Electrochemical Investigations on Bis(azaborolinyl)–Cobalt and –Iron Sandwich Complexes [1]

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Sandwich complexes of Co and Fe with the azaborolinyl (Ab(R)) ligand and derivatives of it are studied with normal pulse-, differential pulse- and cyclic voltammetry at a Pt electrode in THF and CH_2Cl_2 *solutions, one-electron oxidations being observed. The oxidation process of* $[Ab(SiMe_3)]_2Co$ *is complicated by a substitution of the* $SiMe_3$ *group in* $[Ab(SiMe_3)]_2Co^+$ *by an alkyl group of the tetra-alkyl ammonium ion used as supporting electrolyte. The oxidation of the Fe-complexes in the case that R =* $SiMe_3$ *is nearly completely reversible; however with R = H or t-Bu the oxidized products are not stable. The observed trends in redox potentials can be explained with structural and electronic properties of the complexes.*

Introduction

Substitution of two adjacent C atoms in the cyclopentadiene ring by the isoelectronic B(R)N(R′)-group gives 1,2-azaboroline [2–11] from which compounds like $M[C_3H_3BMeNR']_2$, M = Co, Fe; R′ = $SiMe_3$, CMe_3 have been synthesized [6–10] and characterized. X-ray determinations [7–10] revealed the sandwich structure of these complexes. Hereafter, these complexes will be abbreviated as $[Ab(R)]_2M$ with R the substituent on the nitrogen. X-ray structure determinations have revealed that of the twenty possible isomers only three isomers are actually realized in the solid state. Of importance here are one isomer in which both ligand rings have the same –C–B–N–C– sequence (*e.g.* clockwise) and one isomer with opposite –C–B–N–C– sequences (*e.g.* clockwise and anti clockwise). (See Fig. 1). These isomers will be indicated with B–N, B′–N′ and B–N, N′–B′ respectively. Interconversion of the isomers is very unlikely while one ring has to

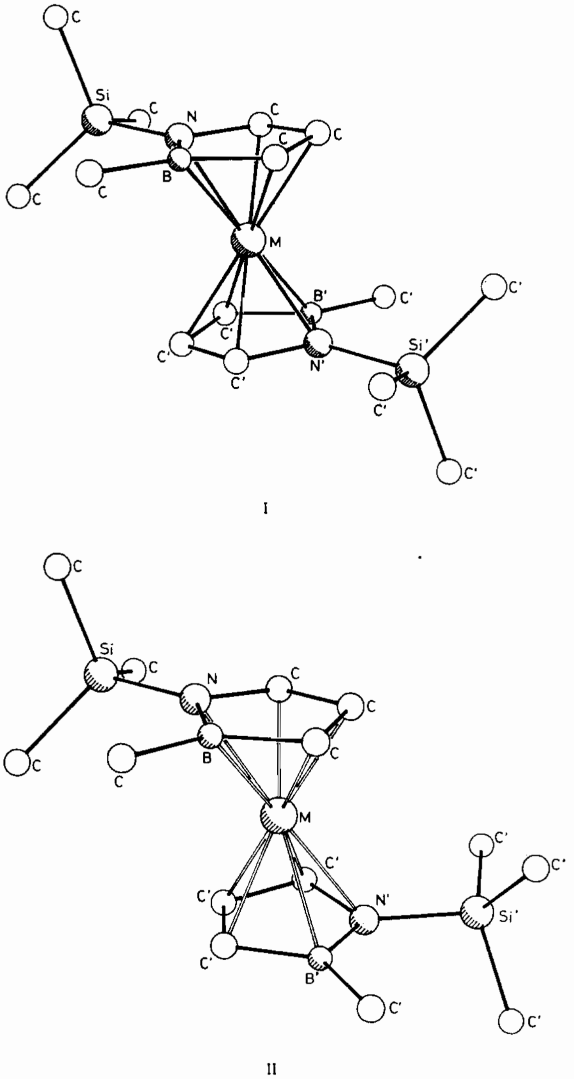

Fig. 1. Molecular structures of the $Co[Ab(SiMe_3)]_2$ Complexes with I. B–N, B′–N′ configuration; II. B–N, N′–B′ configuration.

