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Electrochemical Redox Behaviour of Cobalt and Iron Triazenido Complexes, $[(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)M]^z$

J. G. M. van der LINDEN, A. H. DIX

Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

and E. PFEIFFER

Inorganic Chemistry Laboratory, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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The cobalt(III) complexes, $[(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Co]^+$ *with* $L = PEt_3$, PPh_3, $P(OMe)_3$ *and* $P(OPh)_3$ *and* ArN_3Ar = *di-aryltriazenido anion can be reversibly reduced in a one electron step to the neutral cobalt(II) species at about* -0.2 *to* $+0.1$ *V* vs. *a Ag–AgCl electrode in acetone solutions.*

The iron(II) complexes, $(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Fe$ *with* $L = PPh_3$, $P(OMe)_3$, $P(OPh)_3$ *and CO could be oxidized in the potential range 0.25–0.65 V* vs. *a Ag–AgI electrode in dichloromethane solutions. The new complex,* $[(\eta^5\text{-}C_5H_5)(CO)(NO)(ArN_3Ar)Fe]PF_6$ *was obtained by reaction of* $(\eta^5\text{-}C_5H_5)(CO)(NO)(ArN_3Ar)Fe$ *with* $NOPF_6$.

Introduction

Recently a series of isostructural transition metal triazenido complexes, $[(\eta^5\text{-}C_5H_5)(L)Ar\text{—}\overline{N\text{—}N\text{—}(Ar)\text{—}M}]^z$, z = 0, +1, has been reported for iron and cobalt [1, 2]. The same structure, which comprises a chelating triazenido ligand, was shown for the paramagnetic intermediate of the fluxional complex, $(\eta^5\text{-}C_5H_5)(PPh_3)(ArN_3Ar)Ni$ [3], and apparently exists for metal complexes with several electronic configurations. Whereas, in a single case, M = Co, L = PPh_3, both members of the Co(II)/Co(III) redox couple could be synthesized and characterized, in general only the iron(II) and cobalt(III) complexes were prepared and isolated.

In order to demonstrate the existence of redox couples for all compounds we examined the electrochemical properties of the available complexes. Moreover it would be of interest to observe the substituent effect on the redox potentials of the d^6/d^5 and the d^7/d^6 couples for iron and cobalt, respectively.

TABLE I. Electrochemical Data for the Reduction of the Cobalt Compounds.[a]

Compound[b]		Normal Pulse Voltammetry		Alternating Current Voltammetry		Cyclic Voltammetry		
		$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	E_p (V)	$\Delta E_{1/2}$[c] (mV)	E_p^{cath} (V)	ΔE_p[d] (mV)	$\frac{i_{cathodic}}{i_{anodic}}$
1a	$[(C_5H_5)(PEt_3)(DpTT)Co]PF_6$	−0.230	63	−0.225	115	−0.250	72	1.1
1b	$[(C_5H_5)(PEt_3)(DpClT)Co]PF_6$	−0.125	50	−0.120	115	−0.150	74	1.1
2a	$[(C_5H_5)(PPh_3)(DpTT)Co]PF_6$	−0.135	61	−0.130	115	−0.170	62	1.2
2a′	$[(C_5H_5)(PPh_3)(DpTT)Co]$[e]	−0.130	60	−0.120	100	−0.095[f]	81	0.9[f]
2b	$[(C_5H_5)(PPh_3)(DpClT)Co]PF_6$	−0.010	59	−0.005	109	−0.040	75	1.1
3a	$[(C_5H_5)(P(OMe)_3)(DpTT)Co]PF_6$	−0.105	66	−0.065	120	−0.160	100	1.0
3b	$[(C_5H_5)(P(OMe)_3)(DpClT)Co]PF_6$	+0.015	48	+0.025	105	−0.050	72	1.0
4a	$[(C_5H_5)(P(OPh)_3)(DpTT)Co]PF_6$	+0.065	70	+0.065	107	+0.025	76	1.1
4b	$[(C_5H_5)(P(OPh)_3)(DpClT)Co]PF_6$	+0.125	58	+0.120	123	+0.165	79	1.2

[a] In acetone *vs.* Ag–AgCl electrode. [b] DpTT = *p*-$MeC_6H_4N_3C_6H_4Me$-*p*; DpClT = *p*-$ClC_6H_4N_3C_6H_4Cl$-*p*. [c] Width at half peak height. [d] Cathodic to anodic peak separation. [e] Oxidation of the cobalt(II) complex with [f] E_p^{anod}.

