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Axial Labilization by Macrocyclic Ligands. 3. Kinetics of Axial Substitution in Iron(II) Complexes of Two Tetraimine Macrocyclic Ligands

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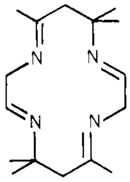
The results of a study of the kinetics of substitution of axial acetonitrile by *N*-methylimidazole in the complexes $FeL^5(An)_2{}^{2+}$ and $FeL^6(An)_2{}^{2+}$ (L^5 and L^6 are macrocyclic ligands with structures as defined below) in acetone solvent are presented. Axial substitution kinetics are consistent with a dissociative (D) mechanism. The activation parameters for these systems are compared with those for four previously studied systems.

Introduction

Axial labilization by macrocyclic ligands is a phenomenon of current research interest.[1-9] In two previous papers, we have reported the results of studies of the axial ligand substitution kinetics in low-spin iron(II) complexes of four synthetic macrocyclic ligands of general formula R_4[14]tetraeneN$_4$ (R = Me (L^1), R = Ph (L^2), R = *p*-MePh (L^3), and R = *p*-MeOPh (L^4)).[1,2] Herein we report the results of further studies of this type, involving the systems indicated in reaction 1. As in the previous four systems (L = L^1–L^4), reaction 1

$$FeL(An)_2{}^{2+} + 2X \overset{S}{\rightleftarrows} FeLX_2{}^{2+} + 2An \qquad (1)$$

$$L = L^5 \text{ or } L^6$$



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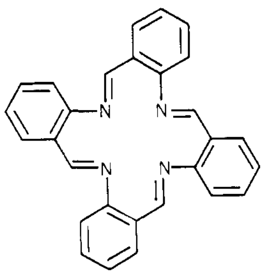

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X = *N*-methylimidazole (MeIm)
An = acetonitrile
S = solvent = acetone

proceeds by a dissociative (D) mechanism. Dissociative rate constants and the associated activation parameters, ΔH^* and ΔS^*, are compared with the corresponding quantities for the previously studied systems.

Experimental Section

Reagents. Reagent grade acetonitrile, acetone, and *N*-methylimidazole were dried and/or purified as previously described.[1,2] All other materials were reagent grade and were used without further purification.

Syntheses. Me$_6$[14]4,11-dieneN$_4$·2HClO$_4$[10] and [Fe(Me$_6$[14]-4,11-dieneN$_4$)(An)$_2$](ClO$_4$)$_2$,[11,12] which serves as a starting material for $FeL^5(An)_2(PF_6)_2$, were prepared by literature methods or modifications thereof.

[FeL⁵(An)₂](PF₆)₂. This compound was prepared by a modification of the procedure described by Busch et al. for the synthesis of $[FeL^5(An)_2](ClO_4)_2$.[13] [Fe(Me$_6$[14]4,11-dieneN$_4$)(An)$_2$](ClO$_4$)$_2$ (3.36 g, 0.0055 mol) was slurried with 50 mL of An, and 0.84 mL of 70% $HClO_4$ was added. The mixture was stirred for 16 h under O_2; then NH_4PF_6 (3.4 g, 0.021 mol) was added in bulk and the resulting white precipitate of NH_4ClO_4 removed by suction filtration. The volume of the filtrate was reduced by one-third with a rotary evaporator, the solution was filtered again, and the filtrate was poured into 75 mL of H_2O, resulting in the formation of pink-violet crystals. These were isolated by suction filtration and quickly taken up in 30 mL of An. The resulting solution was filtered, and 50 mL of diethyl ether was added dropwise with stirring. The pink-violet crystals of product were isolated by suction filtration, washed with ether, and dried under vacuum. The product, $[FeL^5(An)_2](PF_6)_2$, was characterized by IR, NMR, and electronic absorption spectroscopy. IR (KBr pellet): 3000–2890 (w), 1650 (m, sp), 1090 (m, br), 850 (vs, $PF_6{}^-$), 560 cm^{-1} (vs, sp, $PF_6{}^-$). Electronic spectrum (An solution), λ_{max} (ϵ): 355 nm (7980 M^{-1} cm^{-1}), 500 (sh). NMR (nitromethane-d_3, Me$_4$Si reference): δ 1.1 (*gem*-dimethyl), 1.63 (CH_3CN), 2.11 (imine CH_3), 2.67 (bridgehead methylene), 4.5 (methylene, five-membered ring), 7.73 (imine).[13]

