Electrochemical Generation of Low-valent Molybdenum Tri-tertiary Phosphine Complexes: Interactions with Monophosphines and Molecular Nitrogen†

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The electrochemical reduction of the 15-electron molybdenum(III) complex [$MoCl_3$(dpepp)], dpepp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$, has been studied in the presence of PPh_3 under argon and under molecular nitrogen. The primary reduction of the trichloride involves a reversible single-electron transfer to give the unstable 16-electron molybdenum(II) anion [$MoCl_3$(dpepp)]$^-$. Loss of chloride from this anion prior to or following further electron transfer provides two principal pathways to molybdenum(0) products, [Mo(η^6-$C_6H_5PPh_2$)(dpepp)] under Ar or *cis*-[$Mo(N_2)_2$(dpepp)(PPh_3)] under molecular nitrogen, a relatively high potential pathway *via* molybdenum(I) solvated intermediates and a low potential pathway *via trans*-[$MoCl_2$(dpepp)(PPh_3)]. The *cis*-dinitrogen complex is unstable on the preparative time-scale, small amounts of *trans*-[$Mo(N_2)_2$(dpepp)(PPh_3)] are formed, presumably by isomerisation, but the major product is the η^6-arene complex.

Dinitrogen complexes of molybdenum(0) and tungsten(0) with tertiary phosphine co-ligands can be synthesised from molecular nitrogen by chemical or electrochemical reductions of a wide range of starting materials.

For example, sodium-amalgam or magnesium reduction of either [Mo_2Cl_{10}][1] or [$MoCl_3(thf)_3$][2] (thf = tetrahydrofuran) in the presence of PMe_2Ph under molecular nitrogen at 1–5 atm gives the mono-tertiary phosphine products *cis*- and *trans*-[$Mo(N_2)_2(PMe_2Ph)_4$].[3] Electrosyntheses include the formation of the di-tertiary phosphine complexes *trans*-[$M(N_2)_2(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) from molecular nitrogen and metallo-oxide,[4] -imide,[5] -hydrazide,[6] -thiolate or -halide[7] precursors *via* reductions at a mercury-pool cathode and the intermediates and pathways involved in these reactions have been studied in some detail.[4–8]

Here we are concerned with the electrochemistry of certain molybdenum tri-tertiary phosphine systems which possess ligating $PhP(CH_2CH_2PPh_2)_2$ (dpepp). The complex *trans*-[$Mo(N_2)_2$(dpepp)(PPh_3)] can be chemically synthesised in good yield by sodium-amalgam reduction under molecular nitrogen of either *mer*-[$MoCl_3$(dpepp)] or *trans*-[$MoCl_2$(dpepp)(PPh_3)];[9,10] under argon *fac*-[Mo(η^6-$C_6H_5PPh_2$)(dpepp)] is formed, see below. The chemistry and electrochemistry of these triphosphine systems are particularly interesting because the reaction between *trans*-[$Mo(N_2)_2$(dpepp)(PPh_3)] and HCl gives ammonia and *mer*-[$MoCl_3$(dpepp)].[10,11] Thus there is the possibility of constructing a fixation cycle which employs an electroreduction step to regenerate the dinitrogen complex from the trichloride product. Just such a cycle has been demonstrated for tungsten which utilises the {$W(dppe)_2$} framework[6,12] but attempts by Dubois and Turner[13] to exploit the molybdenum–triphosphine system at a polymer coated electrode have been unsuccessful.

Here we describe the application of voltammetric and coulometric techniques to the study of the electron-transfer chemistry of the tridentate tris(tertiary phosphine) systems *mer*-[$MoCl_3$(dpepp)], *trans*-[$MoCl_2$(dpepp)(PPh_3)], *trans*-[$Mo(N_2)_2$(dpepp)(PPh_3)] and *fac*-[Mo(η^6-$C_6H_5PPh_2$)(dpepp)][14] and our attempts to electrosynthesise the dinitrogen complex. Some cursory voltammetric studies of related molybdenum triphosphine systems have been reported.[15]

Results and Discussion

Synthesis of Complexes.—The syntheses of *mer*-[$MoCl_3$(dpepp)] and *trans*-[$Mo(N_2)_2$(dpepp)(PPh_3)] have been described elsewhere.[9,10] The preparation of the dichloride *trans*-[$MoCl_2$(dpepp)(PPh_3)] from the trichloride is straightforward and is described in the Experimental section. Whilst this compound is stable in the solid state, it slowly loses triphenylphosphine in solution (see below).

Initial attempts to prepare the arene complex *fac*-[Mo(η^6-$C_6H_5PPh_2$)(dpepp)] gave an impure product,[14] however we have now been able to find conditions for the isolation of a crystalline material and this is described in the Experimental section.

Electron-transfer Chemistry.—Scheme 1 summarises the electron-transfer steps and intermediates which we believe to be involved in the conversion of *mer*-[$MoCl_3$(dpepp)] to *trans*-[$MoCl_2$(dpepp)(PPh_3)] and thence molybdenum(0) products. Below we discuss the experimental evidence which supports the pathways outlined in this Scheme.

