The Preparation and Oxidation, Substitution, and Protonation Reactions of *trans*-Bis(dinitrogen)tetrakis(methyldiphenylphosphine)tungsten

By **Joseph Chatt, Alan J. Pearman,** and **Raymond L. Richards,*** Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ

The complex *trans*-$[W(N_2)_2(PMePh_2)_4]$ has been prepared. It gives *trans*-$[W(N_2)_2(PMePh_2)_4][FeCl_4]$ with an excess of $FeCl_3$ in ethanol, and $[W(N_2)_2(PMePh_2)_3L]$ (L = NC_5H_5, NC_5H_4Me-3, NC_5H_4Me-4, or $NC_5H_4CO_2H$-4) on treatment with L in tetrahydrofuran (thf). With dppe ($Ph_2PCH_2CH_2PPh_2$) in thf, *trans*-$[M(N_2)_2(PMePh_2)_4]$ (M = Mo or W) give $[M(N_2)_2(PMePh_2)_2(dppe)]$. Treatment of $[W(N_2)_2(PMePh_2)_4]$ with hydrogen chloride in dichloromethane gives dinitrogen (1 mol) and $[WCl_3(NHNH_2)(PMePh_2)_2]$, which with H_2SO_4 in methanol gives hydrazine (0.28 mol) and ammonia (0.23 mol), but mainly ammonia (0.76 mol) and a little hydrazine (0.08 mol) on treatment with 40% aqueous potassium hydroxide.

THE extent of protonation and reduction of the dinitrogen ligand in certain complexes of molybdenum and tungsten is dependent on the tertiary phosphine co-ligands. Thus when dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) is the co-ligand, *e.g.* in *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), protonation by sulphuric acid stops at the $M-NNH_2$ stage, giving *trans*-$[M(HSO_4)(NNH_2)(dppe)_2][HSO_4]$,[1] whereas when PMe_2Ph is the co-ligand, *e.g.* in *cis*-$[M(N_2)_2(PMe_2Ph)_4]$, ammonia is obtained in good yield by reaction with H_2SO_4.[2] We have, therefore, varied the tertiary phosphine ligands which accompany dinitrogen in its complexes in order to isolate intermediate stages on the route to ammonia and to influence the distribution of the final products between hydrazine and ammonia. We have already described some of our preliminary investigations[1,2] and here we describe in detail the preparation of *trans*-$[W(N_2)_2(PMePh_2)_4]$ and some of its oxidation, substitution, and protonation reactions and compare them with those of its analogues.

Molybdenum and tungsten dinitrogen and hydrazido(1 −)-complexes

Complex	Colour	Yield (%)	M.p.[a] (θ_c/°C)	Analysis[b] (%) C	H	N	I.r.[c] (cm^{-1})	N.m.r.[d] (δ/p.p.m.)
trans-$[W(N_2)_2(PMePh_2)_4]$	Orange-red	15	155—157 (decomp.)	59.9 (60.0)	5.4 (5.0)	5.2 (5.4)	1 910s[e] 1 975w[e]	1.77 (m), PCH_3 6.89, PPh
trans-$[W(N_2)_2(PMePh_2)_4][FeCl_4]$	Yellow-brown	45	decomp. >120	50.8 (50.4)	4.4 (4.2)	4.6 (4.5)	1 946[e] 2 020w[e] 377[f]	
$[W(N_2)_2(PMePh_2)_3(NC_5H_5)]$	Purple	25	decomp. >150	57.2 (57.5)	4.9 (4.8)	7.5 (7.6)	1 882[e] 1 558 1 574 1 589 } g	h
$[W(N_2)_2(PMePh_2)_3(NC_5H_4Me\text{-}3)]$	Purple	30	decomp. >130	58.0 (57.9)	5.0 (4.8)	7.4 (7.5)	1 877s[e] 1 578 1 591 } g	h
$[W(N_2)_2(PMePh_2)_3(NC_5H_4Me\text{-}4)]$	Red-brown	28	decomp. >130	57.6 (57.9)	4.8 (4.9)	7.3 (7.5)	1 879[e] 1 582[g]	h
$[W(N_2)_2(PMePh_2)_3(NC_5H_4CO_2H\text{-}4)]$	Green	36	decomp. >100	56.8 (56.1)	4.8 (4.6)	7.3 (7.3)	1 880s[e] 1 571 1 659 1 710 } g	h
$[W(N_2)_2(PMePh_2)_2(dppe)]$	Orange	45	decomp. >150	60.5 (60.1)	5.0 (4.8)	4.9 (5.4)	1 920s[e]	1.2—2.4 (m), PCH_3, PCH_2 6.8—8 (m), PPh
$[Mo(N_2)_2(PMePh_2)_2(dppe)]$	Orange	67	decomp. >140	65.8 (65.7)	5.4 (5.3)	5.7 (5.9)	1 943s[e]	1.0—2.2 (m), PCH_3 + PCH_2 6.7—8.0, PPh
$[WCl_3(NHNH_2)(PMePh_2)_2]$[i]	Grey-brown	74	decomp. >150	43.2 (43.3)	4.3 (4.1)	3.7 (3.9)	3 123w 3 197m 3 356w } j 260ms[l] 300s, br[l]	2.49 (m), PCH_3 5.60 (br s), NH_2[k] 7.23—7.74, Ph 12.10 (t),[m] NH[k] 124.69 (t),[n] WP