Iron(II) Acetate. This compound was prepared as previously described.[14]

FeL⁶(An)₂(BF₄)₂. This compound was synthesized by literature methods.[14] Anal. Calcd for $C_{32}H_{32}N_6B_2F_8Fe$: C, 53.08; N, 11.61; H, 3.62. Found: C, 52.05; N, 11.59; H, 4.02. IR (KBr pellet): 3100–2900 (w), 2280 (w, CH_3CN), 1600 (m), 1580 (m), 1560 (m), 1080 (vs, $BF_4{}^-$), 770 cm^{-1} (m, sp, $BF_4{}^-$). Visible electronic spectrum (An solution), λ_{max} (ϵ): 665 nm (2.3 × 10^3 M^{-1} cm^{-1}), 523 (4.7 × 10^3), 487 (sh).

Physical Methods. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Electronic absorption spectra were obtained with a Perkin-Elmer 552 spectrophotometer. IR spectra were obtained from KBr pellets with a Perkin-Elmer 457 or 683 infrared spectrometer. NMR spectra were measured with a Perkin-Elmer R-24B 60-MHz spectrometer. Cyclic voltammetry was performed at a platinum electrode on a PAR Model 373 potentiostat–galvanostat with a PAR Model 175 universal programmer and a Houston Instruments 2000 X-Y recorder. Voltages were measured against the aqueous saturated calomel electrode (SCE). Ligand substitution kinetics were studied with a Nortech SF-3A Canterbury stopped-flow system, fitted with a mixing cell of path length 2 mm, which has been previously described. Low temperatures were achieved by circulating coolant from a Forma Masterline Model 2800 constant-temperature bath first through a heat exchanger submerged in dry ice/acetone and then through a heat exchanger submerged in the thermostating bath for the stopped-flow system. Temperatures as low as −20 °C could be achieved in this way but could not be closely regulated. Errors in reported temperatures are therefore on the order of ±0.3 °C. Kinetics measurements were performed under N_2 atmosphere, due to the mild oxygen sensitivity of the iron complexes.

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(1) Hamilton, D. E.; Lewis, T. J.; Kildahl, N. K. *Inorg. Chem.* **1979**, *18*, 3364.
(2) Kildahl, N. K.; Lewis, T. J.; Antonopoulos, G. *Inorg. Chem.* **1981**, *20*, 3952.
(3) Holloway, C. E.; Stynes, D. V.; Viuk, C. P. J. *J. Chem. Soc., Dalton Trans.* **1979**, 124.
(4) Martinsen, J.; Miller, M.; Trojan, D.; Sweigart, D. A. *Inorg. Chem.* **1980**, *19*, 2162.
(5) Ashley, K. R.; Leipoldt, J. G.; Joshi, V. K. *Inorg. Chem.* **1980**, *19*, 1608.
(6) Ashley, K. R.; Shyu, S. B.; Leipoldt, J. G. *Inorg. Chem.* **1980**, *19*, 1613.
(7) Pasternack, R.; Parr, G. *Inorg. Chem.* **1976**, *15*, 3087.
(8) Ostrich, I. J.; Lin, G.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1980**, *19*, 619.
(9) Sweigart, D. A.; et al. *Inorg. Chem.* **1981**, *20*, 163.
(10) Tait, A. M.; Busch, D. H. *Inorg. Synth.* **1978**, *18*, 4.
(11) Balkus, K. J. Major Qualifying Project Report No. NK-0029; Worcester Polytechnic Institute: Worcester, MA, 1982.
(12) Goedkin, V. L.; Merrell, P. H.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 3397.
(13) Goedkin, V. L.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 7355.
(14) Kildahl, N. K.; Kolis, J. W.; Beckett, J.; Holland, G. F.; Patz, M. A. *J. Coord. Chem.*, in press.

