Table III. Orbital Exponents (Contraction Coefficients of Double-ζ Expansion Given in Parentheses) and Energies Used in the Extended Hückel Calculations

atom	orbital	ζ_i (c_i)	H_{ii}, eV
Cu	4s	2.20	-11.40
	4p	2.20	-6.06
	3d	5.95 (0.5770), 2.10 (0.6168)	-14.00
S	3s	1.817	-20.00
	3p	1.817	-13.30
Cl	3s	2.033	-30.0
	3p	2.033	-15.0
O	2s	2.275	-32.30
	2p	2.275	-14.80

$(\epsilon_1 - \epsilon_2)^2$. Neglecting the "other terms" and introducing the fitting parameters in eq 8, we obtain semiempirical estimates of the two-electron terms K_{ab} = 1196 cm^{-1} and $J_{aa} - J_{ab}$ = 324 cm^{-1}, to be compared with the ab initio value K_{ab} = 720 cm^{-1} calculated by Charlot et al.[43] for an oxalato-bridged dinuclear compound.

Concluding Remarks

The extent of the twisting distortion (α) in Cu(II) dinuclear complexes with C_2X_4 bridging ligands is found to depend on the nature of the X atoms: the less electronegative X is, the greater the importance of the distortion is. Inclusion of the C_2X_4 fragment into a larger ligand, as in bipyrimidine or benzoquinone, reduces the extent of the distortion. For the analogous Ni(II) complexes with one less electron per metal atom, the planar structure is preferred.

The driving force for the bending of the basal plane of the metal relative to the plane of the C_2X_4 bridge is the strengthening of the metal-axial-ligand bond, for both Cu(II) and Ni(II) complexes. According to this conclusion, when two equivalent axial ligands are present, no bending occurs. This bending has a small effect on the magnetic exchange interactions: the magnetic coupling becomes less antiferromagnetic when the bending angle γ is increased.

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Appendix: Computational Details

The qualitative theoretical discussions in this paper are substantiated by molecular orbital calculations of the extended Hückel type[47] with a modified Wolfsberg-Helmholz formula.[48] Atomic parameters used are shown in Table III.[3,47]

Calculations were performed for the following model complexes: (A) $[(H)_2Cu(\mu\text{-}C_2O_4)Cu(H)_2]^{n-}$ (n = 2, 0); (B) $[Cl(H)_2Cu(\mu\text{-}C_2O_4)Cu(H)_2Cl]^{n-}$ (n = 4, 2); (C) $[(H)_2Cu(\mu\text{-}C_2S_4)Cu(H)_2]^{2-}$; (D) $[(H)_2Cu(\mu\text{-}\mathbf{5})Cu(H)_2]^{2-}$; (E) $[(H)_2Cu(\mu\text{-}\mathbf{6})Cu(H)_2]^{n-}$. Bond distances (Å) and angles used for A and B: Cu-O = 2.00, Cu-H = 1.70, Cu-Cl = 2.60, C-C = 1.54, C-O = 1.25; CCO = 117, HCuH = 90°. Bond distances (Å) and angles (deg) used for C: Cu-S = 2.26, Cu-H = 1.80, C-C = 1.47, C-S = 1.70; CCS = 120. Bond distances (Å) and angles (deg) used for D and E: Cu-O = 1.95, Cu-N = 2.00, C-C(ring) = 1.37, C-C(inter-ring) = 1.47, C-N = 1.37, C-H = 1.08; CCO = 115, ring angles = 120.

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Contribution from the Monsanto Company,
St. Louis, Missouri 63167

Oxygen-Stable Ferrocene Reference Electrodes[1]

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Reference electrodes (RE's) play an important role in electrochemistry, but standard designs suffer from limitations. Ferrocene derivatives have been reported to serve as alternative RE's, but they suffer from poor stability to oxygen, water, and nonaqueous solvents. The previously described ferrocene-based RE's are unstable due to the reaction of ferrocenium ion (Fc^+) with dioxygen. We have found that sufficient methyl substitution of the cyclopentadienyl rings can render ferrocenium stable to O_2, and ring-methylated Fc^+ analogues may be used to fabricate stable RE's. A bis(pentamethylcyclopentadienyl)iron reference electrode is described; its potential is pH independent in aqueous buffer solutions. Unlike any other ferrocene electrodes previously reported, these electrodes are stable in aqueous solvents in air. A new reference standard for use under aerobic conditions is proposed.

