ements of the Al coupling tensor determined above are positive. They then yield $A_{\rm iso} = 12.0$, $A_{\rm dip} = 4.5$ G. The value of $A_{\rm dip}$ for a unit spin density in the Al 3p orbital has been calculated to be 21 G.[5] The coefficients in eq 1 for the Al-benzene complex are thus assessed to be $a^2 \simeq 0.2$, $b^2 \simeq 0.4$. The McConell relation[6] and the spin density, b^2, in the p_π orbital of carbon then predict the proton coupling constant of 9 G in close agreement with the observed value. In the case of Al-ethylene, it has been shown that $a^2 = 0.7$ and $b^2 = 0.15$. It is interesting that the electron migration occurs to a much further extent for the Al-benzene complex.

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Paul H. Kasai,* D. McLeod, Jr.
Union Carbide Corporation, Tarrytown Technical Center,
Tarrytown, New York 10591

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Hydrogenation and Degradation of Carbon Disulfide by Organometallic Cluster Hydride Complexes. Reaction of Carbon Disulfide with $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$

Sir:

It has recently been proposed that transition metal cluster compounds may form the basis for the development of a valuable new class of homogeneous catalysts. This idea is based on the principle that the cooperative interaction of several metal atoms with a given substrate or substrates can produce new and unusual forms of reactivity.[1,2] We have recently been examining the ability of triosmium-hydride cluster complexes to effect the hydrogenation of small molecules[3] and have found that $(\mu\text{-H})_2Os_3(CO)_{10}$ reacts with CS_2 via an unusual dicluster reaction to produce the molecule $(\mu\text{-}S_2CH_2)[(\mu\text{-H})Os_3(CO)_{10}]_2$.[3b] In this reaction each cluster has transferred one hydrogen atom to the carbon atom of the CS_2 molecule and produced a dithiomethylene ligand which then links the two cluster units. In an effort to gain further insight into the mechanism of this unusual reaction we have examined the reaction of $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ with CS_2. To our surprise, we have found an entirely new reaction in which a single cluster complex reacts with one molecule of CS_2, transfers both its hydrogen atoms to the carbon atom, cleaves a single sulfur atom from the original CS_2 unit, and ultimately produces a fractured cluster complex containing inorganic sulfide and a bridging thioformaldehyde ligand.

In a typical reaction 0.12 g of $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ was refluxed in 25 mL of CS_2 solvent for 3 h. The color of the solution changed from purple to orange. The solvent was removed in vacuo, and the product I was isolated (16% yield) by chromatography over alumina.[4] The details of the molecular structure of I have been established through an X-ray crystal structure analysis.[5,6] The molecular structure of I is shown in Figure 1. An inorganic sulfide ligand S(2) is found bonded to all three osmium atoms. The group C(10)-S(1) is a thioformaldehyde ligand which is formally π bonded to atom Os(2), while sulfur atom S(1) simultaneously serves as a bridge between atoms Os(1) and Os(2). Although the hydrogen atoms of the thioformaldehyde ligand were not observed crystallographically, their presence was confirmed by the observation of an AB quartet resonance pattern in the ^{1}H NMR spectrum.[7] We are not aware of any other structural characterizations of a thioformaldehyde ligand and find here that the C-S bond distance at 1.79 (1) Å is very long and approaches that of a single bond.[8,9] There is a metal-metal bond between atoms Os(1) and Os(3), Os(1)-Os(3) = 2.855 (1) Å, but none between Os(1) and Os(2), Os(1)··Os(2) = 3.780 (1) Å, and Os(2) and Os(3), Os(2)··Os(3) = 4.033 (1) Å.