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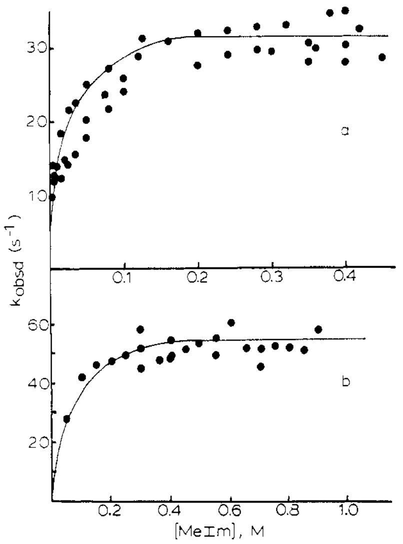

Figure 1. Plots of k_{obsd} vs. [MeIm]. (a) FeL^5(An)$_2^{2+}$: [Fe] = (1–2.5) × 10^{-4} M; [An] = 0.5 or 1.0 M; T = 1 °C. (b) FeL$_6$(An)$_2^{2+}$: [Fe] = (1.5–3.0) × 10^{-4} M; [An] = 0.19 M; T = 1 °C.

Reaction 1 was studied under conditions for pseudo-order kinetics in iron complex. The appearance of iron product was monitored at 410 or 420 nm for FeL^5(An)$_2^{2+}$ and at 595 nm for FeL^6(An)$_2^{2+}$.

Results

Spectrophotometric Titrations. [FeL^5(An)$_2$](PF$_6$)$_2$. The electronic absorption spectra of solutions containing 5 × 10^{-4} M FeL^5(An)$_2^{2+}$ and An in the range between 0.19 and 5.32 M in acetone solvent indicate that for [An] ≥ 1 M, the iron complex exists solely as the bis(acetonitrile) adduct. This concentration or greater of acetonitrile was thus maintained in the iron-containing reactant solution in all of the kinetics experiments. Similarly, spectra of solutions containing 5 × 10^{-4} M FeL^5(An)$_2^{2+}$, 1.0 M An, and MeIm in the range between 0.05 and 0.50 M indicate complete conversion of the bis(acetonitrile) to the bis(*N*-methylimidazole) adduct for [MeIm] ≥ 0.05 M (λ_{max} for FeL^5(MeIm)$_2^{2+}$ = 369 nm). Concentrations of MeIm in excess of 0.05 M were therefore used in all kinetics experiments.

[FeL^6(An)$_2$](BF$_4$)$_2$. Titrations similar to those described for [FeL^5(An)$_2$](PF$_6$)$_2$ using 2.1 × 10^{-4} M [FeL^6(An)$_2$](BF$_4$)$_2$ indicate that the minimum concentrations of An and MeIm required are, respecively, 0.38 and 0.04 M. These concentrations or greater were therefore used in all kinetics experiments involving FeL^6(An)$_2^{2+}$.

Kinetics Studies of Reaction 1, L = L^5. (All concentrations give hereafter are those which prevail *after* dilution by a factor of 2 in the stopped-flow mixing cell.) The kinetics of the L^5 system in acetone were followed at 1 °C by the stopped-flow method under nitrogen atmosphere by monitoring the appearance of bis(*N*-methylimidazole) product at either 410 or 420 nm. Iron concentrations in the range between 1 and 2.5 × 10^{-4} M were used. Low temperature was required to ensure that the reaction rate fell within the stopped-flow range. The reaction is first-order in iron, as shown by strict linearity, over several half-lives, of plots of ln (A_∞ – A) vs. t. Here A is the absorbance of the solution at time t, and A_∞ is the absorbance at equilibrium. The slopes of such plots yield pseudo-first-order rate constants, k_{obsd}, according to the standard integrated first-order rate law.

