Electron-transfer Reactions in Nitrogen Fixation. Part 2.[1] The Electrosynthesis of Ammonia: Identification and Estimation of Products†

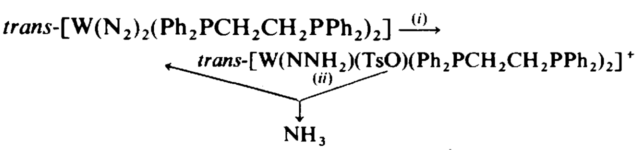
Christopher J. Pickett,* Karl S. Ryder, and Jean Talarmin
AFRC Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ

Protonation of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ with toluene-*p*-sulphonic acid gives the hydrazido cation *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(Ph_2PCH_2CH_2PPh_2)_2]^+$. Reduction of this cation at a Hg-pool electrode in a tetrahydrofuran electrolyte under N_2 (1 atm) affords free ammonia with regeneration of the parent dinitrogen complex in excellent yield. Protonation of the regenerated product allows the system to be cycled and this can be performed in one vessel, the cathode compartment of the electrolysis cell.

The first paper in this series describes the electrosynthesis of complexes such as *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ from molecular nitrogen and precursors which possess the robust framework $M(Ph_2PCH_2CH_2PPh_2)_2$ (M = Mo or W), *e.g.* reaction (1) {conditions: thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$; Hg-pool cathode; −2.7 V *versus* ferrocenium–ferrocene couple; N_2 (1 atm)}.[1] We now show that this framework

$$trans\text{-}[WCl_2(Ph_2PCH_2CH_2PPh_2)_2] \longrightarrow trans\text{-}[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2] \quad (1)$$

(M = W) can mediate the conversion of molecular nitrogen to ammonia. The conversion is achieved by protonation of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ with $4\text{-}CH_3C_6H_4SO_3H$ (TsOH) and reduction of the hydrazido(2−)-product at a mercury-pool cathode in a tetrahydrofuran (thf) electrolyte. The regeneration of the parent dinitrogen complex in the electrolytic step allows the system to be cycled: this can be carried out in one vessel, the cathode compartment of the electrochemical cell, Scheme.



Scheme. (*i*) 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf under N_2 (1 atm), 23.1 °C; (*ii*) $TsOH{\cdot}H_2O$, Hg-pool cathode, −2.6 V *versus* ferrocene–ferrocenium

This paper describes the conditions employed for the protonation and the electronation reactions (*i*) and (*ii*), Scheme, the identification and yields of products, and the *in situ* cycling of the system.

The detection and identification of intermediates involved in the electrosynthesis will be described in Part 3 of this series.[2] A preliminary report of this work has been communicated.[1] The protonation[3] and electronation chemistry[4] of related systems has been reviewed.[4]

Results

Protonation.—*trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ reacts with $4\text{-}CH_3C_6H_4SO_3H$ in thf to give the stable hydrazido(2−)-cation, *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ which can be isolated as its TsO^- salt in good yield, reaction (*i*), Scheme. Details of the preparation and characterisation of this complex are given in the Experimental section. The synthesis is a straightforward extension of preparations described elsewhere.[3]

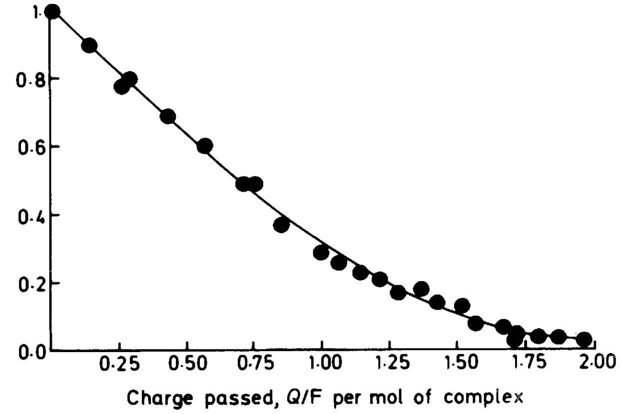


Figure 1. Normalised cell current *versus* charge passed for the reduction of *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ at a mercury-pool cathode in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf

Quantitative studies by ^{31}P n.m.r. spectroscopy show that in solution the protonation reaction proceeds stoicheiometrically; this is important in the cycling of the system as discussed below.

