Electrochemical Behaviour of Organonitrile Dinitrogen Complexes of Molybdenum(0) and Tungsten(0) and the Anchoring of a Dinitrogen Complex to an Electrode Surface

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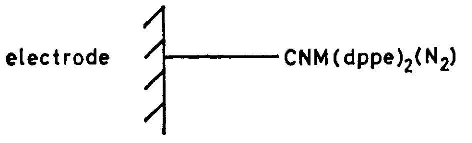
The solution electrochemistry of the complexes $[M(N_2)(RCN)(dppe)_2]$ [M = Mo or W, R = alkyl or aryl, dppe = 1,2-bis(diphenylphosphino)ethane] is reported. This type of complex has been anchored to an electrode surface *via* the organonitrile ligand.

DINITROGEN complexes $[M(N_2)_2(dppe)_2]$ [M = Mo or W; dppe = 1,2-bis(diphenylphosphino)ethane] can be alkylated or protonated at nitrogen in reactions which involve concomitant oxidation of the metal.[1,2] Recently we demonstrated that an electroactive metal complex could be attached to the surface of an electrode *via* a silylation reaction.[3] This paper describes the anchoring to an electrode surface of a metal complex capable of binding dinitrogen, the first step in the development of an electrode capable of mediating the protonation or alkylation of dinitrogen.

It has been shown that organonitriles RCN can replace an N_2 from $[Mo(N_2)_2(dppe)_2]$ yielding $[Mo(N_2)(RCN)(dppe)_2]$.[4] We have anchored an organonitrile to a tin oxide electrode *via* the organic moiety using the methods developed by Murray and his co-workers,[5] and employed the free CN group to bind molybdenum and tungsten also bearing dinitrogen, as shown in (I). In order to facilitate characterisation of the surface species, the solution electrochemistry of $[M(N_2)(RCN)(dppe)_2]$ was investigated.



(I)

RESULTS AND DISCUSSION

Figure 1 shows a typical cyclic voltammogram obtained for $[M(N_2)(RCN)(dppe)_2]$ complexes in tetrahydrofuran (thf)—0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a platinum electrode. The electrochemical parameters are given in Table 1. The results are consistent with Scheme

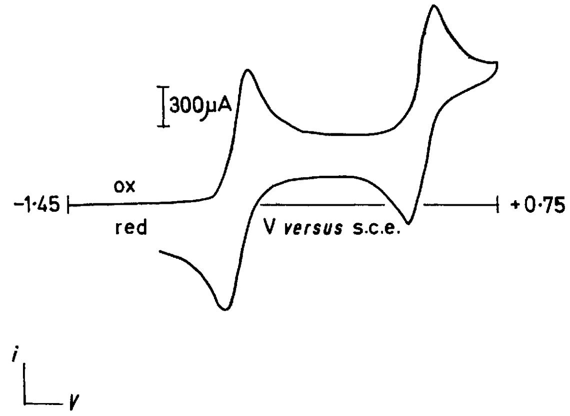


FIGURE 1 Cyclic voltammetry of $[M(N_2)(RCN)(dppe)_2]$ complexes: i–V behaviour of $[Mo(N_2)(Pr^nCN)(dppe)_2]$ in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a platinum electrode. Scan rate = 0.3 V s^{-1}

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[1] J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39.

[2] J. Chatt, *J. Organometallic Chem.*, 1975, **100**, 17.

[3] R. J. Burt, G. J. Leigh, and C. J. Pickett, *J.C.S. Chem. Comm.*, 1976, 959.

[4] T. Tatsumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, 1975, **14**, 2530.

[5] P. R. Moses, L. Wier, and R. W. Murray, *Analyt. Chem.*, 1975, **47**, 1882.

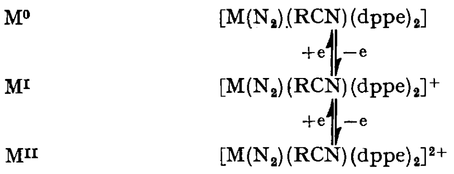
TABLE 1

Current–potential characteristics of the molybdenum(0) and tungsten(0) complexes. $E_{\frac{1}{2}}$ = Half-wave potential = $\frac{1}{2}(E_p^{ox} + E_p^{red}) \simeq (E_p^{ox} - 29\text{mV})$, E_p = peak potential, and j = current. Superscripts 1 and 2 refer to the primary and secondary redox processes respectively; ox and red refer to the oxidation and reduction processes respectively

