

Electron-transfer Reactions in Nitrogen Fixation. Part 1. The Electrosynthesis of Dinitrogen, Hydride, Isocyanide, and Carbonyl Complexes of Molybdenum: Intermediates, Mechanisms, and Energetics†

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Dinitrogen, hydride, carbonyl, and isocyanide complexes of Mo⁰ and W⁰ can be electrosynthesised from the molecular substrates N₂, H₂, etc. and precursors *trans*-[MX₂(Ph₂PCH₂CH₂PPh₂)₂] (M = Mo; X = Cl, Br, I, SPh, or SBuⁿ; M = W; X = Cl), [MoH₂Cl₂(Ph₂PCH₂CH₂PPh₂)₂], or from MoCl₃ and Ph₂PCH₂CH₂PPh₂. Intermediates, mechanisms, and energetics associated with the electrosyntheses are described.

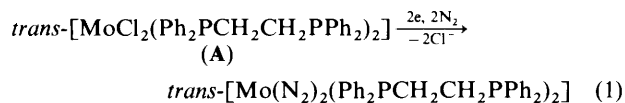
The purpose of the papers in this series is to delineate electron-transfer reactions of transition-metal complexes¹ which are relevant to chemical² and biochemical³ aspects of nitrogen fixation.⁴

The generation by electron transfer of reactive molybdenum intermediates which can bind dinitrogen, dihydrogen, and other substrates has some bearing on the discussion of biological nitrogen fixation and also on the construction of chemical routes to fixed-nitrogen products.^{2,5-7} This work describes intermediates, mechanisms, and energetics associated with the electrosynthesis of dinitrogen, hydride, isocyanide, and carbonyl complexes of molybdenum from the molecular substrates (N₂, CO, H₂, MeNC, and BuⁿNC) and molybdenum halide or thiolate precursors, especially *trans*-[MoCl₂(Ph₂PCH₂CH₂PPh₂)₂]. The electrosyntheses provide new routes to complexes hitherto prepared by chemical reductions,² or indirectly by ligand-displacement reactions.⁸ The formation and reactivities of 16-, 17-, and 18-electron intermediates described here may be of interest in a wider context.

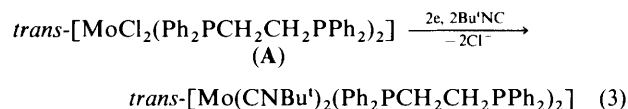
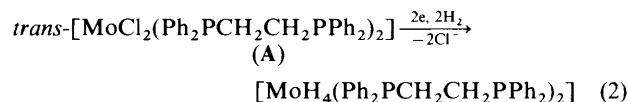
Results and Discussion

Electrosyntheses.—The electrosyntheses were carried out at a mercury-pool electrode in tetrahydrofuran (thf) or dimethylformamide (dmf) containing 0.2 mol dm⁻³ [NBu₄][BF₄], using a divided cell, as detailed in the Experimental section. *In situ* cyclic voltammetry and coulometry were employed to monitor the course of the reductions. Complexes were isolated from the thf electrolyte as solids, and characterised by ¹H n.m.r., ³¹P n.m.r., i.r. spectroscopy, and microanalysis, using the procedures described in the Experimental section. When dmf was used as the electrolyte, products were identified by cyclic voltammetry and ³¹P n.m.r. spectroscopy without prior isolation from the catholyte. All potentials are quoted *versus* the saturated calomel electrode (s.c.e.), against which the ferrocenium-ferrocene couple has an E⁰ value of 0.54 V in thf-0.2 mol dm⁻³ [NBu₄][BF₄].

From *trans*-[MoCl₂(Ph₂PCH₂CH₂PPh₂)₂]. The exhaustive controlled-potential (*ca.* -2.3 V) electrolysis of *trans*-[MoCl₂(Ph₂PCH₂CH₂PPh₂)₂] (A), in a thf electrolyte saturated with gaseous dinitrogen ([N₂] *ca.* 2.6 mmol dm⁻³, 20 °C, 1 atm) gives *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] in good yield (Table 1). Coulometry showed that the electrochemical reduction is an overall two-electron process (1). Under similar conditions,



controlled-potential electrolysis of complex (A) under dihydrogen ([H₂] *ca.* 3.6 mmol dm⁻³, 20 °C, 1 atm) affords the tetrahydride, reaction (2), or, in the presence of other substrates, L (= CO, MeNC, or BuⁿNC), the stable complexes *trans*-[MoL₂(Ph₂PCH₂CH₂PPh₂)₂], *e.g.* reaction (3). Yields are listed in Table 1.



Controlled-potential reductions of complex (A) in the presence of N₂, CO, or BuⁿNC, employing a dmf electrolyte, proceed analogously to those in thf, but, in the *absence* of a substrate, under an atmosphere of argon, the products are determined by the solvent, thf or dmf. This is discussed below.

From other complexes. The tungsten analogue of (A), *trans*-[WCl₂(Ph₂PCH₂CH₂PPh₂)₂] (B), is reduced at a mercury-pool electrode in a thf electrolyte saturated with gaseous dinitrogen to give *trans*-[W(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂]; similarly, under carbon monoxide, electroreduction of (B) affords *cis*- and *trans*-[W(CO)₂(Ph₂PCH₂CH₂PPh₂)₂], Table 1. Whereas the molybdenum dichloride, (A), is reduced cleanly in the presence of BuⁿNC [reaction (3)], electroreduction of (B), under similar conditions, gives a mixture from which low yields of *trans*-[W(CNBuⁿ)₂(Ph₂PCH₂CH₂PPh₂)₂] were isolated.

The electroreduction of *trans*-[Mo(SR)₂(Ph₂PCH₂CH₂PPh₂)₂] (D; R = Ph), in a thf electrolyte under dinitrogen, is relatively straightforward; as with the dichloride, (A), *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] is formed in moderate yield (Table 1). However, under similar conditions, the alkanethiolato-complexes (D; R = Prⁿ or Buⁿ) give poor yields of *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] or *trans*-[Mo(CNBuⁿ)₂(Ph₂PCH₂CH₂PPh₂)₂] in the presence of dinitrogen or BuⁿNC, respectively, Table 1.

The hydrido-complex, [MoH₂Cl₂(Ph₂PCH₂CH₂PPh₂)₂], undergoes the electrosynthetic reactions summarised by Scheme 1 and Table 1. The reduction of the tungsten analogue, [WH₂Cl₂(Ph₂PCH₂CH₂PPh₂)₂] is not accessible in the thf electrolyte.

The 'one-pot' synthesis of *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂-

† Non-S.I. unit employed: atm = 101 325 Pa.