Reference electrodes (RE's) are ubiquitous in electrochemistry, being necessary components of pH probes and other electrochemical sensors. Commonly used reference electrodes (e.g., the saturated calomel electrode (SCE) or the silver/silver chloride electrode) contain an aqueous internal filling solution. At high pressures, the solution being tested may leak back into the reference electrode compartment, contaminating the internal reference solution. This problem may be eliminated by internal pressurization of the reference electrode, but this significantly complicates electrode design and increases cost. In addition, aqueous reference electrodes are not well-suited for use in nonaqueous solvents, since unknown and irreproducible liquid-junction potentials exist between the aqueous and nonaqueous phases. Furthermore, contamination of the sample by water and other ions associated with the reference electrode may occur. For nonaqueous electrochemistry, IUPAC recommends[2] the use of a redox couple such as ferrocene/ferrocenium ion (Fc/Fc^+) as an internal standard. The Fc/Fc^+ couple is an appropriate choice because its potential is largely independent of the solvent.

An alternative to the liquid junction electrode is one based on an entirely solid-state design. Peerce and Bard[3] elegantly fabricated such an electrode by coating poly(vinylferrocene) (PVFc) on platinum. The polymer-coated electrode was brought to a 1:1 ratio of ferrocene to ferrocenium by poising the electrode at the $PVFc/Fc^+$ half-wave potential (0.39 V vs SCE). Although this electrode maintained a constant, reproducible potential in deaerated acetonitrile over 21 h, it was unstable in other nonaqueous solvents, including benzonitrile, DMF, and methanol. The electrode's rapid potential drift in these solvents was attributed to gradual dissolution of $PVFc^+$, and it was predicted that higher molecular weight PVFc should be more useful in a wide range of solvents. In aqueous solution, the potential of the PVFc electrode drifted 150 mV overnight, even with deaeration.

Cross-linking strategies for PVFc were employed by Kannuck and co-workers[4] to prepare RE's with no solubility problems, but

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Table I. Cyclic Voltammetry of Ferrocene Derivatives[a]

		N_2 satd				
sample	concn, mM	scan rate, mV/s	$E_{1/2}$[b]	ΔE_p[c]	$i_{p,c}/i_{p,a}$	O_2 satd $i_{p,c}/i_{p,a}$
Fc	10	25	0.013	0.099	0.97	0.81
1,1′-Me_2	8.2	25	−0.052	0.088	0.94	0.80–0.87
1,1′-$(CO_2H)_2$	10	25	0.431	0.088	0.94	0.84
vinyl	10	25	0.030	0.104	1.04	0.56
OMFc	1.3	100	−0.369	0.161	1.08	0.97–1.08
DMFc	12	25	−0.374	0.177	1.02	1.02
PVFc/Pt		100	0.055	0.185	1.06	*d*
FcPVBC/Pt		100	0.320	0.269	1.04	*d*

[a] The solvent was MeCN, with 0.1 M Bu_4NBF_4 as supporting electrolyte, except for 1,1′-dicarboxyferrocene, which was analyzed at pH 7 in an aqueous phosphate buffer. [b] Volts vs Ag pseudo-RE in MeCN, vs standard Ag/AgCl electrode in water. [c] ΔE_P (volts) is the difference between the anodic and cathodic peak potentials; *iR* compensation was not employed. [d] For the thin-film electrodes, the characteristic Fc/Fc^+ cyclic voltammogram completely disappeared within 25 scans in O_2-saturated MeCN.

this design still suffered from poor stability (lifetimes of 24 h in MeCN and 7 h in H_2O). In a related study, Haimerl and Merz[5] prepared reference electrodes by electrochemically copolymerizing vinylferrocene and vinylpyrrole onto platinum. The electrodes were found to be stable for several hours in deaerated acetonitrile but unstable in the presence of air. Clearly, polymer solubility was not the only important contributor to the stability of these ferrocene-based electrodes, and because of our interest in robust solid-state sensor electrodes, we investigated this problem.

