

## 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 Mo<sup>0</sup> and W<sup>0</sup> can be electrosynthesised from the molecular substrates N<sub>2</sub>, H<sub>2</sub>, etc. and precursors *trans*-[MX<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (M = Mo; X = Cl, Br, I, SPh, or SBu<sup>n</sup>; M = W; X = Cl), [MoH<sub>2</sub>Cl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], or from MoCl<sub>3</sub> and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>. Intermediates, mechanisms, and energetics associated with the electrosyntheses are described.

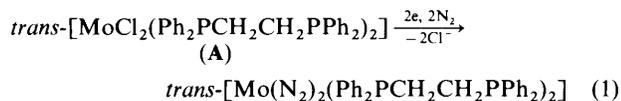
The purpose of the papers in this series is to delineate electron-transfer reactions of transition-metal complexes<sup>1</sup> which are relevant to chemical<sup>2</sup> and biochemical<sup>3</sup> aspects of nitrogen fixation.<sup>4</sup>

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.<sup>2,5-7</sup> This work describes intermediates, mechanisms, and energetics associated with the electrosynthesis of dinitrogen, hydride, isocyanide, and carbonyl complexes of molybdenum from the molecular substrates (N<sub>2</sub>, CO, H<sub>2</sub>, MeNC, and Bu<sup>n</sup>NC) and molybdenum halide or thiolate precursors, especially *trans*-[MoCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]. The electrosyntheses provide new routes to complexes hitherto prepared by chemical reductions,<sup>2</sup> or indirectly by ligand-displacement reactions.<sup>8</sup> The formation and reactivities of 16-, 17-, and 18-electron intermediates described here may be of interest in a wider context.

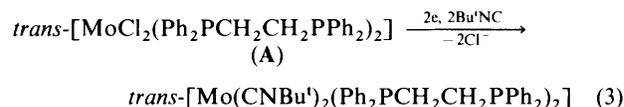
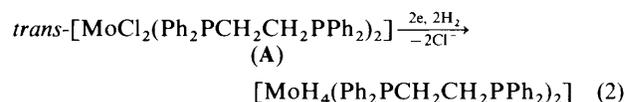
### Results and Discussion

**Electrosyntheses.**—The electrosyntheses were carried out at a mercury-pool electrode in tetrahydrofuran (thf) or dimethylformamide (dmf) containing 0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>], 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 <sup>1</sup>H n.m.r., <sup>31</sup>P 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 <sup>31</sup>P 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 E<sup>0</sup> value of 0.54 V in thf-0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>].

From *trans*-[MoCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]. The exhaustive controlled-potential (*ca.* -2.3 V) electrolysis of *trans*-[MoCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (A), in a thf electrolyte saturated with gaseous dinitrogen ([N<sub>2</sub>] *ca.* 2.6 mmol dm<sup>-3</sup>, 20 °C, 1 atm) gives *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] 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 ([H<sub>2</sub>] *ca.* 3.6 mmol dm<sup>-3</sup>, 20 °C, 1 atm) affords the tetrahydride, reaction (2), or, in the presence of other substrates, L (= CO, MeNC, or Bu<sup>n</sup>NC), the stable complexes *trans*-[MoL<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], *e.g.* reaction (3). Yields are listed in Table 1.



Controlled-potential reductions of complex (A) in the presence of N<sub>2</sub>, CO, or Bu<sup>n</sup>NC, 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*-[WCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (B), is reduced at a mercury-pool electrode in a thf electrolyte saturated with gaseous dinitrogen to give *trans*-[W(N<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]; similarly, under carbon monoxide, electroreduction of (B) affords *cis*- and *trans*-[W(CO)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], Table 1. Whereas the molybdenum dichloride, (A), is reduced cleanly in the presence of Bu<sup>n</sup>NC [reaction (3)], electroreduction of (B), under similar conditions, gives a mixture from which low yields of *trans*-[W(CNBu<sup>n</sup>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] were isolated.

