coefficient for calcite calculated using the following parameters: H^+ diffusion coefficient = $7.46 \times 10\text{-}5$ cm^2s^{-1}, kinematic viscosity of water = 0.01 cm^2s^{-1}, density of calcite = 3.0 g cm^{-3}. The rate of the surface

proton reaction is shown by means of the horizontal line. It can be seen that for small particles the rates of mass transport and interfacial kinetics are approximately equal. However for the small particles (<100µ) used in lake-liming it can be seen that the rate-determining step will be dissolution as opposed to mass transport as hitherto assumed [7-12].

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ELECTROCHEMICAL OXIDATION OF BISCYCLOPENTADIENYLMOLYBDENUM COMPLEXES. EFFECT OF COORDINATED AMIDINES.

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In recent years, much attention has been paid to mechanisms of oxidation-reduction of transition metal and organometallic compounds [1]. The 17- electron species resulting from oxidation are important as catalysts or proposed intermediates in many catalytic processes [2]. They also can undergo a wide variety of reactions, including dimerization, disproportionation, reductive elimination of ligands and activation of ligands after electron transfer to the metal.

In this work we report results of the electrochemical oxidation of two types of complexes, both containing the $MoCp_2$ moiety, with chelated N,N´-diarylacetamidinato ligands (I) and monocoordinated amidines (II)

1	$R_1 = R_2 = H$	X	R
2	$R_1 = H; R_2 = CH_3$	6 Cl	CH_3
3	$R_1 = R_2 = CH_3$	5 Cl	C_6H_5
4	$R_1 = R_2 = OCH_3$		
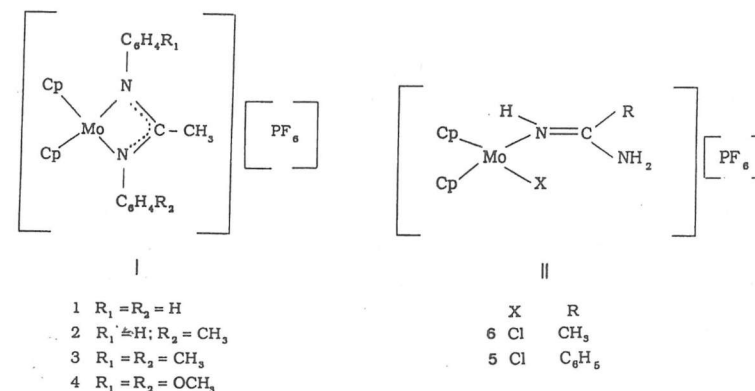
Cyclic voltammetry and controlled potential electrolyses were carried out in order to oxidise and obtain evidence for the mechanism of chemical reactions coupled with the electron transfer.
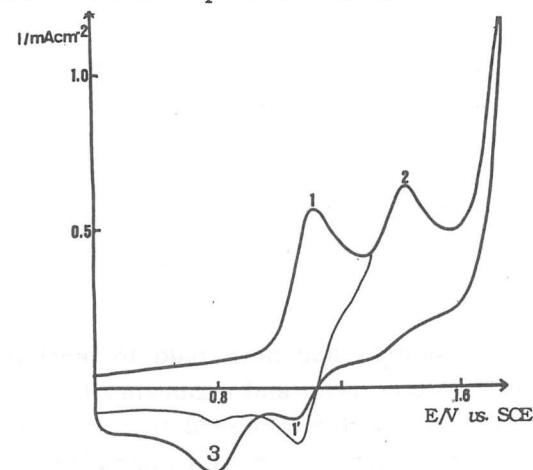

Fig. 1- Cyclic voltammograms of complex 4 (1.1 mmol dm^{-3}) in ACN/[Bu$_4$N][BF$_4$] (0.1 mol dm^{-3}) at a carbon disc electrode. Potential scan rate 0.1 Vs^{-1}.

Figure 1 shows cyclic voltammograms typical of type I complexes in ACN-0.1 mol dm^{-3} [Bu$_4$N][BF$_4$] at a vitreous carbon electrode, in the range 0-1.7 V vs. SCE. It is shown that the complex undergoes two oxidation processes. The first oxidation has all the properties of a reversible one electron transfer process for potential scan rates faster than 0.3 Vs^{-1}, if the scan is reversed before the second oxidation. The second oxidation is irreversible and is associated with peak 3; this corresponds to the reduction of an intermediate produced after the second oxidation, but it is also observed when the scan is reversed before the second oxidation.

