "equatorial" C-H bonds, C(10)-H(1) and C(9)-H(2), and a pair of essentially equivalent "axial" C-H bonds, C(10)-H(3) and C(9)-H(4). In the same way the four CCH angles of 1 can be grouped into a pair of essentially equivalent "equatorial" CCH angles, C(9)-C(10)-H(1) and C(10)-C(9)-H(2), and a pair of essentially equivalent "axial" CCH angles, C(9)-C(10)-H(3) and C(10)-C(9)-H(4).

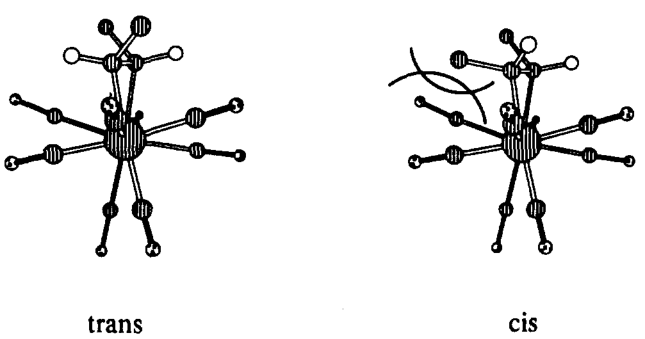

Figure 3. Structures predicted for the *trans*- and *cis*-2-butene adducts of $Os_2(CO)_8$ after replacing appropriate hydrogen atoms in the structure of 1 by methyl carbons (striped circles) (oxygen = dotted circles, hydrogen = open circles). (The methyl hydrogens have been omitted for clarity.)

Table III. Selected Bond Distances and Angles from the Structures of Related Compounds

	C_2H_4[a]	$K[(\eta^2\text{-}C_2H_4)\text{-}PtCl_3]$[b]	$(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)\text{-}Os_2(CO)_8$[c]	C_2H_6[d]
R_{CC}, Å	1.335 (3)	1.375 (4)	1.5225 (26)	1.532 (2)
R_{CH}, Å	1.090 (3)	1.087 (8)	1.097 [7]	1.096 (2)
∠HCH	116.6 (8)	114.9 (6)	107.6 [5]	107.4 (3)
∠CCH	121.7 (4)	121.1 (5)	111.9 [13]	111.5 (3)

[a] Average ground-state structure, as determined by both electron diffraction and vibrational spectroscopy.[27] [b] Neutron diffraction.[11a] [c] Neutron diffraction, this work; error estimates shown in brackets for averaged quantities are standard deviations of the mean. [d] Average ground-state structure, as determined by both electron diffraction and vibrational spectroscopy.[28]

The axial hydrogens are close to two carbonyl ligands (for example, the H(4)-C(1) distance is 2.720 (5) Å and the H(4)-C(8) distance is 2.763 (5) Å) whereas the equatorial hydrogens are close to only one (for example, the H(1)-C(1) distance, 2.718 (4) Å, is much shorter than the H(1)-C(3) distance, 3.088 (5) Å). One would thus expect that substituents would prefer equatorial positions, and this preference is observed. Analysis of the ^1H NMR coupling constants of $(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHMe)Os_2(CO)_8$ shows that the methyl substituent occupies an equatorial position,[10] and the X-ray-determined structure of 2 shows that the carbomethoxy substituent occupies an equatorial position.[5a,c,d] The X-ray-determined structure of 4 (dimethyl fumarate adduct) shows that the trans carbomethoxy substituents both occupy equatorial positions,[5a,c,d] whereas the cis carbomethoxy substituents in 3, the dimethyl maleate adduct, must occupy one axial as well as one equatorial position, and the X-ray-determined structure of 3 shows that they do so.[5a,c,d]

One would thus predict that a cis 1,2-disubstituted olefin would bind less tightly to $Os_2(CO)_8$ than the corresponding trans 1,2-disubstituted olefin, and measurements of olefin exchange rates show that this prediction is correct: the replacement of the *trans*-2-butene in $(\mu\text{-}\eta^1,\eta^1\text{-}trans\text{-}MeCH{=}CHMe)Os_2(CO)_8$ is no faster than the replacement of propene in the corresponding propene adduct, whereas we have been unable to prepare an $Os_2(CO)_8$ adduct of *cis*-2-butene even at 0 °C.[24] Three-dimensional drawings (Figure 3) constructed by Chem3D[25] from the structure

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[17] Error estimates shown in brackets for averaged quantities are standard deviations of the mean; values in parentheses elsewhere were estimated standard deviations based on least-squares calculations.