The dependence of k_{obsd} on the concentration of incoming ligand (MeIm) at a fixed An concentration of 0.5 M is shown in Figure 1a. At MeIm concentrations >0.2 M, the value of k_{obsd} become independent of [MeIm], and the reaction reaches a limiting rate of 31.4 ± 3.3 s^{-1} (the mean value of k_{obsd} for [MeIm] ≥0.20 M) at 1 °C. Further experiments performed at low MeIm concentration indicate an inverse dependence of k_{obsd} on [An]. We have previously shown that axial ligand substitution reactions of low-spin FeL(An)$_2^{2+}$-type complexes proceed by a D mechanism.[1,2] For the FeL^5(An)$_2^{2+}$ system, a D mechanism is indicated both by the attainment of a limiting rate at high concentration of incoming ligand and by rate retardation caused by an excess of leaving ligand, An, at low incoming ligand concentration. We have established[2] that the D mechanism in eq 2–4 adequately accounts for the

$$\mathrm{FeL(An)_2 + MeIm \rightleftarrows FeL(An)(MeIm) + An} \quad K\text{, rapid} \tag{2}$$

$$\mathrm{FeL(An)(MeIm) \rightleftarrows FeL(MeIm) + An} \quad k_{-\mathrm{An}}, k_{\mathrm{An}} \tag{3}$$

$$\mathrm{FeL(MeIm) + MeIm \rightarrow FeL(MeIm)_2} \quad k_{\mathrm{MeIm}} \tag{4}$$

(charges omitted for clarity)

behavior of the L^1–L^4 systems. Under conditions of low [An] and high [MeIm], the full rate law[2] for this mechanism reduces to eq 5, where [Fe]$_T$ = [FeL(An)$_2$] + [FeL(An)(MeIm)]. The

$$\text{rate} = k_{-\mathrm{An}}[\mathrm{Fe}]_\mathrm{T} \tag{5}$$

value of k_{obsd} is thus a direct measure of k_{-An} in the limiting-rate region of the k_{obsd} vs. [MeIm] profile. Assuming that the mechanism in eq 2–4 applies also to the FeL^5(An)$_2^{2+}$ system (vide infra), we conclude that k_{-An} for this system has the value 31.4 s^{-1} at 1 °C.

We have previously discussed the importance of the dissociative rate constant, k_{-An}, and the associated activation parameters, ΔH^* and ΔS^*, in the context of our general program of study of axial labilization by macrocyclic ligands.[1] To determine the latter parameters for the L^5 system, we performed temperature studies of reaction 1 under limiting-rate conditions between –20 and +5 °C. The activation parameters derived from the temperature studies are ΔH^* = 17.8 ±1.6 kcal/mol and ΔS^* = 13.9 ± 5.9 cal/(K mol). The value of k_{-An} at 30 °C, calculated from the Eyring equation, is 9.3 × 10^2 s^{-1}. These results are summarized in Table I, along with those for the other systems studied.

Kinetics Studies of Reaction 1, L = L^6. The kinetics of the L^6 system in acetone were followed at 1 °C under nitrogen atmosphere by monitoring the appearance of bis(*N*-methylimidazole) product at 595 nm. Iron concentrations in the range between 1.5 and 3 × 10^{-4} M were used. Again, low temperature was required to achieve rates compatible with the stopped-flow system. The reaction is first order in iron, pseudo-first-order rate constants being obtained from the usual plots of ln (A_∞ – A) vs. t. The dependence of k_{obsd} on the concentration of MeIm at a fixed An concentration of 0.19 M is shown in Figure 1b. Again, attainment of a limiting rate at high MeIm concentration and rate retardation by An at low [MeIm] indicate that reaction occurs via the D mechanism in eq 2–4. The value of k_{-An}, obtained by averaging the k_{obsd} values for [MeIm] ≥ 0.40 M, is 52 ± 4 s^{-1} at 1 °C. The temperature dependence of k_{-An} in the range between –5 and +5 °C yields ΔH^* = 19.7 ± 3.4 kcal/mol and ΔS^* = 22 ± 12 cal/(K mol). The value of k_{-An} at 30 °C, calculated from the Eyring equation, is 1.7 × 10^3 s^{-1}. The final kinetics parameters obtained for reaction 1, L = L^6, are collected in Table I.

