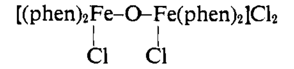
complexes[2–7] having subnormal magnetic moments, which should be amenable to nmr study because exchange coupling in these complexes can significantly decrease the proton nmr line widths.[8] Furthermore there will be no complications due to pseudocontact shifts, and this will greatly simplify the interpretation of their observed isotropic shifts. Of the octahedrally coordinated complexes studied to date by contact shift nmr, only those of nickel(II) have this very desirable feature.

We have begun an investigation of the nmr contact shifts of some of these complexes and in particular wish to report our preliminary results for the complexes $[Fe_2L_4O]Cl_4 \cdot nH_2O$ where L is 1,10-phenanthroline (phen) or the symmetrically substituted dimethylphenanthrolines, 4,7-dimethylphenanthroline (4,7-dmp) and 5,6-dimethyl-1,10-phenanthroline (5,6-dmp). Recent experimental evidence including infrared[4] and conductance[6] data has shown that these complexes contain an oxo bridge and two coordinated chlorides and not two hydroxy bridges as was once believed. Furthermore magnetic measurements[4,6] and Mössbauer spectra[5] suggest that the spin states of the individual iron atoms are $S = {}^5/_2$, and that antiferromagnetic exchange coupling with $J \cong 100$ cm^{-1} and $g = 2.0$ can explain the variation of χ_m with T and the subnormal room-temperature magnetic moment[6] ($\mu_{eff} = 1.78$ BM).



$$[(phen)_2\underset{|\atop Cl}{Fe}{-}O{-}\underset{|\atop Cl}{Fe}(phen)_2]Cl_2$$

The nmr isotropic shifts of these complexes were measured in D_2O at 28° at 60 MHz and are reported in Table I. Of interest is the fact that distinct signals were found for all four protons. Here, save for the 2,9-proton resonance, the half-widths are between 200 and 400 Hz.[9] In low-spin $Fe(phen)_3(ClO_4)_3$ and related complexes[10] the observed half-widths, 40–80 Hz, are much smaller as would be expected and provide further evidence that the binuclear complexes discussed herein do not contain low-spin iron(III). High-spin octahedral d^5 complexes are expected to be magnetically isotropic, and thus we can disregard the pseudocontact term and can attribute the isotropic shifts to a contact interaction only. If J is approximately 100 cm^{-1}, about 50% of the molecules at any time will be in the diamagnetic, $S' = 0$ ground state. Most of the remaining molecules will have energy $2J$, spin $S' = 1$,[11] and will be responsible for the contact shifts.

Table I. Nmr Isotropic Shifts[a]

Compound	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$
$[Fe_2(phen)_4O]Cl_4 \cdot 5H_2O$	−1320	−525	+21	−180
$[Fe_2(4,7\text{-dmp})_4O]Cl_4 \cdot 3H_2O$		−552	(−9)	−210
$[Fe_2(5,6\text{-dmp})_4O]Cl_4 \cdot 4H_2O$		−560	+20	(−22)

[a] The shifts are in cps relative to the appropriate diamagnetic tris-iron (II) complex. Methyl resonances are enclosed in parentheses.

As will be noted, the contact shifts for $[Fe_2(phen)_4O]Cl_4$ follow the pattern (attenuation) expected for a σ mechanism.[12] The very small positive value for $\Delta\nu_{4,7}$ could be explained by a small contribution from a spin polarization mechanism or an extremely minute contribution from a π-delocalization mechanism, which for all practical purposes would be nil. The contact shifts of the methyl-substituted complexes provide further substantiation for a σ-delocalization mechanism because of the small negative values of the methyl proton contact shifts. We have discounted an alternative mechanism whereby the contact shifts in these complexes are due to a combination of both σ and π delocalization such that at the 4,7 protons these two effects numerically cancel each other, causing $\Delta\nu_{4,7} \cong 0$ for $[Fe_2(phen)_4O]Cl_4$. Were this true, one would expect that in $[Fe_2(4,7\text{-dmp})_4O]Cl_4$, the 4,7-$CH_3$ shift would be at least −200 cps owing to the domination of the π mechanism at the 4,7-methyl position. It seems likely that the unpaired spin resides in an orbital of σ symmetry localized mainly on the Fe–O–Fe unit and is then *via* σ bonding partially transferred into the highest filled phenanthroline σ molecular orbital. The success of observing and interpreting the nmr spectra of these complexes means that similar studies can be extended to binuclear oxo-bridged iron(III) species of biochemical significance such as μ-oxo-bis(tetraphenylporphyrin)iron(III).[13]

Such work is at present being initiated in this laboratory along with a study of other binuclear iron(III) complexes in order to ascertain if a σ-delocalization mechanism is prevalent in these complexes.

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(5) R. R. Berrett, B. W. Fitzsimmons, and A. A. Owusu, *ibid.*, *A*, 1575 (1968).

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(7) W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *ibid.*, 90, 6347 (1968).

(8) R. G. Shulman and V. Jaccarino, *Phys. Rev.*, **103**, 1126 (1956); **108**, 1219 (1958).

(9) The spectra showed no evidence of the presence of geometrical isomers which would tend to broaden the resonances and make them asymmetrical.