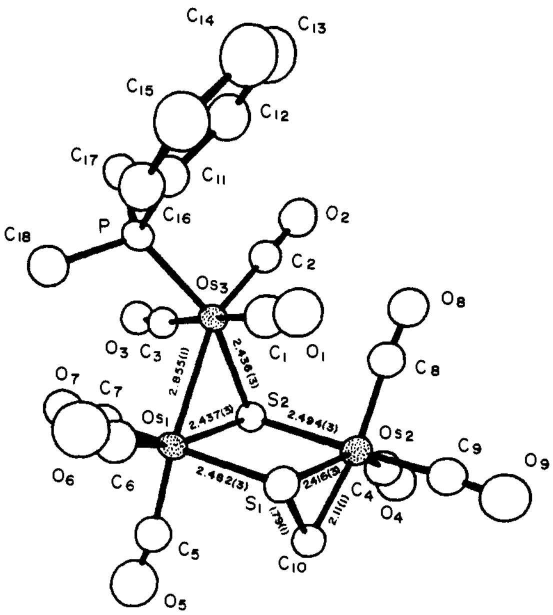

Figure 1. A perspective ORTEP drawing of $(\mu\text{-SCH}_2)(\mu_3\text{-S})Os_3(CO)_9[P(CH_3)_2C_6H_5]$ showing 50% probability ellipsoids and selected bond distances.

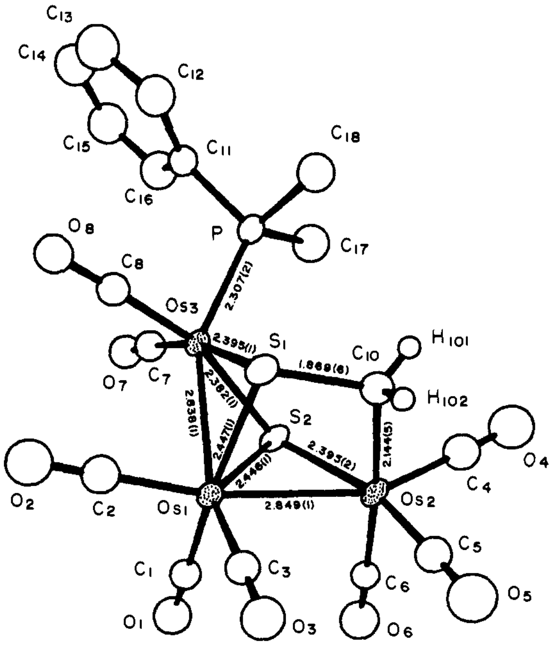

Figure 2. A perspective ORTEP drawing of $(\mu_3\text{-SCH}_2)(\mu_3\text{-S})Os_3(CO)_8[P(CH_3)_2C_6H_5]$ showing 50% probability ellipsoids for all nonhydrogen atoms and selected bond distances.

When refluxed in hexanes solvent, I readily loses 1 mol of carbon monoxide to form the complex $(\mu_3\text{-SCH}_2)(\mu_3\text{-S})Os_3(CO)_8[P(CH_3)_2C_6H_5]$, II (yield 74%).[11] II was also analyzed crystallographically and its molecular structure is shown in Figure 2.[12,13] This compound also contains an inorganic

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sulfide and thioformaldehyde ligand, but the latter now serves as a triple bridge with the sulfur atom S(1) bridging the two osmium atoms Os(1) and Os(3) and the carbon atom C(10) bonded to the third osmium atom Os(2). The thioformaldehyde C(10)–S(1) bond is stretched still further and was found to be 1.869 (6) Å.[7] The hydrogen atoms on the thioformaldehyde ligand were located crystallographically as shown in the figure and also confirmed spectroscopically.[14] Most importantly a metal–metal bond has been formed between atoms Os(1) and Os(2), Os(1)–Os(2) = 2.849 (1) Å. We believe that this compound is formed simply by the loss of one CO from Os(3) in I. Atom S(1) then bonds to Os(3), while C(10) remains bonded to Os(2). Finally a metal–metal bond is formed between Os(1) and Os(2).

We do not wish to speculate about the mechanism of the formation of I at this time, but the important consequences and overriding implications of the reaction are clear. Cluster compounds do possess remarkable abilities to hydrogenate and fragment small substrate molecules like CS_2. The breaking and making of metal–metal bonds may play a key role in these processes and may indeed be a distinct advantage in development of certain cluster catalysts.[15] However, such bond rupture processes will also depend intimately on the use of inert supportive ligands such as the inorganic sulfide ligand in this case, which can maintain the proximity of the metal fragments so that bond making can again occur.

