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Amidinato complexes of dicyclopentadienylmolybdenum. Synthesis and redox properties

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Abstract

Reaction of $[MoCp_2Br_2]$ ($Cp = C_5H_5$), in ethanol containing NEt_3 with a range of diarylamidines, $Ar^1N(H)XNAr^2$ (Ar^1, Ar^2 = Ph, *p*-MeOPh, *p*-MePh, *p*-FPh; X = CH, CMe, CPh), gives the cations $[MoCp_2(Ar^1NXNAr^2)]^+$ in which the amidinato ligands are bidentate. Cyclic voltammetry shows that the 17 electron species obtained after monoelectronic oxidation undergo a slow chemical reaction. The formal oxidation potentials depend on the amidinato X group and are related to those of similar complexes containing the isoelectronic diaryltriazenido ligands (X = N). Cathodic reduction gives species whose stabilities are dependent markedly on the X group. A plausible mechanism is suggested for the reductions.

Introduction

We previously reported [1] the preparation of the complex cations $[MoCp_2(Ar^1NNNAr^2)]^+$, in which the diaryltriazenido ligands form a very stable four-membered ring. Since amidines are isoelectronic with triazenes, they are expected to undergo similar reactions at the metal center, and the synthetic route used previously for the triazenes has indeed been extended with success to amidines, and the new cationic complexes **1–9** were obtained. The purpose of the work described below was to investigate the influence of structural changes within the ligands on the electrochemical properties of the complexes. Some of results described have already been briefly reported [2].

Results and discussion

Synthesis and characterization of the complexes

Reactions of $[MoCp_2Br_2]$ with formamidines, in refluxing ethanol containing NEt_3 gave red solutions from which red crystals of $[MoCp_2(Ar^1NXNAr^2)][PF_6]$ (**1–5**) were isolated. Similar reactions with acetamidine and benzamidines gave the complexes **6** and **7–9**, respectively (see Fig. 1).

The structure was deduced from the analytical and conductivity data and the IR and ^1H NMR spectra (Table 1), as discussed below.

The observed conductivities (78–98 Ω^{-1} cm^2 mol^{-1}) are in keeping with those previously reported for 1 : 1 electrolytes in nitromethane solutions [3].

The IR spectra show absorptions typical of the $MoCp_2$ fragment (ca. 3000 cm^{-1}) and of the PF_6^- anion (840, 560 cm^{-1}). In addition, there are characteristic bands in the 1500–1580 cm^{-1} and 1200–1300 cm^{-1} regions. The bands at 1500–1580 cm^{-1} are assigned to the asymmetrical stretching of the NCN group [1]. The bands are shifted to lower wavenumbers (40–50 cm^{-1}) relative to those for the parent amidines.

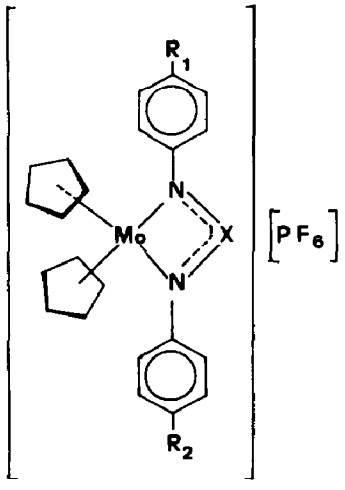
The ^1H NMR spectra display signals from the Cp ring protons (5.95–6.05 ppm) and the amidine protons. These appear at higher fields, than those from the free ligands. Integration of the signals shows that there is one amidinato group for two Cp rings.

Electrochemistry

Cyclic voltammograms were determined using a Pt disc electrode for solutions (ca. 1 mmol dm^{-3}) in MeCN containing $[NBu_4][PF_6]$ (0.1 mol dm^{-3}). The observed data are summarized in Table 2.