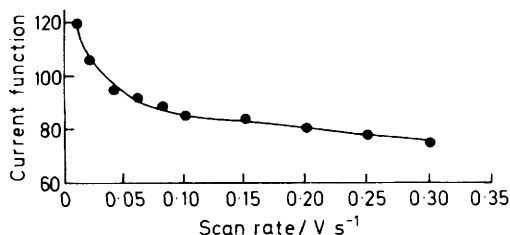
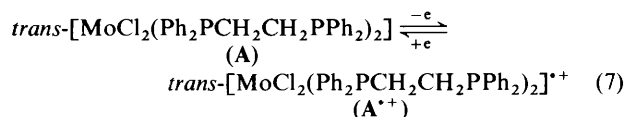


Figure 2. Plot of the current function, F_p^{RED} , versus scan rate, v , showing the deviation towards a 2e process at slow scan rates

chemistry, Figure 2. The independence of F_p^{RED} is diagnostic of diffusion-controlled electron transfer at potentials at and beyond the peak reduction potential, E_p^{RED} . Potential-step responses for solutions of complex (A) in a thf electrolyte, at a platinum electrode stepped from -1.6 to -2.0 V, were also recorded and the resulting transient cathodic current, i_t^{RED} , measured at various times, t , after initiation of the step. The transient current function, $F_t^{\text{RED}} = i_t^{\text{RED}} t^{1/2}$, is essentially independent of t ($t < 4$ s at 22.5°C) and this confirms the mass-transport-limited nature of the primary reduction event.

The number of electrons involved in the primary step was determined from the magnitudes of F_p^{RED} and F_t^{RED} by taking advantage of the observation that complex (A) undergoes a straightforward, reversible, one-electron oxidation to give the stable cation, (A^{*+}) , equation (7) ($E^0 = -0.05$ V), Figure 1(b).



The appropriate current functions for the oxidation, F_p^{OX} and F_t^{OX} , were determined by cyclic voltammetry and potential-step experiments respectively. The ratio $F_p^{\text{RED}}/F_p^{\text{OX}}$ is close to unity at scan rates > 0.1 V s⁻¹, as is apparent from Figure 2; similarly the ratio $F_t^{\text{RED}}/F_t^{\text{OX}}$ is close to unity, provided $t < 4$ s. Both these results show that the reduction involves the initial transfer of a single electron, equation (6).

The reversibility of the one-electron reduction, equation (6), was verified by cyclic voltammetry in thf and dmf electrolytes under various conditions. Figure 1(a) qualitatively shows that the reduction is partially reversible at 0.3 V s⁻¹, 22.5°C , i.e. the peak-current ratio $(i_p^{\text{OX}}/i_p^{\text{RED}})^{\text{RED}}$ is less than unity. At faster scan rates, or lower temperatures, in either thf or dmf electrolytes, the ratio approaches one. A separation in forward and reverse peak potentials, ΔE , close to 60 mV is theoretically associated with reversible one-electron transfer: experimentally we find ΔE for complex (A) is ca. 70 mV (thf electrolyte, 0.1 V s⁻¹, 22.5°C).

The 16-electron parent complex (A) is e.s.r. silent (d^4 , spin state $S = 1$). Electrolysis of (A) in a thf electrolyte at low temperature, followed by freezing of the catholyte and examination by e.s.r. spectroscopy, revealed a weak signal of axial symmetry, $g_\perp = 1.94$, $g_\parallel = 1.98$, which we associate with the generation of paramagnetic $\text{trans-[MoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^{*-}$ ($S = 0.5$).

It is usual to assume that electrochemical reversibility involving fast electron transfer implies the retention of the structural integrity of a molecule,¹⁵ although the generality of this assumption has been criticised.¹⁶ Stable *cis* and *trans* isomers of molybdenum complexes that possess the $\text{Mo}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ framework have E^0 potentials which differ substantially.^{17,18} We find no evidence for the existence of two isomers of (A) in solution from either low-temperature or fast-scan-rate cyclic voltammetry, and therefore conclude that the

Table 2. E^0 Data for primary reductions and oxidations of reactants and products^a

Complex	E^0/V	
	Reduction	Oxidation
$[\text{Mo}(\text{SBU}^n)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.97	-0.20
$[\text{Mo}(\text{SPR}^n)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.96	-0.19
$[\text{Mo}(\text{SPh})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.61	-0.05
$[\text{MoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.68	-0.05
$[\text{MoBr}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.51	+0.01
$[\text{MoI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.34	+0.08
$[\text{WCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-1.74	-0.24
$[\text{MoH}_2\text{Cl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-2.36 ^b	+0.08
$[\text{WH}_2\text{Cl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	< -2.5	-0.07
$[\text{Mo}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.16
$[\text{MoH}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.02
$[\text{Mo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.11
$[\text{Mo}(\text{CO})(\text{Bu}^i\text{NC})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.28
$[\text{Mo}(\text{N}_2)(\text{Bu}^i\text{NC})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.36 ^b
$[\text{Mo}(\text{Bu}^i\text{NC})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.54
$[\text{W}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.15
$[\text{WH}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.14
$[\text{W}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.07
$[\text{W}(\text{Bu}^i\text{NC})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-0.55
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$		+0.54

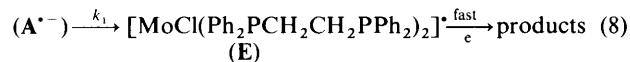
^a All complexes are *trans* isomers except the hydrides: potentials are versus s.c.e. in 0.2 mol dm⁻³ $[\text{NBu}_4][\text{BF}_4]$ -thf. ^b Irreversible process; value is for $E_{p/2}$.

primary one-electron reduction of (A) takes place with retention of the *trans* geometry.¹⁹

The other 16-electron complexes we have studied, $\text{trans-[MX}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ ($M = \text{Mo}$ or W , $X = \text{halide}$ or *thiolate*), also undergo diffusion-controlled, reversible, one-electron reductions to give unstable anions, analogous to the behaviour of (A), equation (6). The formal potentials, E^0 , for these reductions were estimated by cyclic voltammetry and are listed in Table 2. There is a substantial influence of X on the E^0 values, the alkanethiolates being the least easily reduced.

The rate-determining step. The conversion of the intermediate (A^{*-}) into products involves a further electron transfer. This is associated with a current-limiting (rate-determining) chemical step as is evident from the dependence of F_p^{RED} on v at the slower scan rates, Figure 2.

Decomposition of (A^{*-}) by either associative, disproportionation, or dissociative mechanisms could be rate-limiting. Here we show that the dissociative pathway, (8), is operative.



