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 1. 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.

Acknowledgment. We thank the Office of Basic Energy Sciences, U.S. Department of Energy, for support of this research. NMR spectra were run on the Southern New England high field NMR facility which is supported by a grant (RR-798) from the National Institutes of Health.

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

References and Notes

(1) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85,** 451 (1976); (b) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79,** 91 (1979); (c) E. L. Muetterties, *Science*, **196,** 839 (1977).

(2) R. Ugo, *Catal. Rev.*, **11,** 225 (1975).

(3) (a) R. D. Adams and N. M. Golembeski, *J. Am. Chem. Soc.*, **101,** 2579 (1979); (b) R. D. Adams and N. M. Golembeski, *ibid.*, **101,** 1306 (1979).

(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_3·6% 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 $P1$, 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.

(15) G. Huttner, J. Schneider, H. Muller, G. Mohr, J. von Seyerl, and L. Wohlfahrt, *Angew. Chem., Int. Ed. Engl.*, **18,** 76 (1979).

(16) Fellow of the Alfred P. Sloan Foundation 1979–1981.

Richard D. Adams,*[16] Nancy M. Golembeski
John P. Selegue

Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received May 24, 1979

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 ($1/T_1 \leq 5 \times 10^6\ s^{-1}$).

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-

0002-7863/79/1501-5863$01.00/0

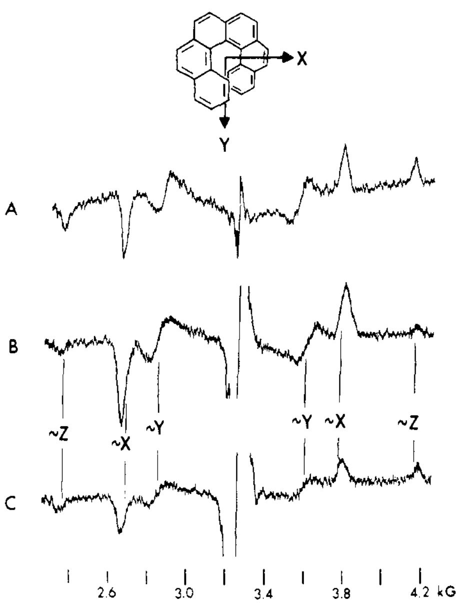


Figure 1. EPR spectra ($d\chi/dB$ vs. B) of triplet hexahelicene in isotropic rigid medium (A) and stretched film with stretch direction parallel to static field (B) and perpendicular to the field (C). All spectra were recorded at 77 K.

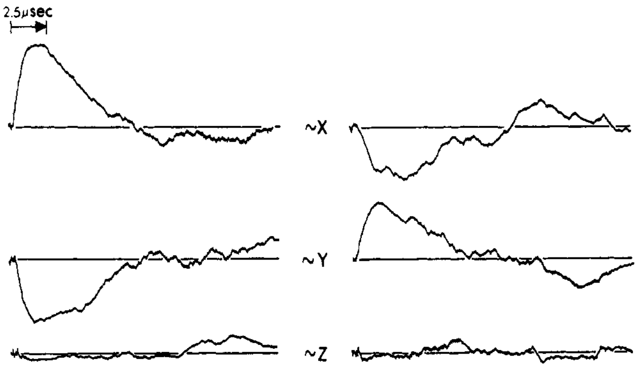


Figure 2. Transient magnetization of hexahelicene triplet in toluene glass at 77 K following excitation by pulsed nitrogen laser (337 nm, 6-ns duration). Signals above the base line are absorptive, below emissive. Each trace is the average of 200 transients, 100 on resonance minus 100 off resonance.

sorptive (Figure 2). In the stretched film with the stretch direction parallel to the field, X peaks are enhanced over Y peaks; i.e., molecules are aligned with X axes parallel to the stretch direction. To determine which directions in hexahelicene correspond to our labels we rely on the assignments of Weigang[2] in which the fluorescence is polarized with electric vector perpendicular to the helix axis and to the twofold rotation axis. The fluorescence from the stretched film is polarized with electric vector parallel to the stretch direction. Our X and Y labels are then attached to the molecular axes as in Figure 1, the Y axis being the twofold rotation axis. The zero-field Hamiltonian for triplet hexahelicene $H = DS_Z{}^2 + E(S_X{}^2 - S_Y{}^2)$ has