Oxidations

All the complexes undergo a one-electron oxidation process that is reversible at scan rates higher than 0.10 V s^{-1} (Fig. 2). The current function $I_p v^{-1/2} c^{-1}$ is



	X	R_1	R_2
1	CH	OMe	OMe
2	CH	OMe	H
3	CH	Me	Me
4	CH	Me	H
5	CH	Me	F
6	CMe	H	H
7	CPh	OMe	H
8	CPh	Me	H
9	CPh	H	H

Fig. 1. Structures of reaction products.

Table 1

Analytical [a], conductimetric [b] and ^{1}H NMR [c] data

	Compound			Analysis (%)			M.p. (°C)	Λ (Ω^{-1} cm^2 mol^{-1})	δ (ppm) (multiplicity; intensity)				
	X	R_1	R_2	C	H	N			Me	OMe	Cp	Ar	CH
1	CH	OMe	OMe	47.41 (47.93)	4.13 (4.02)	4.45 (4.49)	230	81	–	3.75(s;6)	6.00(s;10)	6.91(q;8)	9.50(s;1)
2	CH	OMe	H	48.30 (48.34)	4.01 (3.89)	4.48 (4.70)	235	83	–	3.75(s;3)	5.98(s;10)	7.00(m;9)	9.50(s;1)
3	CH	Me	Me	50.61 (50.52)	4.24 (4.24)	4.59 (4.71)	246	80	2.30(s;6)	–	5.95(s;10)	7.10(q;8)	9.60(s;1)
4	CH	Me	H	50.04 (49.67)	4.13 (3.99)	4.64 (4.83)	239	82	2.30(s;3)	–	5.95(s;10)	7.05(m;9)	9.60(s;1)
5	CH	Me	F	48.08 (48.10)	3.89 (3.87)	4.45 (4.67)	251	78	2.30(s;3)	–	6.00(s;10)	7.05(m;9)	9.60(s;1)
6	CMe	H	H	50.25 (49.67)	4.20 (3.99)	5.00 (4.83)	221	80	2.10(s;3)	–	5.95(s;10)	7.20(m;10)	–
7	CPh	OMe	H	53.87 (53.58)	4.27 (4.02)	4.29 (4.17)	258	79	–	3.70(s;3)	5.98(s;10)	7.10(m;9) 6.60(m;5)	–
8	CPh	Me	H	54.41 (54.89)	4.81 (4.15)	4.35 (4.27)	265	80	2.95(s;3)	–	6.00(s;10)	7.20(m;9) 6.65(m;5)	–
9	CPh	H	H	54.68 (54.22)	4.06 (3.92)	4.51 (4.36)	263	79	–	–	6.05(s;10)	7.25(m;10) 6.70(m;5)	–

[a] Calculated values are given in parentheses. [b] In 10^{-3} mol dm^{-3} nitromethane solutions. [d] In C_6D_6, internal $SiMe_4$.

Table 2

Cyclovoltammetric data for complexes $[MoCp_2Ar^1NXNAr^2][PF_6]$ in acetonitrile–tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) at a Pt electrode

	Compound			$E_p^{a\,a}$ (V)	ΔE (mV)	$I_p^c/I_p^{a\,b}$	$10^{-3}I_p^a v^{-1/2} C^{-1\,b,c}$ (A $V^{-1/2}$ $s^{1/2}$ mol^{-1} cm)	$10^5 D$ (cm^2 s^{-1})	$-E_p^{c\,a}$ (V)	$E_p^c - E_p/2^{c\,b}$ (mV)	$I_p^a/I_p^{c\,b}$	$10^{-3} - I_p^c v^{-1/2} C^{-1\,b,c}$ (A $V^{-1/2}$ $s^{1/2}$ mol^{-1} cm)
	X	R_1	R_2									
1	CH	OMe	OMe	0.83	60	1.0	1.36	2.6	1.58	75	–	2.65
2	CH	OMe	H	0.92	60	1.0	1.37	2.7	1.54	75	–	2.65
3	CH	Me	Me	1.01	65	1.0	1.28	1.4	1.53	75	–	2.40
4	CH	Me	H	1.10	70	0.9	1.43	2.9	1.47	70	–	2.72
5	CH	Me	F	1.08	70	1.0	1.53	3.3	1.50	75	–	2.58
6	CMe	H	H	1.15	70	1.0	1.36	2.6	1.63	75	–	2.55
7	CPh	OMe	H	0.69	60	1.0	1.53	3.3	1.86	70	0.9	1.67
8	CPh	Me	H	0.87	60	1.0	1.51	3.2	1.81	70	0.8	1.53
9	CPh	H	H	0.97	60	1.0	1.51	3.2	1.69	70	0.8	1.50
10	N	Me	H	1.35	90	0.6	1.15	1.9	1.28	70	1.0	1.15