Complex	$^1E_{\frac{1}{2}}$	$^2E_{\frac{1}{2}}$	$^1(E_p^{ox} - E_p^{red})$ [a]	$^2(E_p^{ox} - E_p^{red})$ [a]	$^1(j_p^{red}/j_p^{ox})$ [b]	$(^2j_p^{ox}/^1j_p^{ox})$ [b]	$\tilde{\nu}(N_2)$ [c]
	versus s.c.e.		mV				cm^{-1}
$[Mo(N_2)_2(dppe)_2]$	−0.16	+0.78	64	*d*	1.0	1.0	1 980
$[Mo(N_2)(PhCN)(dppe)_2]$	−0.48	+0.37	62	62	1.0	1.0	1 945
$[Mo(N_2)(MeCN)(dppe)_2]$	−0.58	+0.33	64	64	1.0	1.0	1 920
$[Mo(N_2)(Pr^nCN)(dppe)_2]$	−0.57	+0.35	67	67	1.0	1.0	1 920
$[Mo(N_2)\{Si(CH_2CH_2CH_2CN)(OMe)_3\}(dppe)_2]$	−0.59	+0.34	70	70	1.0	1.0	1 925
$[Mo(N_2)(electrode\text{-}CN)(dppe)_2]$	−0.58		17		1.0		
$[W(N_2)_2(dppe)_2]$	−0.15	+0.79	62	*d*	1.0	1.0	1 950
$[W(N_2)(PhCN)(dppe)_2]$	−0.48	+0.38	56	56	1.0	1.0	1 920
$[W(N_2)(MeCN)(dppe)_2]$	−0.57	+0.32	63	63	1.0	1.0	1 890
$[W(N_2)(Pr^nCN)(dppe)_2]$	−0.57	+0.28	68	68	1.0	1.0	1 895
$[W(N_2)\{Si(CH_2CH_2CH_2CN)(OMe)_3\}(dppe)_2]$	−0.55	+0.31	58	58	1.0	1.0	1 900
$[W(N_2)(electrode\text{-}CN)(dppe)_2]$	−0.56		<17		1.0		
Range	±0.01V	±0.01V	±5 mV	±5 mV	±0.1	±0.1	±5 cm^{-1}

[a] The criteria for one-electron diffusion-controlled reversible oxidation were satisfied: $j_p^{ox}/(\text{scan rate})^{\frac{1}{2}} \simeq$ constant; $(E_p^{ox} - E_{p\frac{1}{2}}^{ox}) = (E_p^{ox} - E_p^{red}) \simeq 60$ mV for the solution complexes. [b] The values $^1(j_p^{red}/j_p^{ox})$ and $(^1j_p^{ox}/^2j_p^{ox})$ were measured at a scan rate of 0.3 V s^{-1}. $^1j_p^{ox}$/[concentration] for the complex $[Mo(N_2)(Pr^nCN)(dppe)_2]$ was within 5% of the value obtained for the ferrocene–ferrocinium couple at the same electrode at 0.3 V s^{-1}. [c] Referring to the parent neutral complexes. [d] Irreversible.

1 in which the complexes undergo *two* successive *reversible* one-electron oxidations in a three-membered electron-transfer series[6] with the metal in oxidation states 0, I, and II. The half-lives, $t_{\frac{1}{2}}$, of the $[M(N_2)(RCN)(dppe)_2]^{n+}$ species have been determined for M = Mo, R = Pr^n, and n = 1 or 2, by the double-potential-step technique[7] and these are compared in Table 2 with the $t_{\frac{1}{2}}$ of $[Mo(N_2)_2(dppe)_2]^+$ measured under the same conditions.[8] The substitution of a dinitrogen ligand by butyronitrile clearly stabilises the higher oxidation states, and indeed $[Mo(N_2)_2(dppe)_2]^{2+}$ is not detectable by cyclic voltammetry at scan rates up to 10 V s^{-1} in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$. The $^1E_{\frac{1}{2}}$ of the organonitrile complexes in Table 1 are considerably more negative than those of $[M(N_2)_2(dppe)_2]$, which suggests that the organonitrile ligands increase electron density on the metal compared to dinitrogen and that this raises the energy of the highest-occupied molecular orbital (h.o.m.o.).[9] A parallel increase in ν(N≡N)[4] and $^1E_{\frac{1}{2}}$ is also observed suggesting that the net σ,π-donor effect of the RCN ligand is transmitted to the *trans*-dinitrogen ligand. The rate-determining step in the decomposition of $[Mo(N_2)_2(dppe)_2]^+$ {and presumably in the parallel decomposition of $[M(N_2)(RCN)(dppe)_2]^+$} is loss of N_2. The stabilisation of organonitrile dinitrogen complexes of M^I and M^{II} compared to the bis(dinitrogen) analogues can therefore be explained by a strengthening of the metal–dinitrogen bond.