Fc^+ is a stabilized 17-electron radical that is stable in aqueous acid but decomposes in neutral or basic solution to give ferrocene and iron hydroxides.[6] The decomposition of Fc^+ solutions was noted by Wahl,[7] Sato[8] used CV to show that DMSO solutions of Fc^+ rapidly decompose in the presence of O_2, and the irreversible behavior of Fc^+ in hydroxylic solvents has been described.[9] Thus, a poised $PVFc/Fc^+$ electrode exposed to air to pH ≥ 7 would be expected to drift as Fc^+ is consumed and would therefore fail in any practical applications. We note that enzyme sensors employing Fc as an electron-transfer mediator may also be expected to drift under circumstances where the decomposition of Fc^+ can compete with its reduction.

It is known that cobaltocene reacts with O_2 via attack on the cyclopentadienyl (Cp) ring.[10] We therefore postulated that Fc^+ reacts in a similar manner and that alkylation of the Cp rings[11] could stabilize Fc^+ to the point where it could be used to prepare robust RE's of practical utility. We report here the discovery that sufficient alkylation of the Cp rings prevents the reaction of ferrocenium ion with oxygen. In addition, we describe the first ferrocene-derived reference electrodes that are stable in air and water.

Results

Cyclic Voltammetry. Cyclic voltammetry (CV) was used to investigate whether dioxygen reacts on an electrochemical time scale with various monomeric and polymeric ferrocene derivatives. The conclusions based on electrochemical measurements were supported by results from spectroscopic studies and GC/MS analysis of the products of the Fc^+/O_2 reaction. The CV results are summarized in Table I. Under anaerobic conditions, the ratio of cathodic to anodic peak currents ($i_{p,c}/i_{p,a}$) was unity within experimental error for all compounds tested. Since no significant background current was observed under O_2, a value of $i_{p,c}/i_{p,a}$ below unity indicates that the oxidized species is consumed in the course of the CV measurement. As the $i_{p,c}/i_{p,a}$ values in Table I show, the oxidized forms of ferrocene, ferrocene-1,1′-dicarboxylic acid, vinylferrocene, and 1,1′-dimethylferrocene do react with oxygen on the CV time scale (scan rates between 25 and 100 mV/s). In contrast, octamethyl- and decamethylferrocenium ($OMFc^+$ and $DMFc^+$) show no measurable reaction with dioxygen under similar conditions. In fact, we have found air-saturated MeCN solutions of decamethylferrocenium hexafluorophosphate to be stable for over 3 years. As seen from Table I, there is no correlation between the half-wave potential and ferrocenium ion stability. However, alkyl substitution of the Cp rings of Fc^+ leads to increased kinetic stability. We note that, given the air-sensitive nature of Fc^+, it would be advantageous to employ ferrocenium as a chemical oxidant under an inert atmosphere.