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TABLE I. Electrochemical Data for the Oxidation of the Azaborolinyl Sandwich Complexes of Iron and Cobalt.[a]

Compound	Solvent	Pulse Voltammetry[b]			Differential Pulse Voltammetry[b]			Cyclic Voltammetry[c]			
		$E_{1/2}$ V	$E_{3/4} - E_{1/4}$ mV	i_d/c mA dm^3 mol^{-1}	E_p V	$w_{1/2}$ mV	i_p/c mA dm^3 mol^{-1}	$(E_{p,a} + E_{p,b})/2$ V	ΔE mV	i_b/i_f	i_p/c mA dm^3 mol^{-1}
$[Ab(t\text{-}Bu)_2Co$	THF	−0.35	85	70	−0.38	109	14	−0.34	70	1.0	59
$[Ab(Et)]_2Co^d$	THF^e	−0.42	66	32	−0.42	96	7	−0.42	92	1.0	33
$[Ab(n\text{-}Bu)]_2Co^d$	THF	−0.41	71	54	−0.39	102	10	−0.40	72	1.0	59
$[Ab(SiMe_3)]_2Co^f$ with B–N, N′–B′ sequence	THF				−0.24						
with B–N, B′–N′ sequence	THF	−0.22	72	68	−0.24	105	6	−0.23	101	0.88	64
mixture of both isomers	THF, CH_2Cl_2	−0.24	70	68	−0.24	95	10	−0.24	82	0.87^g	70
$[Ab(H)]_2Fe$	CH_2Cl_2	0.17	72	38	0.18	125	6	0.19	88	0.26	66
$[Ab(t\text{-}Bu)]_2Fe$	CH_2Cl_2	0.17	95	32	0.19	140	5	0.18	89	0.57	37
$[Ab(SiMe_3)]_2Fe^f$ with B–N, N′–B′ sequence	CH_2Cl_2	0.24	65	53	0.24	115	10	0.24	99	0.97	51
with B–N, B′–N′ sequence	CH_2Cl_2	0.24	66	64	0.24	113	13	0.23	97	0.94	65
mixture of both isomers	CH_2Cl_2, THF	0.23	57	45	0.23	115	11	0.23	113	0.9	70
$[C_5H_5]_2Fe$	THF	0.64	68	62	0.63	96	18	0.64	74	1.0	78
$[C_5H_5]_2Co$	THF	−0.73	61	48	−0.72	105	12	−0.72	68	1.1	54
	reduction	−1.84	53	55	−1.84	93	13	−1.83	70	0.8	66

[a] Potentials *vs.* Ag–AgI(CH_2Cl_2–Bu_4NI) reference electrode. For abbreviations and nomenclature see text. Supporting electrolyte 0.1 *M* Bu_4NClO_4. [b] Scan rate 5 mV/s; differential pulse amplitude 25 mV. [c] Scan rate 200 mV/s. [d] These complexes were generated *in situ* from $[Ab(SiMe_3)]_2Co$. [e] 0.05 *M* Et_4NClO_4 as supporting electrolyte. [f] This refers to C–B–N sequence of both ligands in one molecule: see text. [g] In CH_2Cl_2 this value is 0.96.

be turned 180 °C and therefore some metal-atom bands have to be broken. On the other hand it cannot be excluded that in solution the rings rotate, as in the temperature range from –120 °C to +90 °C no change in the ^{1}H NMR spectra can be observed [7].

In this paper we describe the electrochemical oxidation of some cobalt and iron complexes. Surprisingly the Co complex with R = $SiMe_3$ shows a substitution of R by an alkyl group from the tetra alkyl ammonium ion which is present in the solution as supporting electrolyte. The metallocenes, $[\eta^5\text{-}C_5H_5]_2Fe$ and $[\eta^5\text{-}C_5H_5)_2Co$ are included for comparison.