[a] In sealed evacuated tubes. [b] Calculated values are given in parentheses. [c] Nujol mulls. [d] In CH_2Cl_2 solution, relative to $SiMe_4$. [e] $\nu(N_2)$. [f] $\nu(FeCl_4)$. [g] Pyridine absorptions. [h] Unstable in solvents. [i] Cl 14.7 (14.7%). [j] ν(NH). [k] Disappeared with ^2H_2O (see text). [l] ν(W–Cl). [m] ^3J(NHWP) 91.6 Hz. [n] Phosphorus-31 signal, to high field of $P(OMe)_3$; ^1J(WP) 153.8 Hz (^{1}H-decoupled spectrum).

RESULTS AND DISCUSSION

The complex *trans*-$[W(N_2)_2(PMePh_2)_4]$ was prepared in rather poor yield as in Scheme 1. Its physical properties are shown in the Table and the single N_2-stretching i.r. band and broad single P–Me ^{1}H n.m.r. pattern are consistent with a *trans* structure. Unlike its molybdenum analogue,[3] it may be oxidised by one unit to give a stable species, isolated as the tetrachloroferrate (Scheme 1).

In contrast to its analogues with dppe and PMe_2Ph,

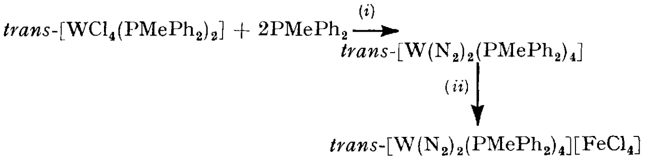
---

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

[2] J. Chatt, A. J. Pearman, and R. L. Richards, *J. Organometallic Chem.*, 1975, **101**, C45.

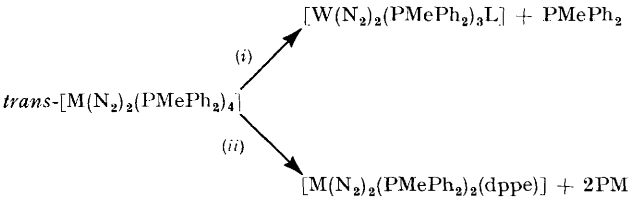
[3] T. A. George and C. D. Siebold, *Inorg. Chem.*, 1973, **12**, 2548.

substitution of the tertiary phosphine ligands of *trans*-$[\mathrm{W(N_2)_2(PMePh_2)_4}]$ by pyridines (one tertiary phosphine) or dppe (two tertiary phosphines) may be carried out,



