dimerization constant for the following equilibrium as

$$2CuA'_{2,o} \rightleftharpoons Cu_2A'_{4,o} \quad K'_{dim} \tag{7}$$

where $K'_{dim} = [Cu_2A'_{4,o}]/[CuA'_{2,o}]^2$. Solvation of acetic acid itself is not expressed explicitly in this formulation and this is why the species are primed. They have estimated $\log K'_{dim} \geq 5.3$ for pure acetic acid by extrapolating to $[H_2O]_0 = 0$ mol dm^{-3}. Recently, Sawada and his coworkers have determined this apparent constant as $\log K'_{dim} = 6.2$ from spectral changes in UV–vis regions.[23]

Kojima et al. have studied the extraction of copper(II) with a series of *n*-carboxylic acids HR into benzene, and found that the extraction constant K_{22} is constant irrespective of the alkyl chain length of an extractant[19]

$$2Cu^{2+} + 3(HR)_{2,o} \rightleftharpoons Cu_2R_4(HR)_{2,o} + 4H^+ \quad K_{22} \tag{8}$$

They have interpreted this constancy on the basis of the regular solution theory.[25] This rule of equality may also be applied to the extraction of a mononuclear complex:

$$Cu^{2+} + 2(HR)_{2,o} \rightleftharpoons CuR_2(HR)_{2,o} + 2H^+ \quad K_{12} \tag{9}$$

Since stoichiometric consideration leads to the following relationship:

$$K_{dim} = K_{22}/(K_{12})^2 \tag{10}$$

these dimerization constants must be identical irrespective of the kind of carboxylic acid HR as extractant dissolved in benzene. Thus

$$K_{dim}(\text{acetic acid}) \simeq K_{dim}(\text{decanoic acid}) \tag{11}$$

According to Hildebrand and Scott[24], the absolute activity, a_i, of species i is interrelated with its mole fraction x_i as follows:

$$\ln a_i = \ln x_i + V_i\phi_s^2(\delta_i - \delta_s)^2/RT \tag{12}$$

where δ_i and δ_s are solubility parameters of a solute i and a solvent s, respectively. V_i is the molar volume of i, and ϕ_s is the volume fraction of the solvent, which may be approximated to unity. As the dimerization constant based on the activity scale is identical in whatever solvent, change in K_{dim} based on the concentration scale may be calculated from the following expression, when the solvent is changed from benzene (B) to acetic acid (E):[20,25-27]

$$RT(\ln K^E{}_{dim} - \ln K^B{}_{dim})/(\delta_B - \delta_E) = V_2(D - 2\delta_2) + V_d(D - 2\delta_d) - 2V_1(D - 2\delta_1) \tag{13}$$

where the subscripts 1, 2, and d denote the species $CuA_2(HA)_2$, $Cu_2A_4(HA)_2$ and $(HA)_2$, respectively. D is a sum of solubility parameters of these two solvents.

The molar volumes and solubility parameters for metal complexes may be evaluated in a common way as:[20,25,26]

$$V_1 = 2 \times 0.9V_d \qquad V_2 = 3 \times 0.9V_d$$

$$\delta_1 = \delta_2 = (1/0.9)^{1/2}\delta_d$$

The following data are available:

$$\delta_d \simeq \delta_E = 13.01 \text{ (cal/cm}^3)^{1/2} \qquad \delta_B = 9.15 \text{ (cal/cm}^3)^{1/2}$$

$$V_d = 57.24 \times 2 \text{ cm}^3/\text{mol} \qquad V_B = 88.85 \text{ cm}^3/\text{mol}$$

Substitution of these numerical values into eq 13 results in

$$\log K^E{}_{dim} - \log K^B{}_{dim} = -0.28 \tag{14}$$

The regular solution theory is constructed on the mole fraction scale, though experimental extraction studies are carried out ordinarily on the molar scale. Fortunately, the dimerization constant on the latter scale can be equated to that on the former one in this case, because the number of species involved is identical for both sides in eq 6, i.e. K_{dim} is a dimensionless constant. Furthermore K'_{dim} equals to K_{dim} on the mole fraction scale, on the assumption that acetic acid is composed primarily of dimeric species $(HA)_2$,[28,29] whose mole fraction is equal to unity. Thus

$$\log K'_{dim}(\text{in acetic acid}) = 6.37 - 0.28 = 6.09 \tag{15}$$

This value agrees well with the experimental one[23] and accounts for the great stability of dinuclear copper(II) acetate in anhydrous acetic acid.[2]

Registry No. HA, 334-48-5; HOAc, 64-19-7; Cu, 7440-50-8; C_6H_6, 71-43-2; copper(II) acetate, 142-71-2; copper(II) decanoate, 28567-33-1.