The current function for the first process is constant for potential scan rates above 0.3 Vs^{-1}, but it increases as the scan rate decreases in the range 0.05-0.30 Vs^{-1}.This gives evidence for an ECE process or a disproportionation of the 17- electron cation formed after loss of one electron.

Complexes 1-3 show similar behaviours and the electrochemical data for these complexes is summarised in the table. The diffusion coefficients were estimated from the current functions presented in the table.

Table- Cyclicvoltammetric data of complexes in ACN/[Bu$_4$N][BF$_4$] (0.1 mol dm^{-3}) at a carbon electrode.

Complex	$^1E_p^a$ (V) [a]	ΔE (mV) [b]	$^1I_p^a/^1I_p^a$ [b]	$10^{-3}\,^1I_p^a v^{-1/2} c^{-1}$ (AV$^{-1/2}$s$^{1/2}$cm mol^{-1}) [b]	$^2E_p^a$ (V)	$10^6 D$ (cm^{2}s^{-1})
1 – [MoCp$_2$(dfam)][PF$_6$]	1.15	60	1.0	1.4	1.75	2.8
2 – [MoCp$_2$(ftam)][PF$_6$]	1.12	65	1.0	1.1	1.70	1.8
3 – [MoCp$_2$(dtam)][PF$_6$]	1.10	60	1.0	1.2	1.61	2.0
4 – [MoCp$_2$(daam)][PF$_6$]	1.02	60	0.9	1.2	1.45	2.1
5 – [MoCp$_2$Cl(bmH)][PF$_6$]	0.85	65	0.9	0.9	1.28	1.1
6 – [MoCp$_2$Cl(amH)][PF$_6$]	0.88	65	1.0	0.9	----	1.2

a) Potentials vs.SCE.
b) Values taken at 0.3 Vs^{-1}.

Controlled potential electrolysis were carried out at potentials slightly above the first oxidation potential. The current against charge plot presented in figure 2 is typical of type I complexes. The current, after some time, assumes values that are higher than expected for a linear decay. This can be explained in terms of the regeneration of the starting complex.
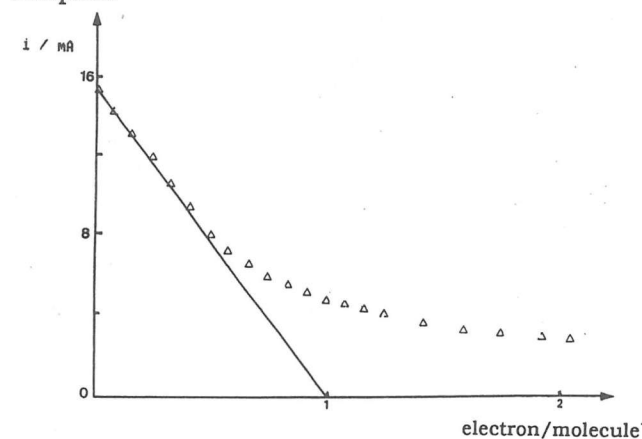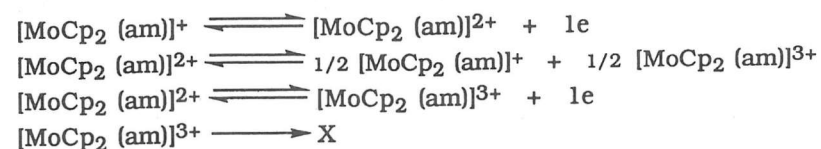

Fig. 2- Plots of charge passed vs. cell current for the electrolysis of 50 μmol of complex 3 in ACN/[Bu$_4$N][BF$_4$] at a Pt gauze electrode.

According to the results presented here the following mechanism can be proposed:

$$[MoCp_2 \, (am)]^+ \rightleftharpoons [MoCp_2 \, (am)]^{2+} + 1e$$
$$[MoCp_2 \, (am)]^{2+} \rightleftharpoons 1/2 \, [MoCp_2 \, (am)]^+ + 1/2 \, [MoCp_2 \, (am)]^{3+}$$
$$[MoCp_2 \, (am)]^{2+} \rightleftharpoons [MoCp_2 \, (am)]^{3+} + 1e$$
$$[MoCp_2 \, (am)]^{3+} \longrightarrow X$$

As espected the potentials for the first oxidation process reflect the electron donating ability of the substituents on the aromatic rings of the acetamidinato ligands. A good linear correlation was observed between the oxidation potentials and the σ^+ Hammett parameters of the substituents. This shows that their influence on the redox orbital is essentially mesomeric.

