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Equilibrium Constants for Dimerization of Several Paramagnetic Iron Thiolate Complexes with the Formula $[Fe(SPh)(L)(L')(\eta\text{-}C_5H_5)]^+$

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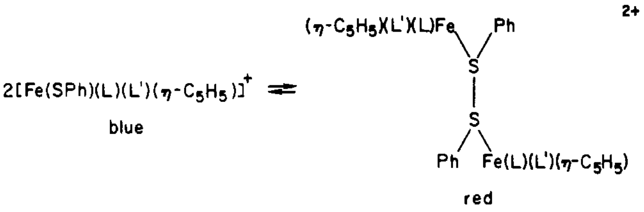
At ambient temperatures, the paramagnetic compounds $[Fe(SPh)(L)(CO)(\eta\text{-}C_5H_5)]PF_6$ (L = $P(OEt)_3$, $P(OPh)_3$) and $[Fe(SPh)(CNR)_2(\eta\text{-}C_5H_5)]BF_4$ (R = $m\text{-}C_6H_4OCH_3$, $m\text{-}C_6H_4CF_3$) exist in solution in equilibrium with diamagnetic dimers containing bridging diphenyl disulfide ligands. Analysis of visible absorption data for solutions of these species at different concentrations provided equilibrium constants for the monomer–dimer equilibria. Dimerization appears to be favored by electron-withdrawing ligands. Values of K_e for the $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$ system in the temperature range 276–294 K were analyzed to provide the parameters ΔH, −12.3 (8) kcal mol^{-1}, and ΔS, −32 (4) eu, for the process of dimerization. The low value of ΔH indicates that when diphenyl disulfide functions as a bridging ligand in this complex the sulfur–sulfur bond is substantially weakened.

Introduction

Oxidations of several organoiron complexes having the general formula $Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$ (L = phosphines, phosphites) yield the cationic complexes $[Fe(SPh)(L)_2(\eta\text{-}C_5H_5)]^+$, stable dark-colored species isolated as BF_4^- or PF_6^- salts.[1] Magnetic moments for these complexes are in accord with their formulation as low-spin iron(III) species. In contrast, oxidation of $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ yields an orange-red diamagnetic product having a bridging diphenyl disulfide ligand, oxidation (electron loss) apparently occurring at the thiolate ligand.[2-4]

Oxidations of the complexes $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ (L = phosphines, phosphites) and $Fe(SPh)(CNR)_2(\eta\text{-}C_5H_5)$ (R = $m\text{-}C_6H_4OCH_3$, $m\text{-}C_6H_4CF_3$) result in the formation of paramagnetic solids having magnetic moments that are lower than the expected values for iron(III) complexes. Behavior of these compounds in solution strongly suggested the existence of an equilibrium between a paramagnetic monomer and diamagnetic dimer:[2,3]



Further study of several of these equilibrium systems is the subject of this paper. It has been possible to obtain values of the equilibrium constants for these reactions by using spectrophotometric techniques, taking advantage of the unique high-wavelength absorption in spectra of the monomers.

Qualitative evidence exists that correlates the donor ability of the ligands L and L′ in $[Fe(SPh)(L)(L')(\eta\text{-}C_5H_5)]^+$ with the propensity to dimerize.[3] The dicarbonyl complex (L = L′ = CO) occurs only as a dimer, and the bis(phosphine) complexes are monomers, whereas the mono(phosphine) or -(phosphite) complexes are mixtures of the two species. There is a difference between mono(phosphine) and -(phosphite) complexes; the dimer is present in solution at room temperature for the phosphite complexes but only at −78 °C for complexes with phosphines. On the other hand, these results could also be explained on the basis of ligand sizes. The goal in this work was to obtain precise data on these equilibria to allow more meaningful comparisons between the various systems and to relate the extent of dimerization to the nature of the other ligands.