SCHEME 1

Table 1 also shows the redox behaviour of the metal(0) organonitrile complexes which carry a remote $Si(OMe)_3$ group on the butyronitrile chain. Clearly the influence of this group on the half-wave potential $^1E_{\frac{1}{2}}$ is negligible. A tin oxide electrode was silylated with $Si(CH_2CH_2CH_2CN)Cl_3$ (Scheme 2) and examined electrochemically in 0.2 mol dm^{-3} $[NBu_4][BF_4]$ solution. Figure 2(*a*) shows the current–potential curve obtained, whilst Figure 2(*b*) shows the curve observed at an untreated tin oxide electrode under the same conditions. Addition of $[Mo(N_2)_2(dppe)_2]$ to the thf solution (*ca.* 5×10^{-3} mol dm^{-3}) caused the appearance of a well defined adsorption wave during the current–potential scan at the organonitrile electrode [Figure 2(*c*)]; the peak separation was 17 mV (theoretically 0 mV) whilst the peak current increased linearly with scan rate and was independent of stirring. No adsorption wave was observed at the un-

TABLE 2

Half-lives of dinitrogenmolybdenum complex cations: the values were determined from the average of three measurements on each of five transients at 292 K

Complex	$t_{\frac{1}{2}}$/s	$E_{\frac{1}{2}}$/V
trans-$[Mo(N_2)(Pr^nCN)(dppe)_2]^+$	32	−0.57
trans-$[Mo(N_2)(Pr^nCN)(dppe)_2]^{2+}$	8	+0.35
trans-$[Mo(N_2)_2(dppe)_2]^+$	16	−0.16

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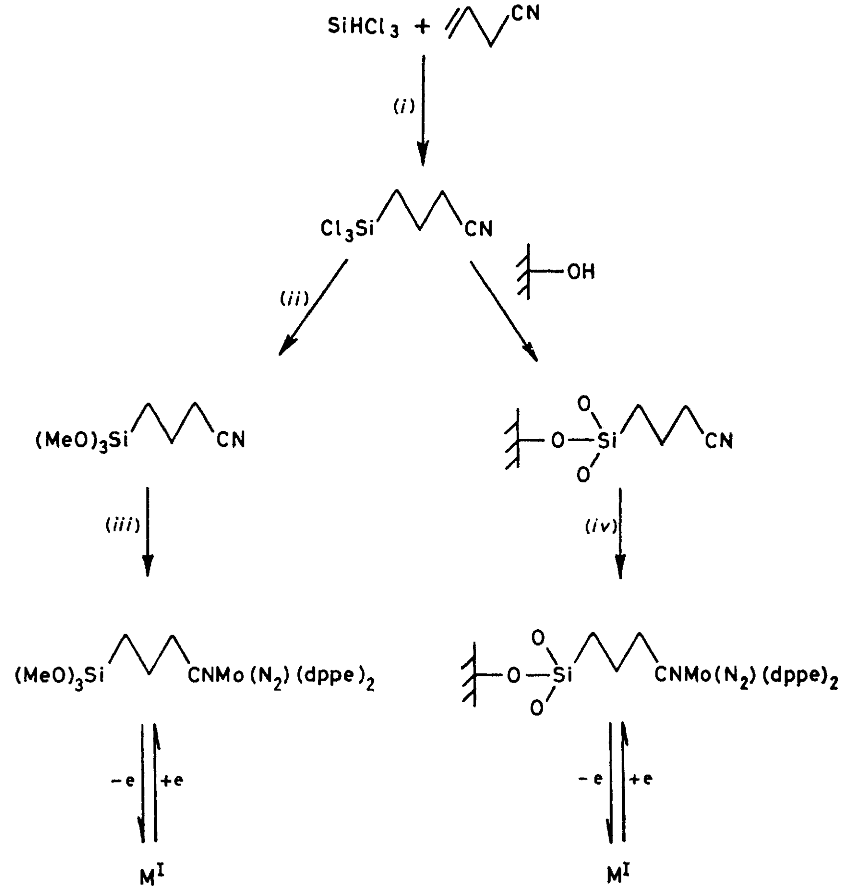
[6] 'Reactions of Molecules at Electrodes,' ed. N. S. Hush, Wiley–Interscience, London and New York, 1971.