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Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters and bond distances and angles for $\mu\text{-}SCH_2(\mu_3\text{-}S)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ and $(\mu_3\text{-}SCH_2)(\mu_3\text{-}S)\text{-}Os_3(CO)_8[P(CH_3)_2C_6H_5]$ (10 pages). Ordering information is given on any current masthead page.

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(4) IR (ν_{CO}, in hexanes solvent): 2080 (w), 2067 (s), 2040 (s), 2005 (vs), 1995 (vs), 1980 (s) cm^{-1}.

(5) Space group $P2_1/c$, No. 14; $a = 10.001$ (2), $b = 13.523$ (3), $c = 18.660$ (5) Å; $\beta = 91.26$ (2)°; 3404 reflections ($F^2 \geq 3.0\sigma(F^2)$) were used in the structure solution and refinement. The structure was solved by the heavy-atom method. All calculations were done on a Digital PDP 11/45 computer using the programs of the Enraf–Nonius SDP library. Final values of the residuals were $R_1 = 0.058$ and $R_2 = 0.067$.

(6) Selected bond angles for I in degrees: Os(3)–Os(1)–S(1) = 96.79 (6), Os(3)–Os(1)–S(2) = 54.78 (6), Os(1)–Os(3)–S(2) = 54.94 (6), Os(1)–S(2)–Os(2) = 100.1 (1), Os(1)–S(2)–Os(3) = 71.27 (7), Os(2)–S(2)–Os(3) = 108.9 (1), Os(1)–S(1)–Os(2) = 101.1 (2), S(1)–Os(1)–S(2) = 79.36 (9), S(1)–Os(2)–S(2) = 79.51 (9), S(1)–Os(2)–C(10) = 45.9 (3), Os(2)–S(1)–C(10) = 58.1 (3), Os(2)–C(10)–S(1) = 76.0 (4), Os(1)–S(1)–C(10) = 101.6 (3), S(2)–Os(2)–C(10) = 87.9 (3).

(7) Presently our samples of I in $CDCl_3$ solvent show two AB quartet resonance patterns. Thus we believe the compound exists as a mixture of two slowly interconverting isomers: isomer 1, δ 3.44 (1 H), 3.60 (1 H) ($J_{AB} = 5.13$ Hz), 2.47 (3 H), 2.32 (3 H), ($^2J_{PH} = 9.3$ Hz), 7.5–7.9 (5 H); isomer 2, 3.57 (1 H), 3.63 (1 H) ($J_{AB} = 5.13$ Hz), 2.30 (6 H) ($^2J_{PH} = 9.45$ Hz, 7.5–7.9 (5 H).

(8) Internuclear distances for C–S single bonds generally lie in the range 1.81–1.86 Å (cf. ref 3 and references therein).

(9) An interesting thioformaldehyde complex has recently been prepared by Roper et al.[10] by the transfer of metal hydride ligands to a thiocarbonyl ligand.

(10) T. J. Collins and W. R. Roper, *J. Organomet. Chem.* **159,** 73 (1978).

(11) II was isolated by chromatography over $Al_2O_3 \cdot 6\%\ H_2O$ and fractional crystallization from a hexane solution: IR (ν_{CO}, in hexanes solvent) 2085 (m), 2052 (s), 2025 (m), 2012 (s), 1980 (m, br) cm^{-1}.

(12) Space group $P\bar{1}$, No. 2; at −35°C, $a = 9.103$ (4), $b = 11.722$ (4), $c = 11.819$ (2) Å; $\alpha = 71.87$ (2), 79.66 (2), 82.20 (3)°; 3668 reflections ($F^2 \geq 3.0\sigma(F^2)$) were used in the structure solution and refinement. Final values of the residuals were $R_1 = 0.037$ and $R_2 = 0.041$.