[a] Potentials vs. SCE. [b] Values taken at 0.200 V s^{-1}. [c] The current function for $FeCp_2/FeCp_2^+$ was 1800 A $V^{-1/2}$ $s^{1/2}$ mol^{-1} cm.

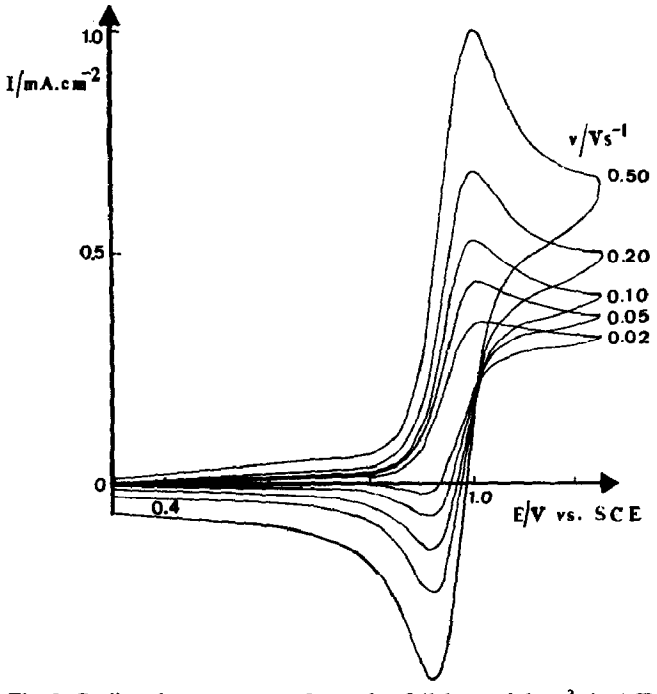


Fig. 2. Cyclic voltammograms of complex **6** (1.1 mmol dm^{-3}) in ACN/[NBu$_4$][PF$_6$] (0.1 mol dm^{-3}) at a Pt disc electrode.

constant for scan rates above 0.10 V s^{-1}, and the diffusion coefficients derived from these values are presented in Table 2. However, at lower scan rates the value of the current function shows that more than one electron is involved, and the ratio of cathodic to anodic peak current becomes < 1. In fact, the cyclovoltammetric behaviour of these complexes parallels that previously observed for the diaryltriazenido [1] (X = N) analogues. The same applies in the case of the exhaustive electrolyses, as can be seen from the current against charge plots presented in Fig. 3.

In the light of the electrochemical evidence it is likely that the complexes undergo disproportionation after the loss of one electron, as follows:

$$[MoCp_2(am)]^+ \rightleftharpoons [MoCp_2(am)]^{2+} + 1\ e^-$$

$$[MoCp_2(am)]^{2+} \rightleftharpoons \tfrac{1}{2}[MoCp_2(am)]^+ + \tfrac{1}{2}[MoCp_2(am)]^{3+}$$

However, this mechanism can only be speculative until chemical and/or spectroscopic evidence is found for reaction intermediates or products. All the complexes undergo a second irreversible oxidation at more positive potentials. The relative peak intensities of both oxidations depend on the scan rate. It is noteworthy that the potentials for the oxidation of amidinato complexes (X = CR) are ca. 200 mV less positive than those for their diaryltriazenido (X = N) analogues. Thus, amidinato ligands are either better σ-donors or worse π-acceptors than triazenido ligands. Similar behaviour was observed for other complexes by Connelly et al. [5].