Cyclic voltammetry (figure 3) shows that type II complexes undergo a monoelectronic and reversible oxidation in ACN-0.1 mol dm^{-3} [Bu$_4$N][BF$_4$], at a carbon disc electrode, to give a product which oxidises at higher potentials.
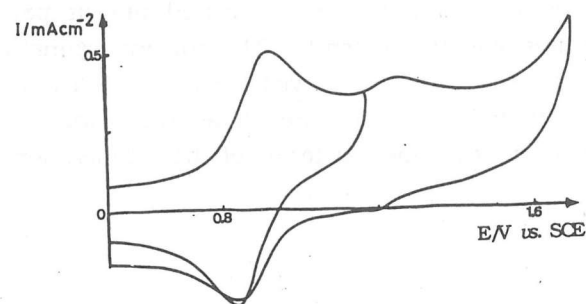

Fig. 3- Cyclic voltammograms of complex 5 (1.0 mmol dm^{-3}) in ACN/[Bu$_4$N][BF$_4$] (0.1 mol dm^{-3}) at a carbon disc electrode. Potential scan rate 0.1 Vs^{-1}.

These complexes are more easily oxidised than type I complexes. Cyclicvoltammetric and controlled potential results do not show any evidence for the disproportionation reaction referred to above for type I complexes.

Kotz *et al.* obtained similar cyclic voltammograms for the complexes [MoCp$_2$X$_2$] [3] and [MoCp$_2$(SR)$_2$] [4]. These authors proposed an oxidatively induced reductive elemination mechanism to explain the behaviour of those complexes.

In order to isolate the oxidation product, controlled potential electrolyses were undertaken together with chemical oxidation using FeCl$_3$. 6H$_2$O.

Figure 4 shows a cyclic voltammogram obtained from an ACN solution of the product of chemical oxidation of complex 5 (A), together with a cyclic voltammogram run after addition of complex 5 to this solution. This shows that complex 5 is completely oxidised and transformed into a product whose oxidation peak appears at the same potential as the second oxidation of complex 5.
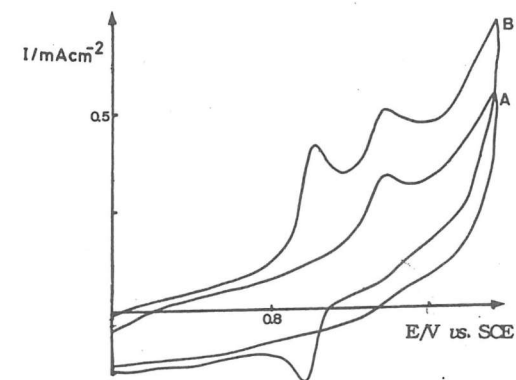

Fig. 4- Cyclic voltammograms of the oxidation product of complex 5 in ACN/[Bu$_4$N][BF$_4$] (A) and after addition of complex 5 to this solution (B). Potential scan rate 0.1 Vs^{-1}.

This work is in progress and we are now looking at the kinetics of the follow-up chemical reaction, by measuring current ratios at different potencial scan rates and using a method described by Nicholson and Shain [5].

The mechanism can be assessed after complete identification of the reaction product.

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WITTIG TYPE REACTIONS INDUCED BY ELECTROGENERATED BASES

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Recently, a great deal of progress has been made in understanding the mechanisms by which organic reactions may be carried out electrochemically and the advantages of these routes have been widely discussed. Therefore, organic chemists become increasingly interested in the possibility of using electrolyses as an alternative to the conventional chemical methods.

It has been shown for several years that the deliberate cathodic generation of anionic bases, in aprotic solvents, may be particularly convenient for preparative purposes since factors such as base strength and concentration can be easily controlled [1].

The synthesis of unsaturated compounds from organophosphorous reagents and carbonyl compounds has been largely explored and olefin formation by means of phosphonate carbanions has been referred as the Wittig-Horner reaction. Different techniques have been employed to generate the carbanion resulting from the phosphonate deprotonation. The technique described here is based on the deprotonation by electrogenerated bases. Compounds which form electrogenerated bases (EGB) by electroreduction, such as azobenzene, are called probases (PB). Lund [2] has shown that stilbene results from the electrolysis, at the azobenzene reduction potential, of a mixture of benzaldehyde, benzyltriphenylphosphonium bromide and azobenzene in N,N-dimethylformamide (DMF). The phosphonate carbanions, however, are generally more reactive than the corresponding phosphoranes, and therefore the phosphonates are less acidic. The possibility of generating the bases *in situ* is, therefore, highly desirable and the success of these reactions has already been preliminary observed [3].

We report here examples of Wittig-Horner reactions carried out electrochemically with different probases.