Primary and Secondary Electron-transfer Reactions of mer-[$MoCl_3$(dpepp)]: *Low Temperature Cyclic Voltammetry.*—Cyclic voltammetry at −20 °C (vitreous carbon disc electrode, thf-0.2 mol dm^{-3} [NBu_4][PF_6]) shows that *mer*-[$MoCl_3$(dpepp)] undergoes reversible, diffusion-controlled one-electron reduction to give anionic [$MoCl_3$(dpepp)]$^-$ as the primary

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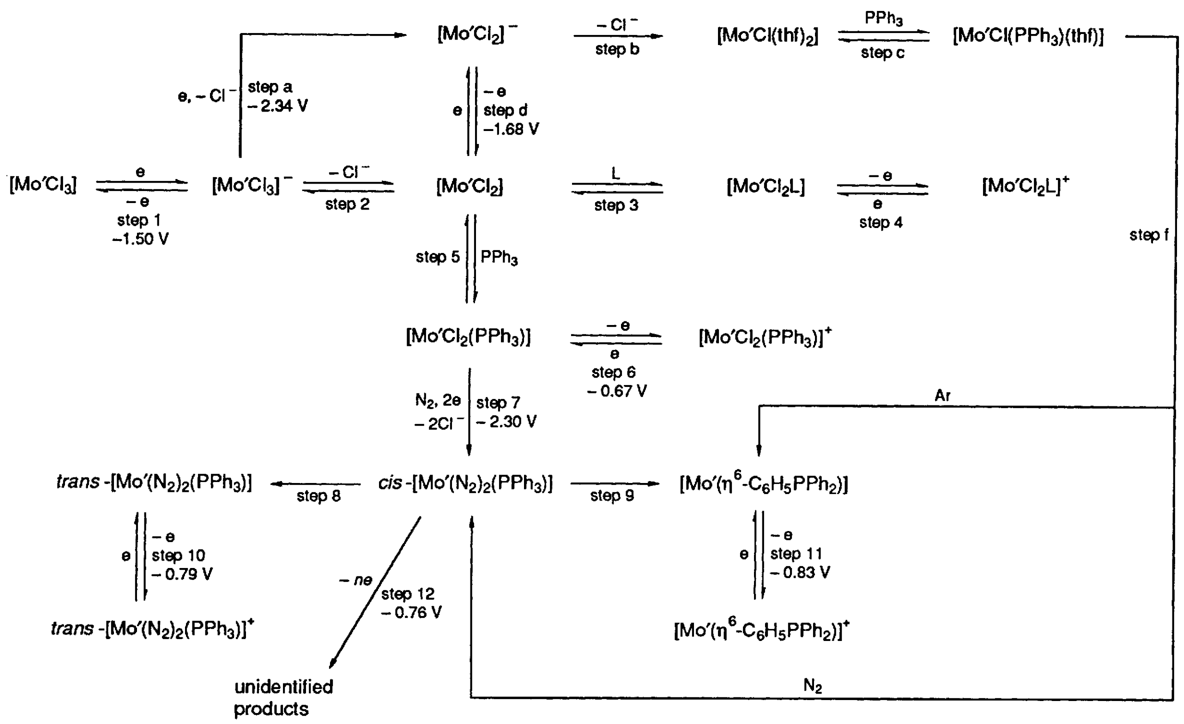
† *Non-SI units employed:* atm = 101 325 Pa, lbf $in^{-2} \approx 6895$ Pa, $F \approx 9.6485 \times 10^4$ C.



Scheme 1 Electron transfer reactions of the molybdenum triphosphine system. In this scheme and in the labelling of the voltammograms the abbreviation Mo′ is used for the {Mo(dpepp)} assembly