As expected, in accord with previous results for triazenido complexes [1], the formal oxidation potentials are sensitive to the nature of the substituents (R^1, R^2) on the aromatic rings. A shift towards less anodic potentials is observed when more

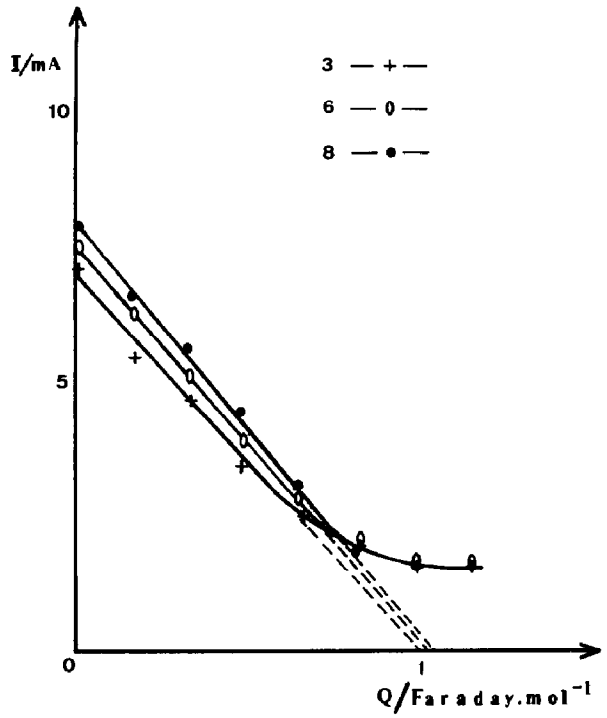


Fig. 3. Plots of charge passed vs. cell current for the electrolysis of 30 μmol of complexes **3**, **6** and **8** in ACN/[NBu_4][PF_6] at a 1 cm^2 Pt gauze electrode.

strongly electron-releasing substituents are present. A good linear correlation (r = 0.991) was found between the oxidation potentials and the Hammett σ^+ parameters for R^1 and R^2. This confirms that the effects of the substituents involve conjugative interaction between the substituent and the reaction centre.

The nature of X also has a marked influence on the E^0 values, as can be seen from the figures in Table 2. Formamidinato complexes (X = CH) are more difficult to oxidise than the acetamidinato complex (X = CMe). This reflects the electron-releasing inductive effect of the methyl group, which enhances the negative charge within the chelated ring and destabilizes the molecular orbital involved. Benzamidinato complexes (X = CPh) are the most readily oxidised, which suggests that overall the phenyl groups supply electrons through the delocalised π-electron system in the ring.

Reductions

All the complexes are reduced at moderately negative potentials. The cyclic voltammograms presented in Fig. 4 are typical of the three types of complexes studied. As expected, the peak potentials are shifted to more cathodic values when more strongly electron-releasing substituents are present. Accordingly amidinato complexes are more difficult to reduce than the corresponding triazenido complexes. The most distinctive feature is that only one reduction peak is observed, whereas two consecutive monoelectronic and reversible peaks were detected for the triazenido complexes.