[18] The axial Mn-CO distance in $Mn_2(CO)_{10}$ is 1.811 (3) Å, whereas the average equatorial Mn-CO distance is 1.856 [7][17] Å; the axial Re-CO distance in $Re_2(CO)_{10}$ is 1.929 (7) Å, whereas the average equatorial Re-CO distance is 1.987 [15][17] Å: Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

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[23] Because the molecules of 1 have no crystallographic site symmetry, the dihedral angle between the Os(1)-Os(2)-C(9) plane and the C(9)-C(10)-Os(1) plane (34.1°) is not exactly the same as the dihedral angle between the Os(2)-C(9)-C(10) plane and the C(10)-Os(1)-Os(2) plane (31.7°). The number reported in the text is the average of these two dihedral angles.

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of 1 clearly show the repulsive interaction that destabilizes the *cis*-2-butene adduct.

The order of relative stability of the $Os_2(CO)_8$ adducts of 1,2-disubstituted olefins (trans > cis) is thus the reverse of that (cis > trans) usually found for the coordination of 1,2-disubstituted olefins, particularly to d^8 metals.[26]

Hybridization of the Ring Carbons in 1. Appropriate structural parameters from 1 have been placed in Table III for comparison with the corresponding parameters for the C_2H_4 units in ethylene, $K[PtCl_3(C_2H_4)]$, and ethane. The $K[PtCl_3(C_2H_4)]$ values used are those from the neutron diffraction structure determination of Bau and coworkers.[11a] The ethylene[27] and ethane[28] parameters are from the average structures in the ground vibrational state determined by Kuchitsu; these values should be the most appropriate ones for comparison with the present neutron diffraction results.[29]

The axial and equatorial C–H bonds of 1 are equivalent in length within the precision of this structure determination, and Table III therefore contains an average value for the C–H bond length of 1. The axial and equatorial CCH angles of 1 are *not* equivalent within the precision of this structure determination, but only their average can be compared with the CCH angles in the other structures, so an average value for the CCH angles of 1 has been placed in Table III.

It is clear from Table III that the ring carbons in 1 have almost completely rehybridized to sp^3. The C–C distance in the coordinated ethylene in $K[PtCl_3(C_2H_4)]$ is only slightly longer than that in free ethylene, showing that little rehybridization has occurred and that the ethylene is largely serving as a σ donor. In contrast, the C–C distance in the coordinated ethylene in 1 is almost as long as the bond between the two sp^3 carbons in ethane. Similarly, the HCH angle in the coordinated ethylene in $K[PtCl_3(C_2H_4)]$ is essentially the same as that of free ethylene, whereas the HCH angle in the coordinated ethylene in 1 is essentially the same as the HCH angle around the sp^3 carbons in ethane; the CCH angle in the coordinated ethylene in $K[PtCl_3(C_2H_4)]$ is essentially the same as that of free ethylene, whereas the CCH angle in the coordinated ethylene in 1 is essentially the same as the CCH angle around the two sp^3 carbons in ethane.

The Os_2C_2 ring in 1 is, like the C_4 ring in cyclobutane, slightly strained. The Os–Os, Os–C, and C–C bond lengths would permit a tetrahedral Os–C–C angle if the Os_2C_2 ring were flat, but the eclipsed interactions that make the ring nonplanar also compress the Os–C–C angles to an average of 104.7 [1]°.[17] This compression would be expected to decrease the s character in the bonds that each ring carbon forms to Os and C, and thus to increase the s character in the bonds that the carbon forms to H. The geometry of the ethylene ligand in 1 does not show the effects observed[30] (an enlarged H–C–H angle and a lengthened C–C distance) when it is incorporated in a really strained ring like cyclopropane. However, some evidence for a strain-induced increase in s character in the C–H bonds of 1 is offered by the value of ^1J(C–H), 135.3 (2) Hz,[31] associated with these bonds. The analogous acyclic system, $(CH_3)_2Os_2(CO)_8$,[32] has a smaller ^1J(C–H), 131 Hz. The value of ^1J(C–H) associated with the Os_2C_2 ring of 1 is about the same as the 134-Hz value of cyclobutane, which is well below the 160-Hz value of cyclopropane but above the 125-Hz value of ethane.[33]

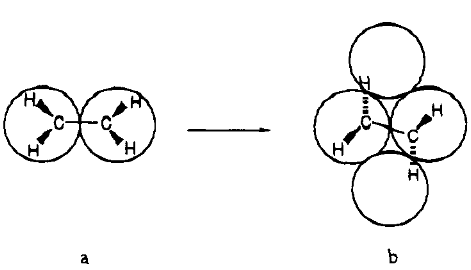

Figure 4. (a) Calculated structure of ethylene on Pt(111). (b) Calculated transition-state structure for dehydrogenation of ethylene on Pt(111).