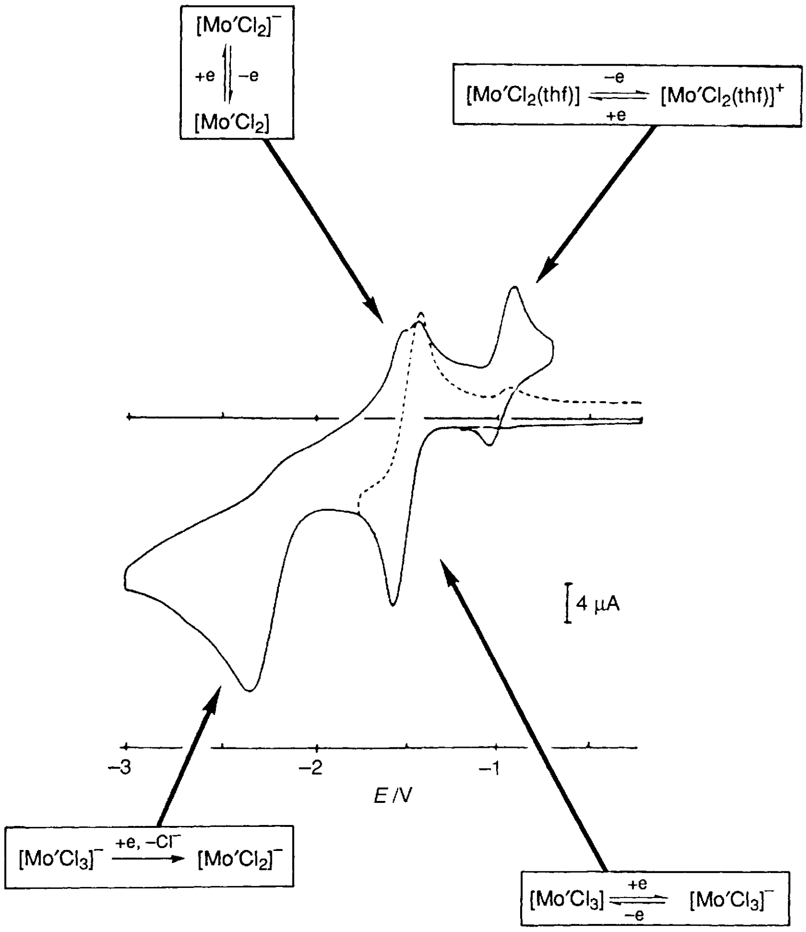


Fig. 1 Low-temperature cyclic voltammetry (−20 °C) of *mer*-[$MoCl_3$(dpepp)] in *thf*-[NBu_4][PF_6]; scan rate 0.20 V s^{-1} at vitreous carbon electrode. The dashed curve shows the partial reversibility of the primary reduction process (step 1): note the partial reversibility of the [$MoCl_2$(thf)(dpepp)]$^{0/+}$ couple at −20 °C (step 4) and the absence of the peak near −1.7 V which is observed at room temperature (Fig. 2). Identical responses are observed under argon or dinitrogen

Table 1 Redox potential data for intermediates and products of the electron-transfer reactions[a]

Species	Process[b]	$E_{\frac{1}{2}}$	or	E_p	$(E_{p/2})$/V
$[MoCl_3(dpepp)]$	$+e_{rev}$; Step 1	-1.50[c]		-1.50	(-1.44)
$[MoCl_3(dpepp)]^-$	$+e_{irr}$; Step a			-2.34	(-2.21)[c]
$[MoCl_2(dpepp)]$	$+e_{rev}$; Step d	-1.68			
$[MoCl_2(dpepp)(thf)]$	$-e_{rev}$; Step 4	-0.99[c]			
$[MoCl_2(dpepp)(PEt_2Ph)]$	$-e_{rev}$; Step 4	-0.73			
	$+2e_{irr}$			-2.42	(-2.35)
$[MoCl_2(dpepp)(PPh_3)]$	$-e_{rev}$; Step 6	-0.67			
	$+2e_{irr}$; Step 7			-2.30	(-2.20)
$[MoCl(dpepp)(thf)_2]$	$+ne_{irr}$			-2.28	(-2.15)
$[MoCl(dpepp)(PPh_3)(thf)]$	$+ne_{irr}$			-2.03	(-1.95)
$[MoCl(dpepp)(PEt_2Ph)(thf)$	$+ne_{irr}$			-2.09	(-2.02)
trans-$[Mo(N_2)_2(dpepp)(PPh_3)]$	$-e_{rev}$; Step 10	-0.79			
cis-$[Mo(N_2)_2(dpepp)(PPh_3)]$	$-ne_{irr}$; Step 12			-0.76	(-0.82)
cis-$[Mo(N_2)_2(dpepp)(PEt_2Ph)]$	$-ne_{irr}$			-0.79	(-0.86)
$[Mo(\eta^6\text{-}C_6H_5PPh_2)(dpepp)]$	$-e_{rev}$; Step 11	-0.83			

[a] Potentials are quoted *versus* the ferrocenium–ferrocene couple and were measured at *ca.* 23 °C (unless otherwise specified) by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][PF_6]$–thf at a vitreous carbon electrode using a scan rate of 0.2 V s^{-1}. [b] The steps are those referred to in Scheme 1 and in the text: e_{rev} implies a reversible one-electron reduction (+e) or oxidation (−e); e_{irr} implies an irreversible oxidation or reduction process, when prefixed by *n*, the number of electrons involved was not determined. [c] Measured at −20 °C.

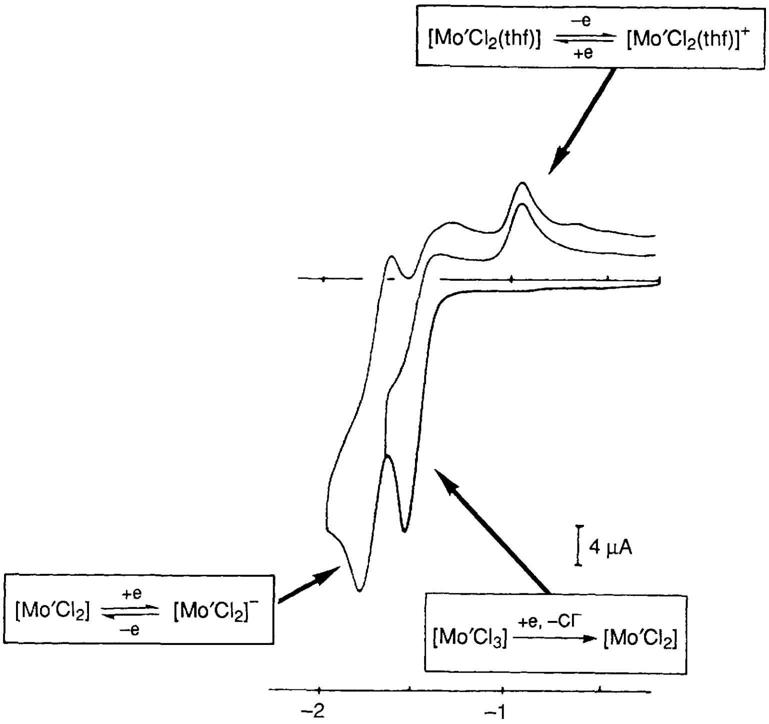


Fig. 2 Room-temperature (20 °C) cyclic voltammetry of *mer*-$[MoCl_3(dpepp)]$ recorded otherwise under the same conditions as those of Fig. 1. The reversible loss of Cl$^-$ from the electrogenerated anion (steps 1 and 2) leads to the formation of $[MoCl_2(dpepp)]$ which reduces reversibly (step d)

product (Fig. 1, Scheme 1: step 1). This molybdenum(II) species is electroactive at −2.34 V (Table 1) where it undergoes an irreversible one-electron reduction, see below (Fig. 1 and Scheme 1, Step a).

