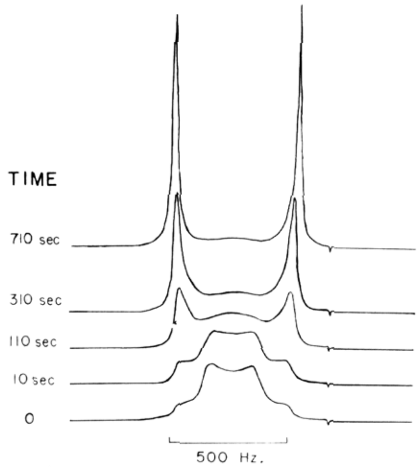

Figure 1. Deuterium NMR spectra of the D_2O component of the cholesteric type I lyomesophase as a function of time. The spectra relate to stages in the process of unwinding of the cholesteric twist by the action of the magnetic field. This unwinding is essentially complete after 710 s in the 58.75-kG field at 25 °C.

oriented perpendicular to the director of the related nematic form, is in the case of type II cholesterics aligned along the magnetic field with no untwisting effect by action of the field.[3] On the other hand, there is a tendency of type I cholesterics to be subject to an untwisting action of the magnetic field, since the helical axis tends to align perpendicular to the magnetic field. In the type I cholesteric thermotropic liquid crystals, the effect of the untwisting as a function of applied field has been studied[3,11] but the dynamics of the process has not.

Aqueous lyotropic systems of nematic liquid crystals are based on the orientational order of disk- or rodlike micelles.[12–14] These have been named type II DM (disk micelles) and type I CM (cylindrical micelles) on the basis of the sign of the magnetic susceptibility anisotropy. The absolute classification as nematic systems is still in doubt because some positional order of the micelles can be detected[14] which depends on the size and character of the containing vessel. We recently reported the first type II lyotropic cholesteric system based on use of pure resolved optically active amphiphiles and, furthermore, illustrated the important relationship of the balanced enantiomer mesophase to the type II nematic system.[8] The helix axis was shown to align along the field direction by studies of polarized microscopy and deuterium NMR of the included D_2O. The balanced optical isomers gave a type II DM mesophase.[8] It is the purpose of this report (a) to show the successful synthesis of a type I cholesteric lyotropic system, (b) demonstrate that the racemic mixture forms a type I CM liquid crystal, (c) provide a photomicrograph of the texture, and (d) show deuterium NMR spectra during the unwinding of the helix in the magnetic field, a dynamic process not hitherto accessible to study in the widely known thermotropic crystals. The composition of the mesophase is (wt %) potassium lauroyl-L-alaninate (D/L racemic mixture for the nematic system) 29.73, potassium sulfate 3.04, 1-decanol 4.8, and D_2O 62.43. The deuterium NMR spectra (for the D_2O signal) of the L mesophase are reproduced in Figure 1. A Bruker WM-250 spectrometer operating at 38.3 MHz equipped with a cryogenic magnet was used to register spectra at 25 °C. The deuterium signals were recorded at 1 ms and 10, 110, 310, and 710 s after placing the sample in the field; the spectra at increasing time are shown from the bottom upward (Figure 1). The racemic mixture of the synthetic detergent formed a type I CM nematic system, and this

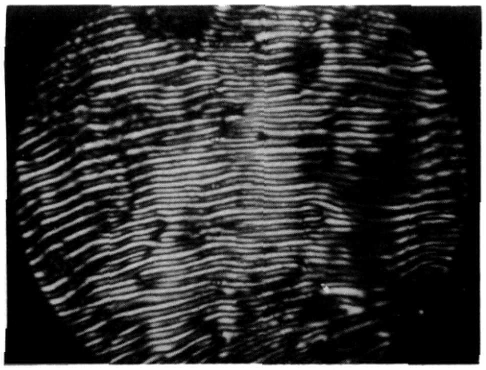

Figure 2. Cholesteric texture observed microscopically between crossed polaroids at 22.2 °C. Sample thickness was 0.2 mm, magnification 100×. The magnetic field was not applied to the sample.