Experimental Section

Synthesis. The complexes used in this study, $[Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)]PF_6$ (L = $P(OEt)_3$, $P(OPh)_3$) and $[Fe(SPh)(CNR)_2(\eta\text{-}C_5H_5)]BF_4$ (R = $m\text{-}C_6H_4OMe$, $m\text{-}C_6H_4CF_3$), were prepared by using the procedures described in the literature.[3] Purity of these samples was confirmed by spectroscopic data and by elemental analyses. Solvents (CH_2Cl_2, CH_3CN) were distilled before use.

Equilibrium Studies. Concentrated solutions of the four compounds listed above are red at room temperature, suggesting that the dimer is the predominant substance in solution. At lower concentrations, the solution assumes the blue color of the monomer. We have illustrated this behavior in Figure 1, a graph of molar absorbance vs. wavelength at various concentrations. Note that both monomers and dimers have major absorption maxima in the 500–550-nm range, while the monomers also have an absorption maxima at 660 or 680 nm.

The strategy chosen to obtain concentration information (and from this a value for the equilibrium constant) was to measure the absorbance of a series of solutions having different total concentrations. The concentration range chosen spanned values in which there occurred the visible change of the solution color between red (dimer) and blue (monomer). Details of this procedure are described below.

Solutions of each compound were prepared by dissolving a weighed sample in the solvent and diluting the solution to a known volume. The measurements were made at ambient temperature, 20 ± 1 °C. A wide range of concentrations was required, and quartz cells with path lengths between 0.01 and 10 cm were chosen so that the absorbance would fall in the range 0.2–2.0. A fresh solution was made for each concentration rather than making dilutions from a stock solution, because of slow decomposition of the samples. Dichloromethane was chosen as solvent in three instances; acetonitrile was used in the case of $[Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)]PF_6$ because of the low solubility of this compound in CH_2Cl_2. It was necessary to correct for decomposition except with the triethyl phosphite complex, which was stable in CH_2Cl_2. This was done by assuming that decomposition was a first-order process and by extrapolating a plot of log $(A - A_\infty)$ vs. t to find the absorbance at $t = 0$. Since A_∞, the absorbance at equilibrium, was unknown, a computer routine was written to choose the value for A_∞ that gave the best linear least-squares fit to the data points. An excellent fit was obtained, and the value of A at mixing could be estimated in this way.

To judge the effect of solvent on the equilibrium, measurements for the triethyl phosphite complex were also made in CH_3CN. Absorbance values for a given concentration were found to be the same as values in CH_2Cl_2, within experimental error.

Absorption measurements on the triethyl phosphite complex in the range 0–21 °C were made on a Gilford 2400-S spectrometer, with

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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.; Rosenhein, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 691-692.

(3) Treichel, P. M.; Rosenhein, L. D.; Schmidt, M. S. *Inorg. Chem.* **1983**, *22*, 3960-3965.

(4) An X-ray diffraction study on $[(Fe(m\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5))_2(\mu\text{-}Ph_2S_2)](BF_4)_2$ has confirmed this structure; manuscript in preparation.

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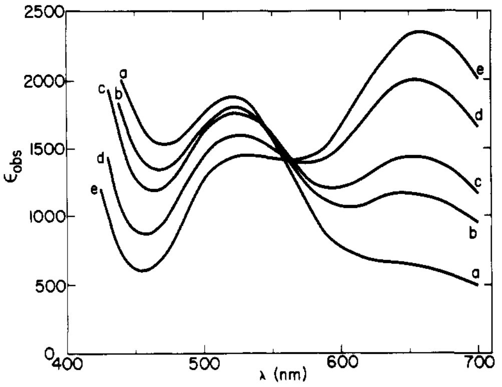

Figure 1. Observed molar absorbance vs. wavelength for [Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$H$_5$)]PF$_6$ at various concentrations: a, 6.60 × 10^{-2} M; b, 1.25 × 10^{-2} M; c, 5.03 × 10^{-3} M; d, 1.53 × 10^{-3} M; e, 4.2 × 10^{-5} M.