SCHEME 1 (*i*) Mg, tetrahydrofuran (thf), $\mathrm{N_2}$; (*ii*) EtOH, excess of $\mathrm{FeCl_3}$

without loss of dinitrogen (Scheme 2). The molybdenum analogue, *trans*-$[\mathrm{Mo(N_2)_2(PMePh_2)_4}]$, may also be substituted, without loss of dinitrogen, by dppe (Scheme 2), but attempts to introduce pyridine ligands lead to its complete loss as the gas. Attempts to introduce such ligands as 2,2′-bipyridine and 1,10-phenanthroline as co-ligands with dinitrogen also lead, for both M = Mo and W, to complete loss of dinitrogen. The pyridine-substituted tungsten complexes were insufficiently stable in solvents in which they were soluble for reliable n.m.r. spectral measurements so their configurations could not be confirmed, but the single $\mathrm{N_2}$-stretching i.r. band indicates a *trans* configuration for the dinitrogen ligands and thus the tertiary phosphines must have the *mer* configuration. Similarly the complexes $[\mathrm{M(N_2)_2(PMePh_2)_2(dppe)}]$ (M = Mo or W) must have *trans*-dinitrogen and *cis*-tertiary phosphine groups.



SCHEME 2 (*i*) M = W, thf, L = $\mathrm{NC_5H_5}$, $\mathrm{NC_5H_4Me}$-3, $\mathrm{NC_5H_4Me}$-4, or $\mathrm{NC_5H_4CO_2H}$-4; (*ii*) M = Mo or W, thf, dppe

The complexes $[\mathrm{M(N_2)_2(PMePh_2)_2(dppe)}]$ (M = Mo or W) could also be prepared directly from dinitrogen by reaction (1). (We are indebted to Dr. P. E. Bevan for this preparation.) This route also allows preparation of the complexes $[\mathrm{M(N_2)_2(PMe_2Ph)_2(dppe)}]$, which are not accessible from *cis*-$[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$ by the method of Scheme 2 owing to extensive decomposition and loss of dinitrogen. The further reactions of these substitution products, especially their protonation, will be described elsewhere.

When treated with sulphuric acid in methanol, *trans*-$[\mathrm{W(N_2)_2(PMePh_2)_4}]$ gives ammonia (1.8 mol), dinitrogen (1.0 mol), and hydrazine (*ca.* 0.1 mol).[1] Similar yields of ammonia (1.9 mol), dinitrogen (1.01 mol), and hydrazine

$$[\mathrm{MCl_4(dppe)}] + 2\mathrm{PMePh_2} + 2\mathrm{N_2} \xrightarrow[\text{thf}]{\text{Mg}} [\mathrm{M(N_2)_2(PMePh_2)_2(dppe)}] + 4\mathrm{MgCl} \quad (1)$$

(*ca.* 0.03 mol) are obtained if hydrogen chloride is used instead of $\mathrm{H_2SO_4}$, but in neither case could intermediates be isolated. If anhydrous hydrogen chloride is used in dichloromethane, however, a grey-green hydrazido(1−)-complex is produced according to equation (2). The hydrazido(1−)-complex shows N–H bands in its i.r. spectrum (Table) and is a non-electrolyte in nitromethane. In its ^{1}H n.m.r. spectrum it shows a P–Me multiplet which indicates equivalent $\mathrm{PMePh_2}$ ligands with moderate P–P coupling (but is not stereochemically diagnostic [4]), a broad singlet which integrates for two protons, and a low-field triplet which integrates for one proton. Of the latter two signals, the broad singlet, which rapidly disappears on addition of $^2\mathrm{H_2O}$, is assigned to the terminal $\mathrm{NH_2}$ group, and the low-field triplet is assigned to the NH group directly attached to the metal. This latter signal does not change on addition of $^2\mathrm{H_2O}$ unless a base, such as $\mathrm{C_5{}^2H_5N}$ is added when the signal disappears over *ca.* 45 min. (Addition of hydroxide causes further reaction, see below.) Thus there appears

$$trans\text{-}[\mathrm{W(N_2)_2(PMePh_2)_4}] + 5\mathrm{HCl} \xrightarrow[20\,^\circ\mathrm{C}]{\mathrm{CH_2Cl_2}} [\mathrm{WCl_3(NHNH_2)(PMePh_2)_2}] + \mathrm{N_2} + 2[\mathrm{PMePh_2H}]\mathrm{Cl} \quad (2)$$