Electronation.—Cyclic voltammetry shows that the complex *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ reduces irreversibly in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ by a diffusion-controlled process.[2] The peak potential for this reduction, E_p^{RED}, occurs at −2.37 V *versus* the ferrocenium–ferrocene couple (fc^+–fc). Accordingly, preparative scale electrolyses were performed in the diffusion-controlled domain at *ca.* 0.2 V negative of E_p^{RED}.

Figure 1 shows a typical plot of the normalised cell current, *I* (cell current/initial cell current) against the charge passed, *Q*; this plot illustrates that the exhaustive electrolysis consumes 2 F mol^{-1} of hydrazido-complex, reaction (2). Following electrolyses the catholyte solution and the aqueous acid-trap were analysed for products as described in the Experimental section and discussed below.

$$trans\text{-}[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+ \xrightarrow{2e} \text{Products} \quad (2)$$

Formation of Ammonia.—Electrolysis of the toluene-*p*-sulphonate complex under a variety of conditions gives

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† *Non-S.I. unit employed:* atm = 101 325 N m^{-2}.

Table. Yields of ammonia produced by electrolysis

Complex	Experiment	Amount of complex (μmol)	Conditions of electrolysis	Gas phase	Amount (absolute) of NH_3 (μmol)	Yield of NH_3 (mol % per mol of complex)
trans-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2][TsO]$	(i)	145	*a*	N_2	33	23
	(ii)	341	*a*	N_2	99	29
	(iii)	120	0.2 mol dm^{-3} $LiClO_4$–thf[a]	N_2	26	21
	(iv)	156	*a*	CO	41	26
	(v)	144	*b*	N_2	28	19
	(vi)	156	*a*	Ar	26	17
	(vii)	141	Co-reduction of $[NBu_4]^+$, −3.2 V[a]	N_2	29	21
	(viii)	136	Not electrolysed[a]	N_2	2	<2
	(ix)	0	Not electrolysed[a]	N_2	0(0.2)	
	(x)	0	Aqueous acid-trap, purged for 2 h	N_2	1	
trans-$[W(NNH_2)F(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$	(xi)	290	*a*	N_2	14	5
	(xii)	144	*b*	N_2	6	4
		±1			±1	±1

[a] Conditions (unless specified otherwise): 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf (30 cm^3); Hg-pool cathode, −2.6 V *versus* fc^+–fc, catholyte purged with gas, aqueous trap of 0.1 mol dm^{-3} HCl (200 cm^3). [b] Conditions as for *a* except electrolyses performed in a closed cell under an atmosphere of N_2 without purging.

ammonia in considerable quantity (20—30% per mol W). Ammonia, retained in the catholyte at the end of electrolysis and purged from the catholyte into the aqueous acid-trap during electrolysis, was identified and estimated by the indolphenol test, as described in the Experimental section.

The Table lists yields of ammonia obtained by exhaustive electrolysis together with data from control experiments. This Table serves to illustrate that ammonia originated from the reduction of the hydrazido(2−)-group of the toluene-*p*-sulphonate complex, reaction (3), and is now discussed.

$$trans\text{-}[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+ \xrightarrow{2e} NH_3\ (0.2\text{—}0.3\ \text{mol}) \quad (3)$$

Background levels of ammonia in the electrolyte and in the acid-trap are insignificant, Table (ix) and (x). Minor amounts of ammonia are released from the complex by the analysis procedure, Table (viii).

Yields of ammonia obtained by electrolysis in the presence of either 0.2 mol dm^{-3}–$[NBu_4][BF_4]$ or –$LiClO_4$ as supporting electrolyte are quite similar, Table (i) and (iii). Reduction of the toluene-*p*-sulphonate complex under extreme conditions, whereby we purposely co-reduce $[NBu_4]^+$, gives no additional ammonia, Table (vii). These results exclude $[NBu_4]^+$ as the source of ammonia.

Comparable yields of ammonia are obtained under N_2, CO, or Ar and in a 'closed system' under N_2, Table (i), (iv), (v), and (vi). These experiments show that the gas-phase dinitrogen is not the source of the ammonia. The slightly lower yields of ammonia obtained under Ar, or with an N_2-depleted electrolyte, Table (v) and (vi), suggests that there is a role for π-acid ligands, N_2 or CO, in the ammonia-forming sequence. This will be discussed in a subsequent paper.[2]

The direct dependence of the formation of ammonia on the presence of the toluene-*p*-sulphonate complex is demonstrated by the increase in the absolute yield of ammonia produced as a consequence of increasing the concentration of *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$, Table (i) and (ii). Furthermore, ammonia formation is specifically linked to the nature of the hydrazido-complex. *trans*-$[W(NNH_2)F(Ph_2PCH_2CH_2PPh_2)_2]^+$, $E_p^{RED} = -2.86$ V *versus* fc^+–fc, was exhaustively electrolysed under conditions similar to those used for the reduction of its closely related toluene-*p*-sulphonate analogue: only meagre yields of ammonia were obtained, Table (xi) and (xii).