The Fate of $[MoCl_3(dpepp)]^-$ *at Room Temperature.*—The primary reduction of *mer*-$[MoCl_3(dpepp)]$ is only partially reversible at room temperature (*ca.* 23 °C) and the major product of the electroreduction is detected as a species which undergoes oxidation near −1 V relative to the ferrocenium–ferrocene couple, Fig. 2. In the presence of PPh_3 the formation of this product is suppressed: a new species is observed which oxidises at a potential identical with that measured for authentic *trans*-$[MoCl_2(dpepp)(PPh_3)]$. This suggests that the product detected in the absence of the phosphine is $[MoCl_2(dpepp)(thf)]$ (Scheme 1, steps 2 and 3). In accord with this assignment we observe corresponding species $[MoCl_2(dpepp)(solvent)]$ with discrete redox potentials in the solvents MeCN or Me_2NCHO. The relative oxidation potentials of the various molybdenum(II) species (Table 1) are consistent with the P_L values for Cl$^-$, thf and PPh_3.[7,16]

The products $[MoCl_2(dpepp)(L)]$ (L = MeCN, Me_2NCHO, PPh_3 or PEt_2Ph) are formed by loss of Cl$^-$ from $[MoCl_3(dpepp)]^-$: the reversibility of this dissociation (Scheme 1, step 2) is demonstrated by the suppression of the formation of $[MoCl_2(dpepp)(thf)]$ in the presence of added Cl$^-$ with a corresponding enhancement of the reversibility of the $[MoCl_3(dpepp)]^{0/-}$ couple (Scheme 1, steps 1 and 2).

The Formation of $[MoCl_2(dpepp)]$.—At room temperature cyclic voltammetry shows that reduction of *mer*-$[MoCl_3(dpepp)]$ generates an intermediate which undergoes quasi-

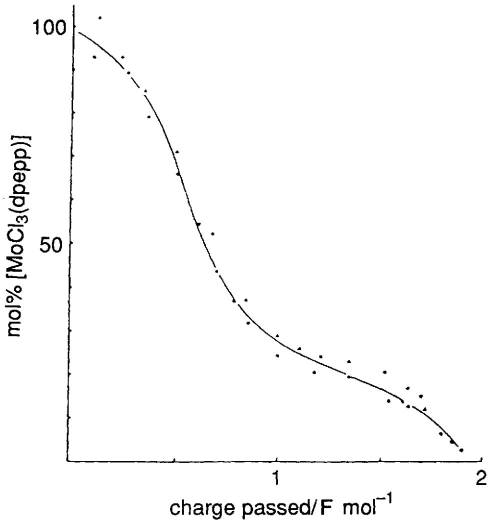


Fig. 3 Charge course for the consumption of $[MoCl_3(dpepp)]$ during bulk electrolysis at −1.6 V in the presence of PPh_3. Note the initial rate of decay corresponds to a one-electron reduction and correlates with the build-up of the primary product *trans*-$[MoCl_2(PPh_3)(dpepp)]$ as shown by Fig. 4: as electrolysis proceeds decomposition of *trans*-$[MoCl_2(dpepp)(PPh_3)]$ takes place to give an electroactive product. The reduction was monitored under dinitrogen

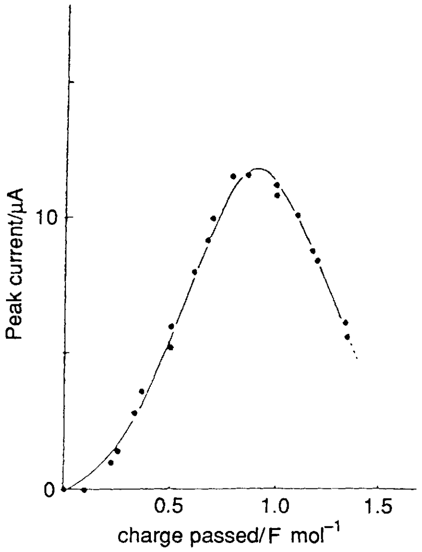


Fig. 4 Charge course to the formation and decay of the primary product of bulk electrolysis of *mer*-$[MoCl_3(dpepp)]$ in the presence of PPh_3 at −1.6 V. The yield of $[MoCl_2(dpepp)(PPh_3)]$ reaches a maximum after the passage of *ca.* 1 F mole^{-1} of the trichloride and thereafter decays. The reduction was monitored under dinitrogen

reversible reduction about 200 mV negative of the primary process, Fig. 2. The formation of this species is suppressed by chloride and at low temperature, Fig. 1. At first sight it is plausible to attribute the quasi-reversible reduction process to the $[MoCl_2(dpepp)(thf)]^{0/-}$ couple, however we dismiss this possibility for the following reasons. (*i*) The potential is independent of solvent. (*ii*) The reduction potential is considerably positive of that observed for *trans*-$[MoCl_2(dpepp)(PPh_3)]$ and this is inconsistent with the relative donicity of the thf and PPh_3.[7,16] (*iii*) Controlled-potential electrolysis at a potential corresponding to the primary reduction in conjunction with *in-situ* voltammetry shows that $[MoCl_2(dpepp)(thf)]$ builds up during the early stage of electrolysis of *mer*-$[MoCl_3(dpepp)]$ but there is no corresponding build-up of the voltammetric peaks associated with the quasi-reversible couple.