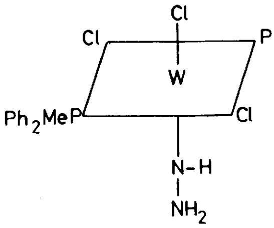
to be only slow exchange of the N–*H* adjacent to the metal, probably as a result of the nitrogen atom's electrons being strongly associated with the metal, thus preventing initial attack by a proton (deuteron) so that a base-catalysed dissociative mechanism can operate, although it is not clear why this process is so slow. The NH_2 resonance is presumed broad because of the nitrogen quadrupole and possible unresolved coupling with the N–*H* atom. The components of the N–*H* low-field triplet are also somewhat broad, possibly because of coupling to the NH_2 group and the nitrogen-quadrupole effect, but the triplet pattern is due to coupling with the two equivalent phosphorus atoms since the ^{1}H-undecoupled ^{31}P spectrum shows two unresolved multiplets with a separation equal to one half that of the outside lines of the N–*H* triplet, *i.e.* both patterns correspond to ^3J(HNWP) 91.6 Hz. The ^{1}H-decoupled spectrum shows a single line (with tungsten satellites) confirming the equivalence of the $\mathrm{PMePh_2}$ groups. Thus the structure of the hydrazido(1−)-complex can be either (A) or (B), which cannot be distinguished by the present data.

The hydrazido(1−)-complex gave hydrazine (0.23 mol) and ammonia (0.28 mol) when treated with $\mathrm{H_2SO_4}$

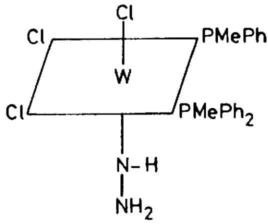
---

[4] J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2796.

in methanol (these values replace the preliminary data of ref. 2), but more ammonia (0.76 mol) and little hydrazine (0.08 mol) were obtained by treating the complex with a large excess of 40% aqueous potassium hydroxide solution. The mechanism of the reduction of the hydrazido(1—)-ligand to ammonia by protic attack is not established, but its exchange behaviour suggests that further attack by a proton must occur preferentially at the terminal nitrogen atom in accord with the mechanism already proposed.[5] The hydrazine may result from the less-favoured attack by strong acid at the α-nitrogen atom to produce a hydrazine complex which is subsequently degraded. Basic (hydroxide) attack would be expected to degrade the N_2H_3 ligand to dinitrogen by dehydrochlorination of the hydrazido(1—)-complex. However, we obtain up to 0.76 mol of ammonia and speculation on the mechanism must await further investigations.



(A)



(B)

The substitution reactions of dinitrogen complexes and the stabilisation of intermediate stages on the route from dinitrogen to ammonia requires a particular balance of tertiary phosphine and other neutral or anionic ligands. In the examples studied here, both substitution of a tertiary phosphine without dinitrogen loss and stabilisation of the hydrazido(1—)-stage have been achieved. However, in closely analogous systems where, for example, PMe_2Ph is the phosphine, loss of dinitrogen occurs in attempted ligand substitutions and only the hydrazido(2—)-reduction stage, *e.g.* in $[MCl_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W),[2,6] has been isolated from protonation studies: neither $[MCl(NNH)(PMe_2Ph)_4]$ nor $[MCl_3(NHNH_2)(PMe_2Ph)_2]$ appear to be sufficiently stable to be isolated from these reactions.

Further investigation of the reactions of the dinitrogen and hydrazido(1—)-complexes prepared in this study is in hand to gain more information on these subtle, but vitally important, ' ligand-balance ' effects.

EXPERIMENTAL

Air-sensitive materials were handled under dinitrogen or by vacuum techniques; non-condensible gases were determined by means of a Töpler pump. N.m.r. spectra were obtained using a JEOL P.S. 100 instrument (with Fourier-transform mode for ^{31}P and some ^{1}H spectra) and i.r. spectra with a Unicam SP 1000 spectrometer. Magnetic moments were measured using a Faraday balance mass spectra with an A.E.I. MS10 instrument, and conductivities with a Portland Electronics conductivity bridge. Analyses were by Mr. A. G. Olney of the University of Sussex Laboratories. The complexes $[WCl_4(dppe)]$,[7] $[MoCl_4(dppe)]$,[8] $[WCl_4(PMePh_2)_2]$,[7] and *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ [3] were prepared as previously described.