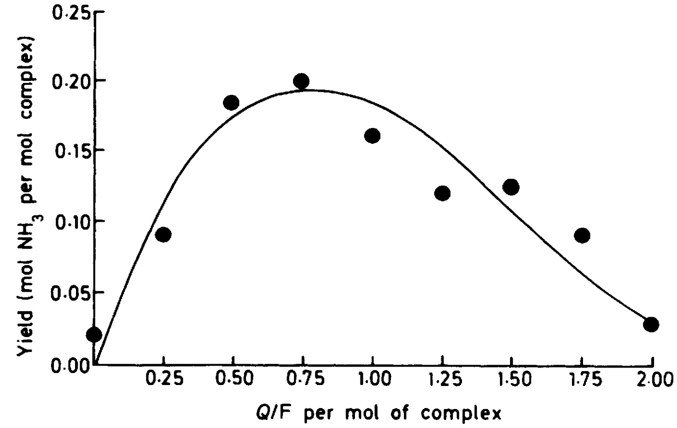

Figure 2. Ammonia retained in cell as function of charge passed

The distribution between the acid-trap and the catholyte of the total ammonia produced varies with the extent of electrolysis and the rate of purging of the system. In typical experiments, ammonia in the catholyte reaches a maximum concentration about half-way through electrolysis, thereafter its concentration falls as it is purged into the aqueous acid-trap, Figure 2. At the end of electrolysis the trap contains 80—90% of the total ammonia produced. The ^{15}N-labelled complex, *trans*-$[W(^{15}N^{15}NH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ was reduced under an atmosphere of $^{14}N_2$ and half-way through the electrolysis, $Q = 1$ F mol^{-1}, the catholyte was examined by ^{15}N n.m.r. spectroscopy. The major resonance in the spectrum is, as expected, free $^{15}NH_3$ ($\delta = -315$ p.p.m., relative to nitromethane). The two other resonances we observe are associated with a metal intermediate and *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$, the final product of electrolysis (see below). (The nature of the intermediate will be discussed in a subsequent paper.[2])

In addition to ammonia small quantities of hydrazine are formed in the electrosyntheses under N_2, yields are typically 1—2 mol% per mol of hydrazido-complex: hydrazine is usually produced in all protolysis reactions of dinitrogen complexes which give ammonia.[4]

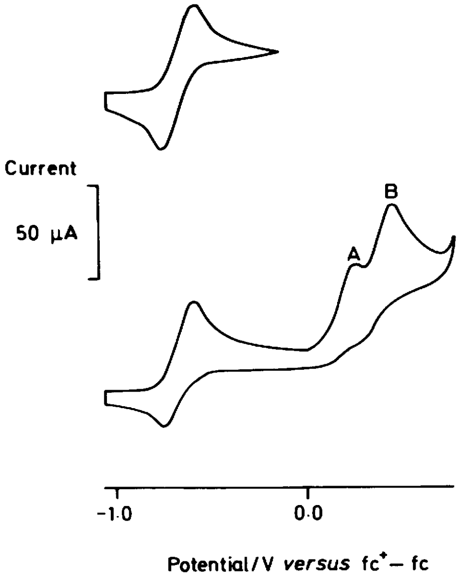

Figure 3. Cyclic voltammogram of product at end of electrolysis

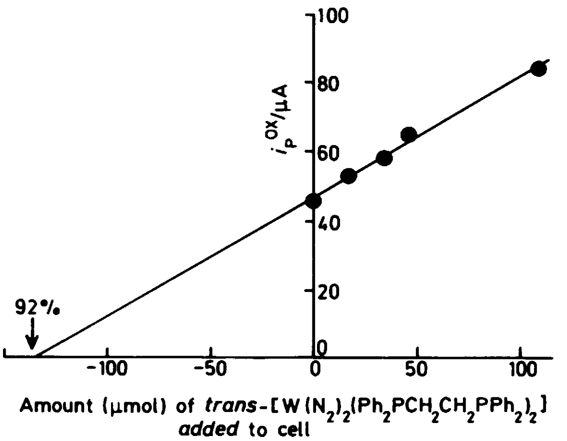

Figure 4. Determination of yield of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$