The rate-determining step cannot involve an associative attack on (A^{*-}) by either solvent or substrate since F_p^{RED} is essentially independent of both and substrate concentration, at all scan rates. Associative attack on other 17-electron molybdenum species is known and proceeds *via* unstable 19-electron intermediates.²⁰ Presumably the low electron affinity of (A^{*-}) and/or the steric protection afforded by the two 1,2-bis(diphenylphosphino)ethane ligands precludes the decomposition of (A^{*-}) by such a route.

The possibility that the decomposition of (A^{*-}) proceeds by a disproportionation pathway (9) is now considered with respect to the equilibrium constant for the disproportionation, K_D , and

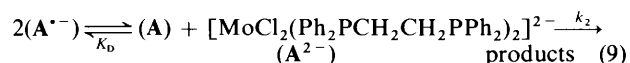
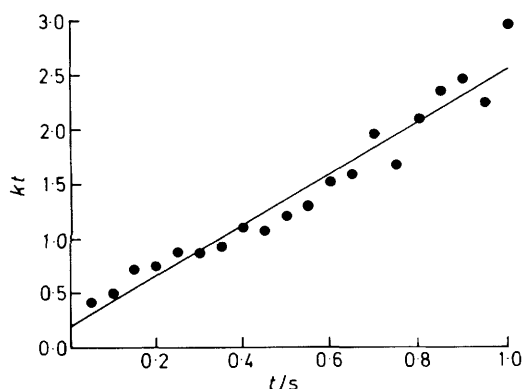
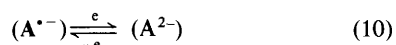


Table 3. Chronoamperometric data for *trans*-[MoCl₂(Ph₂PCH₂CH₂-PPh₂)₂] in thf-0.2 mol dm⁻³ [NBu₄][BF₄] at 49.5 °C

<i>t</i> /s	<i>n</i> _{apparent}	<i>t</i> /s	<i>n</i> _{apparent}
0.05	1.33	0.55	1.73
0.10	1.38	0.60	1.78
0.15	1.51	0.65	1.80
0.20	1.54	0.70	1.86
0.25	1.59	0.75	1.81
0.30	1.59	0.80	1.88
0.35	1.61	0.85	1.91
0.40	1.67	0.90	1.92
0.45	1.66	0.95	1.90
0.50	1.70	1.00	1.95

**Figure 3.** Chronoamperometric *kt* data versus *t*

the first-order rate constant, *k*₂. We know that *E*₂^{0'} for equation (10) must be less than -2.5 V, since we do not observe the direct



reduction of (A^{•-}) before the onset of discharge of the electrolyte. We can therefore calculate an upper limit for *K*_D using equation (11). Thus with the values *E*₂^{0'} < -2.5 V and

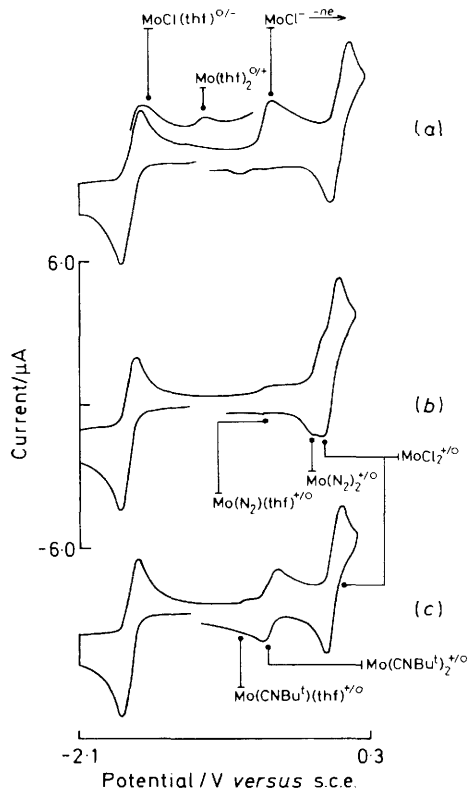
$$K_D = \exp[(nF/RT)(E_2^{0'} - E_1^{0'})] \quad (11)$$

*E*₁^{0'} = -1.68 V [equation (6)] we obtain *K*_D < 10⁻¹⁴ (dimensionless). The decomposition of (A^{•-}) in accord with pathway (9) and the rate law (12) demands a large value of *k*₂ to

$$-d[(\text{A}^{\bullet-})]/dt = K_D k_2 [(\text{A}^{\bullet-})]^2 / [\text{A}] \quad (12)$$

compensate for *K*_D and thereby sustain the regeneration of electroactive (A). The chronoamperometric working curve *n*_{apparent} versus log *K*_D*k*₂*t*, has been simulated by Marcoux²¹ for the general case of disproportionation. Table 3 lists values for *n*_{apparent} at various times *t*, which we have calculated from potential-step measurements on solutions of complex (A) in a thf electrolyte at 49.5 °C. From these and the working curve we obtain values of *K*_D*k*₂ close to 10⁻¹ s⁻¹, i.e. *k*₂ has to be greater than 10¹³ s⁻¹ if the disproportionation mechanism is to operate. Values of *k*₂ > 10¹⁰ s⁻¹ are unreasonable and the proposition of decomposition of (A^{•-}) via the disproportionation pathway (9) is therefore untenable.

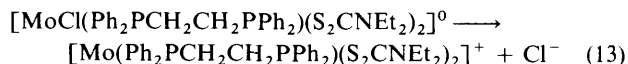
Since associative or disproportionation pathways are improbable, the dissociative mechanism, (8), provides the simplest rationale of our experimental data. The chrono-

**Figure 4.** Ramp-clamp voltammograms of *trans*-[MoCl₂(Ph₂PCH₂CH₂PPh₂)₂]; 0.8 mmol dm⁻³ solution of complex in thf-0.2 mol dm⁻³ [NBu₄][BF₄]; clamp time 17 s, scan rate 0.3 V s⁻¹ at a platinum electrode; [Bu¹NC] = 2.6 mol dm⁻³. In the presence of (a) argon, (b) nitrogen, and (c) Bu¹NC

amperometric working curve, *n*_{apparent} versus log *k*₁*t*, for an electron transfer-chemical reaction-electron transfer (e.c.e.) mechanism²² and the *n*_{apparent} data, listed in Table 3, allow the estimation of *k*₁*t* at various times, *t*. Figure 3 shows the plot of *k*₁*t* versus *t*, from which we obtain *k*₁ = 2.7 ± 0.2 s⁻¹ at 49.5 °C, correlation coefficient 0.973.