Supplementary Material Available: A table of experimental data for distribution of copper(II) between benzene and aqueous solutions at 25 °C (1 page). Ordering information is given on any current masthead page.

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Isolation and Characterization of $Ti(O)(OAr\text{-}2,6Pr^i{}_2)_2(NC_5H_4\text{-}4NC_4H_8)_2$ ($OAr\text{-}2,6Pr^i{}_2$ = 2,6-Diisopropylphenoxide; $NC_5H_4\text{-}4NC_4H_8$ = 4-Pyrrolidinopyridine): A Mononuclear Aryloxide Compound Containing a Terminal Titanium(IV)–Oxo Group

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Received February 16, 1989

The last few years have seen a burgeoning of research interest into the structure and reactivity of early-transition-metal compounds containing terminal oxo ligands.[1-5] However, despite this activity, there is still a dearth of examples of group 4 metal compounds containing this functional group.[1] During our studies of the group 4 metal organometallic chemistry supported by sterically demanding aryloxide ligation, we have been able to obtain an η^2-imine derivative of titanium, which serves as a useful precursor to low-valent aryloxide derivatives of this metal.[6] We wish to report here on the reactivity of this compound toward water, a reaction that under suitable circumstances allows the isolation of a mononuclear oxo derivative of titanium(IV).[3]

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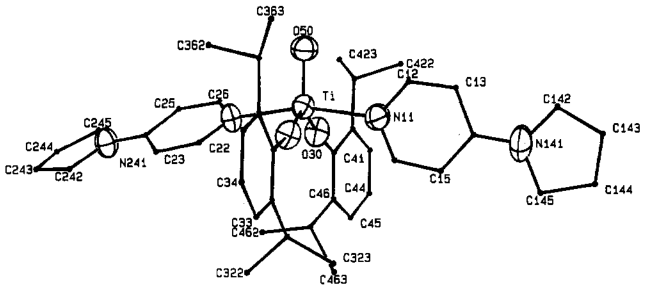

Figure 1. ORTEP view of 2 emphasizing the central coordination sphere.

Results and Discussion

The treatment of the η^2-iminoacyl compound Ti(OAr-2,6Pr$^i_2$)$_2$(η^2-Bu^{t}NCCH$_2$Ph)(CH$_2$Ph)[7] (OAr-2,6Pr$^i_2$ = 2,6-diisopropylphenoxide) with pyridine (1 equiv) in hydrocarbon solvents leads to the rapid formation of the η^2-imine compound Ti(OAr-2,6Pr$^i_2$)$_2$[η^2-Bu^{t}NC(CH$_2$Ph)$_2$](NC$_5$H$_5$) (**1**), in almost quantitative yields.[6] The formulation of **1** as being a titanium(IV) compound containing an azametallacycle ring was supported by structural studies. Entirely consistent with this notion is the fact that **1** reacts with water ($\geq$1 equiv) in hydrocarbon solvents to liberate the organic amine compound HN(Bu^t)CH(CH$_2$Ph)$_2$, which can be isolated from the reaction mixture in 70–85% yields. The other products from the hydrolysis reaction include 2,6-diisopropylphenol as well as yellow, sparingly soluble titanium-containing compounds. However, when the reaction is carried out in the presence of 4-pyrrolidinopyridine it is possible to obtain a crystalline yellow precipitate of a compound of stoichiometry [Ti(O)(OAr-2,6Pr$^i_2$)$_2$(NC$_5$H$_4$-4NC$_4$H$_8$)$_2$] (**2**). A single-crystal X-ray diffraction analysis of **2** confirmed the stoichiometry and furthermore showed the compound to be mononuclear, containing a terminal oxo ligand (Figure 1). The fractional coordinates and isotropic thermal parameters for **2** are collected in Table I while some selected bond distances and angles are given in Table II. The central TiN$_2$O$_3$ core of the molecule can be seen to adopt a trigonal-bipyramidral arrangement about the titanium metal center (Figure 1, Table II), with trans, axial pyridine ligands. The equatorial plane of **2** consists of the oxo group as well as the oxygen atoms of the two aryloxide ligands. The angle between the sterically more demanding aryloxide groups has opened up to 132.4 (3)°. The Ti–N distances of 2.194 (8) and 2.214 (7) Å and Ti–O (aryloxide) distances of 1.863 (6) and 1.879 (6) Å are in the range reported for other pyridine[8] and aryloxide[9] derivatives of titanium(IV). Of obvious specific interest is the Ti–O(oxo) distance of 1.657 (6) Å found in **2**. There have previously only been four reported structural studies on titanium compounds that contain terminal oxo ligands and three of these involve porphyrin type coligation.[1] The distance found in **2** is significantly shorter than that reported for the complex anion [TiOCl$_4$]$^{2-}$ (1.79 Å),[10] but is slightly larger than the average value of 1.62 Å reported for the series of neutral porphyrin compounds of stoichiometry (por)Ti(O).[11,12]

