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ELECTROCHEMICAL OXIDATIONS OF VARIOUS INDENYL—IRON COMPLEXES

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Summary

The preparation of several diindenyliron and cyclopentadienyl(indenyl)-iron species is reported, and their relative eases of oxidation is determined by cyclic voltammetry to be: $Ind_2Fe > (Ind)(Cp)Fe > Cp_2Fe$; and $(1,3\text{-}Me_2\text{-}Ind)_2Fe > (1\text{-}MeInd)_2Fe > Ind_2Fe$.

Introduction

Ferrocene is known to undergo one electron oxidation to give the ferricenium ion, $Fe(C_5H_5)_2^+$; chemical reagents such as HNO_3 are appropriate to carry out this conversion [1]. This reaction has also been investigated by various electrochemical techniques, with an $E_{1/2}$ for the ferrocene—ferricenium ion couple being assigned a value of +0.31 to 0.34 V vs. SCE, in acetonitrile [2] or 90% ethanol [3-5].

An extraordinary amount of work has been done on the electrochemistry of substituted ferrocenes [3-5] and various correlations of oxidation potential values with numerical parameters associated with the substituent groups have been made with some success [4,5]. As might be expected electron-donating substituents facilitate the ease of oxidation of the complex and electron-withdrawing groups impede the process. For example, substitution by one and then a second methyl group (an electron donor vs. hydrogen) causes a moderate decrease in the $E_{1/2}$ value for this oxidation.

No studies on oxidations of indenyliron complexes have yet been reported, except for brief mention of the oxidation of diindenyliron [6]. It might be assumed, of course, that the oxidation of indenyliron complexes should be well defined processes since the indenyl and cyclopentadienyl ligands are congeners. There is a report concerning the reduction of the diindenylcobalt(III) cation [7]; the $E_{1/2}$ value for this process shows that this species is harder to reduce than is the cobalticenium ion in formamide. Conversely, then, the neutral diindenylcobalt complex is easier to oxidize than cobaltocene.

In conjuction with other work [8,9] we had the opportunity to prepare several indenyliron complexes. It seemed appropriate to look at the various oxidation processes of these species.

Experimental

Prepared by published methods were: diindenyliron [10], cyclopentadienyl(indenyl)iron [8], and bis(1,3-dimethylindenyl)iron [9]. 1-Methylindene was prepared from lithium indenide and methyl iodide. Other syntheses are described below. Instruments used in the characterization of these species were: PMR: Varian T-60; mass spectra: AEI MS-9. Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Cyclic voltammetry data were obtained using a PAR-Model 170 electrochemistry apparatus and are given in Table 1. A cell having the conventional three electrode geometry was used; this was constructed with a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (aq. KCl) reference electrode.

Synthesis of (MeInd)$_2$Fe

This black compound was prepared from Li[1-MeInd] and $FeCl_2$ in a manner analogous to the preparation of $(Ind)_2Fe$ [10]; yield, 45 %, m.p. 76-80° (dec.). Identification was made by peak mass match from the high resolution spectrum. Found: 314.07558[*]. $^{12}C_{20}{}^{1}H_{18}{}^{56}Fe$ calcd.: 314.07575.

PMR spectrum (CS_2). The PMR spectrum showed the presence of approximately equal amounts of two isomers (expected because of the dissymmetry imposed by the methyl groups of this species): δ(ppm) 1.84 s and 2.03 s, int. 3, CH_3; 3.74 (2 overlapping doublets, $J = 2$ Hz), 4.15 (d, $J = 2$ Hz) and 4.26 (d, $J = 2$ Hz) total intensity 2, protons on C(2) and C(3); 6.86 s int. 4, protons on C(4), C(5), C(6), C(7). Attempts to separate these isomers were unsuccessful.

Synthesis of MeCp(Ind)Fe

This compound was prepared in a manner similar to that described for the preparation of Cp(Ind)Fe [8], from Na[MeCp] and Ind_2Fe, in 62% yield; m.p. 42-43°C. Anal.: Found: C, 72.13; H, 5.49; Fe, 22.36; mol. wt. 250 (by mass spec.) $C_{15}H_{14}Fe$ calcd.: C, 72.03; H, 5.64; Fe, 22.33%. Parent peak mass match: Found: 250.04540; $^{12}C_{15}{}^{1}H_{14}{}^{56}Fe$ calcd.: 250.04440.

PMR spectrum (CS_2): δ(ppm) 1.53 s int. 3, CH_3; 3.47 (t, $J = 2$ Hz) int. 2 and 3.60 (t, $J = 2$ Hz) int. 2, C_5H_4 protons; 3.90 (t, $J = 2$ Hz) int. 1, indenyl C(2) proton; 4.87 (d, $J = 2$ Hz) int. 2, indenyl C(1) and C(3) protons; 6.84 m, int. 2, and 7.35 m int. 2 indenyl C(4), C(5), C(6), and C(7) protons.

Synthesis of Cp(1-MeInd)Fe

This was also carried out in a manner similar to that described in the literature for Cp(Ind)Fe [8], except prolonged refluxing of the reactants (5 h)

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[*] No impurities were detectable by PMR.

was necessary. Purification by chromatography on alumina separated the product, a purple-colored oil (12%) from the black starting material, (1-MeInd)$_2$Fe (18% recovery). Identification was made by parent peak mass match in the high resolution mass spectrum. Found 250.04452. $^{12}C_{15}{}^{1}H_{14}{}^{56}Fe$ calcd.: 250.04440.