We therefore suggest that this major species is five-co-ordinate $[MoCl_2(dpepp)]$ generated by loss of chloride from $[MoCl_3(dpepp)]^-$ (Scheme 1, step 2). The quasi-reversible nature of the $[MoCl_2(dpepp)]^{0/-}$ couple (Scheme 1, step d) is suggested by the observation that the peak separation $E_p^{red} - E_p^{ox}$] increases from 90 mV at 0.02 V s^{-1} to 250 mV at 0.5 V s^{-1}.[17,18] The retardation of the heterogeneous electron transfer could be a consequence of a high activation energy barrier arising from a geometric rearrangement of $[MoCl_2(dpepp)]$.[19,20]

Low-temperature voltammetry provides some evidence for an isomeric form of $[MoCl_2(dpepp)]$. At −20 °C $[MoCl_3(dpepp)]^-$ undergoes irreversible reduction as shown by Fig. 1. This process leads to the formation of a species which oxidises near −1.6 V *versus* ferrocenium–ferrocene to give $[MoCl_2(dpepp)(thf)]$ (Scheme 1, steps d and 3). Although the oxidation potential is near that assigned to $[MoCl_2(dpepp)]^-$ the potentials are not identical. The complex $[MoCl_2(dpepp)]$ could exist in several forms encompassed by trigonal-bipyramidal and square-pyramidal geometries: the ligand dpepp and related tridentate phosphines are known to exhibit both meridional and facial arrangements in metal complexes.[21–23]

Electron-transfer Chemistry and Reactivity of trans-$[MoCl_2(dpepp)(PPh_3)]$.—Cyclic voltammetry on freshly prepared solutions of *trans*-$[MoCl_2(dpepp)(PPh_3)]$ exhibit a well defined, diffusion-controlled reversible one-electron oxidation at −0.67 V *versus* ferrocenium–ferrocene (Scheme 1, step 6) and an irreversible reduction at E_p −2.3 V. The latter process tends towards a two-electron process at slow scan rates (Scheme 1, step 7). The redox potentials for both oxidation and reduction are close to those observed for *trans*-$[MoCl_2(dppe)_2]$; these are at −0.59 and −2.25 V *versus* ferrocenium–ferrocene respectively.[7] Evidently the dichlorides of the square-planar $\{Mo(dpepp)(PPh_3)\}$ and $\{Mo(dppe)_2\}$ assemblies have similar frontier orbital energies.

Solutions of *trans*-$[MoCl_2(dpepp)(PPh_3)]$ are not indefinitely stable. On standing in thf at ambient temperatures slow decomposition occurs and voltammetry reveals the formation of several products. Among these *mer*-$[MoCl_3(dpepp)]$ is clearly identifiable. The instability of *trans*-$[MoCl_2(dpepp)(PPh_3)]$ explains why bulk electrolyses of *mer*-$[MoCl_3(dpepp)]$ carried out at −1.6 V in the presence of PPh_3 deviate from 1 F mol^{-1} coulometry as illustrated by Fig. 3 and why the product *trans*-$[MoCl_2(dpepp)(PPh_3)]$ builds-up and decays as shown by Fig. 4. The regeneration of *mer*-$[MoCl_3(dpepp)]$ during electrolysis accounts for coulometric *n* values greater than one.

In contrast the complex *trans*-$[MoCl_2(dppe)_2]$ is indefinitely stable in solution and we attribute the instability of *trans*-$[MoCl_2(dpepp)(PPh_3)]$ to reversible loss of PPh_3 with following irreversible chemistry: a parallel instability is exhibited by the solvato species $[MoCl_2(dpepp)(thf)]$ (Scheme 1, steps 3 and 5).

A possible irreversible step is the disproportionation of five-co-ordinate $[MoCl_2(dpepp)]$. Although we have been able to identify *mer*-$[MoCl_3(dpepp)]$ we have not been able to isolate and characterise molybdenum-(I) or -(0) co-products from the decay of the molybdenum(II) species.

The Electrochemistry of trans-$[Mo(N_2)_2(dpepp)(PPh_3)]$, *fac*-$[Mo(\eta^6\text{-}C_6H_5PPh_2)(dpepp)]$ *and Products of Electroreduction of trans*-$[MoCl_2(dpepp)(PPh_3)]$ *under* N_2 *and* Ar.—The molybdenum(0) complexes *trans*-$[Mo(N_2)_2(dpepp)(PPh_3)]$ and *fac*-$[Mo(\eta^6\text{-}C_6H_5PPh_2)(dpepp)]$ each undergo a reversible one-electron oxidation at −0.79 and −0.83 V *versus* ferrocenium–ferrocene respectively (Table 1; Scheme 1, steps 10 and 11). Cyclic voltammetry shows that under molecular nitrogen at 1 atm the irreversible reduction of *trans*-$[MoCl_2(dpepp)(PPh_3)]$ gives a dinitrogen containing species, Fig. 5. The oxidation of this species occurs at E_p = −0.76 V *versus* ferrocenium–ferrocene, *i.e.* close to the oxidation potential of *trans*-$[Mo(N_2)_2(dpepp)(PPh_3)]$. However the electrogenerated