The transfer of the second electron in mechanism (8) is assumed to take place at the electrode in so far as we have analysed our data in terms of an e.c.e. mechanism. Reduction of an electroactive intermediate by (A^{•-}) in solution, the closely related e.c.c. pathways, is also possible.²³

In a related electrochemical study of complexes such as [MoCl(Ph₂PCH₂CH₂PPh₂)(S₂CNET₂)₂]⁺ we found that the rate of Mo-Cl bond cleavage following single electron transfer is markedly influenced by the nature of the solvent: reaction (13) is about ten times faster in CH₃CN than it is in thf.¹⁰ This



contrasts with the insensitivity of the rate of Mo-Cl cleavage to solvent after single-electron reduction of (A). In the former case a separation of positive and negatively charged species occurs, a process favoured by the solvent of higher dielectric constant, CH₃CN. In the latter case, loss of Cl⁻ from (A^{•-}) does not involve 'ion-pair separation' and the rate is consequently insensitive to the solvent.

Detection and identification of intermediates. The electrochemical reduction of complex (A) or its analogues to stable closed-shell products involves the generation of (15-18)-electron intermediates in which the Mo(Ph₂PCH₂CH₂PPh₂)₂

Table 4. Detection potentials* of intermediates

Precursor	Substrate	$E_{p/2}/V$	Assignment	
$trans-[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$	Bu ¹ NC	-0.75	$trans-[Mo(Bu^1NC)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$	
	N ₂	-0.62	$trans-[Mo(N_2)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$	
	H ₂	-0.54	$[MoH_2(thf)(Ph_2PCH_2CH_2PPh_2)_2]$	
	CO	-0.48	$trans-[Mo(CO)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$	
	thf	-1.18	$trans-[Mo(thf)_2(Ph_2PCH_2CH_2PPh_2)_2]$	
$trans-[MoI_2(Ph_2PCH_2CH_2PPh_2)_2]$	thf	ca. 1.6	$trans-[MoCl(thf)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	thf	-1.58	$trans-[MoI(thf)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[Mo(SBu^a)_2(Ph_2PCH_2CH_2PPh_2)_2]$	-1.44	$trans-[Mo(SBu^a)(thf)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[Mo(SPh)_2(Ph_2PCH_2CH_2PPh_2)_2]$	-1.34	$trans-[Mo(SPh)(thf)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$	-0.70	$trans-[Mo(dmf)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$	-0.66	$[MoCl(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[MoBr_2(Ph_2PCH_2CH_2PPh_2)_2]$	-0.63	$[MoBr(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[Mo(SBu^a)_2(Ph_2PCH_2CH_2PPh_2)_2]$	-0.60	$[Mo(SBu^a)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[MoI_2(Ph_2PCH_2CH_2PPh_2)_2]$	-0.59	$[MoI(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[Mo(SPh)_2(Ph_2PCH_2CH_2PPh_2)_2]$	-0.48	$[Mo(SPh)(Ph_2PCH_2CH_2PPh_2)_2]^-$	
	$trans-[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$	Bu ¹ NC + N ₂	-0.35	$trans-[Mo(N_2)(Bu^1NC)(Ph_2PCH_2CH_2PPh_2)_2]$
		Bu ¹ NC + CO	-0.38	$trans-[Mo(CO)(Bu^1NC)(Ph_2PCH_2CH_2PPh_2)_2]$

* Versus the s.c.e. in thf-0.2 mol dm⁻³ [NBu₄][BF₄].

framework is retained. Ramp-clamp voltammetry allows the detection of these intermediates and the analysis of their oxidation potentials provides a means for their identification.

Figure 4 shows a series of voltammograms of (A) in a thf electrolyte which were recorded in the absence of a substrate (a), and in the presence of N₂ (b) or Bu¹NC (c), using a 20-s cathodic clamp. The formation of stable, closed-shell products is clearly evident. Under N₂ the reversible couple associated with the oxidation of $trans-[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ is observed, in the presence of Bu¹NC the $trans-[Mo(Bu^1NC)_2(Ph_2PCH_2CH_2PPh_2)_2]^{+/0}$ couple is detected, Figure 4(b) and (c) respectively. However, the more informative features of the voltammograms are the small peaks observed in the presence of substrates and the peaks detected under argon in their absence.

The peaks which are observed near -1.6, -1.1, and -0.65 V in Figure 4(a) are suppressed in the presence of N₂, CO, H₂, or Bu¹NC and, in each case, a single new peak appears associated with the oxidation of an unstable intermediate, Figure 4(b) and (c). The oxidation potentials, $E_{p/2}^{OX}$, of these species are listed in Table 4. It is evident from this Table that $E_{p/2}^{OX}$ varies according to the nature of the substrate present; from this we infer that a substrate molecule is bound in each of the intermediates.

The intermediates are too unstable to characterise by conventional spectroscopy but we have shown by earlier work that the linear-free-energy relationship (14) can be used to

$$E_{\frac{1}{2}}^{OX} = E_s + \beta P_L \quad (14)$$

identify unstable species, e.g. $trans-[Mo(N_2)(NH_3)(Ph_2PCH_2CH_2PPh_2)_2]^{18}$ in solution. We have therefore used a modified form of this relationship, equation (15), to analyse the $E_{p/2}^{OX}$

$$E_{p/2}^{OX} = \text{Constant} + \beta P_L \quad (15)$$

data listed in Table 4. Because the concentrations of the intermediates we detect are low, $E_{p/2}^{OX}$ is more accurately measurable than is $E_{\frac{1}{2}}^{OX}$; we assume that the $E_{p/2}^{OX}$ values parallel the thermodynamic trend of $E_{\frac{1}{2}}^{OX}$. Figure 5 shows the plot of $E_{p/2}^{OX}$ versus P_L , which is linear with a correlation coefficient of 0.992. Thus the substrates, N₂, CO, Bu¹NC, and Cl⁻ bind to a common site. The oxidation potential of $trans-[Mo(CO)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$ is coincident with that of the intermediate detected under CO; we therefore identify the common site with $trans-[Mo(thf)(Ph_2PCH_2CH_2PPh_2)_2]$. The

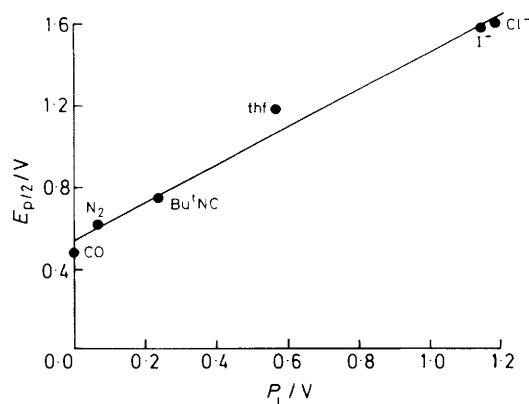


Figure 5. Detection potentials, $E_{p/2}^{OX}$, versus ligand parameter of substrate, P_L

peaks which we associate with the oxidation of the intermediates $trans-[MoCl(thf)(Ph_2PCH_2CH_2PPh_2)_2]^-$ and $trans-[MoL(thf)(Ph_2PCH_2CH_2PPh_2)_2]$, L = N₂ or Bu¹NC, are located in Figure 4: the $E_{p/2}^{OX}$ potentials of these and related species are assigned in Table 4. The reversible oxidation of $trans-[MoI(thf)(Ph_2PCH_2CH_2PPh_2)_2]^-$ is well resolved from that of the $trans-[MoI_2(Ph_2PCH_2CH_2PPh_2)_2]^{0/-}$ couple (Figure 6) and is included in the correlation.