(13) Selected bond angles for II in degrees: Os(2)–Os(1)–Os(3) = 91.11 (1), Os(1)–S(2)–Os(2) = 72.11 (4), Os(1)–S(2)–Os(3) = 72.01 (4), Os(2)–S(2)–Os(3) = 116.42 (5), Os(1)–S(1)–Os(3) = 71.76 (4), Os(2)–C(10)–S(1) = 107.2 (3), Os(1)–S(1)–C(10) = 97.3 (2), Os(3)–S(1)–C(10) = 109.1 (2), S(1)–Os(1)–S(2) = 81.85 (5), S(1)–Os(3)–S(2) = 84.29 (5), Os(1)–Os(3)–P = 149.61 (4).

(14) This compound also appears to exist in solution as a mixture of isomers: isomer 1, δ 0.58 (1 H,), 2.43 (1 H) ($J_{AB} = 11.5$ Hz), 2.29 (3 H), 2.31 (3 H) ($J_{PCH_3} = 11.1$ Hz), 7.25–7.60 (5 H); isomer 2, 2.67 (1 H), 1.21 (1 H) ($J_{AB} = 11.6$, $J_{PCH_2} = 4.9$ Hz), 2.35 (6 H) ($J_{PCH_3} = 10.0$ Hz), 7.25–7.60 (5 H). All couplings and shifts have been verified through ^{31}P decoupling. The presence of phosphorus coupling to the thioformaldehyde methylene in isomer 2 suggests that the methylene group and phosphorus ligand are both attached to the same metal atom. Thus, isomer 1 must be the one which was examined crystallographically.

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Richard D. Adams,*[16] Nancy M. Golembeski
John P. Selegue
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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Intersystem Crossing in Hexahelicene

Sir:

Sapir and Van der Donckt[1] have shown that, although the energies of the first excited triplet states of coronene and hexahelicene are almost equal, their rates of intersystem crossing and of triplet decay are different, both processes being more rapid in hexahelicene. Weigang and co-workers[2] have suggested that, owing to the helical structure of hexahelicene, there is an enhanced mixing between singlet and triplet $\pi\pi^*$ states. We report here magnetic resonance studies of the triplet states of coronene, hexahelicene, and heptahelicene which probe the crossing into the triplet manifold. We include coronene as a check of our experimental methods since its triplet state has been studied extensively by optically detected magnetic resonance.[3,4] We used the fast detection X band apparatus previously described[5] for observation of magnetization following short pulses (~6 ns) of optical excitation. The method permits determination of early populations of spin sublevels in the presence of appreciable rates of spin lattice relaxation ($1/T_1 \leqslant 5 \times 10^6\ s^{-1}$).

Studies of the helicenes would best be carried out in single-crystal hosts, but we have had no success in finding any.[6] We therefore carried out our experiments in rigid glasses and in stretched films in which substantial molecular oreintation may be achieved.[7] Although the degree of orientation of hexahelicene in a stretched polyethylene film is not so large as those of planar hydrocarbons, it is sufficient to permit identification of the principal axes of the triplet splitting tensor, and in conjunction with the time resolved experiments to determine the predominant path of triplet excitation.

In rigid isotropic toluene glass or in unstretched polyethylene films, coronene exhibits the expected X band EPR spectrum. Observation of the transient magnetization following pulsed laser excitation reveals that the low-field XY peak is initially emissive and the high-field XY peak initially absorptive (XY is the molecular plane). The result is in accord with earlier findings.[3,4] In the stretched polyethylene film with stretch direction parallel to the static field the Z component is almost absent, indicating orientation with stretch direction in the molecular plane.

In hexahelicene at random orientation, absence of the sixfold rotation axis is obvious (Figure 1); the X–Y peaks are resolved. Labeling the peaks as in Figure 1 (low-field member of low-field pair and high-field member of high-field pair X and the other two Y), we find, in our transient experiments, that low-field X is initially absorptive, low-field Y initially emissive, high-field X initially emissive, and high-field Y initially ab-