[7] W. M. Schwarz and I. Shain, *J. Phys. Chem.*, 1965, **69**, 30.

[8] C. M. Elson, *Inorg. Chim. Acta*, 1976, **18**, 209.

[9] C. J. Pickett and D. Pletcher, *J. Organometallic Chem.*, 1975, **102**, 327.

treated SnO_2 electrode [Figure 2(*d*)] in the presence of $[Mo(N_2)_2(dppe)_2]$. The ${}^1E_{\frac{1}{2}}$ of the adsorption process (*c*) is -0.58 V *versus* standard calomel electrode (s.c.e.), very close to that observed for the oxidation potential of $[Mo(N_2)\{Si(CH_2CH_2CH_2CN)(OMe)_3\}(dppe)_2]$ in solution. This establishes the anchoring of the $\{Mo(N_2)(dppe)_2\}$ function (Scheme 2) to the electrode.



SCHEME 2 Synthesis of silyl cyanide complexes of Mo^0, and electrode modification. ‡—OH represents the surface hydroxyl groups on the tin oxide electrodes. (*i*) Reflux (8 h), H_2PtCl_6 catalyst; (*ii*) excess of MeOH + NEt_3; (*iii*) $[Mo(N_2)_2(dppe)_2]$, toluene; (*iv*) $[Mo(N_2)_2(dppe)_3]$, thf

A similar process was observed when $[W(N_2)_2(dppe)_2]$ was allowed to react in thf with the organonitrile electrode but the surface coverage was lower. Table 3 shows the surface coverage Γ estimated by integration of the *i*–*t* curves [Figure 2(*c*)]. This value is compared with calculated and estimated surface coverages of anchored species characterised previously.[3,10] In each estimate of Γ the electrochemical area has been assumed to be equal to the geometric area. This is of course a crude approximation,[10] but the values suggest high surface coverages.

TABLE 3

Surface coverage of anchored species

Anchored electroactive species	$10^{10}\Gamma$ / mol cm^{-2}	Ref
SnO_2 electrode–*N*-methylpyridinium	0.8	10
SnO_2 electrode–$CNMo(N_2)(dppe)_2$	1.0	*
SnO_2 electrode–$CNW(N_2)(dppe)_2$	*ca.* 0.1	*
SnO_2 electrode–$[SFe_4S_4(SR)_3]^{2-}$	30	3
Calculated for monolayer	6.0	*

* This work.

We have demonstrated that the residue $Mo(N_2)(dppe)_2$ may be reversibly oxidised whether it is in solution or bound to a tin oxide electrode. The complexes *trans*-$[Mo(N_2)_2(dppe)_2]$ and *trans*-$[Mo(N_2)(RCN)(dppe)_2]$ can be alkylated and protonated to give molybdenum(II) products of the form $[Mo(N_2R)X(dppe)_2]$ (R = H or alkyl, X = halide). In order to achieve an electrocatalytic reduction of dinitrogen we need to couple *oxidation* of the anchored dinitrogen complex by RX with a *reduction* from the electrode.

The reaction of $[Mo(N_2)(Pr^nCN)(dppe)_2]$ with EtBr in thf produces $[MoBr(N_2CH_2CH_2CH_2CH_2O)(dppe)_2]$ in which the nitrile has been lost.[11] We had hoped to carry out analogous reactions using the $M(N_2)(dppe)_2$ residue bound to the electrode surface *via* the cyano-link.

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[10] P. R. Moses and R. W. Murray, *J. Amer. Chem. Soc.*, 1976, **98**, 7435.

[11] G. J. Leigh and C. J. Pickett, unpublished work.

Clearly the alkyl halide is not a suitable substrate since dissociation of the molybdenum from the electrode would occur. The reaction of electrode-bound dinitrogen complexes with acids remains to be investigated.