trans-*Bis(dinitrogen)tetrakis(methyldiphenylphosphine)tungsten*, *trans*-$[W(N_2)_2(PMePh_2)_4]$.—Magnesium turnings (5 g) and *trans*-$[WCl_4(PMePh_2)_2]$ (5.0 g) were pumped *in vacuo* for 1 h. Tetrahydrofuran (thf) (125 cm^3) and methyldiphenylphosphine (2.3 cm^3, 2.0 mol) were then added and the mixture vigorously stirred under dinitrogen for 18 h. The dark red-black solution was then filtered to remove excess of magnesium and the solvent removed *in vacuo*. The residue was pumped for a further 1 h at 20 °C then diethyl ether (75 cm^3) was added. The resulting mixture was filtered and the solid washed with diethyl ether (25 cm^3) then discarded. The two ether fractions were combined and the solvent removed *in vacuo*. Toluene (30 cm^3) and methanol (100 cm^3) were added to give a red *precipitate* of *trans*-$[W(N_2)_2(PMePh_2)_4]$ which was filtered off, washed with methanol, and dried (10^{-3} mmHg, 20 °C).* The mother liquor deposited more solid, on standing at 0 °C, which was filtered off, washed with methanol, dried, and combined with the first product [total yield 1.0 g (14%)].

trans-*Bis(dinitrogen)tetrakis(methyldiphenylphosphine)tungsten*(I) *Tetrachloroferrate*(III), *trans*-$[W(N_2)_2(PMePh_2)_4][FeCl_4]$.—Anhydrous ethanol (50 cm^3) was added to *trans*-$[W(N_2)_2(PMePh_2)_4]$ (0.2 g) and anhydrous $FeCl_3$ (0.2 g) and the mixture was stirred for 0.5 h. The yellow-brown *precipitate* of *trans*-$[W(N_2)_2(PMePh_2)_4][FeCl_4]$ was filtered off, washed with a little methanol then diethyl ether, and dried (10^{-3} mmHg, 20 °C) (0.1 g), μ_{eff} 1.8 B.M., Λ 18 S cm^2 mol^{-1} in *ca.* 10^{-3} mol dm^{-3} $PhNO_2$ solution.

trans,mer-*Bis(dinitrogen)tris(methyldiphenylphosphine)pyridinetungsten*, *trans,mer*-$[W(N_2)_2(PMePh_2)_3(NC_5H_5)]$.—Pyridine (0.5 cm^3) was added to a solution of *trans*-$[W(N_2)_2(PMePh_2)_4]$ (0.6 g) in thf (50 cm^3) and the solution was heated under reflux under dinitrogen until it was purple (10 min). After cooling the solution to 20 °C and filtering it, the solvent was removed *in vacuo* and the resulting purple oil was triturated with diethyl ether to give a purple solid which was filtered off, washed with ether, and dried. Recrystallisation from thf–OEt_2 gave purple *crystals* (0.1 g).

Adducts of the other substituted pyridines were prepared in a similar manner and their physical properties are shown in the Table. Reactions with 2,2′-bipyridine and 1,10-phenanthroline were carried out under similar conditions, but in both cases dinitrogen (2 mol per W atom) was evolved and the dark brown solids obtained after removal of solvent were not further characterised, except to show that they had no N_2-stretching i.r. band.

trans-*[1,2-Bis(diphenylphosphino)ethane]bis(dinitrogen)bis(methyldiphenylphosphine)tungsten*, *trans*-$[W(N_2)_2(PMePh_2)_2(dppe)]$.—(*a*) The complex *trans*-$[W(N_2)_2(PMePh_2)_4]$ (0.47 g) and dppe (0.18 g) were heated under reflux in thf (30 cm^3) for 0.5 h under dinitrogen. After cooling

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27×10^{-24} A m^2.

[5] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1977, 1852.

[6] J. Chatt and R. L. Richards, *Proc. 2nd Climax Molybdenum Conf.*, ed. P. C. H. Mitchell, Oxford, 1976, p. 242.

[7] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J.C.S. Dalton*, 1972, 1064.

[8] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

to 20 °C the solvent was removed *in vacuo* and diethyl ether was added to give a red oily solution which deposited an orange solid on standing for 18 h at 0 °C. This was filtered off and recrystallised from thf–OEt_2 as orange *prisms* (0.21 g).