was verified by standard methods in a separate experiment.[6,15] The initial powder doublet[13] at 1 ms has very rounded features, indicating a high intrinsic line width of the constituent doublet components. The untwisting of the helix is almost complete after 710 s, and the constituent peaks of the doublet can be seen to have this rather large line width on the order of 16% of the powder pattern splitting in the lower spectrum. Further studies are in progress to quantify this new kinetic effect in terms of line shapes. The typical cholesteric texture was observed in the polarizing microscope (Figure 2), and further studies of the screw pitch are in progress. The detergent prepared for this study also shows type II cholesteric behavior in other regions of the phase diagram.

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(11) Kamezawa, N. *J. Magn. Reson.* **1976**, *21*, 211; **1977**, *27*, 325.

(12) Fujiwara, F. Y.; Reeves, L. W.; Suzuki, M.; Vanin, J. A. In "Solution Chemistry of Surfactants", Proceedings of National Colloid Symposium, Knoxville, TN, June 1978; Mittal, K. L., Ed.; Plenum Press: New York.

(13) Fujiwara, F. Y.; Reeves, L. W. *J. Phys. Chem.* **1980**, *84*, 653.

(14) Amaral, L. Q.; Pimentel, C. A.; Tavares, M. R.; Vanin, J. A. *J. Chem. Phys.* **1979**, *71*, 2940; (b) Amaral, L. Q.; Tavares, M. R. *Mol. Cryst. Liq. Cryst. Lett.*, in press.

(15) Fujiwara, F. Y.; Reeves, L. W. *Can. J. Chem.* **1978**, *56*, 2178.

Radical Coupling of Mercaptide Ligands upon Oxidation of Organometallic Mercaptide Complexes

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We have reported the characterization of 17e mercaptide complexes $[Fe(C_5H_5)(dppe)SPh]PF_6$ (dppe = 1,2-bis(diphenylphosphino)ethane)[1] and $[Fe(C_5H_5)(PMe_3)_2SPh]PF_6$.[2] These complexes were prepared by oxidation of an appropriate 18e precursor using mild oxidizing agents, the ease of oxidation reflecting the electron-rich character of these species. We have also prepared $[Fe(C_5H_5)[P(OPh)_3]_2SPh]BF_4$.[3] These complexes are blue and paramagnetic; they have magnetic moments of ~1.9 μ_B, appropriate for low-spin d^5 metal complexes.

The oxidation of $Fe(C_5H_5)(CO)_2SPh$ is in striking contrast to this work. When an acetone solution of this complex is treated with $NOPF_6$, NO evolves and an orange solid is obtained (69% yield). Analyses[4] of this material indicate the formula $[Fe(C_5H_5)(CO)_2SPh]PF_6$, but the compound is diamagnetic. An NMR spectrum (CD_3CN) shows a singlet resonance for cyclopentadienyl protons along with a multiplet in the phenyl proton region. Two ν(CO) absorptions (KBr disk) occur at 2060 s and 2025 s cm^{-1} which are appropriate for $[Fe(C_5H_5)(CO)_2L]^+$ complexes. The most reasonable formula which accords with these data is dimeric, having $Fe(C_5H_5)(CO)_2$ groups linked by a bridging diphenylsulfide ligand, viz.

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(1) Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191–197.

(2) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.*, in press.

(3) Rosenhein, L. D.; Treichel, P. M., unpublished results.

(4) Elemental analyses have been obtained for all new compounds reported.