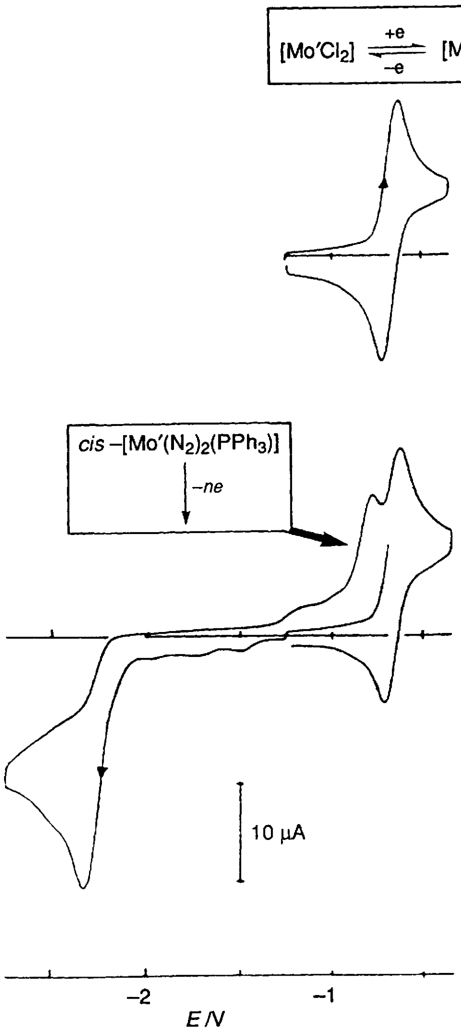


Fig. 5 Cyclic voltammograms of *trans*-[$MoCl_2$(dpepp)(PPh_3)] prepared by electroreduction of *mer*-[$MoCl_3$(dpepp)] in the presence of PPh_3; (*a*) shows the reversible oxidation of the dichloride to the monocation (step 6), (*b*) shows the irreversible reduction under molecular nitrogen to *cis*-[Mo(N_2)$_2$(dpepp)(PPh_3)] (step 7) and the *irreversible* oxidation of this species (step 12). Conditions are as for Fig. 2

species, unlike the chemically prepared complex, oxidises quite irreversibly. This irreversibility cannot be attributed to the presence of Cl^- because this anion has no effect on the voltammetry of *trans*-[Mo(N_2)$_2$(dpepp)(PPh_3)]. Therefore it is evident that a new but closely related dinitrogen complex has been generated. We have recently shown that the oxidations of *cis*- and *trans*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] and their tungsten analogues occur at virtually identical potentials, but the oxidation of the *cis* compounds are *irreversible* whereas those of the *trans* isomers are *reversible*.[3] It therefore seems most likely that the electrogenerated species is *cis*-[Mo(N_2)$_2$(dpepp)(PPh_3)].

Attempts to electrosynthesise on a preparative scale *cis*- or *trans*-[Mo(N_2)$_2$(dpepp)(PPh_3)] by electroreduction of *mer*-[$MoCl_3$(dpepp)] or *trans*-[$MoCl_2$(dpepp)(PPh_3)] under 1 atm of molecular nitrogen at room temperature have met with limited success. Two molybdenum products were identified in the catholyte following bulk preparative electrolysis under dinitrogen. Cyclic voltammetry of the catholyte following exhaustive reduction showed that *fac*-[Mo(η^6-$C_6H_5PPh_2$)(dpepp)] was formed as the major product. Monitoring the electrolysis by difference Fourier-transform IR spectroscopy showed the growth of a new absorption band at 1979 cm^{-1}. The frequency corresponds to that measured from an authentic sample of *trans*-[Mo(N_2)$_2$(dpepp)(PPh_3)] in the electrolyte, however the yield of this product was only 7% after the consumption of 2 F mol^{-1} of the starting material. We note that successful chemical syntheses of *trans*-[Mo(N_2)$_2$(dpepp)(PPh_3)] are carried out at 0 °C and at 5 atm.[10] Attempts chemically to synthesise *trans*-[Mo(N_2)$_2$(dpepp)(PPh_3)] under 1 atm at room temperature gave erratic yields ranging from 0 to 20% with the product contaminated with *fac*-[Mo(η^6-$C_6H_5PPh_2$)(dpepp)]. Furthermore it has been shown that ligating dinitrogen is lost from *cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] at about 200 times the rate as from *trans*-[Mo(N_2)$_2$(dppe)$_2$].[24] This suggests that under ambient conditions reversible loss of N_2 from *cis*-[Mo(N_2)$_2$(dpepp)(PPh_3)] leads to the irreversible formation of the η^6-arene complex (Scheme 1, step 9) at a rate which is faster than isomerisation to the stable *trans* isomer (Scheme 1, step 8); the reversible isomerisation of *cis*- and *trans*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] has been reported recently.[3]

Other Pathways to Molybdenum(0) *Products: Electron-transfer Reactions of* [$MoCl_2$(dpepp)].—The quasi-reversible reduction of [$MoCl_2$(dpepp)] under argon gives an unstable anion which is attacked by solvent or phosphine. Thus cyclic voltammetry shows that in the presence of PPh_3 two reduction peaks are observed. The more negative of these, at $E_p = -2.28$ V *versus* ferrocenium–ferrocene, decreases with increasing concentration of the phosphine whilst the more positive, at -2.03 V, is enhanced. These redox processes must be associated with the binding of thf or PPh_3, respectively, to a Mo centre and they are linked in the voltammetry by an isopotential point.[25–27] This demonstrates that the species reduced at -2.28 and -2.03 V are in equilibrium.