The ethylene carbons may not be completely rehybridized to sp^3 in all dimetallacyclobutanes. A recently prepared dirhodacyclobutane[34] has a C–C distance of only 1.49 (1) Å.

Comparison of 1 with C_2H_4 on Pt(111). The C–C bond length in 1 is close to the C–C distance within ethylene chemisorbed at low temperature on Pt(111); the latter has been measured at 1.49 (3) Å by NEXAFS[35] and estimated as 1.51 Å from vibrational data.[36] However, the NEXAFS study also suggested that the chemisorbed ethylene retained some double-bond character, and that its C–C bond order was about 1.2.[35] Ethylene that is chemisorbed in "di-σ-bonded" fashion is rehybridized to different extents on different metals,[37] so not all such chemisorbed ethylenes will resemble 1 to the extent that ethylene on Pt(111) does.

The nonplanar geometry of the Os_2C_2 ring in 1 resembles the twisted structure calculated for the transition state for ethylene dehydrogenation on arrays of Pt atoms and proposed on Pt(111).[38] The proposed process begins with an eclipsed conformation (Figure 4a) analogous to a planar Os_2C_2 ring; the methylene groups are then rotated 30° in opposite directions about the C–C bond, and that bond is rotated 20° parallel to the surface—producing a structure (Figure 4b) like that of 1. (The methylene groups of 1 are rotated out of an eclipsed conformation by about 33°.[39]) On Pt(111) this puckering brings the "axial" hy-

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[25] Chem3D is a trademark of Cambridge Scientific Computing, Inc.

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drogens of the ethylene close to the two nearest-neighbor Pt atoms. The diosmacyclobutane 1 is thus not only a good vibrational[3] model for ethylene chemisorbed on Pt(111) but a good structural one as well.

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Supplementary Material Available: A stereoview of the unit cell for 1 (1 page); a listing of observed neutron structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

Theoretical Study of the Sandwich Compounds *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ and *commo*-1,1′-Si(1,2,3-$SiC_2B_4H_6$)$_2$

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A theoretical study of the sandwich compounds *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (I) and *commo*-1,1′-Si(1,2,3-$SiC_2B_4H_6$)$_2$ (II) was conducted by using MNDO–SCF semiempirical molecular orbital theory. In agreement with experiment, the calculations show that the silicon atoms in both I and II are slipped toward the boron sides of the C_2B_3 carborane bonding faces. This slip distortion was found to be the result of Si(s)–cage carbon antibonding interactions and an enhancement in intracage bonding on slippage. Preference for a Si(IV) oxidation state in I and II and a Si(II) state in (η^5-C_5H_5)$_2$Si (III) could be explained on the basis of strong antibonding interactions in the LUMO's of I and II that are not present in the HOMO of III. A comparison of the MNDO results with Xα–scattered wave SCF molecular orbital calculations in which silicon harmonics up through $l = 2$ were used for II and III indicates that Si(d) orbital participation is not important in complex bonding.

Introduction

The number of main-group metallacarboranes that have been synthesized and structurally characterized has increased greatly in the past 5 years. Most of these compounds result from the reaction of a metal ion, or metal-containing group, with the dianions *nido*-1,2-$C_2B_9H_{11}^{2-}$, *nido*-2,3-$C_2B_4H_6^{2-}$, or their derivatives.[1,2] Depending on the metal and its oxidation state, the heteroatom can be incorporated into the polyhedral structure of the carborane to form either the respective closo or the commo complexes. In the icosahedral system, structures of the commo complexes of Al(III),[3,4] Ga(III),[5] and Si(IV)[6] have been reported, while, in the pentagonal-bipyramidal system, the structures of the commo complexes of Si(IV)[7,8] and Ge(IV),[9,10] with *nido*-2-[$Si(CH_3)_3$]-3-[R]-2,3-$C_2B_4H_4^{2-}$ (R = H, $Si(CH_3)_3$, CH_3), are known.

There have been numerous structural reports on *closo*-1-Sn-2-$Si(CH_3)_3$-3-R-2,3-$C_2B_4H_4$ (R = $Si(CH_3)_3$, CH_3, H)[1,11,12] and their adducts with monodentate,[13] bidentate,[12,14,15] bis(bidentate),[13] and tridentate[16] Lewis bases. Similar, though less extensive, studies have been reported for the analogous Ge(II)[17,18] and Pb(II)[19,20] metallacarboranes. In the icosahedral system, structural studies

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