Formation of trans-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$.—Under an atmosphere of dinitrogen, the metal product obtained after the exhaustive electrolysis is *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$. The complex is formed essentially quantitatively, reaction (4). The evidence for this is as follows. The complex was

$$trans\text{-}[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+ \xrightarrow[N_2]{2e} trans\text{-}[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2] \quad (4)$$

identified as a product at the end of reduction by three separate techniques: ^{31}P n.m.r. and i.r. spectroscopy, and cyclic voltammetry.

Examination of the catholyte by ^{31}P n.m.r. spectroscopy showed that a single phosphorus-containing metal product is formed. The chemical shift of the singlet resonance (W satellites), δ 94.8 p.p.m. relative to trimethyl phosphite, is identical with that of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ recorded under the same conditions. Work-up of the catholyte gave an orange solid which showed by i.r. spectroscopy the characteristic $\nu(N_2)$ of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ at 1 950 cm^{-1} (Nujol). Examination of the catholyte by cyclic voltammetry showed a major reversible one-electron oxidation process at −0.69 V *versus* fc^+–fc, this is identical with that observed for an authentic sample of the bis(dinitrogen) complex.

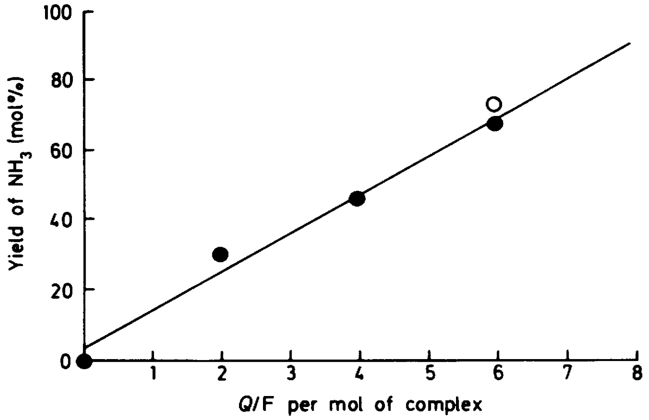

Figure 5. Yield (mol %) of NH_3 for successive protonation–reduction cycles: (●) in trap, (○) trap + catholyte

The yields of the bis(dinitrogen) complex were determined by quantitative cyclic voltammetry, a technique we have used extensively elsewhere.[5] Figure 3 shows the cyclic voltammogram for the product *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ which is present in the catholyte at the end of electrolysis. Before we consider the measurement of yields, we must eliminate a possible source of confusion, the nature of the peaks A and B in Figure 3. Neither peak is a consequence of the oxidation of other products in the catholyte. Peak A is merely the secondary oxidation process of the product; peak B arises from the attack of TsO^- on the dinitrogen complex following its secondary oxidation. Addition of $[NBu_4][TsO]$ to a solution of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf gives a voltammogram identical to that of the catholyte.

The peak current, i_p^{ox}, is directly proportional to the concentration of the product. So as to avoid unnecessary sources of error (in particular, variation in the effective area of the working electrode from one experiment to the next) we have used the 'method of addition' to determine yields. Weighed samples of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ were added to the catholyte and i_p^{ox} was measured after each successive addition. Figure 4 shows a typical plot of i_p^{ox} *versus* the amount (µmol) of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ added; from the intercept we obtain the amount (µmol) of complex contained in the 'unspiked' sample. Yields of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ measured in this way were in the range (85—95) ± 5 mol% per mol of *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$. For example, the yield of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ corresponding to experiment (i) in the Table was 92 ± 5%.

In Situ *Protonation–Reduction Cycles.*—The hydrazido-complex was exhaustively electrolysed under dinitrogen as previously described, Table (i). At the end of electrolysis 2.2 mol equivalents of $TsOH{\cdot}H_2O$ were added to the catholyte and after *ca.* 5 min the electrolyses was recommenced. The initial cell current was close to that observed at the beginning of the first cycle. Following exhaustive electrolysis a further 2.2 mol equivalents of $TsOH{\cdot}H_2O$ were added to the catholyte and the electrolysis repeated once more. The yield of ammonia after the three electrolysis cycles was 73 mol% per mol of *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$. The 23% yield for a single reduction, Table (i), is quite typical; that we obtain a 73% yield after three reductions (performed over a period of *ca.*

6 h) provides good evidence that the system is robust and that *in situ* cycling is possible. The plot of yield of ammonia *versus* number of cycles is shown in Figure 5.