The electroreduction of *trans*-[Mo(SR)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (D; R = Ph), in a thf electrolyte under dinitrogen, is relatively straightforward; as with the dichloride, (A), *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] is formed in moderate yield (Table 1). However, under similar conditions, the alkanethiolato-complexes (D; R = Pr<sup>n</sup> or Bu<sup>n</sup>) give poor yields of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] or *trans*-[Mo(CNBu<sup>n</sup>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] in the presence of dinitrogen or Bu<sup>n</sup>NC, respectively, Table 1.

The hydrido-complex, [MoH<sub>2</sub>Cl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], undergoes the electrosynthetic reactions summarised by Scheme 1 and Table 1. The reduction of the tungsten analogue, [WH<sub>2</sub>Cl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] is not accessible in the thf electrolyte.

The 'one-pot' synthesis of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>-

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



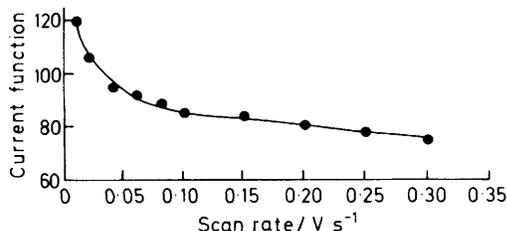
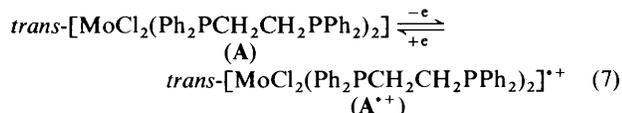


Figure 2. Plot of the current function,  $F_p^{\text{RED}}$ , versus scan rate,  $v$ , showing the deviation towards a 2e process at slow scan rates

chemistry, Figure 2. The independence of  $F_p^{\text{RED}}$  is diagnostic of diffusion-controlled electron transfer at potentials at and beyond the peak reduction potential,  $E_p^{\text{RED}}$ . 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,  $i_t^{\text{RED}}$ , 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  $22.5^\circ\text{C}$ ) 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  $F_p^{\text{RED}}$  and  $F_t^{\text{RED}}$  by taking advantage of the observation that complex (A) undergoes a straightforward, reversible, one-electron oxidation to give the stable cation,  $(A^{+\cdot})$ , equation (7) ( $E^{0'} = -0.05$  V), Figure 1(b).



The appropriate current functions for the oxidation,  $F_p^{\text{OX}}$  and  $F_t^{\text{OX}}$ , 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<sup>-1</sup>, 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<sup>-1</sup>,  $22.5^\circ\text{C}$ , 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,  $\Delta E$ , close to  $60$  mV is theoretically associated with reversible one-electron transfer: experimentally we find  $\Delta E$  for complex (A) is ca.  $70$  mV (thf electrolyte,  $0.1$  V s<sup>-1</sup>,  $22.5^\circ\text{C}$ ).

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  $\text{trans-[MoCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^{+\cdot}$  ( $S = 0.5$ ).

It is usual to assume that electrochemical reversibility involving fast electron transfer implies the retention of the structural integrity of a molecule,<sup>15</sup> although the generality of this assumption has been criticised.<sup>16</sup> 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.<sup>17,18</sup> 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<sup>a</sup>

Complex	$E^{0'}/\text{V}$	
	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
$[\text{Mo}(\text{SP}^n)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	-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 <sup>b</sup>	+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 <sup>b</sup>
$[\text{Mo}(\text{Bu}^i\text{NC})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$		-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

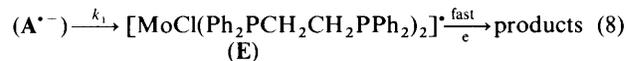
<sup>a</sup> All complexes are *trans* isomers except the hydrides: potentials are versus s.c.e. in  $0.2$  mol dm<sup>-3</sup>  $[\text{NBu}_4][\text{BF}_4]$ -thf. <sup>b</sup> Irreversible process; value is for  $E_{p/2}$ .