Table I. Fractional Coordinates and Isotropic Thermal Parameters for **2**

atom	x	y	z	B,[a] Å^2
Ti	0.25931 (5)	−0.01365 (9)	0.07877 (4)	3.32 (3)
O(30)	0.2095 (2)	0.0337 (3)	0.1124 (2)	4.0 (1)
O(40)	0.3300 (2)	−0.0722 (4)	0.0931 (2)	4.6 (1)
O(50)	0.2364 (2)	−0.0006 (4)	0.0197 (1)	4.5 (1)
N(11)	0.3017 (2)	0.1360 (4)	0.0883 (2)	4.4 (2)
N(21)	0.2284 (2)	−0.1712 (4)	0.0856 (2)	3.6 (1)
N(141)	0.3783 (3)	0.4224 (5)	0.1179 (2)	6.3 (2)
N(241)	0.1885 (2)	−0.4787 (4)	0.1047 (2)	4.7 (1)
C(12)	0.3034 (3)	0.2052 (6)	0.0550 (3)	4.9 (2)
C(13)	0.3286 (3)	0.2996 (6)	0.0624 (3)	5.3 (2)
C(14)	0.3541 (3)	0.3286 (6)	0.1079 (3)	4.7 (2)
C(15)	0.3530 (4)	0.2555 (7)	0.1426 (3)	6.7 (3)
C(16)	0.3266 (4)	0.1637 (6)	0.1311 (3)	6.9 (3)
C(22)	0.1951 (3)	−0.1975 (5)	0.1135 (2)	4.2 (2)
C(23)	0.1800 (3)	−0.2976 (6)	0.1214 (2)	4.1 (2)
C(24)	0.2015 (3)	−0.3788 (5)	0.0984 (2)	4.0 (2)
C(25)	0.2353 (3)	−0.3512 (5)	0.0678 (3)	4.5 (2)
C(26)	0.2482 (3)	−0.2492 (6)	0.0632 (2)	4.6 (2)
C(31)	0.1680 (3)	0.0662 (5)	0.1320 (2)	3.4 (2)
C(32)	0.1763 (3)	0.0684 (5)	0.1810 (2)	3.9 (2)
C(33)	0.0824 (3)	0.1327 (6)	0.1732 (3)	5.1 (2)
C(35)	0.0747 (3)	0.1291 (6)	0.1255 (3)	4.9 (2)
C(36)	0.1162 (3)	0.0950 (5)	0.1036 (2)	3.8 (2)
C(41)	0.3838 (3)	−0.0942 (5)	0.1094 (2)	3.3 (2)
C(42)	0.4203 (3)	−0.1023 (5)	0.0786 (3)	4.2 (2)
C(43)	0.4761 (3)	−0.1223 (7)	0.0965 (3)	5.3 (2)
C(44)	0.4965 (3)	−0.1362 (7)	0.1436 (3)	6.1 (2)
C(45)	0.4603 (3)	−0.1298 (6)	0.1735 (3)	5.3 (2)
C(46)	0.4046 (3)	−0.1078 (6)	0.1578 (3)	4.3 (2)
C(142)	0.3820 (4)	0.5005 (7)	0.0834 (4)	8.4 (3)
C(143)	0.4014 (5)	0.5967 (8)	0.1118 (5)	12.4 (5)
C(144)	0.4312 (5)	0.5664 (7)	0.1575 (4)	10.4 (4)
C(145)	0.4052 (4)	0.4532 (7)	0.1656 (3)	8.1 (3)
C(242)	0.1519 (3)	−0.5119 (6)	0.1352 (3)	5.4 (2)
C(243)	0.1539 (4)	−0.6289 (7)	0.1321 (3)	8.4 (3)
C(244)	0.1955 (4)	−0.6569 (7)	0.1082 (4)	11.1 (3)
C(245)	0.2145 (3)	−0.5654 (6)	0.0850 (3)	6.3 (2)
C(321)	0.2315 (3)	0.0381 (6)	0.2116 (3)	5.2 (2)
C(322)	0.2241 (4)	−0.0469 (8)	0.2459 (4)	8.9 (3)
C(323)	0.2614 (4)	0.1294 (8)	0.2375 (4)	8.8 (3)
C(361)	0.1070 (3)	0.0857 (6)	0.0510 (3)	4.8 (2)
C(362)	0.0839 (4)	−0.0218 (7)	0.0365 (3)	8.4 (3)
C(363)	0.0682 (4)	0.1669 (7)	0.0243 (3)	7.9 (3)
C(421)	0.3988 (3)	−0.0873 (7)	0.0265 (3)	5.9 (2)
C(422)	0.4167 (5)	0.019 (1)	0.0121 (4)	10.9 (4)
C(423)	0.4178 (5)	−0.170 (1)	−0.0019 (4)	12.8 (4)
C(461)	0.3647 (3)	−0.1041 (7)	0.1905 (3)	5.9 (2)
C(462)	0.3406 (4)	−0.2086 (8)	0.1958 (4)	11.1 (3)
C(463)	0.3912 (5)	−0.056 (1)	0.2371 (4)	14.0 (5)
C(701)	0.4497 (5)	0.3385 (9)	0.3524 (4)	9.8 (3)*
C(702)	0.4809 (5)	0.274 (1)	0.3838 (4)	11.6 (4)*
C(703)	0.4979 (5)	0.173 (1)	0.3670 (4)	11.5 (4)*
C(704)	0.4797 (6)	0.153 (1)	0.3209 (5)	13.2 (4)*
C(705)	0.4478 (6)	0.224 (1)	0.2908 (5)	15.5 (5)*
C(706)	0.4331 (5)	0.320 (1)	0.3087 (4)	11.8 (4)*