Conclusions

Formation of Ammonia.—We have shown for the first time that the robust diphosphine complex *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ can yield substantial quantities of ammonia and that this can be achieved by successive protonation and electronation reactions.

Regeneration of trans-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$.—Whereas protolysis reactions of mono-tertiary phosphine complexes such as *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ give ammonia in high yield,[6] such reactions invariably lead to the partial or complete degradation of the MP_4 core (M = Mo or W). We have shown that an MP_4 core can be retained in an ammonia-producing reaction sequence; crucially *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ is regenerated by electrolysis under dinitrogen.

Recycling the System.—Since Chatt *et al.*[6] first reported that the protolysis of the dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ gives ammonia, reaction (5), there has existed the

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{H^+} 2NH_3 + N_2 + \text{degradation products} \quad (5)$$

engaging possibility that a cyclic conversion of molecular nitrogen to ammonia might be achieved at room temperature and pressure using mediators possessing an MP_4 core. We have now shown that this can be substantially realised.

Final Remarks.—That ammonia and *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ are formed by electrolysis of *trans*-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ in the presence of dinitrogen is unambiguous. How this occurs will be shown in a later paper[2] to depend primarily on the ability of the toluene-*p*-sulphonate complex to undergo both reductive cleavage of the W–OTs bond and deprotonation of the hydrazido-group, reactions (6) and (7). Reaction (7) furnishes protons which attack the reduced hydrazido-intermediate generated *via* reaction (6).

$$trans\text{-}[W^{IV}(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+ \xrightarrow{2e} [W^{II}(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2] + TsO^- \quad (6)$$

$$trans\text{-}[W^{IV}(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2]^+ \xrightarrow{-H^+} [W^{II}(NNH)(TsO)(Ph_2PCH_2CH_2PPh_2)_2] \quad (7)$$

Experimental

Preparation of trans-$[W(NNH_2)(TsO)(Ph_2PCH_2CH_2PPh_2)_2][TsO]\cdot H_2O$.—trans-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (0.84 g, 0.81 mmol) was dissolved in thf (60 cm^3) under dinitrogen (1 atm). Toluene-*p*-sulphonic acid hydrate (3.2 g, 16.8 mmol) was added as the solid and the resulting solution stirred for $\frac{1}{2}$ h; during this period the orange solution turned pale brown. The volume of the reaction mixture was reduced to *ca.* 15 cm^3 *in vacuo*. The resulting solution was dropped slowly under dinitrogen into distilled water (200 cm^3) with vigorous stirring whereby a cream coloured precipitate was formed. The precipitate was filtered off, washed with ether (3 × 50 cm^3) and dried at room temperature *in vacuo* (crude yield 0.92 g, 85%). Recrystallisation from thf–ether gave buff-coloured needles. Overall yield 0.76 g, 70%; m.p. 174 °C (decomp.) (Found: C, 57.4; H, 4.90; N, 2.10. Calc. for $C_{66}H_{66}N_2O_7P_4S_2W$: C, 57.8; H, 4.85; N, 2.05%). ^1H N.m.r. (CD_2Cl_2), δ 7.5—6.7 (m, 48 H, aromatic), 4.60 (br, s, 2 H, NH), 2.97 (m, 8 H, PCH_2CH_2P), 2.35 (br, s, 6 H, $CH_3C_6H_4SO_3$) relative to $SiMe_4$. ^{31}P-{^1H} N.m.r. (thf), δ −103.9 (s, W satellites) relative to $P(OMe)_3$.

Instrumentation.—Electrochemical measurements were made using a Hi-Tek DT-101 potentiostat, a Chemical Electronics 01 waveform generator and a Chemical Electronics integrator. Cyclic voltammograms were recorded on a Philips PM8043 X-Y recorder.

Infrared and u.v.–visible spectra were obtained using Pye-Unicam spectrometers type SP2000 and SP1800 respectively. ^1H N.m.r. and ^{31}P n.m.r. spectra were recorded on a JEOL FX90Q Fourier-transform spectrometer.

Electrosyntheses.—Electrolyses were performed in a four-compartment three-electrode cell.[1] The procedure employed for Experiment (i), Table, is typical and we therefore describe it here.