PMR spectrum (CS$_2$). δ(ppm) 2.38 s, int. 3, CH_3; 3.51 s, int. 5, C_5H_5; 3.85 (d, J = 2 Hz) int. 1 and 4.62 (d, J = 2 Hz) int. 1, indenyl C(2) and C(3) protons: 6.80 m int. 2 and 7.40 m, int. 2, indenyl C(4), C(5), C(6) and C(7) protons.

Attempted synthesis of Cp(1,3-Me$_2$Ind)Fe

Refluxing of NaCp and (1,3-Me$_2$Ind)$_2$Fe in tetrahydrofuran for 4 h gave no product, but 50% starting material recovery and decomposition.

Discussion

The syntheses of the diindenyliron and cyclopentadienyl(indenyl)iron species were accomplished by the routes defined in eqns. 1 and 2.

$$FeCl_2 + 2Li[C_9H_5R_2] \rightarrow (C_9H_5R_2)_2Fe + 2LiCl \quad (1)$$

$$(C_9H_5R_2)_2Fe + Na[C_5H_4R'] \rightarrow (C_5H_4R)(C_9H_5R_2)Fe + Na[C_9H_5R_2] \quad (2)$$

R_2 = H, H; H, Me; Me, Me; R' = H, Me

The compound (1-MeInd)$_2$Fe was formed as a mixture of two geometric isomers, in approximately equal amounts according to the PMR spectrum. The two isomers differ in the relative orientation of the two methyl groups.

One-electron oxidations were observed for each of the indenyliron complexes using cyclic voltammetry, with CH_2Cl_2 as a solvent. The potentials for these oxidations, measured as the average of the cathodic and anodic peak voltages, ($E_{1/2} = \frac{1}{2}[E_{p,a} + E_{p,c}]$ vs. SCE (sat. KCl)) are recorded in Table 1. Also included are data for the oxidation of ferrocene in this solvent. It may be observed that this $E_{1/2}$ value for ferrocene, 0.488V vs. SCE, is dissimilar to the values for this oxidation measured in other solvents. This is not unexpected, however; the difference between values in different solvent systems results from the different ligand junction potentials between solvent and the aqueous medium in

TABLE 1

CYCLIC VOLTAMMETRY DATA ON INDENYL- AND CYCLOPENTADIENYL-IRON COMPLEXES[a]

Compound	$E_{p,a}$	$E_{p,c}$	$E_{p,a}-E_{p,c}$	$\frac{1}{2}[E_{p,a} + E_{p,c}]$
(Cp)$_2$Fe	0.510	0.465	0.045	0.49
(MeCp)$_2$Fe	0.425	0.345	0.080	0.39
(Cp)(Ind)Fe	0.375	0.325	0.050	0 35
Cp(1-MeInd)Fe	0.338	0.283	0.052	0.31
(MeCp)IndFe	0.316	0.264	0.052	0.29
(Ind)$_2$Fe	0.243	0.181	0.062	0.21
(1-MeInd)$_2$Fe	0.164	0.084	0.080	0.12
(1,3-Me$_2$Ind)$_2$Fe	0.049	−0.017	0.066	0.02

[a] Cathodic and anodic peak potentials in volts vs. saturated calomel electrode (aq. KCl). Solutions in CH_2Cl_2 (5×10^{-3} *M*) with $[n\text{-}Bu_4N]ClO_4$ (0.1 *M*) as base electrolyte. Scan rate = 200 mV sec^{-1}.

the reference electrode. Nonetheless, comparisons made here between oxidations of complexes in the same solvent (CH_2Cl_2) are valid.

These data indicate that the ease of oxidation, as measured by the $E_{1/2}$ values, increases with replacement of a cyclopentadienyl ligand by an indenyl ligand. Thus in the series Cp_2Fe, Cp(Ind)Fe, $(Ind)_2Fe$, the measured $E_{1/2}$ values are 0.49, 0.35 and 0.21 V. A similar series of methylcyclopentadienyl complexes were recorded: $(MeCp)_2Fe$, 0.39 V; MeCp(Ind)Fe, 0.29 V; $(Ind)_2Fe$, 0.21 V. These data are in accord with the earlier observations concerning the relative ease of cobaltocenium and diindenylcobalt(III) reduction [7].

The methyl group, a better electron donating group than hydrogen, is expected to make the coordinated hydrocarbon a better donor to the metal, effecting negative charge build-up on the metal. This in turn would suggest that the tendency toward oxidation, the loss of an electron from a (primarily) metal orbital, should be enhanced. The series of $E_{1/2}$ values for $(Ind)_2Fe$, $(1\text{-MeInd})_2Fe$, and $(1,3\text{-Me}_2Ind)_2Fe$ are 0.21, 0.12, and 0.02 V, bearing out this assumption. A similar comparison between Cp(Ind)Fe (0.35 V) and Cp(1-MeInd)Fe (0.31 V) or MeCp(Ind)Fe (0.29 V) can also be made.

The $E_{1/2}$ values for all of these iron complexes suggest their facile oxidation can be accomplished even by weak oxidizing agents, and by analogy to ferrocene chemistry, it is not unreasonable to expect that the oxidized species should be isolable. However except for $(1,3\text{-Me}_2Ind)_2Fe$ which can be oxidized to a stable cation $[(1,3\text{-Me}_2Ind)_2Fe]^+$ using oxidizing agents such as $AgPF_6$ [9], our attempts to oxidize these complexes have so far not led to isolation of the oxidized species.

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