a jacketed cell compartment connected to a circulating temperature bath containing an ethylene glycol–water mixture. Temperatures below 20 °C were chosen because the samples had to remain stable over several hours and because a lower temperature shifted the equilibrium toward the region [dimer] > > [monomer] where the most accurate information could be obtained. The complex [Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$H$_5$)]PF$_6$ was used in this study since it is the most stable in solution. About 1 h was required between measurements to allow equilibration of temperature, as determined by the stabilization of absorbance readings. Absorbance measurements were made at only 660 nm. Concentrations were corrected for the change in solvent density with temperature.[5]

Results

Absorbances of a series of solutions having different concentrations are governed by the following three mathematical equations:

$$K = \frac{C_D}{C_M{}^2} \quad \text{(equilibrium constant expression)} \qquad (1)$$

$$C_T = C_M + 2C_D \quad \text{(mass balance)} \qquad (2)$$

$$A = \epsilon_M b C_M + \epsilon_D b C_D \quad \text{(Beer's law)} \qquad (3)$$

in which C_M and C_D refer to monomer and dimer concentrations, C_T is the total concentration based on single metal units, ϵ_M and ϵ_D are extinction coefficients for monomer and dimer at specified wavelengths, and b is the cell path length. Since neither monomer or dimer can be obtained in pure form, the values of ϵ_M and ϵ_D are not directly measurable. Our initial approach to obtain these values was to measure absorbances over a range of high and low concentrations and extrapolate to infinite concentration and dilution, assuming that only dimer and monomer, respectively, should exist under these limiting conditions. Then, at low concentrations, a graph of A/b vs. C_T should produce a straight line through the origin with a slope of ϵ_M, and at high concentrations, a graph of b/A vs. $1/C_T$ should pass through the origin and have a slope of $2/\epsilon_D$. Such plots are illustrated for [Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$H$_5$)]PF$_6$ in Figures 2 and 3. At low concentration (Figure 2), the predicted linear behavior is observed and the extinction coefficients of the monomer can be determined from the slope. From the graph at high concentrations (Figure 3), it is similarly possible to obtain a value of $\epsilon_D(515)$, but at 660 nm, the line had not yet reached linear behavior and cannot be extrapolated through the origin. Limits of solubility prevented measurements at concentrations higher than those shown. It would have been possible to proceed on the designated course at this point either by assuming that ϵ_D at 650 nm is zero or by using data at 515 nm only. We were not comfortable with the former course of action, which would introduce an error of indeterminate magnitude in the calculation. The latter procedure was attempted, but it also appeared to be unsatisfactory, since values of K_e obtained from different sets of data (different C_T values) were inconsistent. This was probably a consequence of the fact tht the 515-nm absorptions due to the monomer and dimer were not very different per metal unit; as a consequence, the overall absorption did not vary markedly as the ratio of monomer to dimer changed.

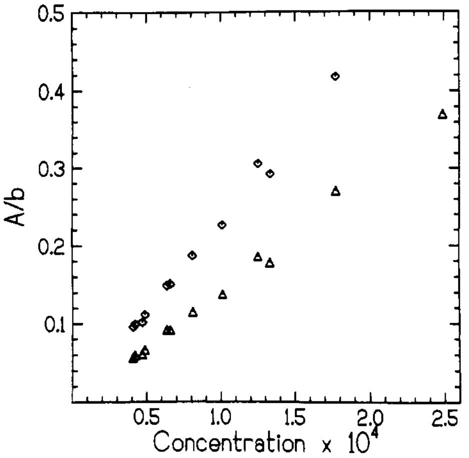

Figure 2. A/b vs. C_T at low concentrations for [Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$H$_5$)]PF$_6$: ◇, 660-nm data; △, 515-nm data.

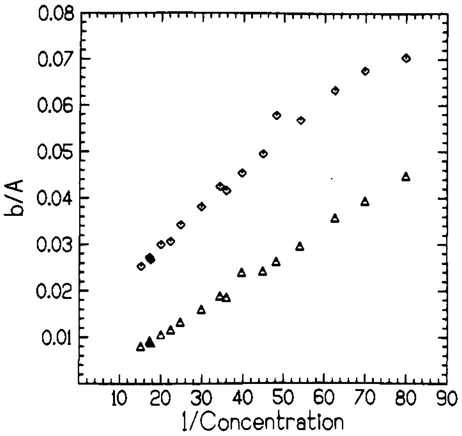

Figure 3. b/A vs. $1/C_T$ at high concentrations for [Fe(SPh)(CO)(P(OEt)$_3$)(η-C$_5$H$_5$)]PF$_6$: ◇, 660-nm data; △, 515-nm data.