EXPERIMENTAL

Preparation of Tin Oxide Electrodes.—A slow stream of dinitrogen was passed through a solution of 5% antimony pentachloride in tin tetrachloride and the resulting vapour was allowed to react in air on glass plates which were maintained at 300 °C. The bluish white, lustrous, conducting deposits, which were *ca.* 25×10^{-6} m thick, displayed current–potential characteristics essentially identical to those previously reported for other antimony-doped tin oxide electrodes.[12]

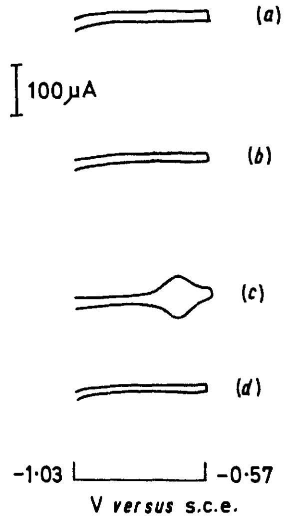

FIGURE 2 Current-potential curves on tin oxide electrodes: (*a*) tin oxide electrode with residual surface hydroxyl groups cyanosilylated, scan rate 0.3 V s^{-1} in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$; (*b*) unmodified electrode, same conditions as (*a*); (*c*) as for (*a*) + *ca.* 5×10^{-3} mol dm^{-3} $[Mo(N_2)_2(dppe)_2]$; (*d*) as for (*b*) + *ca.* 5×10^{-3} mol dm^{-3} $[Mo(N_2)_2(dppe)_2]$

The tin oxide electrodes were modified by allowing them to react with a 10% solution of $Si(CH_2CH_2CH_2CN)Cl_3$ in toluene at room temperature for 75 h. The silylated electrodes were washed five times with toluene (*ca.* 50 °C) and were vacuum dried at room temperature for 3 h. The silylation reaction and electrode cleansing were performed under an atmosphere of dry dinitrogen.

Electrochemical Methods and Instrumentation.—The electrochemical instrumentation, cells, supporting electrolyte, and solvent-purification methods have been described previously.[13,14] The measurements on the tin oxide electrodes were made in a cell of similar construction to that described by Kuwana *et al.*[15] I.R. compensation was not employed in the electrochemical measurements. The reference electrode was either a saturated calomel electrode which probed the working electrode *via* a KCl-saturated aqueous agar bridge or a silver wire immersed in the thf supporting electrolyte solution. In the latter case a ' pilot species ', ferrocene or *trans*-$[Mo(N_2)_2(dppe)_2]$, was employed to standardise the potential scale against that of the calomel–agar reference system. All the measurements were made in argon- or dinitrogen-purged solutions under an atmosphere of the noble gas.

Preparation of Ligands and Complexes.—The trichlorosilane $Si(CH_2CH_2CH_2CN)Cl_3$, was prepared from $SiHCl_3$ (Cambrian Chemicals Ltd.) and allyl cyanide by the method of Belyakova[16] [b.p. 108 °C (7 mmHg);* yield 90%].

The trichlorosilane (15 g, 0.08 mol) was added dropwise to a cooled solution of MeOH (30 cm^3) in Et_2O (150 cm^3) containing triethylamine (26 g, 0.24 mol). After the addition was completed the precipitated $[NHEt_3]Cl$ was filtered off. The product distilled as a clear colourless liquid, after removal of solvent, at 65 °C (0.1 mmHg), yield 80%, ν(CN) at 2 240 cm^{-1}. Hydrogen-1 n.m.r. spectrum (δ) (neat tetramethylsilane as external standard): 3.7—3.9 (s, 9 H, CH_3O), 2.6—2.8 (m, 2 H, CH_2), 1.8—2.2 (s, 2 H, CH_2), and 1.0—1.2 p.p.m. (m, 2 H, CH_2). Complexes $[Mo(N_2)(RCN)(dppe)_2]$ (R = alkyl or aryl) were prepared according to Hidai and his co-workers.[4] The tungsten analogues were prepared similarly except that the reaction mixtures were illuminated by 50-W tungsten-filament lamps.[11] The complexes will be described in detail elsewhere.

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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[14] D. B. Clark, M. Fleischmann, and D. Pletcher, *J. Electroanalyt. Chem.*, 1972, **36**, 137.

[15] T. Kuwana, R. K. Darlington, and D. W. Leedy, *Analyt. Chem.*, 1964, **36**, 2023.

[16] Z. V. Belyakova, S. A. Golubtsov, and T. M. Yakusheva, *Zhur. obshchei Khim.*, 1965, **35**, 1183.