In the second paper in this series,[2] we discussed the experimental justification for the mechanism proposed in eq 2–4. Specifically, when we monitored reaction 1 at a wavelength characteristic of the mixed complex, FeL(An)(MeIm)$^{2+}$, for the systems in which L = L^1–L^4, we observed a very rapid absorbance increase, followed by a relatively much slower absorbance decrease at this wavelength. Further, the rate constant extracted from the slow absorbance decrease was equal to that obtained by monitoring either the appearance

Table I

L	$k_{-\mathrm{An}}$, s^{-1}	ln $k_{-\mathrm{An}}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(K mol)	$E_{1/2}$-(Fe$^{\mathrm{II}}$–Fe$^{\mathrm{III}}$), V vs. SCE
L^5	929	6.83	17.8 ± 1.6	13.9	0.89
L^1	195	5.27	16.2 ± 2.5	5.3	0.97
L^4	14.8	2.69	19.5 ± 3.8	11.7	1.12
L^6	1700	7.41	19.7 ± 3.4	21.8	1.18
L^3	8.5	2.14	21.8 ± 0.3	17.5	1.22
L^2	4.4	1.48	21.7 ± 2.1	16.0	1.25

of this bis(N-methylimidazole) product or the disappearance of the bis(acetonitrile) reactant. We concluded from these observations that replacement of the first axial An by MeIm occurs much more rapidly than replacement of the second and, consequently, that our k_{obsd} values measure the rate of replacement of the second An molecule.

Of the two systems reported here, only $\mathrm{FeL^6(An)_2}^{2+}$ was amenable to an investigation of this type. When reaction 1 for this system was monitored at 548 nm, a wavelength intermediate between $\lambda_{\max}$ values for $\mathrm{FeL^6(An)_2}^{2+}$ (523 nm) and $\mathrm{FeL^6(MeIm)_2}^{2+}$ (595 nm), results similar to those obtained for the L^1–L^4 systems were obtained: a very rapid absorbance increase, followed by a relatively much slower absorbance decrease, was observed. This sequence of absorbance changes undoubtedly reflects very rapid formation and subsequent disappearance of the mixed complex, $\mathrm{FeL^6(An)(MeIm)}^{2+}$. The validity of the mechanism in eq 2–4 for the $\mathrm{FeL^6(An)_2}^{2+}$ system therefore seems likely. Unfortunately, experimental proof of the relative rates of replacement of the first and second An molecules could not be otained for the $\mathrm{FeL^5(An)_2}^{2+}$ species, since the wavelengths of maximum absorbance for all three iron complexes (bis(acetonitrile), mixed, and bis(N-methylimidazole)) lie outside the accessible wavelength range of our stopped-flow system. Rates of reaction 1 for this system were monitored at 410 or 420 nm, on the low-energy tail of an absorption band for $\mathrm{FeL^5(MeIm)_2}^{2+}$. However, given the structural similarity between this system and the others, it seems likely that eq 2–4 apply. We have assumed this to be the case in interpreting our data.

Cyclic Voltammetry of the $\mathrm{FeL(An)_2}^{2+}$ Systems. Cyclic voltammetric measurements were performed in acetonitrile solvent containing 0.1 M tetrabutylammonium perchlorate for the entire series of complexes $\mathrm{FeL(An)_2}^{2+}$, L = L^1–L^6. Measurements were performed with use of a Pt working electrode and referenced to the aqueous saturated calomel electrode. In all cases, well-defined, reversible redox cycles were observed for the $\mathrm{Fe^{II}}$–$\mathrm{Fe^{III}}$ couple. The results of the electrochemical measurements are presented in Table I.