The electrolysis cell was charged with the electrolyte solution under dinitrogen (80 cm^3, 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf). The hydrazido complex (0.202 g, 145 μmol) was dissolved in the electrolyte (*ca.* 30 cm^3) contained in the catholyte chamber. Electrolysis of the complex was initiated at the mercury-pool cathode (nominal area 9.2 cm^2, −2.6 V *versus* fc$^+$–fc). The electrolyte was steadily stirred with a Teflon-coated magnetic follower and continuously purged with a slow stream of dinitrogen gas (pre-saturated with thf vapour) throughout the electrolysis. The cell current of *ca.* 20 mA decayed to *ca.* 0.5 mA after the passage of 1.8 F per mol of hydrazido-complex whilst the colour of the catholyte changed from pale brown, through brown-red, to orange. At the end of electrolysis samples were removed by syringe from the catholyte and trap for analysis as described below. The trap was found to contain 18 mol% per mol of hydrazido complex initially present, the catholyte 5%, giving a total yield of ammonia of 23%, Table (i). About 1% of hydrazine was detected in the catholyte. The yield of dinitrogen complex was found to be 92%, Figure 4.

Analysis of Products.—Ammonia was determined by the 'indophenol test' which employs two separate reagents, (**A**) and (**B**); AnalaR chemicals for these reagents were supplied by B. D. H. Ltd. [Reagent (**A**): phenol (10 g), $Na_2[Fe(CN)_5(NO)]$ (50 mg), distilled water (1 l); reagent (**B**): sodium hydroxide (5 g), sodium hypochlorite (1 mol dm^{-3}, 5.65 cm^3), distilled water to 1 l]. The reagents are stored at 4 °C. Reagent (**A**) (10 cm^3) was added to 1 cm^3 of the trap solution with thorough mixing, reagent (**B**) (10 cm^3) was added and the solution again thoroughly mixed. After 1 h the characteristic blue colour was fully developed and the optical density (o.d.) of the solution was measured at 625 nm. The catholyte was tested for ammonia in the following way. A sample (1 cm^3) was added to aqueous HCl (0.1 mol dm^{-3}, 1 cm^3) which precipitates the metal complex, reagents (**A**) and (**B**) (10 cm^3 each) were added and the solution was filtered to remove the precipitated solids. The colour was allowed to develop for 1 h and the o.d. of the filtrate was measured as before. Control experiments show that there are no discernible interferences in the test procedure used for the catholyte and that it is reproducible. Yields of ammonia were estimated from a standard curve.

Hydrazine present in the catholyte was estimated using the reagent pdmab; 'AnalaR' chemicals for this reagent were supplied by B. D. H. Ltd. [*p*-dimethylaminobenzaldehyde (1.2 g), ethanol (60 cm^3), concentrated hydrochloric acid (*ca.* 35% w/v, 6 cm^3)]. The test procedure on the catholyte was as follows. The catholyte (5 cm^3) was added to aqueous HCl (0.1 mol dm^{-3}, 5 cm^3) and the precipitated complex *trans*-

$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ was removed by filtration. The filtrate (5 cm^3) was added to the reagent (10 cm^3) together with more HCl (0.1 mol dm^{-3}, 10 cm^3). The o.d. of the resulting solution was measured at 458 nm and hydrazine was estimated from a standard curve.

trans-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ present in the catholyte at the end of electrolysis was determined as follows. A known volume of the catholyte (8—10 cm^3) was removed from the cell by a gas-tight syringe and transferred carefully to a two-compartment, three-electrode cyclic voltammetry cell. The peak current, i_p^{ox}, for the primary oxidation of the product at -0.69 V *versus* fc^+–fc was measured at a scan rate of 0.2 V s^{-1} at the platinum wire working electrode. Accurately weighed samples of analytically pure *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ were successively added to the catholyte and, after each addition, i_p^{ox} was remeasured. From the plot i_p^{ox} *versus* amount of complex added (μmol) the yield of *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ can be estimated, Figure 4. In a separate experiment we have found that the plot of i_p^{ox} *versus* concentration of the dinitrogen complex shows excellent linearity over the range of concentration which was obtained in our electrolysis experiments.

The principal source of error in estimating the yield of complex is associated with accurately measuring the volume of the catholyte in the electrolysis cell. This is less important in the case of ammonia yields because the bulk of this product is in the acid-trap.

Acknowledgements

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