Failing to obtain satisfactory values of K in this initial procedure, we chose a different approach. This involved a fit of the available data at each wavelength to eq 4. This

$$\frac{A}{b} = \frac{\epsilon_D - 2\epsilon_M}{8K} + \frac{\epsilon_D C_T}{2} + \frac{(2\epsilon_M - \epsilon_D)(1 + 8KC_T)^{1/2}}{8K} \qquad (4)$$

equation, derived by combining eq 1–3, gives the measured quantity A/b as a nonlinear function of total concentration C_T with three parameters (ϵ_D, ϵ_M, K). A least-squares fit of experimental data to this equation would have the advantage of using all the available data in a single determination of K at each wavelength.

Since no assumptions were made in the derivation, eq 4 may be regarded as equivalent to Beer's law. At low C_T values the value of A/b goes to zero as predicted. However at high total concentrations, A/b approaches $\epsilon_D C_T/2$ only if ϵ_D is not close to zero. If ϵ_D is close to zero, as was expected for the 650-nm data, A/b approaches $[2\epsilon_M(1 + 8KC_T)^{1/2}]/8K$. (This is because the measured absorption will be due to the monomer even though most of the compound is in the dimeric form.) Thus a graph of A/b vs. C_T (or b/A vs. $1/C_T$ such as that in

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[5] Morgan, S. O.; Lowry, H. H. *J. Phys. Chem.* **1930**, *34*, 2385–2432.

Table I. Extinction Coefficients and Equilibrium Constants for $[Fe(SPh)(L)(L')(\eta\text{-}C_5H_5)]^+$ Complexes[a]

compd	λ, nm	ϵ_M, M^{-1} cm^{-1}	ϵ_D, M^{-1} cm^{-1}	K	residuals[b]
$[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$	515	1380 (20)	3892 (64)	344 (117)	R
	660	2429 (23)	79 (53)	106 (7)	NR
$[Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)]PF_6$	515	1072 (26)	3405 (56)	940 (269)	R
	660	2043 (47)	−268 (59)	436 (53)	NR
	660[c]	2167 (70)	0[d]	715 (114)	NR
$[Fe(SPh)(m\text{-}CNC_6H_4OMe)_2(\eta\text{-}C_5H_5)]BF_4$	550	1338 (30)	7446 (117)	802 (100)	R
	680	3101 (52)	505 (73)	444 (50)	R
$[Fe(SPh)(m\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5)]BF_4$	540	1279 (54)	7829 (129)	1900 (291)	R
	680	3477 (89)	4 (33)	1617 (166)	NR

[a] Calculated by nonlinear least-squares fit of data. [b] R = random, NR = nonrandom residual plot. [c] Values calculated by the extrapolative procedure (see text): at 515 nm, $\epsilon_M = 1510$ M^{-1} cm^{-1} and $\epsilon_D = 3750$ M^{-1} cm^{-1}; at 660 nm, $\epsilon_M = 2290$ M^{-1} cm^{-1}. [d] Lower bound for ϵ_D fixed at 0.0.

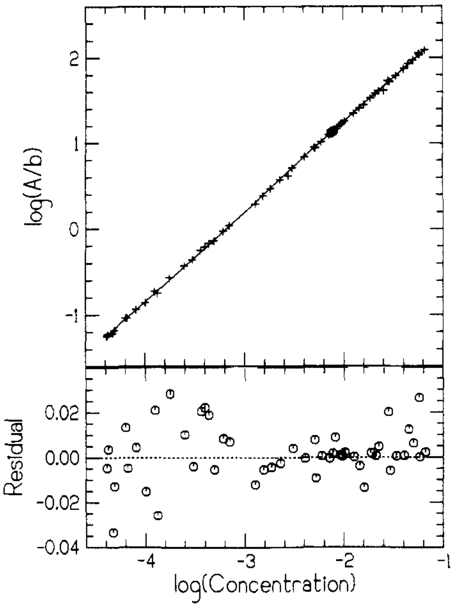

Figure 4. log (A/b) vs. log C_T at 515 nm for $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$ with a plot of residuals (bottom). The solid line is the curve derived by FIT to accommodate these data.