We will now consider the nature of these derivatives of [$MoCl_2$(dpepp)]$^-$. One plausible candidate for the PPh_3 ligated species is the simple adduct [$MoCl_2$(dpepp)(PPh_3)]$^-$. However this species can be eliminated because we have established that the reduction of independently synthesised [$MoCl_2$(dpepp)(PPh_3)] occurs at -2.30 V *versus* ferrocenium–ferrocene. Similarly we find that [$MoCl_2$(dpepp)(PEt_2Ph)] reduces at -2.42 V whereas the intermediate generated from [$MoCl_2$(dpepp)] in the presence of PEt_2Ph reduces at -2.09 V. It seems likely therefore that these derivatives of the one-electron reduction of [$MoCl_2$(dpepp)] are the neutral molybdenum(I) monochloro species [MoCl(dpepp)(L)] or [MoCl(dpepp)(L)(thf)] where L = PPh_3, PEt_2Ph or thf. A stable rhenium(I) species [ReCl(dppe)$_2$] related to the former five-co-ordinate species is known,[28] however we favour the latter assignment because *trans*-[MoCl(dppe)$_2$(thf)] also reduces near -2.1 V *versus* ferrocenium–ferrocene (Scheme 1, steps b and c).

Under argon, electrochemical reduction of [$MoCl_3$(dpepp)] gives the arene complex [Mo(η^6-$C_6H_5PPh_2$)(dpepp)] directly as shown by the voltammogram of Fig. 6(*a*). Under dinitrogen, but otherwise under the same conditions, the appearance of a new oxidation peak at $E_p = -0.76$ V is evident, which corresponds to the oxidation of *cis*-[Mo(N_2)$_2$(dpepp)(PPh_3)], Fig. 6(*b*). Notably, reduction at -1.7 V also leads to the formation of some [Mo(N_2)$_2$(dpepp)(PPh_3)] and, in the presence of PEt_2Ph, to the corresponding dinitrogen complex.

The reduction of the five-co-ordinate intermediate [$MoCl_2$(dpepp)] at -1.7 V provides a relatively high-potential route to the unstable *cis*-dinitrogen species. Direct reduction of the six-co-ordinate *trans*-[$MoCl_2$(dpepp)(PPh_3)] and *trans*-[$MoCl_2$(dppe)$_2$] require potentials *ca.* 0.5 V more negative. This may explain the otherwise puzzling observation that the chemical synthesis of *trans*-[Mo(N_2)$_2$(dppe)$_2$] from *trans*-[$MoCl_2$(dppe)] requires magnesium or sodium amalgam but amalgamated zinc can be successfully employed in the chemical reduction of *trans*-[$MoCl_2$(dpepp)(PPh_3)] to the analogous dinitrogen compound. Whereas the latter dichloride can lose PPh_3 to give the more easily reducible [$MoCl_2$(dpepp)] inter-