[a] Asterisks denote values for isotropically refined atoms. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for **2**

Ti–O(30)	1.879 (6)	Ti–O(40)	1.863 (6)
Ti–O(50)	1.657 (6)	Ti–N(11)	2.194 (8)
Ti–N(21)	2.214 (7)		
O(30)–Ti–O(40)	132.4 (3)	O(30)–Ti–O(50)	114.2 (30)
O(30)–Ti–N(11)	88.3 (3)	O(30)–Ti–N(21)	87.4 (3)
O(40)–Ti–O(50)	113.3 (3)	O(40)–Ti–N(11)	86.3 (3)
O(40)–Ti–N(21)	85.4 (3)	O(50)–Ti–N(11)	96.4 (3)
O(50)–Ti–N(21)	99.4 (3)	N(11)–Ti–N(21)	164.1 (3)
Ti–O(30)–C(31)	171.5 (6)	Ti–O(40)–C(41)	167.3 (6)

The ^{1}H NMR spectrum of **2** is straightforward. Interpretation of the infrared spectrum is not straightforward with a number of bands in the 850–1050-cm^{-1} region. However, a band at 930

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Table III. Crystallographic Data for **2**

$TiO_3N_4C_{48}H_{64}$
fw: 792.97
$a = 24.597\ (4)$ Å
$b = 12.962\ (1)$ Å
$c = 29.373\ (4)$ Å
$\beta = 102.524\ (7)°$
$V = 9142\ (4)$ Å^3
$Z = 8$

space group: $C20/c$ (no. 15)
$T = 21$ °C
$\lambda = 0.70930$ Å
$\rho_{calc} = 1.152$ g cm^{-3}
$\mu = 2.25$ cm^{-1}
$R(F_o) = 0.059$
$R_w(F_o) = 0.065$

cm^{-1} is shifted to 891 cm^{-1} when $^{18}OH_2$ was used in the synthesis of **2**. Much smaller shifts were observed (≤5 cm^{-1}) for the remaining bands, and hence we assign the band at 930 cm^{-1} as being due to the terminal titanium–oxo stretching frequency.