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

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  $\text{W}$ ,  $X = \text{halide}$  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.

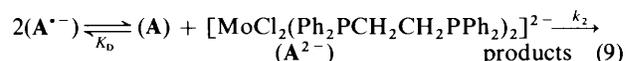
*The rate-determining step.* The conversion of the intermediate  $(A^{+\cdot})$  into products involves a further electron transfer. This is associated with a current-limiting (rate-determining) chemical step as is evident from the dependence of  $F_p^{\text{RED}}$  on  $v$  at the slower scan rates,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

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



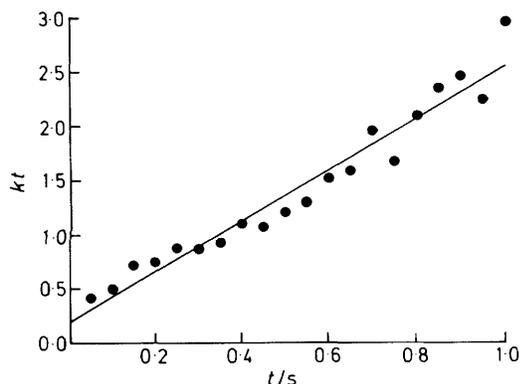
The rate-determining step cannot involve an associative attack on  $(A^{+\cdot})$  by either solvent or substrate since  $F_p^{\text{RED}}$  is essentially independent of both and substrate concentration, at all scan rates. Associative attack on other 17-electron molybdenum species is known and proceeds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

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

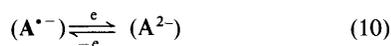


**Table 3.** Chronoamperometric data for *trans*-[MoCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>)<sub>2</sub>] in thf-0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>] at 49.5 °C

<i>t</i> /s	<i>n</i> <sub>apparent</sub>	<i>t</i> /s	<i>n</i> <sub>apparent</sub>
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  $(\text{A}^{\bullet-})$  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

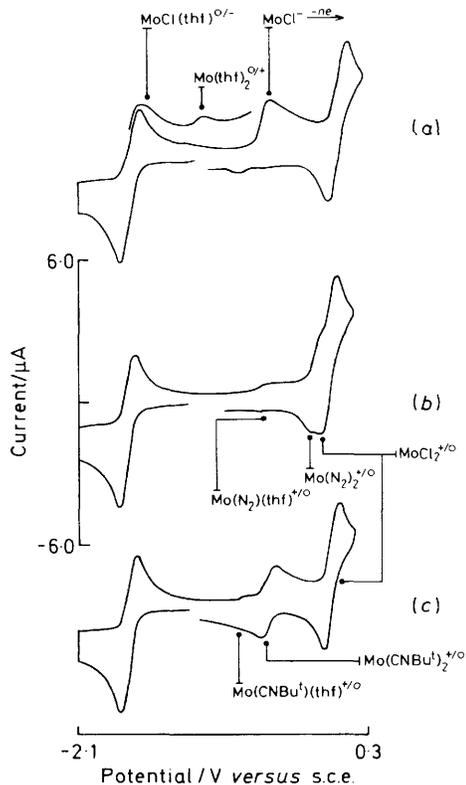
$$K_D = \exp[(nF/RT)(E_2^{0'} - E_1^{0'})] \quad (11)$$

$E_1^{0'} = -1.68$  V [equation (6)] we obtain  $K_D < 10^{-14}$  (dimensionless). The decomposition of  $(\text{A}^{\bullet-})$  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  $n_{\text{apparent}}$  versus  $\log K_D k_2 t$ , has been simulated by Marcoux<sup>21</sup> for the general case of disproportionation. Table 3 lists values for  $n_{\text{apparent}}$  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  $10^{-1} \text{ s}^{-1}$ , i.e.  $k_2$  has to be greater than  $10^{13} \text{ s}^{-1}$  if the disproportionation mechanism is to operate. Values of  $k_2 > 10^{10} \text{ s}^{-1}$  are unreasonable and the proposition of decomposition of  $(\text{A}^{\bullet-})$  via the disproportionation pathway (9) is therefore untenable.