Discussion

The results of the studies reported in this paper, along with results from earlier studies, are collected in Table I. It is to be noted that ΔH^* and ΔS^* are large and positive for both the L^5 and L^6 systems, lending further support to the D mechanism, eq 2–4. Further conclusions can be drawn from the results in Table I. At the outset of this study, it was our goal to demonstrate that a quantitative correlation exists between the structure of a macrocyclic ligand and its ability to labilize ligands in the axial coordination sites in transition-metal complexes containing the macrocycle. The obvious problem lies in how to represent macrocycle structure quantitatively. Relevant to this problem Busch and co-workers have shown[15] that a very clear quantitative relationship exists between specific structural features of macrocyclic ligands and the half-wave redox potential, $E_{1/2}$, for oxidation or reduction of the central metal ion in complexes containing these ligands, as long as the axial ligand is held fixed. The half-wave redox potential can therefore be used to represent the macrocycle structure in quantitative terms. We have previously shown that for the systems L^1–L^4, both the dissociative rate constant for axial ligand substitution and the activation enthalpy governing the temperature dependence of this rate constant correlate well with $E_{1/2}$ for the $\mathrm{Fe^{II}}$–$\mathrm{Fe^{III}}$ couple. Figure 2a shows a plot of ln $k_{-\mathrm{An}}$ vs. $E_{1/2}(\mathrm{Fe^{II}}$–$\mathrm{Fe^{III}})$ for all six systems thus far investigated, and Figure 2b shows the corresponding plot for ΔH^*. The L^5 system clearly fits the trend we have previously established between both ln $k_{-\mathrm{An}}$ and ΔH^* and macrocyclic ligand donor ability, represented quantitatively by the $E_{1/2}$ values. The trend indicates that, as the donor ability of the macrocyclic ligand increases, as reflected in a decreasing value of $E_{1/2}$, the axial ligand substitution rate increases and the activation enthalpy decreases. For reactions occurring by the D mechanism this may be interpreted in terms of decreasing metal–axial ligand bond strength with increasing in-plane donation by the macrocyclic ligand. In contrast to the L^5 system, however, the L^6 system clearly does not fit the established correlations. On the basis of the redox potential for this system, we would predict $k_{-\mathrm{An}}$ and ΔH^* values similar to those for the L^3 system; specifically, we would anticipate that ΔH^* should be approximately 21.5 kcal/mol and $k_{-\mathrm{An}}$ (30 °C) should be about 10 s^{-1}. The observed rate differs by a factor of 170 from the expected value! At present, we have no experimentally based explanation for the failure of this system to fit the correlation so nicely established by data on the other five. Clearly, however, the macrocyclic ligand L^6 is unique in two respects among those investigated thus far. First, it is a 16-membered ring system; and second, it has benzo substituents. It is well-known from extensive electronic spectral studies by Busch and co-workers that the ligand field strengths of 16-membered rings are substantially less than those of 14-membered rings on both Co(III) and Ni(II).[16,17] It is reasonable that this holds true for Fe(II) as well. If so, it is possible that, in acetone solution, the low-spin $\mathrm{FeL^6(An)_2}^{2+}$ complex exists in spin equilibrium with a small concentration of the corresponding high-spin species and that rapid ligand exchange occurs at the labile iron(II) center in the latter. That ligand substitution occurs rapidly in high-spin complexes of iron(II) has been well established.[18] The ligand-exchange

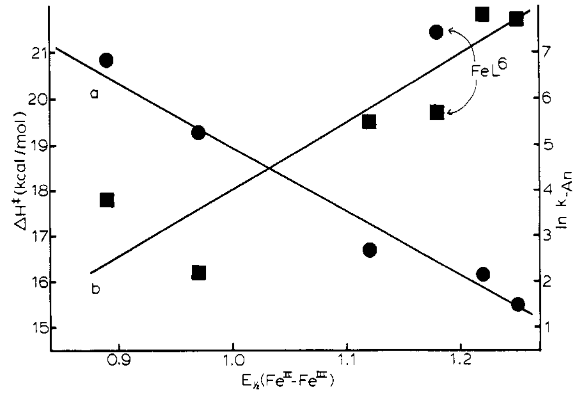

Figure 2. (a) Plot of ln $k_{-\mathrm{An}}$ vs. $E_{1/2}(\mathrm{Fe^{II}}$–$\mathrm{Fe^{III}})$ for the $\mathrm{FeL(An)_2}^{2+}$ series. (b) Plot of ΔH^* vs. $E_{1/2}(\mathrm{Fe^{II}}$–$\mathrm{Fe^{III}})$ for the $\mathrm{FeL(An)_2}^{2+}$ series.