Experimental

The complexes were synthesized as described in the literature [6–8]. Electrochemical measurements were made with a three electrode Bruker E 310 instrument. Controlled potential electrolyses were carried out with a Wenking LB 75M potentiostat and a Birtley current integrator. Voltammograms were displayed on a X–Y recorder (BD 30 Kipp en Zonen, Delft), a Textronix 564 B storage oscilloscope or a Nicolet Explorer II model 206. Normal pulse (NP) and differential pulse (DP) voltammograms were obtained at a scan rate of 5 mV/s with a pulse frequency of 2 pulses per second; differential pulse amplitude was 25 mV. Cyclic voltammograms (CV) were taken with scan rates of (0.05–10 V/s. A platinum disk working electrode (geometric area 7.8 mm^2) and a platinum auxiliary electrode were used. Measurements were made on approximately 5 × 10^{-3} mol dm^{-3} complex solutions in CH_2Cl_2 or THF with 0.1 mol dm^{-3} Bu_4NClO_4 or Bu_4NPF_6 as supporting electrolyte. Potentials are referred to a Ag–AgI (0.05 mol dm^{-3} Bu_4NI; 0.4 mol dm^{-3} Bu_4NClO_4 in CH_2Cl_2) reference electrode [12]. This reference electrode was positioned as close as possible to the working electrode utilising a Luggin probe to minimize iR drop. No external iR compensation was employed. Only very small differences in potentials between THF and CH_2Cl_2 solutions were observed, at most 0.02 V. These may be ascribed to differences in liquid junction potentials or to not compensated iR losses. CH_2Cl_2 (p.a. Merck) was dried over 4 Å molecular sieve and used as such. THF was distilled from sodium-benzophenone mixtures as described before [13]. Both solvents were deoxygenated by freezing procedures. The potential range of the thus purified THF was –2.5 – +1.4 V and of the CH_2Cl_2 – 2.0 – +2.0 V. All manipulations were carried out in a glovebox in which a dry and oxygen-free nitrogen atmosphere was maintained.

Results

The cobalt and iron azaborolinyl sandwich complexes can be oxidized in a one electron transfer process. The electrochemical data including a comparison with cobaltocene and ferrocene are summarized in Tables I and II. The number of electrons n obtained from controlled potential electrolyses clearly show that these oxidations are one electron transfer processes. Also the various determined current functions, i_l/c, i_p/c and $i_p/v^{1/2}$, as compared with the metallocenes, indicate a one electron transfer, although for the last two parameters this comparison is strictly only valid for reversible cases. Despite some efforts no reductions of the neutral compounds were seen in THF solutions up to the limit of the potential range of the solvent.

Comparison of the isomers

By careful fractional sublimation procedures it is possible to separate although in small quantities, the two isomers in a pure form. As the data show there is no difference in the electrochemistry of these isomers and a mixture therefrom. So further experiments were made on the normally obtained isomeric mixtures.

It has to be noted that the occurrence of the different isomers has been observed only in the solid state.

Cobalt complexes $[Ab(R)]_2Co$, R = alkyl, $SiMe_3$

The alkyl substituted complexes exhibited a one electron oxidation wave, dependent on the substituent R in the potential range –0.35 to –0.42 V (NP). This is a chemically reversible process for in the cyclic voltammograms the peak current ratio i_b/i_f = 1. The complex with R = t-Bu was prepared as described elsewhere [8] whereas the complexes with R = n-Bu and Et were generated *in situ* from $[Ab(SiMe_3]_2Co$ (*vide infra*).

The electrochemical oxidation of $[Ab(SiMe_3)]_2$-Co occurred at *ca.* –0.23 V (NP) with Bu_4NClO_4 or Bu_4NPF_6 as the supporting electrolyte.

In the reverse scan of the cyclic voltammogram a new electrode process is observed (Fig. 2) at approximately –0.40 V (CV, $E_{p,c}$), indicating that a chemical follow-up reaction generated a new electro active species (EC-mechanism). Plots of peak current ratios (i_b/i_f) and of the anodic current function ($i_{p,a}/v^{1/2}$) both as a function of the scan rate were employed for diagnosis of this mechanism [14]. Bulk electrochemical oxidation of the complex, carried out at 0.00 V gave, after the passing of one equivalent of charge, a solution that could be reduced at –0.70 V with again the equivalent of one charge; the cyclic voltammogram of this final solution shows the characteristics of $[Ab(nBu)]_2Co^{0/+}$ redox couple at –0.40 V (CV). With Et_4NClO_4 as the supporting

TABLE II. Controlled Potential Electrolyses of the Metal Sandwich Complexes.[a]