(*b*) (*P. E. Bevan's method*). Methyldiphenylphosphine (1.7 g) was added to [WCl_4(dppe)] (4.45 g) and magnesium (5 g) in thf (200 cm^3) and the mixture was stirred under dinitrogen for 18 h. It was then filtered and the solvent removed from the resulting dark red-brown solution *in vacuo*. The residue was dissolved in benzene (100 cm^3), filtered (using Celite), and the filtrate was reduced to about one third of its volume *in vacuo*. Methanol (80 cm^3) was then added and orange *crystals* formed after allowing the solution to stand for 18 h at 0 °C. These were filtered off, washed with methanol, dried, and shown to be identical to the product from (*a*) by i.r. spectroscopy and analysis (3.5 g). Although the yields from methods (*a*) and (*b*) are the same (45%), (*b*) is obviously the better route since it involves fewer steps.

trans-[1,2-*Bis(diphenylphosphino)ethane*]*bis(dinitrogen)-bis(methyldiphenylphosphine)molybdenum*, *trans*-[$Mo(N_2)_2(PMePh_2)_2$(dppe)], was similarly prepared by route (*a*) from *trans*-[$Mo(N_2)_2(PMePh_2)_4$] or by route (*b*) from [$MoCl_4$(dppe)] and its properties are shown in the Table.

trans-*Trichloro*[*hydrazido*(1−)]*bis(methyldiphenylphosphine)tungsten*, *trans*-[$WCl_3(NHNH_2)(PMePh_2)_2$].—Dichloromethane (40 cm^3) and hydrogen chloride (10 mol equiv.) were condensed at −196 °C on to *trans*-[$W(N_2)_2(PMePh_2)_4$] (0.59 g) *in vacuo*. On warming to 20 °C, dinitrogen (14.34 cm^3, 1.07 mol equiv.) was evolved with the formation of a red solution which was stirred for 4 h, during which time it became pale and some white solid precipitated. After filtration, the solution was reduced in volume *in vacuo* to *ca.* 5 cm^3. Methanol (5 cm^3) and diethyl ether (60 cm^3) were then added to give a pale grey-brown *solid* which was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C) (0.3 g). The complex is essentially non-conducting in $MeNO_2$ (Λ *ca.* 2 S cm^2 mol^{-1}) and its molecular weight in $C_2H_4Cl_2$ (523, calc. 722), although rather low, shows it to be a monomer.

Reactions of trans-[$WCl_3(NHNH_2)(PMePh_2)_2$].—(*a*) *With* H_2SO_4 *in methanol*. Concentrated H_2SO_4 (0.07 cm^3, 22.5 mol) was added, *in vacuo*, to the hydrazido(1−)-complex (0.042 g) in methanol (30 cm^3) and the mixture was stirred for 160 h; dihydrogen (0.3 mol) was evolved. The solvent was then removed *in vacuo* at 20 °C and the reaction flask filled with argon. Distilled water was added, the mixture was filtered, and the residue washed with distilled water, under argon. The washings and the initial filtrate were then combined, transferred to an all-glass distillation apparatus, 40% w/v KOH solution (10 cm^3) added, and the mixture distilled to small volume into 1 N H_2SO_4 (*ca.* 10 cm^3). The resulting solution was made up to a known volume with distilled water and aliquot portions were tested for ammonia (indophenol) and hydrazine (*p*-dimethylaminobenzaldehyde). Addition of $Tl_2[SO_4]$ to the reaction mixture had little effect on the yield of ammonia (0.24 mol) and hydrazine (0.23 mol).

(*b*) *With aqueous potassium hydroxide solution*. The hydrazido(1−)-complex (0.05 g) was placed in the all-glass distillation apparatus and 40% w/v potassium hydroxide solution (10 cm^3) was added under argon. The mixture was then distilled to near dryness into H_2SO_4 (10 cm^3) and the resulting solution was tested, as above, for ammonia (0.76 mol) and hydrazine (0.08 mol).

We thank Messrs. I. G. Pickard and S. N. Anderson for experimental assistance.

[7/766 *Received*, 6*th May*, 1977]