Related species $[W(thf)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and $[W(N_2)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$ have been postulated as intermediates which arise by flash photolysis of $trans-[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ in thf. The former is thought to react rapidly with N₂ to give the latter, which in turn reacts at a slower rate with N₂ to regenerate the parent complex.^{24,25}

We assign the major peak observed in the voltammetry of complex (A) under argon in the thf electrolyte to the irreversible oxidation of a moderately stable intermediate $trans-[MoCl(Ph_2PCH_2CH_2PPh_2)_2]^-$ (E^-), which is located in Figure 4(a). Our evidence for this assignment is as follows. The complexes $trans-[MoX_2(Ph_2PCH_2CH_2PPh_2)_2]$, X = halide or thiolate, all show major peaks in a similar potential domain; Table 4 lists the characteristic $E_{p/2}^{OX}$ values of these species. The $E_{p/2}^{OX}$ values differ, thus we conclude that an X⁻ ligand is retained at the molybdenum centre. Current-function data show that (E^-) is formed after the transfer of two electrons, which is consistent

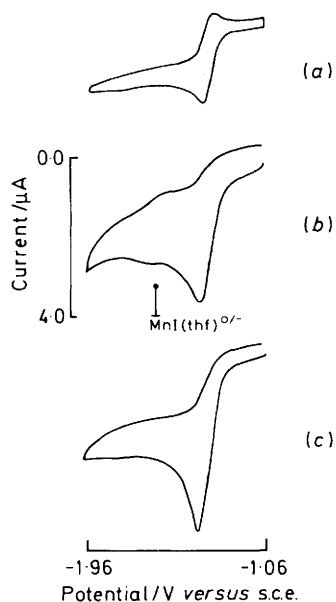


Figure 6. Cyclic voltammetry of $trans\text{-}[\text{MoI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ in thf - $0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{BF}_4]$ at a platinum electrode, scan rate 0.3 V s^{-1} . In the presence of argon at -10 (a) and 25°C (b) and in the presence of CO at 25°C (c)

with the generation of a molybdenum(0) species. If, as is reasonable, we assume the $\text{Mo}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ framework is preserved, three formulations are possible: $[\text{MoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^{2-}$, $[\text{MoCl}(\text{thf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$, and $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$, a 16-electron intermediate. The dianion is clearly untenable since we know its oxidation occurs at a potential more negative than -2.5 V ; the 18-electron anion we have already identified with the oxidation near -1.6 V , Figure 5, thus we assign the oxidation observed at -0.66 V to $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$.

Stable species related to $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$, (E^-), are known. Hidai and co-workers²⁶ have prepared $trans\text{-}[\text{Mo}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ and shown that in the solid state it possesses a square-pyramidal geometry (CO is apical). This species reacts with a wide range of donor, π -acid, and certain anionic ligands to give stable 18-electron octahedral adducts.^{26,27} Recently we described²⁸ the synthesis and structure of $[\text{ReCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$. It possesses a trigonal-bipyramidal geometry (Cl is axial) but reacts selectively with ligands. Whereas it binds CO and isocyanides, it does not co-ordinate N_2 , thf, or anionic ligands.

Although moderately stable on the voltammetric time-scale, (E^-) cannot be prepared by controlled-potential electrolysis as on this longer time-scale it decomposes. Thus controlled-potential reduction of complex (A) under argon in a thf electrolyte always gives a mixture of products. The ^{31}P , ^1H n.m.r. and i.r. spectra of the solids isolated from the catholyte show that this mixture contains $[\text{MoH}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$, $trans\text{-}[\text{Mo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$, and 'free' $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ as major components. This parallels the thermal decomposition of $trans\text{-}[\text{Mo}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ in thf.²⁹

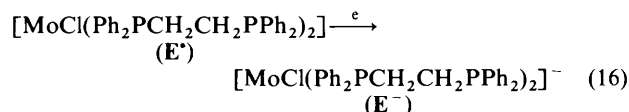
In contrast, the reduction of (A) under argon in a dmf electrolyte produces a dark red catholyte in a clean two-electron process. This catholyte contains a single, stable molybdenum(0) species which we formulate as $trans\text{-}[\text{Mo}(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$, (F), an analogue of $trans\text{-}[\text{Mo}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ and $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$. The reasons for this formulation are as follows. First,

the ^{31}P n.m.r. spectrum of (F) in the dmf electrolyte shows a singlet resonance consistent with the retention of a square-planar array of P atoms. Secondly, the reaction between (F) and Bu^1NC results in the rapid formation of $trans\text{-}[\text{Mo}(\text{Bu}^1\text{NC})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$; similarly with N_2 or with CO the bis(dinitrogen) or dicarbonyl analogues are formed, respectively. Thirdly, irradiation of a solution of $trans\text{-}[\text{Mo}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ with a tungsten-filament lamp generates a species which has identical redox characteristics to those of (F); thus (F) cannot possess a co-ordinated Cl^- . Finally, we exclude the possibility that (F) is the decarbonylation product, $trans\text{-}[\text{Mo}(\text{CO})(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$,²⁶ because $trans\text{-}[\text{Mo}(\text{CO})(\text{Bu}^1\text{NC})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is not formed in its reaction with Bu^1NC . Thus far the observations are consistent with the formulation of (F) as either $trans\text{-}[\text{Mo}(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ or $trans\text{-}[\text{Mo}(\text{dmf})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$. It has been shown that dmf functions as a powerful donor ligand when co-ordinated *via* its O atom to a molybdenum(0) centre, indeed, $\nu(\text{CO})$ in the complex $trans\text{-}[\text{Mo}(\text{CO})(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is comparable to $\nu(\text{CO})$ in the anion $trans\text{-}[\text{Mo}(\text{CO})(\text{N}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$.^{18,30} On this basis we suggest that a *single* dmf ligand is sufficient to stabilise the molybdenum centre of (F) in a 16-electron configuration, *cf.* $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$.