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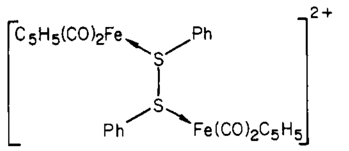

This complex, as a BF_4^- salt, can be made independently in the reaction of $[Fe(C_5H_5)(CO)_2(THF)]BF_4$ and diphenyl disulfide in CH_2Cl_2, using a 2:1 ratio of these reactants. Facile displacement of THF from the precursor is well-known.[5] This compound is soluble in CH_3CN but decomposes slowly to $[Fe(C_5H_5)(CO)_2(PhSSPh)]BF_4$[4] and known $[Fe(C_5H_5)(CO)_2(CH_3CN)]BF_4$. The former compound is also formed from $[Fe(C_5H_5)(CO)_2(THF)]BF_4$ and diphenyl disulfide when these species are reacted in a 1:1 molar ratio. This compound is believed to have a monodentate disulfide ligand.[6] The structure of this compound and its formation from $[Fe(C_5H_5)(CO)_2\text{-}\mu\text{-}PhSSPh\text{-}Fe(CO)_2(C_5H_5)]^+$ under mild conditions argue strongly for the proposed structure of the disulfide-bridged dinuclear complexes.[7]

Oxidations of the related compounds $Fe(C_5H_5)(CO)(L)SPh$[4,8] ($L = P(OPh)_3$, $P(OEt)_3$, PPh_2Me, $PPhMe_2$, PMe_3) were carried out with $AgPF_6$ (for the phosphine complexes) or $NOPF_6$ (for the phosphite complexes). Dark colored products were obtained from each reaction, for which analyses also confirm a stoichiometry $[Fe(C_5H_5)(CO)(L)SPh]X$ ($X = PF_6$ or BF_4).[4] Magnetic moments between 0.5 and 1.0 μ_B were measured for these species at ambient temperatures. Concentrated solutions of the phosphite complexes are red, but dilution caused a color change to blue. The phosphine complexes are blue at room temperature. A reversible blue-red color change can be induced by temperature variation; the higher temperature color is blue while cooling causes the solution to become red. These data suggest an equilibrium between blue 17e monomer and red 18e dimer, viz.,

$$2[Fe(C_5H_5)(CO)(L)SPh]^+ \rightleftharpoons [Fe(C_5H_5)(CO)(L)\text{-}\mu\text{-}PhSSPh\text{-}Fe(C_5H_5)(CO)(L)]^{2+}$$

We have maintained that the facile oxidation of electron-rich complexes is a consequence of the destabilization accorded to HOMO orbitals of primarily metal character by the donation of electronic charge from good donor ligands.[1] The removal of an electron from this orbital would leave an unpaired electron to reside in an orbital which is primarily of metal character. In 17e, d^5 octahedral complexes (such as the $[Fe(C_5H_5)(L)_2SPh]^+$ complexes mentioned above) there usually is no chemical reactivity associated with the unpaired electron. Radical reactions at a metal site are encountered with other types of 17e complexes such as $Mn(CO)_5$, a d^7 five-coordinate species. Our observation of what is apparently a ligand-based radical reaction in these 17e mercaptide species is of some interest in this frame of reference. Only a few other examples of ligand-centered radical reactions have come to our attention.[9]

We suspect that the HOMO in $Fe(C_5H_5)(CO)_2SPh$ is not a metal orbital at all but is in fact a sulfur lone-pair orbital. We base this assumption on PES data and theoretical calculations for $Mn(CO)_5X$ species (X = Cl, Br, I) which indicate that the HOMO is a halogen lone pair.[10] The extrapolation to metal thiolate complexes seems a reasonable one. If so, the oxidation of $Fe(C_5H_5)(CO)(L)SPh$ species ($L = CO$, $P(OR)_3$, PR_3) might be assumed to occur by loss of an electron from a sulfur orbital, giving a radical site located at sulfur. This then reacts in typical radical fashion to give the dimeric product.

A few complexes containing an organic disulfide ligand bridging two metals are known; this includes three organometallic species[11] and several other coordination compounds.[12] A potential bioinorganic interest in related complexes involving metals complexed to the sulfur containing amino acids is noted.

It is our belief that these results are most significant in directing attention to the possibility of a range of radical reactions at ligands not anticipated previously. We are currently investigating this problem in this broader context.

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(5) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153-162.