TABLE II. Electrochemical Data for the Oxidation of the Cobalt Complexes.[a]

Compound[b]	Normal Pulse Voltammetry		AC Voltammetry		Cyclic Voltammetry		
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	E_p (V)	$\Delta E_{1/2}$[c] (mV)	E_p^{anodic} (V)	ΔE_p[d] (mV)	$\frac{i_{anodic}}{i_{cathodic}}$
1a	1.340	53	1.345	100	1.380	65	1.0
1b	1.550	65	1.550	113	1.600	74	1.0
2a	1.330	63	1.330	125	1.340	61	1.2
2a'	1.285	67	1.320	160	1.345	e	–
2b	1.545	70	1.555	135	1.590	76	1.2
3a	1.330		1.320	125	1.425	111	1.1
3b	1.550	52	1.550	100	1.580	71	1.1
4a	1.430	50	1.430	108	1.460	71	1.1
4b	1.575	58	1.585	125	1.610	82	1.1

[a] In acetone *vs.* Ag–AgCl electrode. [b] For abbreviations and numbering of the complexes see Table I. [c] Width at half peak height. [d] Anodic to cathodic peak potential separation. [e] No cathodic wave observed.

Results and Discussion

Cobalt Complexes

The electrochemical redox behaviour of the cobalt(III) compounds, $[(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Co]^+\text{-}PF_6^-$, has been studied at a platinum electrode *vs.* a Ag–AgCl electrode in acetone solutions. The various techniques used (pulse, AC and cyclic voltametry) show that all these complexes are easily reduced to the neutral cobalt(II) compounds in the potential range –0.2 to +0.1 V (Table I). The experimental data obtained with these various techniques are in good agreement with each other. In the cyclic voltammograms corresponding anodic peaks were observed indicating that the formed cobalt(II) complexes can be re-oxidized. The ratio of the cathodic to the anodic peak currents, being nearly one, indicates the occurrence of a chemically reversible redox couple. This is further supported by the electrochemical oxidation carried out on one of the synthesized cobalt(II) compounds, $[(\eta^5\text{-}C_5H_5)(PPh_3)\text{-}(DPTT)Co]$ [2]. Identical half wave potentials for both the reduction of the cobalt(III) and the oxidation of the cobalt(II) complexes were found.

Thus it may be concluded that this series of cobalt triazenido compounds exhibits a chemically reversible one-electron transfer according to

$$[(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Co]^+ + e \rightleftarrows [(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Co]$$

Apparently all cobalt(II) species are stable compounds in acetone solutions. We anticipate that the phosphite complexes, $(\eta^5\text{-}C_5H_5)\{P(OR)_3\}(ArN_3Ar)\text{-}Co(II)$, can be synthesized by chemical reduction of the cobalt(III) complexes. These compounds could not be prepared before [2] because $Co\{P(OR)_3\}_2X_2$ as required starting material is not known.

The influence of the ligand L on the half wave potentials irrespective of the substituents on the triazenido ligands comprises a potential range of 0.3 V.

Increasing $E_{1/2}$ values are observed in the order L = $PEt_3 < PPh_3 < P(OMe)_3 < P(OPh)_3$, which is in accordance with the increasing positive charge on the metal atom due to the decreasing basicity of the ligands in that order.

The influence of the substituents present on the aryl groups of the triazenido ligand on the $E_{1/2}$ values is about 120 mV going from the para methyl (DpTT) to the para chloride (DpClT) substituted ligand.

Comparing for both ligands, ArN_3Ar and L = PR_3, their influence on the charge of the central metal atom, the triazenido ligand seems to be the most effective, although the para substituent on this ligand exerts its influence over six bonds, *vs.* the two bonds for the groups R on the ligand L. So we conclude tentatively that the valency electron is mainly located on the cobalt–nitrogen four-membered ring.

In the potential range studied to –2.0 V no indication was obtained for a further reduction of the formed cobalt(II) compounds.

For the oxidation of the cobalt(III) complexes well defined pulse polarographic and AC voltammetric waves were recorded and the data are summarized in Table II. Limiting currents per unit concentration were the same for these oxidations as those observed for the reductions of these cobalt(III) complexes indicating that here also one electron processes are operating. In the cyclic voltammograms

TABLE III. Electrochemical Data for the Oxidation of the Iron Complexes.[a]

Compound[b]	Normal Pulse Voltammetry		AC Voltammetry		Cyclic Voltammetry		
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	E_p (V)	$\Delta E_{1/2}$ (mV)	E_p^{anodic} (V)	ΔE_p[d] (mV)	$\frac{i_{anodic}}{i_{cathodic}}$
$(C_5H_5)(PPh_3)(DpTT)Fe$	0.225	76	0.225	126	0.255	68	1.0
$(C_5H_5)(PPh_3)(DpClT)Fe$	0.360	93	0.340	124	0.388	92	1.0
$(C_5H_5)(P(OMe)_3)(DpTT)Fe$	0.365	115	0.360	138	0.420	122	1.0
$(C_5H_5)(P(OMe)_3)(DpTT)Fe$	0.510	123	0.480	165	0.510	82	1.0
$(C_5H_5)(P(OPh)_3)(DpTT)Fe$	0.520	73	0.510	145	0.540	76	1.2
$(C_5H_5)(P(OPh)_3)(DpClT)Fe$	0.660	76	0.650	148	0.685	85	1.0
$(C_5H_5)(CO)(DpTT)Fe$	0.910	69	0.883	123	0.940	101	1.4
$(C_5H_5)(CO)(DpClT)Fe$	1.010	51	1.015	133	1.065	[e]	–

[a] In CH_2Cl_2 *vs.* Ag–AgI electrode. [b] For abbreviations see Table I. [c] Width at half peak height. [d] Anodic to cathodic peak potential separation. [e] No cathodic wave observed.

the corresponding reduction waves are observed. The anodic to cathodic peak current ratio, slightly above unity, indicates that some decomposition of the oxidized products occurred. The half-wave potentials are mainly centered around two positions: at 1.3 V for those compounds containing the para methyl substituted triazenido ligand (DpTT) and at 1.5 V for the para chloride substituted ligand (DpClT) cobalt complexes. No influence of the ligand L is noted.