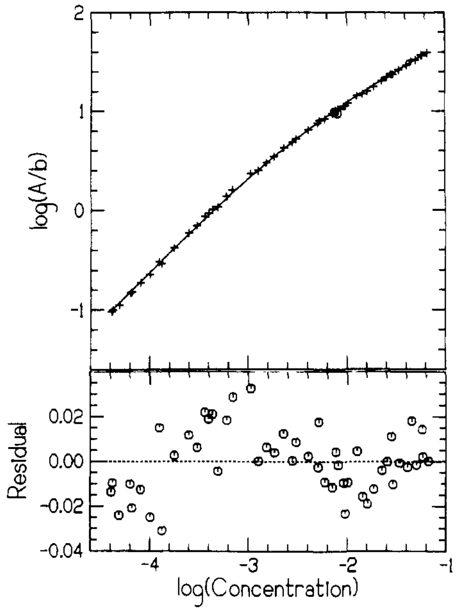

Figure 5. log (A/b) vs. log C_T at 660 nm for $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$ and the derived relationship from FIT, with a plot of residuals (bottom).

Figure 3) for the 650-nm data will not be linear.

Because the dependent variable, A/b, varied over several orders of magnitude while the estimated relative error in measurement remained roughly constant, the data were transformed to a logarithmic basis for the fitting procedure, which was carried out by a nonlinear least-squares program.[6] The log–log analyses had the effect of weighing the data more evenly and reducing the statistical correlation between the parameters. All three parameters, ϵ_M, ϵ_D, and K, were allowed to vary. This analysis provided the values for these parameters given in Table I. The values for the extinction coefficients for the triethyl phosphite compound are within 10% of the values obtained by the extrapolated procedure described above. The experimental data and calculated values from the least-squares analysis for this compound are portrayed in Figure 4 and 5. Data points whose values were more than 3.0 standard deviations from the predicted values were excluded from the final fitting calculation and are not shown on the graphs; it was necessary to discard no more than four points from each data set.

On the log–log scale, the extreme of each line segment should ideally reach Beer's law behavior, forming a straight line with a slope of 1.0. Different y intercepts indicate different extinction coefficients for the monomer and dimer at a given wavelength. It can be seen that at the lower wavelength, both monomer and dimer have similar extinction coefficients per metal unit, since the two ends of the curve are nearly collinear. At high concentrations and with the higher wavelength data, Beer's law behavior is not reached, since the slope does not become 1.0. This would appear to be the result of the nonlinearity of the relationship discussed above between A/b and C_T when ϵ_D is very small. In the case of $[Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)]PF_6$ the value of ϵ_D at 660 nm that gave the best fit occurred below zero. Since this is unreasonable, values obtained for ϵ_M and K when ϵ_D is assigned the value of zero are also included in Table I.

Since the log–log scale compresses the data and makes the fit look better than it actually is, residual plots ($(A/b)_{obsd} - (A/b)_{calcd}$) have been included in these figures. The graph for the residuals for the 515-nm data (Figure 4) are random, as expected. However, there may be some nonrandom character to the residuals from the 660-nm data (Figure 5). The magnitude of the deviation is not large enough to raise questions about the basic interpretation of the data; nonetheless, this may indicate the existence of additional, secondary processes in solution.

Standard deviations for the values of ϵ_M, ϵ_D, and K were obtained from the least-squares program and are included in Table I. The extinction coefficients appear quite accurate. The values of K derived from the 660-nm data have uncertainties of about 10%, which appears to be a reasonable value considering the accuracy of the method. Values of K derived from the 550-nm data are less precisely identified, which seems

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(6) Erhardt, W. C. FIT: A Nonlinear Regression Subroutine, University of Wisconsin—Madison, 1977.