Experimental Section

Synthesis of $Ti(O)(OAr\text{-}2,6Pr^i{}_2)_2(NC_5H_4\text{-}4NC_4H_8)_2$ (2). To a solution of $Ti(OAr\text{-}2,6Pr^i{}_2)_2[Bu^tNC(CH_2Ph)_2](py)$ (**1**) (0.50 g, 0.67 mmol) in benzene (25 mL) was added 4-pyrrolidinopyridine (0.30 g, 2.01 mmol). The mixture was stirred vigorously while water (12.1 μL, 0.67 mmol) was slowly added. After the mixture was stirred for 12 h, the benzene solvent was allowed to evaporate down slowly whereupon yellow crystals of the product began to form. The crystals were washed with hexane and dried under vacuum. Yield = 0.27 g (50%). Anal. Calcd for $TiC_{48}H_{64}N_4O_3$, (**2**)·C_6H_6: C, 72.71; H, 8.14; N, 7.07. Found: C, 71.85; H, 9.05; N, 7.29. ^{1}H NMR (C_6D_6, 30 °C): δ 3.23 (septet, C*H*Me$_2$), 1.29 (d, CH*Me*$_2$), 8.55 (d, ortho protons on pyridine ring), 6.11 (d, meta protons on pyridine ring), 2.68 (d), 1.36 (d, ortho and meta protons on pyrrolidine ring). Infrared (Nujol mull): ν(Ti–O), 930 cm^{-1}; ν(Ti–^{18}O), 891 cm^{-1}. Other IR bands (cm^{-1}): 3056 (w), 3022 (w), 2956 (s), 2924 (s), 2854 (s), 1612 (s), 1532 (s), 1484 (m), 1460 (s), 1434 (s), 1412 (s), 1378 (w), 1342 (w), 1330 (m), 1270 (s), 1224 (m), 1210 (m), 1180 (w), 1158 (w), 1110 (w), 1096 (w), 1066 (w), 1042 (w), 1014 (s), 930 (m), 894 (m), 874 (w), 816 (w), 804 (w), 748 (m), 706 (w), 682 (m), 660 (w).

$Bu^tN(H)CH(CH_2Ph)_2$. The organic amine was obtained from the hydrolysis supernatant by preparative TLC on silica eluted with a 1:1 benzene/hexane mixture. Yields typically were 70–85%. ^{1}H NMR (C_6D_6, 30 °C): δ 3.36 (broad, N*H*), 3.13 (quintet, C*H*(CH$_2$Ph)$_2$), 2.72 (AB pattern of doublets, CH(C*H*$_2$Ph)$_2$), 0.91 (s, C*Me*$_3$), 6.8–7.3 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): 29.5 (C*Me*$_3$), 51.1 (*C*Me$_3$), 43.8 (*C*H$_2$Ph), 56.1 (C*H*), 126.3, 128.5, 130.0, 140.5 (CH$_2$*Ph*). High-resolution MS: calcd for $C_{19}H_{25}N$, 268.2065; found, 268.2061.

Crystallographic Studies

Selected crystal data and data collection parameters are collected together in Table III. A suitable crystal was mounted in a glass capillary in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement by using the scattering angles of 25 reflections in the range 14.3° < θ < 17.2° as measured by the computer-controlled diagonal slit method of centering. Systematic absences and subsequent least squares refinement indicated the space group $C2/c$ (no. 15). The data were collected at room temperature by using the ω–θ scan technique. The scan rate varied from 2 to 20°/min in ω, and data were collected to a maximum 2θ of 45°. Moving-crystal, moving-counter background counts were made by scanning an additional 25% above and below the scan width. The counter aperture was adjusted as a function of θ. For intense reflections an attenuator (factor 12.9) was automatically inserted in front of the detector. As a check on crystal and electronic stability, three standard reflections were remeasured every 5000 s of beam time. No decay in standards was observed.