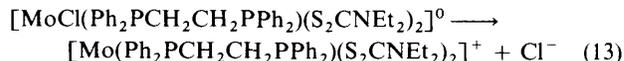
Since associative or disproportionation pathways are improbable, the dissociative mechanism, (8), provides the simplest rationale of our experimental data. The chrono-

**Figure 4.** Ramp-clamp voltammograms of *trans*-[MoCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]; 0.8 mmol dm<sup>-3</sup> solution of complex in thf-0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>]; clamp time 17 s, scan rate 0.3 V s<sup>-1</sup> at a platinum electrode; [Bu<sup>1</sup>NC] = 2.6 mol dm<sup>-3</sup>. In the presence of (a) argon, (b) nitrogen, and (c) Bu<sup>1</sup>NC

amperometric working curve,  $n_{\text{apparent}}$  versus  $\log k_1 t$ , for an electron transfer-chemical reaction-electron transfer (e.c.e.) mechanism<sup>22</sup> and the  $n_{\text{apparent}}$  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  $k_1 = 2.7 \pm 0.2 \text{ s}^{-1}$  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  $(\text{A}^{\bullet-})$  in solution, the closely related e.c.c. pathways, is also possible.<sup>23</sup>

In a related electrochemical study of complexes such as [MoCl(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)(S<sub>2</sub>CNET<sub>2</sub>)<sub>2</sub>]<sup>+</sup> 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 CH<sub>3</sub>CN than it is in thf.<sup>10</sup> 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, CH<sub>3</sub>CN. In the latter case, loss of Cl<sup>-</sup> from  $(\text{A}^{\bullet-})$  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(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>

**Table 4.** Detection potentials\* of intermediates

Precursor	Substrate	$E_{p/2}/V$	Assignment
$trans-[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$	Bu <sup>1</sup> NC	-0.75	$trans-[Mo(Bu^1NC)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$
	N <sub>2</sub>	-0.62	$trans-[Mo(N_2)(thf)(Ph_2PCH_2CH_2PPh_2)_2]$
	H <sub>2</sub>	-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 <sup>1</sup> NC + N <sub>2</sub>	-0.35	$trans-[Mo(N_2)(Bu^1NC)(Ph_2PCH_2CH_2PPh_2)_2]$
	Bu <sup>1</sup> 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<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>].

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 N<sub>2</sub> (b) or Bu<sup>1</sup>NC (c), using a 20-s cathodic clamp. The formation of stable, closed-shell products is clearly evident. Under N<sub>2</sub> 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 Bu<sup>1</sup>NC 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 N<sub>2</sub>, CO, H<sub>2</sub>, or Bu<sup>1</sup>NC 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.

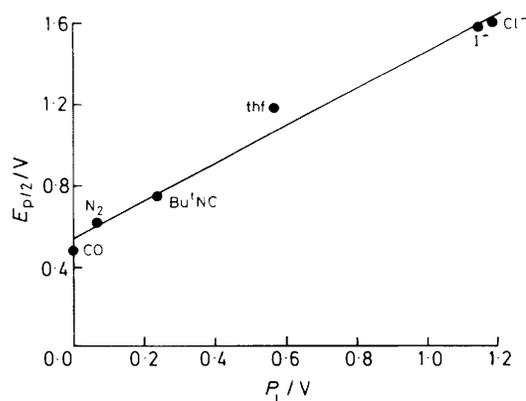
The intermediates are too unstable to characterise by conventional spectroscopy but we have shown by earlier work that the linear-free-energy relationship (14) can be used to

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

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, N<sub>2</sub>, CO, Bu<sup>1</sup>NC, and Cl<sup>-</sup> 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