(7) Green, J. R.; Margerison, D. "Statistical Treatment of Experimental Data"; Elsevier: Amsterdam, 1978.

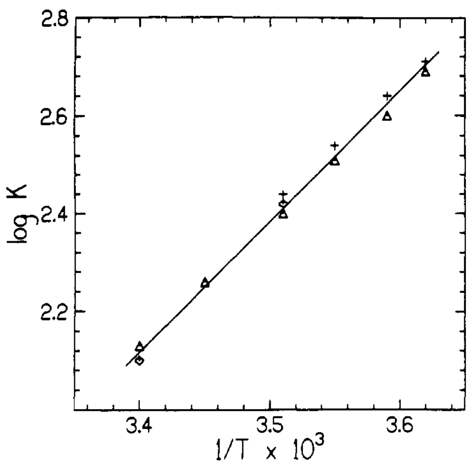

Figure 6. log K vs. $1/T$ for $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$: +, $C_T = 7.94 \times 10^{-3}$ M; Δ, $C_T = 9.18 \times 10^{-3}$ M; ◇, $C_T = 9.09 \times 10^{-3}$ M.

to be in accord with our earlier assumption that the absorption at this wavelength should be rather insensitive to the ratio of monomer to dimer.

For one compound, $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$, a study was carried out on the dependence of K_e with temperature. The 660-nm absorption data were used for samples of this compound is the range 276–294 K. Equilibrium constants were calculated with ϵ_M and ϵ_D values assumed constant in this temperature range. Figure 6 is a graph of log K vs. $1/T$. From this graph, values of ΔH (−12.3 (8) kcal mol^{-1}) and ΔS (−32 (4) eu) for the association process are obtained.

Discussion

In a previous paper,[3] we described the oxidation of several $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ compounds (L = phosphines, phosphites) and of $Fe(SPh)(CNR)_2(\eta\text{-}C_5H_5)$ (R = $p\text{-}C_6H_4CF_3$), $m\text{-}C_6H_4OMe$). Products of these reactions are dark-colored solids with magnetic moments less than the value predicted for a low-spin iron(III) system. In solution, variations of color with dilution and with changes in temperature suggested the existence of an equilibrium between monomer and dimer. Chemical evidence, and more recently a crystal structure study,[4] has confirmed a structure for the dimer having a bridging diphenyl disulfide ligand group. Thus the monomer–dimer equilibrium involves the association of two monomers via sulfur–sulfur bond formation.

The goal of this study was to obtain information on this type of equilibrium for several systems. Ultimately, we hoped to obtain equilibrium constant values and other thermodynamic parameters such as the value of ΔH for sulfur–sulfur bond formation. The availability of these data would permit comparison between systems to assess the influences of electronic and steric factors on the position of the equilibrium. It would also permit comparison of the values for the sulfur–sulfur bond energy between the free and complexed ligand.

The procedure by which values for the constants were obtained, described in detail in the previous section of this paper, involved absorbance measurements on solutions in which total concentration was varied. However to use Beer's law to obtain monomer and dimer concentrations, it was first necessary to obtain extinction coefficient values for both species. Initially, an extrapolative method to obtain the extinction coefficients was attempted. When this approach proved only partially successful, a second approach was undertaken that involved a nonlinear least-squares fit of data with the theoretical model derived from three basic equations (the equilibrium constant expression, mass balance, and Beer's law).