The structure was solved by using the Patterson heavy-atom method to reveal the position of titanium atoms. The remaining heavy atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structures, but their positions were not refined. All calculations including the full-matrix least-squares refinement were performed by using Enraf-Nonius' SDP on a VAX computer.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063) for support of this research.

Registry No. 1, 109284-20-0; 2, 121919-40-2; *t*-BuNC(CH$_2$Ph)$_2$, 121935-24-8; *t*-BuN(H)CH(CH$_2$Ph)$_2$, 121935-25-9.

Supplementary Material Available: Listings of crystal data and data collection parameters, hydrogen atom parameters, anisotropic thermal parameters, and full bond distances and angles (14 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Temperature, Pressure, and Electrolyte Dependence of the Ferrocene/Ferrocenium Electron Self-Exchange in CD_3CN

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Received May 1, 1989

We are studying the effects of elevated pressures on electron-transfer kinetics,[1,2] and the classic system ferrocene–ferrocenium is of interest. Wahl and co-workers[3] made an extensive study at atmospheric pressure via NMR spectroscopy some years ago. In the course of our research it appeared that our rate constants were somewhat larger than those reported by Wahl. Some results reported by Weaver et al.[4] also indicate a systematic difference with the earlier values. We have reinvestigated the system using 200-MHz NMR spectroscopy primarily in the hope of obtaining some more precise k values, which would be helpful in our elevated pressure work.

It is believed that ΔV^* measurements on a variety of electron-transfer reactions will aid in testing theories and providing more insight into detailed mechanisms. The ferrocene–ferrocenium case is attractive because formally 0/+1 interaction is involved and interpretation of the results may be facilitated in comparison to that of reactions involving more highly charged reactants. Unfortunately, there are experimental difficulties, particularly because of the fast exchange rate, which makes it hard to obtain extensive and/or precise ΔV^* values. We report here our best efforts in this case.

Experimental Section

Materials. Ferrocene (Fe(cp)$_2$) was purchased from Alfa Chemical Co. and was twice vacuum-sublimed. $Fe(cp)_2PF_6$ was prepared according to the literature.[3] Anal. Calcd: C, 36.29; H, 3.05; P, 9.35; F, 34.44. Found: C, 36.33; H, 2.97; P, 9.20; F, 32.33. The characteristic absorption band of ferrocenium was found at 617 ± 1 nm. The extinction coefficient was determined, from three independent experiments at 617 nm, to be 513.3 ± 9.5 M^{-1} cm^{-1} in acetonitrile under an argon atmosphere. Acetonitrile-d_3 was obtained from MSD Isotopes Merck, dried over 4-Å molecular sieves (activated at about 200 °C under vacuum), degassed by three freeze–pump–thaw cycles, and stored in an evacuated bulb in the dark until used. $Co(cp)_2PF_6$ was obtained from Strem Chemicals and used without further purification.

^{1}H NMR Measurements at 1 atm. Details of the sample preparations are given in ref 5. Proton NMR spectra were collected on a Nicolet NT200WB instrument. The aquisition parameters were a 4.5-μs pulse width, a 500-ms postaquisition delay, a 14 000-Hz sweep width, a 32K block size, and 500–4000 scans. Temperature readings were calibrated by using the method of Raiford et al.[6], corrected to 200 MHz, by adding a capillary of methanol to the experimental sample. The self-exchange rate was found to lie near the "fast-exchange" region. Therefore, the rate constants for electron exchange could be determined from eq 1,[3] where

$$k = \frac{4\pi x_D x_P (\delta\nu)^2}{(W_{DP} - x_P W_P - x_D W_D)C_{tot}} \tag{1}$$

x_D and x_P are the mole fractions of diamagnetic and paramagnetic species, W_{DP}, W_P, and W_D are the NMR line widths (hertz) at half-height for the mixed, pure paramagnetic, and pure diamagnetic samples, respectively, $\delta\nu$ is the difference in resonance frequency (hertz) between

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0020-1669/89/1328-3604$01.50/0