These observations suggest strongly that the one electron oxidation occurs mainly on the nitrogen chain of the triazenido ligand. Accordingly the substituent effect (about 220 mV) is enhanced compared with the value observed by the reductions.

Iron Complexes

The electrochemical data for the oxidation of the iron(II) complexes, $(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Fe$, at a platinum electrode are summarized in Table III. The quoted data were obtained in dichloromethane *vs.* Ag–AgI electrode, since especially the carbonyl complexes decomposed during the measurements in acetone. However, no significant differences in $E_{1/2}$ values for the other compounds were observed and all the data are comparable [4].

In the cyclic voltammograms the corresponding cathodic peaks were observed indicating that with the exception of the carbonyl complexes the formed iron(III) compounds can be reduced. The i_{anodic} to $i_{cathodic}$ ratio is about one. Like the cobalt compounds the iron(II) and (III) triazenido complexes constitute a chemically reversible redox couple:

$$(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Fe \rightleftarrows [(\eta^5\text{-}C_5H_5)(L)(ArN_3Ar)Fe]^+ + e$$

As compared with the Cobalt(II)/(III) redox couples described above the $E_{1/2}$ values for these iron(II)/(III) couples are found in a more positive potential range (0.2–0.7 V), as expected since for iron a d^6/d^5 and for cobalt a d^7/d^6 electronic configuration change is involved.

The influence on $E_{1/2}$ of the substituents (Me, Cl) of the aryl groups of the triazenido ligand is of the same order (120 mV) for both these iron and cobalt redox couples. Also the influence of the ligand L is of the similar magnitude and the same order for the ease of oxidation is observed, L = $PPh_3 > P(OMe)_3 > P(OPh)_3 >$ CO. This is somewhat surprising, since the ^1H NMR data [1] showed for the iron compounds a much stronger dependence of the chemical shifts of the cyclopentadienyl protons on the group L deviating from the order of basicity.

Chemical oxidation of the iron complexes was attempted by reaction with $AgPF_6$ and $NOPF_6$, respectively. Whereas with $AgPF_6$ no reaction was observed, reaction with $NOPF_6$ led to complete decomposition of the products except for the carbonyl complexes. Reaction of $(\eta^5\text{-}C_5H_5)(CO)(ArN_3Ar)Fe$ with $NOPF_6$, however, did not give the Fe(III) species, but the diamagnetic compounds, $[(\eta^5\text{-}C_5H_5)(NO)(CO)(ArN_3Ar)Fe]PF_6$, which according to IR and ^1H NMR spectra contain monodentate triazenido ligands.

A similar reaction involving the opening of the iron–nitrogen ring might account for the decomposition of the carbonyl complexes during the measurements in a donor solvent such as acetone and cannot be strictly excluded for an iron(III) carbonyl species in CH_2Cl_2.

Experimental

The cobalt and iron complexes were prepared according to the literature [1, 2]. $[(C_5H_5)(CO)$-

(NO)(DpTT)Fe]PF_6 was prepared by addition of solid $NOPF_6$ to a solution of $(C_5H_5)(CO)(DpTT)Fe$ in CH_3CN at 0 °C and subsequent precipitation by addition of excess diethyl ether. *Anal.*: C, 42.1; H, 3.57; F, 20.4; N, 9.78. $C_{20}H_{19}F_6FeN_4O_2P$ requires: C, 43.8; H, 3.50; F, 20.8; N, 10.2.

The electrochemical measurements were made with a three electrode Bruker E310 instrument with platinum working and auxiliary electrodes. Measurements were made on *ca.* 10^{-3} mol dm^{-3} depolarizer in 0.1 mol dm^{-3} Bu_4NClO_4 in acetone or dichloromethane solutions. Potentials are referred to a Ag–AgCl (0.1 mol dm^{-3} LiCl–acetone) electrode [5] or a Ag–AgI (0.42 mol dm^{-3} Bu_4NI–dichloromethane) electrode [6].

Normal pulse voltammograms (2.0 pulses per second) and AC voltammograms (amplitude 10 mV peak to peak, frequency 77.5 Hz) were recorded at a scan rate of 5 mV $second^{-1}$, using a X–Y recorder (BD 30, Kipp, Delft). Cyclic voltammograms were taken with a scan rate of 200 mV $second^{-1}$. All measurements were made in an inert atmosphere (N_2) in a glove box.

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