In the following section we consider how the intermediates arise *via* secondary electronation reactions.

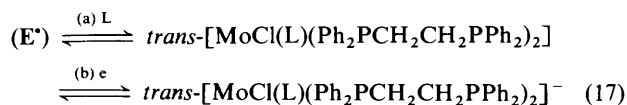
Secondary electronation. The reduction of complex (A) to closed-shell products involves two, discrete, single-electron-transfer reactions. The primary electronation gives ($\text{A}^{\cdot-}$) which loses Cl^- to generate (E^{\cdot}) as discussed earlier. The identification of species involved in the second electron-transfer reaction(s) is crucial to an understanding of the electrocatalytic sequence. The constraints on the nature of the electroactive species are as follows. First such species must be 15- or 17-electron intermediates in which the $\text{Mo}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ framework is retained. Secondly, directly or indirectly, they must give rise to the 16- and 18-electron species described above. Finally, the potentials at which they are reduced must be near or more positive than that associated with the primary electronation of (A), *i.e.* -1.7 V .

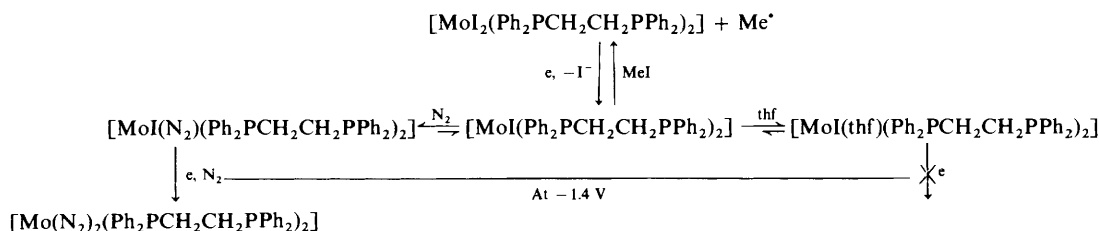
Superficially, reaction (16), the one-electron reduction of



$trans\text{-}[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$, (E^{\cdot}), fulfils such requirements; (E^{\cdot}) is the immediate product of Cl^- loss from ($\text{A}^{\cdot-}$) and (E^{\cdot}) is detected as an intermediate which oxidises irreversibly about 1 V more positive than does ($\text{A}^{\cdot-}$). Although not strictly a thermodynamic potential difference, this is indicative of a considerable driving force for the heterogeneous (or homogeneous) reduction of (E^{\cdot}).

Whilst reaction (16) provides a simple interpretation of the observed chemistry, it is neither the exclusive secondary electron-transfer step, nor indeed a dominant one. Because the loss of Cl^- from ($\text{A}^{\cdot-}$) is slow, (E^{\cdot}) is generated throughout the diffusion layer, *i.e.* away from the electrode. Consequently (E^{\cdot}) has the opportunity of reacting with solvent or substrate molecules (L), prior to secondary electronation, pathway (17). This pathway will be significant if the equilibrium (17a) is favourable and the 17-electron intermediates formed are





Scheme 2.

appropriately electroactive, (17b). The second condition is readily satisfied. We have shown that the couple in which $L = \text{thf}$ occurs about 100 mV more positive than does the (A^{\ominus}) – (A^{\ominus}) couple. Because the P_L values of the substrates $L = \text{N}_2$, CO, or isocyanides are more positive than P_{thf} , the reduction of the 17-electron intermediates $\text{trans}[\text{MoCl}(\text{L})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ will also be favourable. Demonstrably, $\text{trans}[\text{MoCl}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ reduces irreversibly at $E_{p/2}^{\text{RED}} = -0.97 \text{ V}$.³¹

Convincing support for the preceding equilibrium (17a) comes from a parallel study of the voltammetry of $\text{trans}[\text{MoI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$. The primary reduction of this complex is a one-electron process which is considerably less reversible than is the reduction of (A) under similar conditions, Figure 6. Although the loss of I^- from the 17-electron anion $\text{trans}[\text{MoI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ is rapid, under argon *two-electron transfer does not take place at the primary reduction potential*, instead $\text{trans}[\text{MoI}(\text{thf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is detected at a potential about 200 mV more negative than that for the first electron transfer. Thus, in the absence of a substrate, secondary electronation is 'isolated' from the primary electronation step because $\text{trans}[\text{MoI}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is trapped by thf, *cf.* pathway (17a). In the presence of N_2 , CO, or Bu^iNC the irreversible reduction peak is enhanced and the current approaches that for a two-electron process; correspondingly the peak for $\text{trans}[\text{MoI}(\text{thf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is suppressed. This shows that although the concentration of thf is more than a factor of 10^3 higher, the substrates N_2 , CO, and Bu^iNC compete effectively for the $\text{trans}[\text{MoI}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ site and give electroactive products. Clearly the equilibrium of the site with thf is reversible and rapid. Five-co-ordinate low-valent molybdenum species are known to react with alkyl halides, which they homolytically cleave.³¹ The voltammetry of $\text{trans}[\text{MoI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ under argon in the presence of MeI shows a catalytical peak current, i_p^{RED} , which is initially proportional to the concentration of the alkyl halide. This is suppressed in the presence of N_2 , CO, and other substrates, in accord with the competition of these substrates for $\text{trans}[\text{MoI}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$. Scheme 2 summarises the chemistry of $\text{trans}[\text{MoI}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$.

The detection of $\text{trans}[\text{MoCl}(\text{thf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ (and its iodo-analogue) is concordant with pathway (17), but the question which arises is why do we not detect corresponding substrate-ligated species such as $\text{trans}[\text{MoCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$? The 17-electron complex $\text{trans}[\text{MoCl}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ has been shown to undergo an irreversible one-electron reduction by cyclic voltammetry in a thf electrolyte.³¹ This demonstrates that the 18-electron anion is unstable, thereby accounting for the detection of $\text{trans}[\text{Mo}(\text{CO})(\text{thf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ rather than $\text{trans}[\text{MoCl}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ in the voltammetry of (A) under CO, reaction (18). A parallel substitution lability of