Absorbance data were collected at two wavelength absorptions. Monomer and dimer had similar absorptions at lower wavelengths (515 nm for the phosphite complex and 540 or 550 nm for the isocyanide complexes). The monomer also had a higher wavelength absorption in the red region (660 or 680 nm). Similar absorptions are also seen for complexes like $[Fe(SPh)(L)_2(\eta\text{-}C_5H_5)]^+$, which do not dimerize (L = phosphines, phosphites); this absorption accounts for the dark color of these species. In principle, two sets of data at different wavelengths should provide values for the equilibrium constant. However the lower wavelength data are judged to provide considerably less accurate concentration values since the extinction coefficients of monomer and dimer are not very different (per metal unit). Because the absorbances of monomer and dimer per metal unit are similar, the absorbance will be relatively insensitively to the amount of association. Thus larger random errors in the equilibrium constant values are likely if these data are used. Values for the equilibrium constants for the four systems studied are given in Table I. Results from absorbance data for low wavelengths are also included for comparison. The higher wavelength data produce equilibrium constant values with an estimated accuracy of about ±10%, quite good considering the experimental difficulties encountered. The standard deviations of K calculated from the lower wavelength are somewhat larger (10–30%) as predicted.

A comparison between K_e values is quite interesting. The values for the two isocyanide complexes are 444 (50), for the complex with $m\text{-}CNC_6H_4OCH_3$ ligands, and 1617 (166), for the complex with $m\text{-}CNC_6H_4CF_3$ ligands, dimerization occurring to a significantly larger extent for the latter system. Electrochemical data obtained in our laboratories several years ago indicated that the latter isocyanide has a greater electron-withdrawing ability than the former, a result also anticipated on the basis of substituent parameter values.[8] It is unlikely that the two meta-substituted aryl isocyanides present a significantly different steric profile. Thus it is reasonable to argue that the electron-withdrawing ligands favor dimerization. Indeed, this conclusion is consistent with qualitative differences seen previously with various $[Fe(SPh)(L)(L')(\eta\text{-}C_5H_5)]^+$ species; i.e., dimerization is favored for dicarbonyl complexes vs. mono- and bis(phosphine) complexes, and for the phosphite complexes relative to the phosphine complexes.

The significant difference between the equilibrium constant values for the triethyl (K_e = 106 (7)) and triphenyl phosphite (K_e = 715 (114)) complexes is more difficult to rationalize. It is hard to believe that there is much difference in electron-donor properties of these ligands, though perhaps triphenyl phosphite is a slightly better acceptor.[9] On the other hand, triphenyl phosphite is a more sterically demanding ligand,[10] and if steric features determine the result, the order of K_e should be reversed. This further reinforce the conclusion that electronic factors are significant.

Perhaps the most interesting part in this project concerns measurement of values of K_e as a function of temperature and derivation of the thermodynamic parameters ΔH and ΔS for the dimerization process. This was done for one compound, $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$, by using 660-nm absorption data in the range 276–294 K. Results of this study were quite good, as judged by adherence to a straight line of a graph of log K_e vs. $1/T$ (Figure 6). The values of ΔH for the dimerization process is −12.3 (8) kcal mol^{-1}. The entropy change is measured at −32 (4) eu, the magnitude and negative sign being reasonable for this type of process. The ΔH value may be compared to the value of the sulfur–sulfur bond dissociation energy in diphenyl disulfide, estimated at 55 kcal

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(8) Essenmacher, G. J.; Treichel, P. M. *Inorg. Chem.* **1977**, *16*, 800–806.
(9) For example, see: Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953–2956.
(10) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956–2965.

mol^{-1}.[11] A lengthening of the sulfur–sulfur bond (2.26 Å in $[(Fe(CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5))_2(Ph_2S_2)](BF_4)_2$[4] vs. 2.023 (1) Å in Ph_2S_2[12]) occurs in conjunction with the observed decrease in bond strength.

We should qualify this comparison of bond strengths by observing that the free-ligand value was obtained from gas-phase measurements whereas our result comes from a solution reaction and will presumably be influenced by solvation effects. Also, it seems reasonable that repulsion of positive charges for the two monomers may be contributing to the weakening of the sulfur–sulfur bond in the disulfide-bridged complex. This point certainly warrants further study. Nonetheless, we still believe that there is merit to our earlier contention[2,3] that the sulfur–sulfur bond is weakened by back-bonding from the metal to a sulfur–sulfur antibonding orbital. It is also conceivable that the monomer, a radical species, is stabilized by ligands that are good donors. More study needs to be directed to this question in the future.