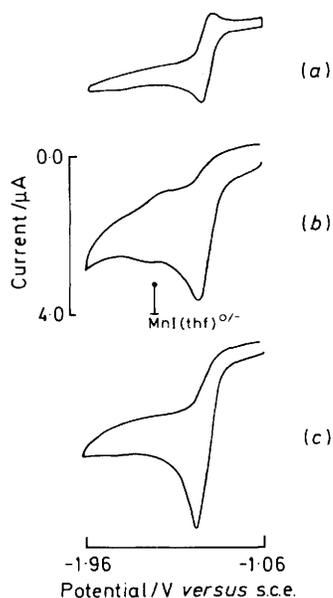


**Figure 5.** Detection potentials,  $E_{p/2}^{OX}$ , versus ligand parameter of substrate,  $P_L$

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 = N<sub>2</sub> or Bu<sup>1</sup>NC, 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 N<sub>2</sub> to give the latter, which in turn reacts at a slower rate with N<sub>2</sub> to regenerate the parent complex.<sup>24,25</sup>

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<sup>-</sup> 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  $trans\text{-}[\text{Mo}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$  in  $\text{thf}$ - $0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{BF}_4]$  at a platinum electrode, scan rate  $0.3 \text{ V s}^{-1}$ . In the presence of argon at  $-10$  (a) and  $25^\circ\text{C}$  (b) and in the presence of CO at  $25^\circ\text{C}$  (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  $-2.5 \text{ V}$ ; the 18-electron anion we have already identified with the oxidation near  $-1.6 \text{ V}$ , Figure 5, thus we assign the oxidation observed at  $-0.66 \text{ V}$  to  $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ .

Stable species related to  $[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ , ( $\text{E}^-$ ), are known. Hidai and co-workers<sup>26</sup> 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,  $\pi$ -acid, and certain anionic ligands to give stable 18-electron octahedral adducts.<sup>26,27</sup> Recently we described<sup>28</sup> 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  $\text{N}_2$ , thf, or anionic ligands.

Although moderately stable on the voltammetric time-scale, ( $\text{E}^-$ ) 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  $^{31}\text{P}$ ,  $^1\text{H}$  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.<sup>29</sup>

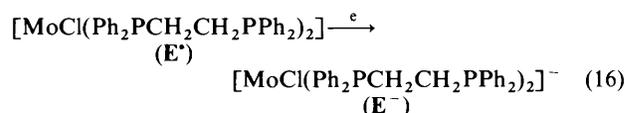
In contrast, the reduction of (A) under argon in a dmf electrolyte produces a dark red catholyte in a clean two-electron process. This catholyte contains a single, stable molybdenum(0) species which we formulate as  $trans\text{-}[\text{Mo}(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ , (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  $^{31}\text{P}$  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  $\text{Bu}^1\text{NC}$  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  $\text{N}_2$  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  $\text{Cl}^-$ . Finally, we exclude the possibility that (F) is the decarbonylation product,  $trans\text{-}[\text{Mo}(\text{CO})(\text{dmf})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ ,<sup>26</sup> 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  $\text{Bu}^1\text{NC}$ . 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  $trans\text{-}[\text{Mo}(\text{CO})(\text{N}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^-$ .<sup>18,30</sup> 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.

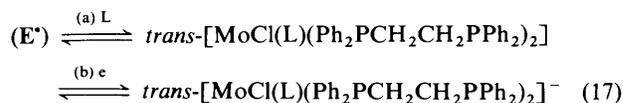
**Secondary electronation.** The reduction of complex (A) to closed-shell products involves two, discrete, single-electron-transfer reactions. The primary electronation gives ( $\text{A}^{\cdot-}$ ) which loses  $\text{Cl}^-$  to generate ( $\text{E}^{\cdot}$ ) as discussed earlier. The identification 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.*  $-1.7 \text{ V}$ .