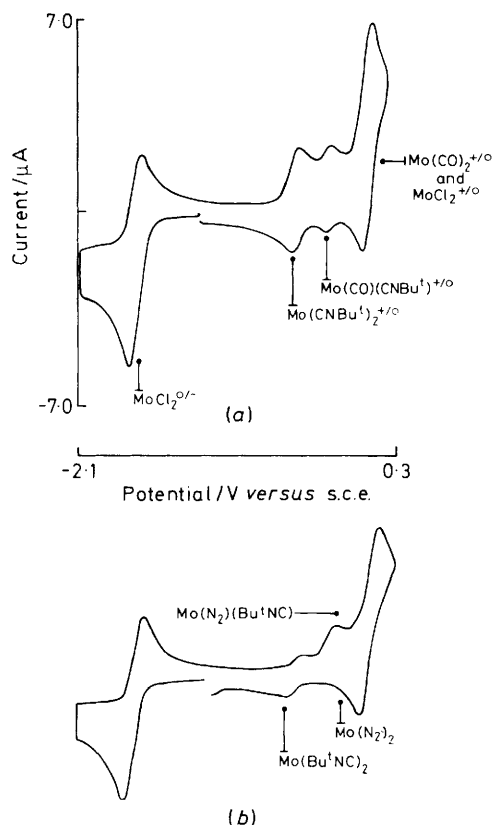
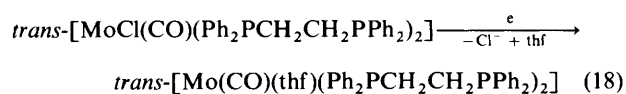
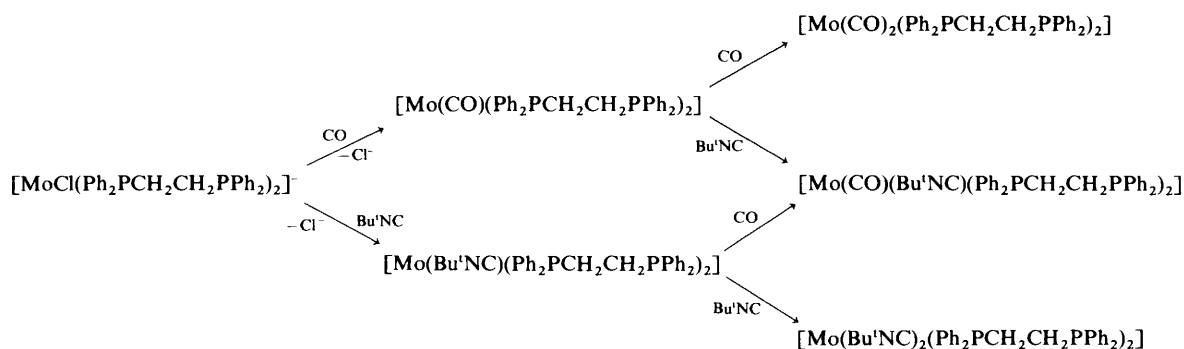


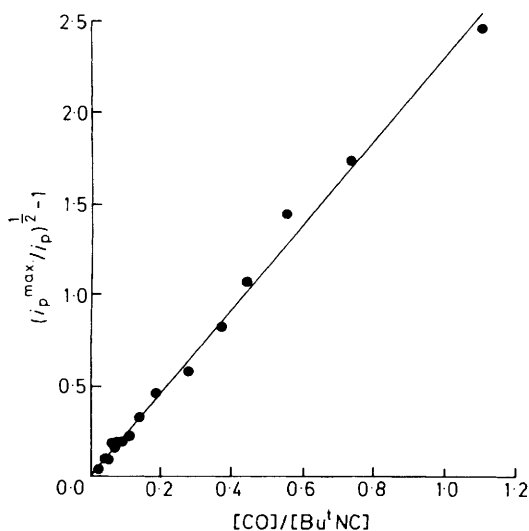
Figure 7. Ramp-clamp voltammograms in the presence of Bu^iNC , 5.2 mmol dm^{-3} , and co-substrates CO (a) or N_2 (b); conditions otherwise as for Figure 4

anionic ligands in the complexes $\text{trans}[\text{Mo}(\text{N}_2)\text{X}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$, $\text{X} = \text{N}_3^-$ or CN^- , has been noted.¹⁸

The discrimination between substrates by molybdenum sites. We wished to know whether the molybdenum sites generated by the electronation of complex (A) in thf were capable of discriminating between strongly binding π -acid substrates. We have therefore probed the product distribution which arises as a consequence of the reduction of (A) in the presence of *co-substrates*, CO and Bu^iNC , by ramp-clamp voltammetry. A cathodic clamp of 20 s imposes a concentration profile of stable products in the diffusion layer which does not relax significantly on the time-scale of the detection ramp, *ca.* 5 s. The peak currents associated with the reversible oxidations of the products under these near-steady-state conditions are taken as a measure of their relative concentrations at the electrode. We find that the peak current, i_p , for the product $\text{trans}[\text{Mo}(\text{CNBu}^i)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ increases smoothly as the ratio $[\text{CO}]/[\text{Bu}^i\text{NC}]$ decreases. It is naturally at a maximum, i_p^{max} , in the absence of CO provided $[\text{Bu}^i\text{NC}] > 5 \text{ mmol dm}^{-3}$, *i.e.* $\text{trans}[\text{Mo}(\text{Bu}^i\text{NC})(\text{thf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is sup-



Scheme 3.

Figure 8. Dimensionless plot for the competitive substrates CO and BuⁿNC

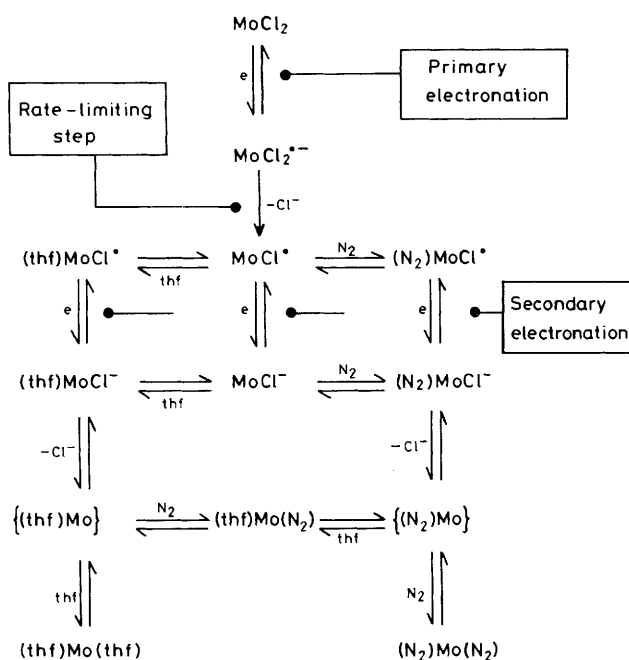
pressed (see above). Correspondingly, the concentration of *trans*-[Mo(CO)(BuⁿNC)(Ph₂PCH₂CH₂PPh₂)₂] increases and then decreases with decreasing [CO]/[BuⁿNC]. Qualitatively the concentration of *trans*-[Mo(CO)₂(Ph₂PCH₂CH₂PPh₂)₂] responds to changes in [CO]/[BuⁿNC] in the expected sense, but accurate measurement of the appropriate peak current is excluded by the overlap with the (A⁺)–(A⁰) couple, Figure 7(a).