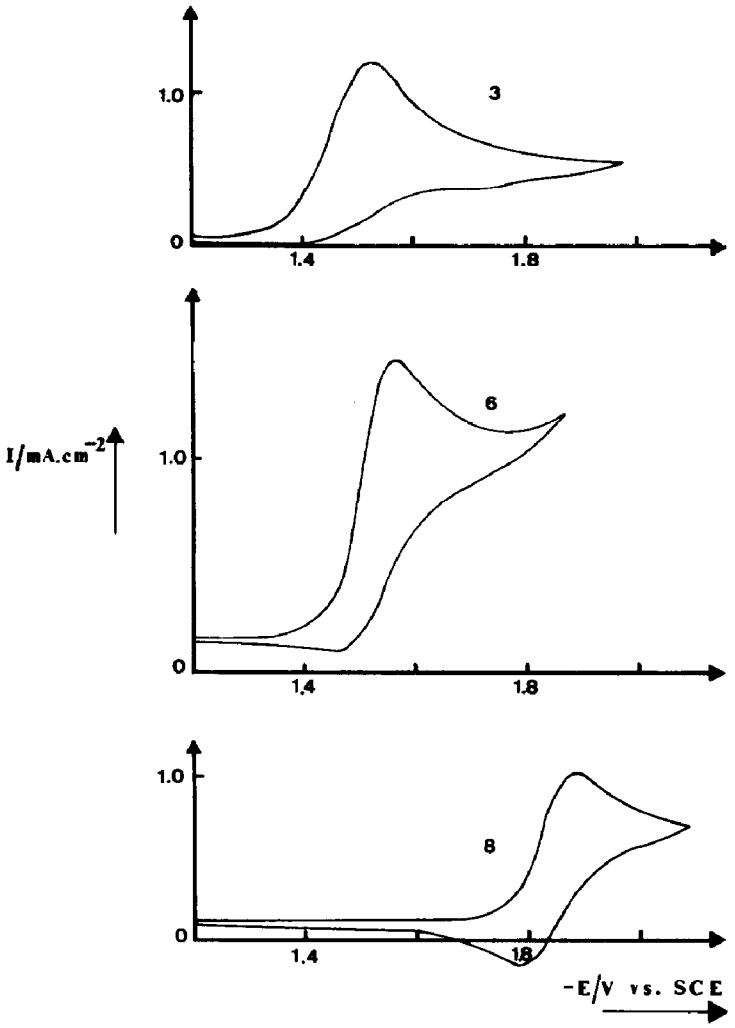


Fig. 4. Cyclic voltammograms of complexes **3** (1.0 mmol dm^{-3}), **6** (1.1 mmol dm^{-3}) and **8** (1.3 mmol dm^{-3}) in ACN/$[NBu_4][PF_6]$ (0.1 mol dm^{-3}). Potential scan rate 0.20 V s^{-1}.

As can be seen from Fig. 4, the stability of the reduction products depends on the X group, and decreases in the order CPh > CMe > CH. It is also noteworthy that only when X = CPh is the current function for the reduction similar to that observed for the oxidation. The other complexes show higher values for the current function in the reduction. This clearly shows that the subsequent chemical reaction reaction contributes to the overall number of electrons involved.

In order to throw light on these features, constant-potential electrolyses were carried out at potentials ca. 100 mV more negative than the peak potential. As can be seen from Fig. 5, plots of current vs. charge were linear. However, the number of electrons is related to the X group; thus when X = CPh, complete electrolysis requires one faraday per mole, in agreement with the cyclovoltammetric data, whereas when X = CMe two electrons per molecule are required. Hence, on the longer time scale of the electrolysis, an overall two-electron process is observed. When X = CH a two-electron process seems to occur at the beginning, but the