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(15) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

(16) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968.

(17) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029.

(18) Sisley, M. J.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1982**, *21*, 1141.

process may thus occur as indicated in eq 6 and 7.

$$\underset{\text{LS}}{\mathrm{FeL^6(An)_2^{2+}}} \rightleftarrows \underset{\text{HS}}{\mathrm{FeL^6(An)_2^{2+}}} \quad K\text{, rapid} \qquad (6)$$

$$\underset{\text{HS}}{\mathrm{FeL^6(An)_2^{2+}}} + 2\mathrm{MeIm} \rightarrow \underset{\text{LS}}{\mathrm{FeL^6(MeIm)_2^{2+}}} \quad \text{rapid} \qquad (7)$$

Examination of the temperature dependence of the NMR spectrum of an acetone solution of $FeL^6(An)_2^{2+}$ should allow detection of the high-spin component. At (presumably) higher temperatures, the concentration of high-spin component should increase, giving rise to substantial isotropic shifts in the resonances of the ligand protons. We currently lack facilities for performing these experiments, so the explanation must remain speculative at the present time.

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Registry No. $[FeL^5(An)_2](PF_6)_2$, 57139-48-7; $FeL^6(An)_2(BF_4)_2$, 62637-62-1; An, 75-05-8; MeIm, 616-47-7.

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Phosphite Complexes of Copper(I) Containing Chloride, Tetrahydroborate, and (Ethoxycarbonyl)trihydroborate

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Complexes have been studied of the type $[(RO)_3P]_yCuX$, where $y = 2$ or 3, R = CH_3 or C_2H_5, and X = Cl, BH_4, or $H_3BCOOC_2H_5$. Characterization has been by elemental analysis, IR, molecular weight, and NMR data. The hydroborate complexes show bidentate coordination to the copper. In contrast to the case of phosphine and phosphite BH_4^- complexes, both IR and NMR spectra show that at room temperature reaction of excess phosphite ligand with $[(RO)_3P]_2CuH_3BCOOC_2H_5$, R = CH_3 or C_2H_5, results first in a tris(phosphite) complex and ultimately in complete replacement of the (ethoxycarbonyl)trihydroborate.

Introduction

It is well-known that the tetrahydroborate ion (BH_4^-) and its derivatives have been studied for a variety of reasons in organic and inorganic chemistry. Organic chemistry has provided a wealth of information regarding their use as selective reducing agents in both organic and organometallic synthesis.[1] Inorganic chemists have studied the covalent coordination complexes of BH_4^- and have found them to be of theoretical and practical interest. Theoretical interest arises from the variety of M–H–B bonding modes and the fluxional behavior exhibited by the hydroborate moiety,[2,3] whereas practical interest results from selective reducing behavior, which has recently been reported.[4]