Reaction Compound	Oxidation[b] n_{ox} (V_{ox}, V)	Reduction[b] n_{red} (V_{red}, V)	Color Changes
$[Ab(SiMe_3)]_2Co \rightarrow [Ab(n\text{-}Bu)]_2Co^+$			green to brown
B–N, B′–N′ configuration	1.0 (0.00)		
mixture of both isomers	1.0 (0.00)		
$[Ab(n\text{-}Bu)]_2Co^+ \rightarrow [Ab(n\text{-}Bu)]_2Co$			brown to yellow-green
B–N, B′–N′ configuration		0.9 (–0.70)	
mixture of both isomers		0.9 (–0.55)	
$[Ab(SiMe_3)]_2Fe$			red(brown) to brown-yellow
B–N, B′–N′ configuration	0.9 (+0.45)		
mixture of both isomers	1.0 (+0.45)		
$[Ab(H)]_2Fe$	1.0 (+0.37)		orange-yellow to green
$[Ab(t\text{-}Bu)]_2Fe$	1.0 (+0.45)		orange-yellow to green
$[\eta\text{-}C_5H_5]_2Fe \rightarrow [\eta\text{-}C_5H_5]_2Fe^+ \rightarrow [\eta\text{-}C_5H_5]_2Fe$	1.0 (+0.70)	1.0 (+0.40)	brown to blue to brown
$[\eta\text{-}C_5H_5]_2Co \rightarrow [\eta\text{-}C_5H_5]_2Co^+ \rightarrow [\eta\text{-}C_5H_5]_2Co$	1.0 (–0.30)	1.0 (–0.95)	red-brown to green to red-brown

[a] In CH_2Cl_2 (0.1 *M* Bu_4NClO_4). [b] n is the number of electrons counted with the oxidation or reduction reactions. Potentials in parentheses *vs.* Ag–AgI reference electrode.

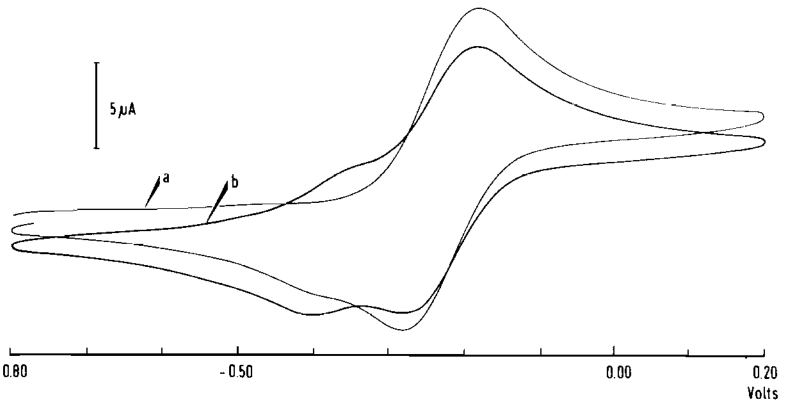

Fig. 2. Cyclic voltammogram of $Co[Ab(SiMe_3)]_2$ (0.1 *M* Bu_4NClO_4, THF) at a scan rate of 200 mV s^{-1}. a) First scan; b) 30th scan.

electrolyte the same reaction pattern is observed, with the generation of a redox couple at –0.42 V (CV) which now points to the formation of the $[Ab(Et)]_2Co^+$ species. Obviously in the oxidized form there has been a substitution of $SiMe_3$ by the alkyl group of the supporting electrolyte.

The neutral cobalt complex, $[Ab(SiMe_3)]_2Co$ also turned out to be reactive towards the tetraalkyl ammonium ion, however the reaction is very slow as compared with the oxidized form of the complex. To study this substitution reaction, differential pulse voltammograms were recorded, during a period of 24 hours, of a CH_2Cl_2 solution containing this cobalt complex and Bu_4NPF_6 as the supporting electrolyte. The formation of the substitution product is readily seen after 1–2 hours and the intensities of their peaks at –0.29 and –0.36 V increased steadily at the expense of the original oxidation peak at –0.21 V (Fig. 3). The peak at –0.36 V arises from the alkyl substituted complex $[Ab(Bu)]_2Co$, while the peak at –0.29 V is attributed to the oxidation of an intermediate mixed ligand complex, $[Ab(SiMe_3)][Ab(R)]Co$. In the following reaction scheme the redox couples and their substitution reactions are summarized.

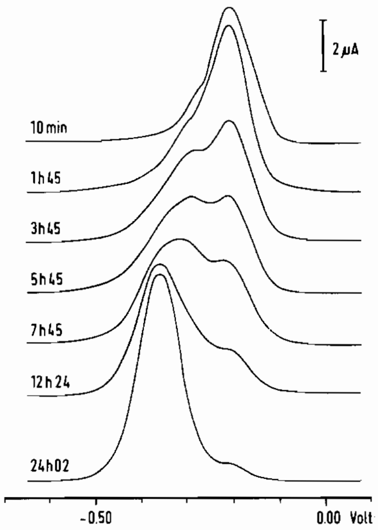

Fig. 3. The formation of the $Co(AbR)_2$ complex from the N-trimethyl substituted complex in dichloromethane (0.1 *M* Bu_4NPF_6) followed with differential pulse voltammetry.