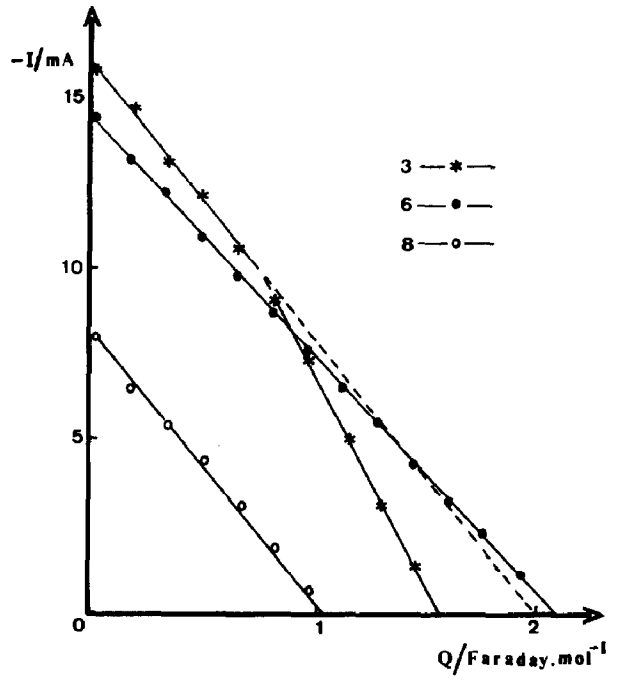


Fig. 5. Plots of charge vs. cell current for the electrolysis of 26 μmol of complexes **3**, **6** and **8** at a 1 cm^2 Pt gauze electrode.

change of slope indicates that the overall reaction becomes monoelectronic as electrolysis proceeds.

These observations suggest the following mechanism:

$$[MoCp_2(am)]^+ + 2\,e^- \rightleftharpoons [MoCp_2(am)]^- \qquad E$$

$$[MoCp_2(am)]^- + [MoCp_2(am)]^+ \rightleftharpoons {}_2[MoCp_2(am)] \qquad C_1$$

$$[MoCp_2(am)]^- \rightarrow \text{decomposition products} \qquad C_2$$

When X = CMe the reduced species undergo the decomposition reaction C_2, but when X = CH reaction C_1 becomes predominant after the reduced species have reached a certain concentration.

Conclusion

The influence of structural changes within the ligands can affect the tendency of the complexes to undergo redox reactions. It has also been shown that the stability of the 19- and 20-electron species obtained after reduction very much depends on the nature of the ligands, since it varied markedly even for coordination of very closely related ligands.

Experimental

All reactions were carried out under nitrogen by Schlenk techniques. Acetonitrile (Merck) was purified by a standard method [6] immediately prior to use. Tetrabutyl-

ammonium hexafluorophosphate was prepared as previously described [1], as was complex $[MoCp_2Br_2]$ [7,8]. The synthesis of formamidines and acetamidine was based on a method described by Roberts [9], and benzamidines were prepared by a published method [10].

The ^1H NMR spectra were recorded on a JEOL JNM 100 PFT spectrometer with deuterated acetone solutions. IR spectra were recorded with a Shimadzu 435 spectrometer as KBr pellets and were calibrated with a polystyrene film. Conductivity data were determined with a Radiometer CDM3 conductivity meter, calibrated with a standard KCl solution. Elemental analyses were performed at the Centro de Quimica Estrutural.

Synthesis of $[MoCp_2(MeOPhNCHNPhOMe)][PF_6]$ (1)

A solution of $[MoCp_2Br_2]$ (0.38 g; ca. 1 mmol), 1,3-di-*p*-anisylformamidine (0.40 g; ca. 1.5 mmol) and triethylamine (1 ml) in ethanol was heated under reflux for ca. 1 h. The solution was filtered and partly evaporated, and, an excess of $[NH_4][PF_6]$ was added to give an orange-red solid, which was filtered off, washed with water, dried, and recrystallised from acetone petroleum spirit as red crystals of the title compound (yield: 80%, 0.50 g).

Complexes **2–9** were prepared similarly.

Electrochemistry

Cyclic voltammetry was carried out under nitrogen with a two-compartment, three-electrode electrochemical cell, a Hi-Tek DT 2101 potentiostat and a Hi-Tek PPR 1 waveform generator. Voltammograms were recorded on a Philips PM 8041 *X–Y* recorder. Controlled potential electrolyses were performed with a H-type three-electrode, three-compartment cell with 1 cm^2 Pt gauze working and auxiliary electrodes. The amount of complex was 25–50 μmol, and the charge passing was monitored with a Hi-Tek DIBS 2 integrator.

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