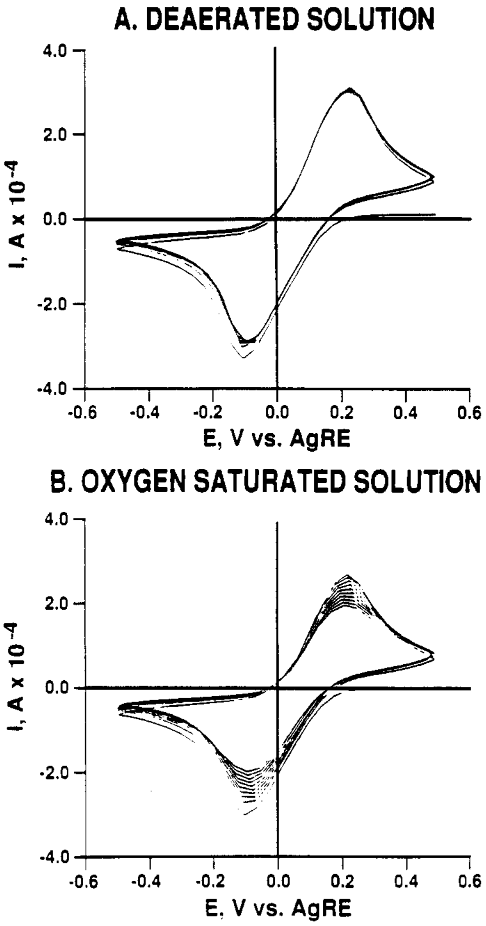

Figure 1. Cyclic voltammograms of poly(vinylferrocene) films deposited on Pt wire: (A) in the absence of O_2; (B) in the presence of O_2. Conditions: 0.1 M Bu_4NBF_4 in MeCN; scan rate 100 mV/s. See Table I for $E_{1/2}$, ΔE_p, and $i_{p,c}/i_{p,a}$.

The cyclic voltammograms of poly(vinylferrocene) (PVFc) on Pt in the absence and presence of oxygen are shown in Figure 1. The peak current is stable under anaerobic conditions. The decrease in peak current with each cycle for the oxygen-saturated solution demonstrates the rapid reaction of ferrocenium with dioxygen in acetonitrile. Similar results for a polymer (FcPVBC) prepared by quaternizing (dimethylamino)ferrocene with poly(vinylbenzyl chloride) are given in the supplementary material, along with a kinetic study for the O_2/FcPVBC reaction as determined by double potential step chronoamperometry (DPSC).[12]

Ferrocene/Ferrocenium Carbon Paste Electrodes. The stability of decamethylferrocene and ferrocene carbon paste electrodes, as well as an unloaded carbon paste electrode, was measured in air-saturated standard buffer solutions from pH 2 to 10. Figure

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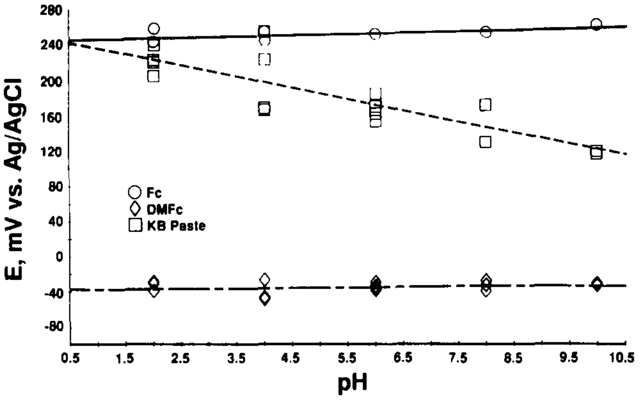

Figure 2. pH response of carbon paste electrodes loaded with Ketjenblack carbon alone (KB paste), carbon plus Fc/$FcPF_6$, and carbon plus DMFc/$DMFcPF_6$.

2 shows a plot of electrode potential of the paste electrodes vs pH taken over a 2-day period. Both loaded electrodes exhibit potentials essentially independent of pH ($E_{DMFc} = -35.6$ mV, $E_{Fc} = 252.7$ mV (mean values)), while the unloaded paste electrode shows a pH dependence of ca −13 mV/pH.

Clearly, at the loading levels used, the ferrocene/ferrocenium couple (decamethyl or unsubstituted) dominates the electrode potential, accounting for the lack of pH response. The pH independence of the DMFc/$DMFc^+$ paste electrode potential and its stability in air were expected because of the stability of the decamethylferrocenium ion described above. The stability of the ferrocene paste electrode may be explained by the fact that the paste is essentially an infinite reservoir of ferrocene and ferrocenium ions in a hydrophobic matrix. As the ferrocenium ion is consumed at the paste/buffer interface (by reaction with O_2 or hydroxide), it is replenished from the bulk. Since the potential of the electrode is determined at the interface, a constant potential was observed over the course of our measurements. In the case of PVFc/Fc^+ electrodes composed of a thin film of electroactive polymer coated on a Pt wire, the reservoir of Fc^+ is finite, and decomposition of Fc^+ leads to a drift in potential.