Extensive studies on arylphosphine–copper complexes of tetrahydroborate and substituted tetrahydroborates have shown that arylphosphine and substituted arylphosphine ligands influence the mode and strength of attachment of the hydroborate to the metal.[2,3] In contrast, alkylphosphines and arylarsines and -stibines fail to stabilize copper with respect to reduction by tetrahydroborate.[5] The effect of phosphites as ligands in tetrahydroborate complexes is relatively unexplored. A few phosphite complexes of first-row transition metals with halides or perchlorate have been reported, e.g. $[(RO)_3P{\cdot}CuX]_3$ and $[(RO)_3P{\cdot}AgX]_3$[6-9] and $[(RO)_3P(RO)_3P{\cdot}CuX]_3$, $[(PhO)_3P]_2{\cdot}CuX$, and $[(EtO)_3P]_4CuClO_4$.[8-10] In addition, monomeric tetrakis(trialkyl and triaryl phosphite)nickel(0) complexes have been prepared by Tolman.[11] However, the only report of monomeric (phosphite)copper complexes containing hydroborate and comparable to those obtained with phosphine ligands has been from our work.[3a,d] We wish to report the preparation and characterization of new phosphite complexes of copper(I): $[(RO)_3P]_3CuCl$ (R = C_2H_5, CH_3) and $[(RO)_3P]_2CuBH_3R'$ (R = C_2H_5, CH_3; R' = H, $COOC_2H_5$). The relative ease of replacement of the hydroborate by the phosphite at room temperature is a characteristic that differentiates these complexes from their phosphine counterparts, and this will also be discussed.

Experimental Section

General Techniques. Infrared spectra were taken on a Beckman IR-20A spectrometer. ^1H NMR spectra were obtained with a Varian XL-100, A-60, and EM-360 or JEOL 90Q spectrometer. Chemical shifts were based upon internal references (Me_4Si, (^1H), $BF_3{\cdot}OEt_2$ (^{11}B), 85% H_3PO_4 (^{31}P), or known solvent). Vapor pressure osmometry was performed on a Mechrolab, Inc., Model 301A osmometer at 37 °C with chloroform solvent. Conductivity of the complex solutions was measured with a General Radio Co. Type 1608-A impedance bridge and a submersible conductivity cell with cylindrical plates and a cell constant of 1.1626 cm^{-1}. Spectral grade acetonitrile and nitromethane were used for the conductance measurements. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Percent yields in the synthesis of the complexes were comparable to triphenylphosphine complexes[3b] and ranged from 70 to 80%.

Materials. Diborane,[12] borane carbonyl,[3b,13] and potassium (ethoxycarbonyl)trihydroborate[14] were prepared by previously published

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(1) "Sodium Borohydride"; Thiokol/Ventron Division: Danvers, MA 01923; and references therein.

(2) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(3) (a) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1978**, *17*, 3708. (b) *Ibid.* **1979**, *18*, 531. (c) *Ibid.* **1980**, *19*, 587. (d) *Ibid.* **1981**, *20*, 1731. (e) *J. Chem. Soc., Chem. Commun.* **1977**, 137.

(4) Sorrell, T. N.; Spillane, R. J. *Tetrahedron Lett.* **1978**, 2473. (b) Sorrell, T. N. *Ibid.* **1978**, 4985. (c) Fleet, G. W. J.; Fuller, C. J.; Harding, P. J. C. *Ibid.* **1978**, 1437. (d) Fleet, G. W. J.; Harding, P. J. C. *Ibid.* **1979**, 975. (e) Sorrell, T. N.; Pearlman, P. S. *J. Org. Chem.* **1980**, *45*, 3449.

(5) Lippard, S. J.; Ucko, D. A. *Inorg. Chem.* **1968**, *7*, 1051.

(6) Arbuzov, A. E. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1171.

(7) Davies, T. L.; Ehrlich, P. *J. Am. Chem. Soc.* **1936**, *58*, 2151.

(8) Azanovskaza, M. M. *Zh. Obshch. Khim.* **1957**, *27*, 1363; *Chem. Abstr.* **1958**, *52*, 2738*h*.

(9) Arbuzov, A. E.; Zorastrova, V. M. *Dokl. Akad. Nauk SSSR* **1952**, *84*, 503; *Chem. Abstr.* **1952**, *46*, 10038*f*.

(10) Bergerhoff, V. G. *Z. Anorg. Allg. Chem.* **1964**, *327*, 139.

(11) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(12) Freegard, G. F.; Lang, L. H. *Chem. Ind.* (*London*) **1965**, *11*, 471.

(13) Malone, L. J.; Parry, R. W. *Inorg. Chem.* **1967**, *6*, 817.

0020-1669/83/1322-0592$01.50/0