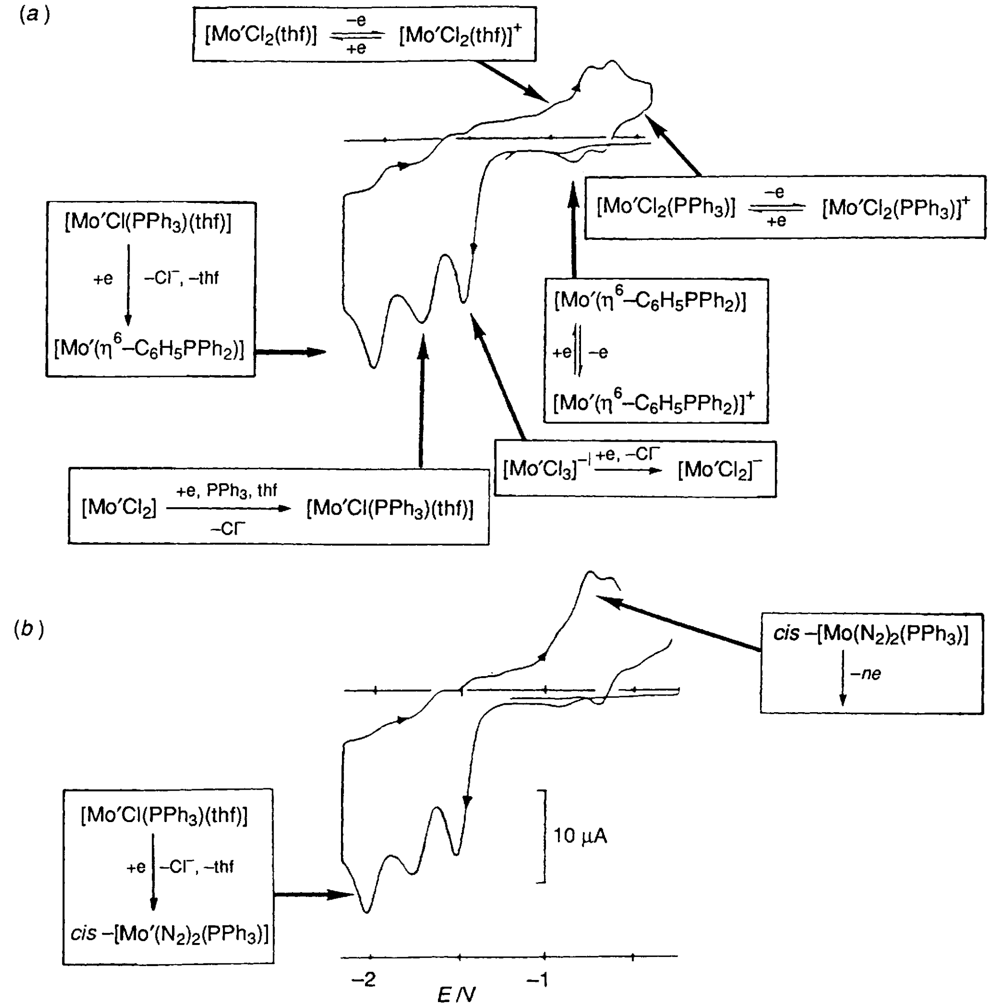


Fig. 6 Cyclic voltammograms showing the sequential reduction of *mer*-[MoCl$_3$(dpepp)] in the presence of PPh$_3$. A cathodic hold for 15 s shows that (*a*) under argon the arene and the dichloride are formed and (*b*) under molecular nitrogen the irreversible oxidation of *cis*-[Mo(N$_2$)$_2$(dpepp)(PPh$_3$)] is also detected

mediate, a corresponding pathway for the former dichloride is not available.

Experimental

Solvents and Reagents.—The purification of thf and the preparation of supporting electrolytes [NBu$_4$][BF$_4$] and [NBu$_4$][PF$_6$] have been described previously.[7,29] The syntheses of *mer*-[MoCl$_3$(dpepp)] and *trans*-[Mo(N$_2$)$_2$(dpepp)(PPh$_3$)] and general experimental procedures utilised in the syntheses described below have been reported previously.[9,10]

Electrochemical Apparatus and Measurements.—Apparatus and instrumentation used in this study have been described elsewhere together with general procedures for voltammetry and controlled-potential electrolyses.[7,29]

Preparation of [MoCl$_2$(dpepp)(PPh$_3$)].—To a flask containing 2 g (excess) of amalgamated zinc, PPh$_3$ (0.92 g, 3.5 mmol) and thf (20 cm^3) was added [MoCl$_3$(dpepp)] (0.43 g, 0.58 mmol). The mixture was stirred under argon for 6 h at room temperature. The solution was filtered, methanol (50 cm^3) added, and the solution cooled to 0 °C. After 2 h red-orange fibrous crystals were isolated by filtration, washed with methanol and pentane, and dried under a flow of N$_2$. The product (0.21 g, 0.21 mmol) was isolated in 31% yield with 0.5 thf of crystallization (Found: C, 64.85; H, 5.30; Cl, 7.25; P, 12.50. Calc. for C$_{54}$H$_{52}$Cl$_2$MoO$_{0.5}$P$_4$: C, 64.90; H, 5.25; Cl, 7.10; P, 12.40%). IR(KBr): ν(MoCl) 310 cm^{-1}. μ_{eff} = 2.75 (Gouy method).

The product can be recrystallised by dissolving in thf solution containing 10% PPh$_3$ and adding methanol as described above.

When the above reaction was carried out under 60 lbf in^{-2} of molecular nitrogen using an excess of amalgamated zinc, for 20 h, *trans*-[Mo(N$_2$)$_2$(dpepp)(PPh$_3$)] was isolated in 28% yield. Under similar conditions *trans*-[Mo(N$_2$)$_2$(dpepp)(PPh$_3$)] can be prepared from *trans*-[MoCl$_2$(dpepp)(PPh$_3$)] using either sodium amalgam or amalgamated zinc in 75 and 42% yields respectively.

Preparation of [Mo(η^6-C$_6$H$_5$PPh$_2$)(dpepp)].—Tetrahydrofuran (40 cm^3, degassed with argon) was added to a mixture of [MoCl$_3$(dpepp)] (2.0 g, 2.7 mmol), PPh$_3$ (2.12 g, 8.06 mmol) and 1% sodium amalgam (150 g) under argon at 0 °C. The mixture was stirred for 3 h after which the suspension was decanted from the amalgam and filtered twice through a layer of Celite. The volume of solvent was reduced to about 10 cm^3 by bubbling molecular nitrogen through the solution. Methanol (60 cm^3) was added slowly over a period of 1 h to cause the precipitation of yellow-orange crystals of product. The product was collected by filtration and washed with methanol and pentane and dried *in vacuo*. Yield: 1.8 g (75%). ^{31}P-{^{1}H} NMR (C$_6$D$_6$, 80.984 MHz, 23 °C, [Mo(η^6-C$_6$H$_5$P$_x$Ph$_2$){(Ph$_2$P$_b$CH$_2$CH$_2$)$_2$P$_a$Ph}]): δ 103.15 (dt, 1, J_{PP} = 14.30, J_{PP} = 3.71 Hz, P$_a$), 78.08 (d, 2, P$_b$), −10.84 (d, 1, P$_x$) (δ relative to 85% H$_3$PO$_4$).

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