$$D/hC = 0.088 \pm 0.001 \text{ cm}^{-1}$$

$$E/hC = -0.006 \pm 0.001 \text{ cm}^{-1}$$

The zero-field state $|T_Y\rangle$, i.e., the eigenstate of S_Y with eigenvalue zero is predominantly excited following photoexcitation at 337 nm. Our data do not exclude excitation into $|T_Z\rangle$ with $P_Z/P_Y = (0.4 \pm 0.2)$ where P_Z and P_Y are relative probabilities of excitation of $|T_Z\rangle$ and $|T_Y\rangle$. In heptahelicene, surprisingly, the $|T_X\rangle$ and $|T_Y\rangle$ states are almost energetically degenerate. $D/hC = \pm 0.084 \pm 0.002 \text{ cm}^{-1}$, $E/hC = \pm 0.002 \pm 0.001 \text{ cm}^{-1}$, but that the degeneracy is accidental, different from the degeneracy imposed by symmetry as in coronene, is demonstrated by the transient experiment. No observable transients at the X–Y positions are observed, owing to the superposition of the emissive and absorptive signals. Unfortunately, we were unable to incorporate heptahelicene into films which would have permitted selective orientation.

In summary, observation of the transient magnetization in triplet hexahelicene demonstrates that the predominant path of intersystem crossing leads to population of the $|T_Y\rangle$ state, and that a small rate of population of $|T_Z\rangle$ is not excluded.

Acknowledgments. This work has been supported by the National Science Foundation. We are grateful to Professor Melvin Newman for our supply of hexahelicene and to Professor R. H. Martin for heptahelicene. We are especially indebted to Professor John Scandrett for indispensable help in making the signal averaging work.

References and Notes

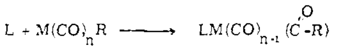
(1) M. Sapir and E. Van der Donckt, *Chem. Phys. Lett.*, **36**, 108 (1975).
(2) O. E. Wergang, J. A. Turner, and P. A. Trouard, *J. Chem. Phys.*, **45**, 1126 (1966).
(3) M. A. El Sayed, W. R. Moomauw, and J. B. Chodak, *Chem. Phys. Lett.*, **20**, 11 (1973).
(4) K. Ohno, N. Nishi, M. Kihoshita, and H. Inokuchi, *Chem. Phys. Lett*, **33**, 293 (1975).
(5) S. S. Kim and S. I. Weissman, *J. Mag. Reson.*, **24**, 167 (1976).
(6) We have prepared solid solutions of hexahelicene in triptycene, but they undergo such efficient photodecomposition of the hexahelicene that they are useless for our purposes. The only product which we have identified is an abundant supply of hydrogen atoms.
(7) J. J. Dekkers, G. P. Hoornweg, C. Maclean, and N. H. Velthorst, *Chem. Phys. Lett.*, **19**, 517 (1973).

S. S. Kim, S. I. Weissman*
Department of Chemistry, Washington University
St. Louis, Missouri 63130
Received May 10, 1979

Kinetic and Thermodynamic Control of the Methyl Migration (CO Insertion) Reaction by Strong Lewis Acids

Sir:

The activation of metal-coordinated carbon monoxide and in particular the alkyl migration reaction is a subject of considerable fundamental and technological importance.[1-3] As shown in eq 1, this reaction involves the migration of the alkyl



$$\mathrm{L + M(CO)_nR \longrightarrow LM(CO)_{n-1}(\overset{O}{\overset{\|}{C}}{-}R)} \qquad (1)$$

group onto one of the coordinated carbonyls accompanied by the addition of a ligand to an alkyl metal carbonyl forming a metal-acyl complex. For the special case of an anionic metal carbonyl, alkyl migration is accelerated by small alkali metal ions, which ion pair with the metal carbonyl.[4] As with reaction 1, an incoming ligand is still required for this cation assisted reaction. In the course of studying the potentially more general molecular Lewis acid assistance of alkyl migration (a reaction which would not be confined to anionic alkyl metal carbonyls), we were surprised to find a very fast methyl migration reaction in the absence of added CO. The mechanism of formation, structure, and reactivity of these novel methyl migration products are discussed below.

The addition of $AlBr_3$ to $Mn(CO)_5(CH_3)$ or $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)$ in toluene solution leads to a rapid color change in each case and the appearance of new low-frequency acyl infrared bands, small shifts in terminal CO stretching frequencies, and a downfield shift in the methyl ^1H NMR resonance. These features are known from recent work in our laboratory to be characteristic of Lewis acid coordinated metal

0002-7863/79/1501-5864$01.00/0