$$\begin{tikzcd}
{[Ab(SiMe_3)]_2Co} \arrow[r, "+R_4N^+", "\text{slow, hours}"'] \arrow[d, shift left, "\begin{array}{l}-e\\ -0.21V\end{array}"] & {[Ab(SiMe_3)][Ab(R)]Co} \arrow[r, "R_4N^+", "\text{slow hours}"'] \arrow[d, shift left, "\begin{array}{l}-e\\ -0.29V\end{array}"] & {[Ab(R)]_2Co} \arrow[d, shift left, "\begin{array}{l}-e\\ -0.36V\end{array}"] \\
{[Ab(SiMe_3)]_2Co^+} \arrow[r, "R_4N^+", "\text{fast seconds}"'] \arrow[u, shift left, "+e"] & {[Ab(SiMe_3)][Ab(R)]Co^+} \arrow[r, "R_4N^+", "\text{fast seconds}"'] \arrow[u, shift left, "+e"] & {[Ab(R)]_2Co^+} \arrow[u, shift left, "+e"]
\end{tikzcd}$$

(Potentials (DP) refer to the case of 0.1 *M* Bu_4NPF_6 in CH_2Cl_2).

Iron Complexes $[Ab(R)]_2Fe$, *R = H, t-Bu and* $SiMe_3$

The oxidation of the separate isomers (I, II) of $[Ab(SiMe_3)]_2Fe$ as well the mixture of both isomers have i_b/i_f values close to one, indicating nearly 100% reversibility on the cyclic voltammetric timescale. In contrast with this are the low i_b/i_f ratios for $[Ab(H)]_2Fe$ and $[Ab(t\text{-}Bu)]_2Fe$ (see Table I) which indicate that the oxidized products suffer chemical degradation reactions. Indeed a cyclic voltammetry taken after exhaustive electrolyses of a solution containing $[Ab(t\text{-}Bu)]_2Fe$ shows only 30% of the original concentration. The reason for this lability of the oxidized complexes with R = H or t-Bu is not clear.

In contrast with $[Ab(SiMe_3)]_2Co$ the corresponding Fe complex and its oxidized form show no substitution activity of the $SiMe_3$ group.

Discussion

Compared with the metallocenes the cobalt complexes are oxidized at higher potentials than cobaltocene (about −0.24 V *versus* −0.73 V), whereas in contrast with this the oxidation potentials for the iron complexes are found at clearly lower potentials as now compared with ferrocene (about 0.20 V *versus* 0.64 V). An explanation for this behaviour may be found in the altered electron contribution of the azaborolinyl rings compared with the cyclopentadienyl ligands. The lowering of the $E_{1/2}$ value for the iron complexes may be due to the fact that the azaborolinyl rings possess stronger donor but weaker acceptor properties than the cyclopentadienyl groups [15], *i.e.* the iron atom in azaborolinyl sandwich complexes has a higher electron density than in ferrocene and consequently is to be oxidized at lower potentials.

On the other hand the higher oxidation potential of the cobalt complexes can be understood from the molecular structures. All azaborolinyl cobalt sandwich complexes investigated by X-ray analysis up to now show slipped rings so that the three ring carbon atoms are closer to the cobalt atom than the BN group [7]. This indicates that the cobalt atom tries to avoid the unfavourable 19 electron configuration present in cobaltocene. As a result the cobalt atom in azaborolinyl cobalt complexes has a lower electron density than in cobaltocene and is oxidized at higher potential. Indeed the azaborolinyl cobalt complexes are considerably more stable and are less sensitive to oxygen than cobaltocene itself.

Another result of interest is the difference in the $E_{1/2}$ values between $N{-}SiMe_3$ and the N–alkyl substituted complexes. The electron withdrawing character of the $SiMe_3$ group decreases the electron density on the nitrogen atom, leading to a weaker donor capacitiy of the ring towards the metal atom and thus to higher oxidation potentials. The fast substitution of $SiMe_3$ by R in $[Ab(SiMe)_3]_2Co^+$ and $[Ab(SiMe_3)][Ab(R)]Co^+$ is easily understood. The oxidation of the cobalt atom causes a stronger electron shift from the azaborolinyl rings to the metal. This shift weakens the N–Si bond so that substitution by alkyl groups is facilitated.

The results of our electrochemical investigations agree well with the structural and chemical properties of the azaborolinyl metal sandwiches.

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