(10) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **91**, 3442 (1969).

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(13) I. A. Cohen, *ibid.*, **91**, 1980 (1969).

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The Thiophilic Addition of Phenyllithium to Thiobenzophenone

Sir:

Stabilization of an anion or radical by a sulfur atom adjacent to the site of formal electron localization is well documented.[1] Nucleophilic attack on sulfur has also been studied extensively in recent years.[2] We

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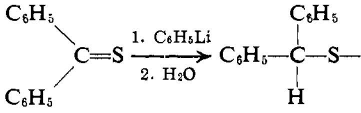
(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 71–84; C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, pp 27–28, 55–60; G. Cilento, *Chem. Rev.*, **60**, 147 (1960); D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 8, 639 (1969).

(2) J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968); D. C. Owsley, G. K.

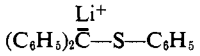
wish to report a reaction which illustrates both phenomena and reveals the possibility of inverse addition of organometallics to carbon–heteroatom multiple bonds.

Reaction of phenyllithium in ether–benzene with equimolar thiobenzophenone at −70 or 25° gives immediate decolorization of the blue thioketone solution. Aqueous quenching followed by extractive and triturative or chromatographic work-up gives a 30–40% isolated yield of benzhydryl phenyl sulfide (**1**).[3] Quenching the reaction solution immediately after disappearance of the blue color of thiobenzophenone with methanol-O-*d* (94 atom % *d*) gives **1** with 84% deuterium at the benzhydryl carbon, as shown by pmr and mass spectrometry, suggesting **2** as a reaction intermediate.



$$(C_6H_5)_2C{=}S \xrightarrow[2.\ H_2O]{1.\ C_6H_5Li} C_6H_5{-}\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}S{-}C_6H_5$$

1



$$(C_6H_5)_2\overset{Li^+}{\bar{C}}{-}S{-}C_6H_5$$

2

$(C_6H_5)_3C{-}S^*$ **3**

$(C_6D_5)_2CHSC_6H_5$ **4**

The possibility that thiobenzophenone and phenyllithium react by initial addition to carbon to give the anion or radical **3** which rearranges to **2** or its precursor[4] is discounted by the observation that thiobenzophenone-d_{10} reacts with phenyllithium to give benzhydrylphenyl-d_{10} sulfide (**4**) containing less than 3% S-phenyl-d_5 material.[5] Reaction of thiobenzophenone with phenylmagnesium bromide produces **1** in 10% yield. *n*-Butylbenzhydryl sufide is obtained in 25% yield (glpc) by reaction of *n*-butyllithium with thiobenzophenone.

Although reports of the reactions of arylthioketones and organometallics usually stress the formation of tetraarylethylene sulfides and tetraarylethylenes,[6] products resulting from thiophilic attack on thiocarbonyls are precedented with organometallics,[7] radicals,[8] diazo compounds,[9] and other nucleophiles.[10,11] It has been suggested that the polarization of a thiocarbonyl group is toward a negative carbon from a positive sulfur on the basis of dipole moment measurements.[12] The present results are consistent with initial thiophilic attack on sulfur by the organometallic to give an intermediate stabilized anion, but we cannot discount the prior intermediacy of radicals. The mode of addition is inverse to that usually observed for the reaction of carbon–heteroatom multiple bonds and organometallics. Further study of the scope[13] and mechanism of this reaction is in progress.

Acknowledgment. We are grateful to the Alfred P. Sloan Foundation and the Public Health Service (GM 12595) for support.

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(3) The product was unambiguously identified by spectral and melting point comparisons with authentic material prepared by the reaction of thiophenol and diphenyldiazomethane: A. Schoenberg, O. Schutz, and J. Peter, *Ber. Deut. Chem. Ges. B*, **62**, 1663 (1929).

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(5) The location of the deuterated phenyl rings was determined by mass spectrometry. The fragmentation of **1** shows major peaks for $[C_6H_5S]\cdot^+$ and $[(C_6H_5)_2CH]^+$. The fragmentation of **4** shows the former peak unshifted and the latter peak 10 amu higher.

(6) E. Campaigne, "Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., p 942; the formation of the episulfides and ethylenes could involve intermediates analogous to **2**, as could a number of other reactions of thiocarbonyl compounds.

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Cycloaddition Reactions of Cycloheptatriene and 2,5-Dimethyl-3,4-diphenylcyclopentadienone[1]

Sir:

Following the prediction of concerted cycloadditions of order greater than [4 + 2] made by Woodward and Hoffmann in 1965,[2] several examples of the [6 + 4] cycloaddition reaction were discovered.[3] Although the [6 + 4] cycloaddition elucidated herein has been mentioned briefly,[3e,4] we wish to report preliminary evidence concerning the concertedness of this reaction, and, in addition, to outline the complexity of the reaction paths observed.

Cycloheptatriene and 2,5-dimethyl-3,4-diphenylcyclopentadienone (VII) form 1:1 adducts I, mp 145–146°, II, mp 171° (needles) and mp 196–197° (prisms), III, mp 199–200°, and IV, mp 158–159°, a decarbonylated 1:1 adduct V, mp 198–199°, and a 2:1 adduct VI, mp 225–226°.[5]

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