We assume that CO and BuⁿNC compete for the molybdenum sites according to the unidirectional reactions shown by Scheme 3; this is qualified later. A simple derivation shows that indiscriminate binding of CO or BuⁿNC requires equation (19)

$$[(i_p^{\max.}/i_p)^{\frac{1}{2}} - 1] = k_{rel}[\text{CO}][\text{Bu}^n\text{NC}]^{-1} \quad (19)$$

to obtain with $k_{rel} = 1.0$. The i_p data were analysed accordingly and the appropriate dimensionless plot is shown in Figure 8. The linearity of this plot is excellent (correlation coefficient = 0.997), but the slope, k_{rel} , is 2.3 ± 0.1 . This deviation from the statistical value of unity is accommodated by a rate of reaction of CO at each site 2.3 times greater than the rate of reaction of BuⁿNC at the same site.

We have assumed that the predominant reaction pathway involves the initial binding of CO or BuⁿNC to *trans*-[MoCl(Ph₂PCH₂CH₂PPh₂)₂]⁻, rather than to (E⁺) with subsequent fast electron transfer. The electrochemistry of *trans*-[MoI₂(Ph₂PCH₂CH₂PPh₂)₂] clearly shows the viability of the latter pathway (see above) but we have not explored the



Scheme 4.

implications of this. Nevertheless, CO is preferentially 'fixed' by the (A) + 2e reduction system.

The co-substrates N₂ + BuⁿNC give rise to *trans*-[Mo(N₂)(BuⁿNC)(Ph₂PCH₂CH₂PPh₂)₂] in an analogous fashion: this species has been postulated as an intermediate in substitution reactions but has not hitherto been detected,³² Figure 7(b).

Conclusions

Both under argon and in the presence of dinitrogen, the reduction chemistry of *trans*-[MoX₂(Ph₂PCH₂CH₂PPh₂)₂] is summarised by Scheme 4. General conclusions with respect to this Scheme and the earlier discussion are as follows.

(1) The critical free-energy barrier in the electrochemical sequence is the primary single-electron-transfer step. This is sensitive to X, less so to the metal, Mo or W; E^0 increases in the order X = BuⁿS < Cl < PhS < Br < I; W < Mo (Table 2).

(2) The rate-determining step is the dissociation of X⁻ which follows the single electron transfer. The leaving-group ability of X⁻ follows the order X⁻ = BuⁿS⁻ ≈ PhS⁻ ≈ Cl⁻ < Br⁻ < I⁻; Cl⁻ loss is faster at Mo^I than at W^I.

(3) From synthetic, energetic, and kinetic standpoints, BuⁿS⁻

is the least favourable ligand at Mo^{II} for reductive formation of the dinitrogen complex or other molybdenum(0) complexes.

(4) Dinitrogen can promote secondary electronation: the electron flux associated with the reduction of *trans*-[MoI₂-(Ph₂PCH₂CH₂PPh₂)₂] is greater under N₂ than it is under argon.

(5) Competition between substrates such as CO and Bu¹NC for electrogenerated molybdenum sites is non-statistical: ligation of CO is favoured over Bu¹NC binding by a discrimination factor of 2.3 ± 0.1.

Experimental

Precursor Complexes.—The complexes *trans*-[MX₂(Ph₂PCH₂CH₂PPh₂)₂] (M = Mo, X = SPh, SP^r, or SBUⁿ; ³³M = Mo or W, X = Cl; M = Mo, X = Br or I³⁴) and [MH₂Cl₂-(Ph₂PCH₂CH₂PPh₂)₂] (M = Mo or W)³⁵ were prepared by literature methods^{33,35} or by modification or extension of described procedures.³⁴ The purification of solvents and electrolyte has been described earlier.³⁶

Electrochemical Measurements.—Cyclic voltammetry and potential-step measurements were carried out in a thermostatted two-compartment three-electrode cell. The working electrode was a platinum wire of nominal area 0.0814 cm²; this was probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; platinum or tungsten auxiliary electrodes were employed. A Hi-Tek Instruments Ltd. type DT201 potentiostat and type PPR1 waveform generator provided potentiodynamic controls; current-potential or time responses were recorded using a Philips type PM8043 X-Y recorder and a Datalab type DL901 transient recorder.

Controlled-potential electrolyses were carried out in a four-compartment, three-electrode H-type cell. The working electrode was a mercury pool of nominal area 9.2 cm². A platinum-gauze counter electrode was employed which was separated from the working-electrode compartment by two glass frits (porosity 2); this formed a chamber isolating the catholyte from the anolyte. A Luggin capillary probed the mercury pool and in conjunction with a compartment containing a silver wire immersed in the electrolyte formed the pseudo-reference electrode system. Potentiostatic control and *in situ* cyclic voltammetric monitoring of the course of the electrolyses were carried out using the instrumentation described above. The charge passed during electrolysis was monitored using a Chemical Electronics Integrator.

Electrosyntheses.—Typically, 100 mg of complex contained in 30 ml of electrolytes was electrolysed under the appropriate atmosphere until the cell current was *ca.* 5% of the initial current; this corresponded to the passage of 2–2.3 Faradays mol⁻¹. The catholyte was removed by a gas-tight syringe and transferred to a Schlenk flask. Removal of the solvent, thf, under vacuum at room temperature left a mixture of product and supporting electrolyte, [NBu₄][BF₄]. The latter is readily soluble in CH₃CN or MeOH, whereas the neutral bis(diphosphine) complexes are essentially insoluble; thus the catholyte residue was repeatedly extracted with either of these solvents (4 × 10 cm³) leaving the metal product which was then removed and recrystallised from diethyl ether–thf. All manipulations subsequent to electrolysis were carried out with degassed solvents under dinitrogen or argon.

Other Measurements.—Products obtained by electrosynthesis were examined for purity by cyclic voltammetry, as described above, and by i.r. (Nujol), ¹H and ³¹P-{¹H} n.m.r. spectroscopy. Infrared spectra were recorded on a Pye-Unicam type SP2000

spectrophotometer, n.m.r. spectra on a JEOL type FX90Q Fourier-transform spectrometer. E.s.r. spectra were recorded on a Bruker type ER200 D-SRC spectrometer.

Acknowledgements

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