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

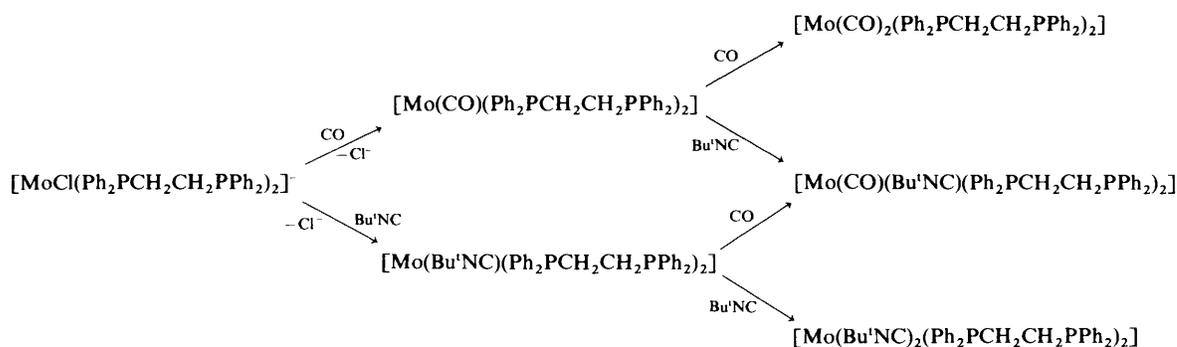


$trans\text{-}[\text{MoCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ , ( $\text{E}^{\cdot}$ ), fulfils such requirements; ( $\text{E}^{\cdot}$ ) is the immediate product of  $\text{Cl}^-$  loss from ( $\text{A}^{\cdot-}$ ) and ( $\text{E}^{\cdot}$ ) is detected as an intermediate which oxidises irreversibly about  $1 \text{ V}$  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 ( $\text{E}^{\cdot}$ ).

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  $\text{Cl}^-$  from ( $\text{A}^{\cdot-}$ ) is slow, ( $\text{E}^{\cdot}$ ) is generated throughout the diffusion layer, *i.e.* away from the electrode. Consequently ( $\text{E}^{\cdot}$ ) 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 3.

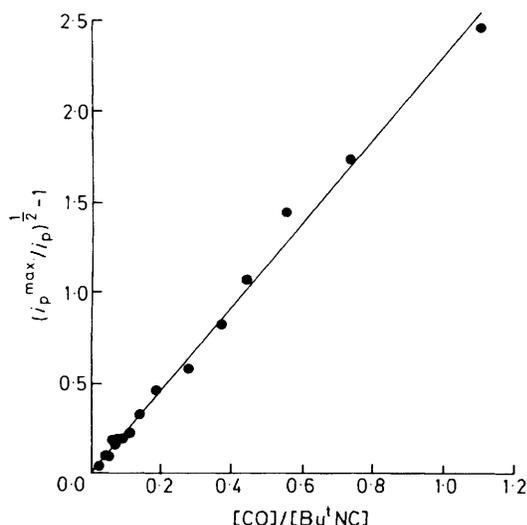


Figure 8. Dimensionless plot for the competitive substrates CO and Bu<sup>n</sup>NC