The use of a DMFc/$DMFc^+$ carbon paste electrode as an RE requires that it be stable to oxidation or reduction from components in the test solution. In cases where such reactions could occur, i.e in the presence of Ag^+ or $FeCl_4^-$, the electrode should be isolated from the test solution with a porous frit, as is the convention with standard RE's (e.g. Ag/AgCl or I/I_2).

Reference Electrodes for Nonaqueous Electrochemistry. The above results lead us to conclude that the air-stable DMFc/$DMFc^+$ couple could have some advantages over Fc/Fc^+ as a reference couple for nonaqueous electrochemistry, especially in the presence of oxygen. We recommend two methods for utilizing the DMFc/$DMFc^+$ couple as a reference standard. First, by analogy with Gritzner and Kuta,[2] DMFc may be added as an internal standard to the test solution. An alternative method, which avoids contamination of the test solution, is to construct a compartmentalized reference electrode with a porous frit junction. For example, equimolar amounts of DMFc and $DMFcPF_6$ are dissolved to give a 0.004 M solution in MeCN that contains the supporting electrolyte. The reference solution is added to a glass tube with a porous frit at one end, a Pt wire is inserted into the tube, and the electrode is inserted into the MeCN test solution. Similar reference electrodes may be prepared for a variety of solvents. This technique allows electrochemical potentials to be measured in aerated solvents. More general use of DMFc/$DMFc^+$ as a reference will require comparisons of pseudothermodynamic reference potentials over a range of solvents.

Conclusions

It has been demonstrated that, unlike the ferrocenium ion itself, octa- and decamethylferrocenium ions are stable to molecular oxygen in solution at room temperature. In addition, it has been shown that the reported instability of ferrocene-based reference electrodes results from the reaction of the ferrocenium ion with dioxygen. These observations allow the construction of improved organometallic reference electrodes. A new reference standard for nonaqueous electrochemistry has been proposed for use under aerobic conditions, along with a mode of implementation. We are now exploring several extensions of this work, including ring-alkylated analogues of PVFc, for use in entirely solid-state designs, and O_2-stable ferrocenium derivatives with widely varying redox potentials, for use as stable electron-transfer mediators in enzyme electrodes.

Experimental Section

Materials and Methods. Ferrocene and its derivatives were obtained from Strem Chemicals (Newburyport, MA), except for octamethylferrocene, which was prepared by the literature procedure.[13] Poly(vinylferrocene) coatings on Pt wire were prepared by the published method of Peerce and Bard.[3]

Electrochemical Apparatus and Procedures. Cyclic voltammetry was performed on computer-controlled equipment described previously.[14] Electrode potential measurements in aqueous buffers were made by using a Fisher Scientific ACCUMET pH meter. Electrochemistry was performed in MeCN or THF (Burdick and Jackson) with 0.1 M tetrabutylammonium tetrafluoroborate (Southwest Analytical) as supporting electrolyte, except for measurements of 1,1′-dicarboxyferrocene, which were done in water (pH 7, phosphate buffer). Standard buffer solutions (Fisher Scientific) were employed when the pH stability of the reference electrodes was tested.

Electrode Preparation. Carbon paste was prepared by mixing 2 g of Ketjenblack carbon (Akzo Chemie American, Chicago, IL) with 24 mL of high-purity mineral oil (Aldrich). The loaded ferrocene/ferrocenium carbon pastes were prepared by grinding together 0.1 g of the ferrocenium salt with 0.1 g of the ferrocene compound followed by mixing with ca. 0.1 g carbon paste. Carbon paste electrodes were fabricated by using heat-shrinkable Teflon to form a small cup at the end of a platinum-disk electrode. The cup was packed with the paste and smoothed with a small spatula.

Acknowledgment. We thank a reviewer for his helpful comments.

Supplementary Material Available: A textual presentation of the details for the synthesis of FcPVBC, the chemical oxidation of (vinyl)Fc, and the reaction of Fc^+ with O_2 on a preparative scale and the descriptions of CV and additional electrochemical studies and graphs for the DSPC and CV analyses (9 pages). Ordering information is given on any current masthead page.

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