(6) The synthesis of this compound under mild conditions argues strongly for this structure. Infrared data [ν(CO) at 2068 s and 2025 s cm^{-1}] similar to data on many other $[Fe(C_5H_5)(CO)_2L]^+$ complexes support this formulation. NMR data only confirm the stoichiometry. However, the NMR spectrum of an analogous compound, $Fe(C_5H_5)(CO)_2(CH_3SSCH_3)]BF_4$, shows proton resonances at δ 5.76, 2.98, and 2.80, intensities 5:3:3, confirming the different methyl proton environments expected for such a structure.

(7) Raman data might have provided further evidence for this structure, since disulfide groups show characteristic strong absorptions. However, attempts to obtain Raman data were frustrated by the decomposition of the sample under laser irradiation. A crystal structure study is under way which should verify the proposed structure.

(8) Prepared by reactions of $Fe(C_5H_5)(CO)_2SPh$ with L in toluene and fully characterized.[4]

(9) Waterman, P. S.; Giering, W. P. *J. Organomet. Chem.* **1978**, *155*, C47-C50. Reinhart, K. L.; Michejda, C. J.; Kittle, P. A. *J. Am. Chem. Soc.* **1959**, *81*, 3162-3163. Connelly, N. J.; Kitchen, M. D.; Stansfield, R. F. D.; Whiting, S. M.; Woodward, P. *J. Organomet. Chem.* **1978**, *155*, C34-C36. El Murr, N.; Sheats, J. E.; Geiger, W. E.; Holloway, J. D. L. *Inorg. Chem.* **1979**, *18*, 1443-1446.

(10) Lichtenberger, D. E.; Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1973**, *12*, 702-705.

(11) Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *Gazz. Chim. Ital.* **1976**, *106*, 971-991. *Isr. J. Chem.* **1977**, *15*, 153-159. Abel, E. W.; Khan, A. R.; Kite, K.; Orrell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1980**, 1169-1174.

(12) Stein, C. A.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2212-2216. Warner, L. G.; Kodooka, M. M.; Seff, K. *Ibid.* **1974**, *13*, 2529-2534. Nosco, D. L.; Elder, R. C.; Deutsch, E. *Ibid.* **1980**, *19*, 2545-2551 and references therein.

First Authentic Example of a Difference in the Structural Organometallic Chemistry of Zirconium and Hafnium: Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$

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The road to understanding the structures of $(C_5H_5)_4M$, M = Ti, Zr, and Hf, has been long and filled with crystallographic pitfalls. All three structures were determined initially in the early 1970s. An accurate determination showed that $(C_5H_5)_4Ti$ has two σ- and two π-bonded ligands.[1] Poor quality X-ray studies indicated that $(C_5H_5)_4Zr$ has one σ- and three π-bonded groups,[2] while $(C_5H_5)_4Hf$ was formulated with two σ- and two π-cyclopentadienyl units.[3] In retrospect this was most unusual because (1) zirconium and hafnium differ only slightly (but significantly) in chemical behavior and never in the structure of organometallic derivatives[4] and (2) the crystallography of $(C_5H_5)_4Zr$ and $(C_5H_5)_4Hf$ suggested some serious problems. In particular, that of $(C_5H_5)_4Zr$ was questioned.[1] However, our group showed in 1978 that the one σ three π mode was correct even though the initial X-ray work was faulty.[5] It was supposed that $(C_5H_5)_4Hf$, when properly determined, would likewise prove to be of one σ three π formulation. However, we now report the results of an accurate study of $(C_5H_5)_4Hf$: the compound is correctly viewed as $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$. The original work was in error in that the *c* axis was given only half its true value. The apparent disorder in the space group $P\bar{4}2_1m$ does not exist in the proper choice of $P\bar{4}2_1c$. The molecule is shown in Figure 1.

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(1) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Takats, J. *J. Am. Chem. Soc.* **1971**, *93*, 3592.

(2) Kulishov, V. I.; Brainina, E. M.; Bokiy, N. G.; Struchkov, Yu. T. *Chem. Commun.* **1970**, 475.

(3) Kulishov, V. I.; Brainina, E. M.; Bokiy, N. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1972**, *36*, 333.

(4) See, for example, the tabulation in: Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.*, in press.

(5) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238.

0002-7863/81/1503-692$01.00/0