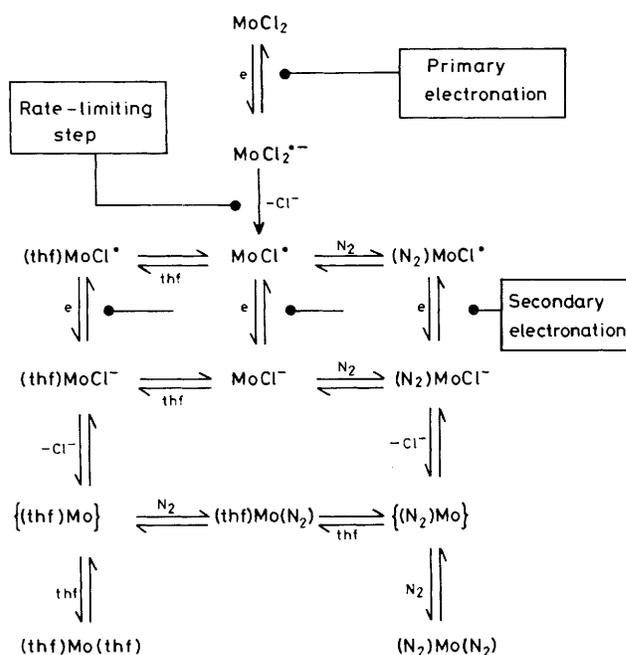
pressed (see above). Correspondingly, the concentration of *trans*-[Mo(CO)(Bu<sup>n</sup>NC)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] increases and then decreases with decreasing [CO]/[Bu<sup>n</sup>NC]. Qualitatively the concentration of *trans*-[Mo(CO)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] responds to changes in [CO]/[Bu<sup>n</sup>NC] in the expected sense, but accurate measurement of the appropriate peak current is excluded by the overlap with the (A<sup>+</sup>)–(A<sup>0</sup>) couple, Figure 7(a).

We assume that CO and Bu<sup>n</sup>NC 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 Bu<sup>n</sup>NC 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  $2.3 \pm 0.1$ . 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 Bu<sup>n</sup>NC at the same site.

We have assumed that the predominant reaction pathway involves the initial binding of CO or Bu<sup>n</sup>NC to *trans*-[MoCl(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sup>-</sup>, rather than to (E<sup>+</sup>) with subsequent fast electron transfer. The electrochemistry of *trans*-[MoI<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] 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 N<sub>2</sub> + Bu<sup>n</sup>NC give rise to *trans*-[Mo(N<sub>2</sub>)(Bu<sup>n</sup>NC)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] in an analogous fashion: this species has been postulated as an intermediate in substitution reactions but has not hitherto been detected,<sup>32</sup> Figure 7(b).

## Conclusions

Both under argon and in the presence of dinitrogen, the reduction chemistry of *trans*-[MoX<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] 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 = Bu<sup>n</sup>S < Cl < PhS < Br < I; W < Mo (Table 2).

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

(3) From synthetic, energetic, and kinetic standpoints, Bu<sup>n</sup>S<sup>-</sup>

is the least favourable ligand at Mo<sup>II</sup> 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*-[MoI<sub>2</sub>-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] is greater under N<sub>2</sub> than it is under argon.

(5) Competition between substrates such as CO and Bu<sup>1</sup>NC for electrogenerated molybdenum sites is non-statistical: ligation of CO is favoured over Bu<sup>1</sup>NC binding by a discrimination factor of 2.3 ± 0.1.

## Experimental

**Precursor Complexes.**—The complexes *trans*-[MX<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (M = Mo, X = SPh, SP<sup>r</sup>, or SBU<sup>n</sup>; <sup>33</sup>M = Mo or W, X = Cl; M = Mo, X = Br or I<sup>34</sup>) and [MH<sub>2</sub>Cl<sub>2</sub>-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (M = Mo or W)<sup>35</sup> were prepared by literature methods<sup>33,35</sup> or by modification or extension of described procedures.<sup>34</sup> The purification of solvents and electrolyte has been described earlier.<sup>36</sup>

**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 cm<sup>2</sup>; 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 cm<sup>2</sup>. 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<sup>-1</sup>. 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, [NBu<sub>4</sub>][BF<sub>4</sub>]. The latter is readily soluble in CH<sub>3</sub>CN 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 cm<sup>3</sup>) 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), <sup>1</sup>H and <sup>31</sup>P-{<sup>1</sup>H} 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

We thank Mr. K. S. Ryder for valuable experimental assistance, Dr. D. J. Lowe for help and advice in the recording of e.s.r. spectra, Mr. C. J. Macdonald for recording n.m.r. spectra and for microanalyses, and Dr. R. L. Richards for help in measuring gas solubility and advice in the preparation of the thiolato-complexes.

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*Received 10th September 1984; Paper 4/1561*