Registry No. $[Fe(SPh)(CO)(P(OEt)_3)(\eta\text{-}C_5H_5)]PF_6$, 76452-73-8; $[Fe(SPh)(CO)(P(OPh)_3)(\eta\text{-}C_5H_5)]PF_6$, 76468-63-8; $[Fe(SPh)(n\text{-}CNC_6H_4OMe)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-64-9; $[Fe(SPh)(n\text{-}CNC_6H_4CF_3)_2(\eta\text{-}C_5H_5)]BF_4$, 87681-66-1.

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(12) Sacerdoti, M.; Gilli, G.; Domiano, P. *Acta Crystallogr., Sect. B* **1975**, *B31*, 327–328.

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Cleavage of the Rhenium–Methyl Bond of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ by Protic and Halogen Electrophiles: Stereochemistry at Rhenium

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Reaction of (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ ((+)-(*S*)-**1**) with HX gives (+)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ (X = Cl, (+)-(*S*)-**2**; X = Br, (+)-(*R*)-**3**; X = I, (+)-(*R*)-**4**; X = OSO_2CF_3, (+)-(*R*)-**5**; X = $OCOCF_3$, (+)-(*R*)-**6**; X = OCHO, (+)-(*R*)-**7**; X = $OSO_2\text{-}p\text{-}C_6H_4CH_3$, (+)-(*R*)-**8**) in 63–85% yields and ≥99% retention of configuration at rhenium. The corresponding reactions of (±)-**1** give (±)-**2**–(±)-**8** (69–89%). Triflate (+)-(*R*)-**5** and halides (+)-(*S*)-**2** and (+)-(*R*)-**3** are configurationally and chemically less stable than the other cleavage products. Reactions of (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ with (+)-(*R*)-**5**, (+)-(*S*)-**2**/$AgPF_6$, (+)-(*R*)-**3**/$AgPF_6$, and (+)-(*R*)-**4**/$AgPF_6$ give (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+X^-$ ((+)-(*SS*)-$\mathbf{9}^+X^-$) of ≥99% diastereomeric purity. Reaction of (+)-(*R*)-**7** with $(CH_3)_3SiCl$ gives $HCO_2Si(CH_3)_3$ and (+)-(*S*)-**2** in 98% ee. Reaction of (+)-(*R*)-**5** with CO (2000 psi) gives (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+CF_3SO_3^-$ in 78% ee. Reaction of (+)-(*S*)-**1** with Cl_2, Br_2, and I_2 gives essentially racemic **2**, **3**, and **4**, respectively. The mechanisms of these reactions, and absolute configuration assignments, are discussed. Products **2**–**8** are characterized by microanalysis and NMR, IR, mass, UV, ORD, and CD spectroscopy.

Introduction

There have been numerous studies of the stereochemistry of metal–carbon bond cleavage by electrophilic reagents.[3] The majority of these have focused on the stereochemistry at carbon.[3,4] In many cases where the stereochemistry at the metal was examined,[3,5] substantial racemization was observed.[5a–c]

We have found that a number of remarkably stereospecific ligand-based transformations[6] can be observed with easily resolved[7] chiral $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(L)$ compounds. Many of these have obvious applications in asymmetric organic synthesis, provided that the ligand (L) can be detached from the rhenium without significant epimerization or racemization of its chiral centers. Our preliminary results indicate that this is easily accomplished.[8] However, another important consideration in any ligand detachment reaction is the stereochemical fate of the rhenium. If the metal moiety can be recovered in enantiomerically pure form, then it can be recycled without an additional optical resolution and its utility as a "chiral auxiliary"[9] for asymmetric organic synthesis is greatly enhanced.

In this paper, we describe reactions of racemic and optically active forms of the methyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**)[7,10] with a series of protic acids HX and halogens X_2. High chemical yields of the new complexes $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$[11] are obtained. The reactions with HX are shown to proceed with essentially complete retention of configuration at rhenium. Chemical transformations that establish the reaction stereochemistry are also described.

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