Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy of Hydrazido(2 –)-, Imido-, and Nitrido-complexes of Molybdenum and Tungsten

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Nitrogen-15 chemical shifts and coupling constants are reported for the range of hydrazido(2⁻)complexes $[MX({}^{15}NR^{1}R^{2})(dppe)_{2}]^{+} \{X = CI, Br, I, or HSO_{4}; M = Mo or W; R^{1} = H, R^{2} =$

Me, or Et [and ${}^{15}N_2R^{1}R^2 = {}^{15}N^{15}N(CH_2)_3CH_2$]; dppe = Ph₂PCH₂CH₂PPh₂}, [W(NCPrⁿ)(${}^{15}N^{15}NH_2$)-(dppe)₂]HSO₄, and [MX₂(${}^{15}N^{15}NH_2$)(PMe₂Ph)₃] (X = Cl, l, or HSO₄). Nitrogen-15 n.m.r. spectroscopy is used to demonstrate the formation of hydrazido(2⁻)-complexes by the reaction of *trans*-[M(${}^{15}N_2$)₂-(dppe)₂] and [M(${}^{15}N_2$)₂(dppe)(depe)] (depe = Et₂PCH₂CH₂PEt₂) with HBr, and to monitor the reaction of [Mol₂(${}^{15}N^{15}NH_2$)(PMe₂Ph)₃] with HI in thf to give ${}^{15}NH_3$. Chemical shift data are also reported for the imido-complex cations [MoX(${}^{15}NR$)(dppe)]⁺ (X = Cl, Br, or OMe; R = H or Me) and the nitrido-complexes [Mo(${}^{15}N$)(S₂CNEt₂)₃], [MX(${}^{15}N$)(dppe)₂], [ReCl₂(${}^{15}N$)(PPrⁿPh₂)₂], [ReCl₂(${}^{15}N$)(PMe₂Ph)₃], and [ReCl(${}^{15}N$)(dppe)₂]Cl.

During our investigations of the activation of the dinitrogen molecule at metal sites,¹ we have shown that a reasonable mechanism for the reduction of dinitrogen to ammonia at such a site (particularly tungsten or molybdenum) is as shown in the Scheme.

We have discussed the relevance of such mechanisms to the action of nitrogenase and the potential use of ¹⁵N n.m.r. spectroscopy to observe intermediates, as in the Scheme, in the functioning enzyme.^{2,3} In this paper we describe the chemical shifts of a range of complexes of the particularly stable hydrazido(2–)-stage of reduction and for a number of imido- and nitrido-complexes which are components of the Scheme. We also show examples of the use of ¹⁵N n.m.r. spectroscopy in monitoring reactions of the dinitrogen and hydrazido(2–)-ligands, and in the structural assignment of an imido-complex.

Results and Discussion

Hydrazido(2-)-ligand Chemical Shifts and Coupling Constants.—The n.m.r. and related data in Table 1 greatly extend the information already published,⁴ and allow better comparisons due to the use of standard conditions [such as the use of NN-dimethylformamide (dmf) solvent, as far as possible] and susceptibility corrections (see Experimental section).

In the hydrazido(2–)-ligand $M=N_x-N_\beta H_2$ the singly bonded, protonated nitrogen (N_p) is more highly shielded than the nitrogen (N_x) doubly bonded to the metal, as expected. The ranges of δ ⁽¹⁵N) are, for N_p, -226 (±12) p.p.m. in the Mo and -241 (±12) in the corresponding W complexes, and for N_x, -68 (±10) in the Mo and -88 (±10) in the corresponding W complexes. The higher shielding, by *ca.* 14 p.p.m., in the tungsten complexes compared to corresponding complexes of molybdenum is remarkably constant for the range of ligands N₂, N₂R, N₂H₂, and N₂HR, both for N_x and N_p. As illustrated in the Figure, there is a linear correlation with unit slope of the nitrogen shifts in the tungsten and molybdenum complexes, given by equation (1), with a correlation co-

$$\delta(^{15}N)$$
 (W complex) $-14 = \delta(^{15}N)$ (Mo complex) (1)

efficient of 0.996. We notice that the ¹⁵N shifts in mononitrosyl $[M(\eta^5-C_5H_5)(CO)_2(NO)]$ and dinitrosyl $[M(\eta^5-C_5H_5)Cl(NO)_2]$ 'piano-stool' complexes of molybdenum and







Figure. Graph of $\delta(^{15}N)$ in a molybdenum complex versus $\delta(^{15}N)$ for corresponding tungsten complex of the types $ML^{-15}N_2$, $ML^{-}N_2R,\ ML^{-}N_2H_2$, and $ML^{-}N_2HR$ (ML = metal + co-ligands): $^{15}N_x$ denoted by + and $^{15}N_\beta$ by O

tungsten are similarly related.⁵ The imido-complexes [MBr- $(^{15}NH)(dppe)_2$]⁺ (dppe = Ph₂PCH₂CH₂PPh₂) (Table 2) diverge slightly from this relationship.

In the hydrazido(2–)-complexes, as in diazenidocomplexes,⁶ the N_{β} resonance shows a nuclear Overhauser effect (n.O.e.) with proton decoupling. Table 1. Nitrogen-15 n.m.r. data for hydrazido(2-)-complexes a

	$\delta(^{15}N_{\alpha}^{corr.})/$	$\delta(^{15}N_{\beta}{}^{corr.})/$	¹ J(¹⁵ N ¹⁵ N)/	¹ J(¹⁵ N _β H)/	/			
Complex	p.p.m.	p.p.m.	Hz	Hz	$J_{\rm other}/{\rm Hz}$	Solvent	Temp./K	Ref.
trans-[MoF(¹⁵ N ₂ H ₂)(dppe) ₂]BF ₄	- 79.9	- 240.5	10.8	86	${}^{2}J(NP) = 6$ ${}^{2}J(FN) = 77,$ ${}^{3}J(FN) = 12.9$	CH₂Cl₂	298 291	4 t.w.
	75.7 °	-233.3	n.r.	87	<u> </u>	dmf	291	t.w.
trans-[MoBr(¹⁵ N ₂ H ₂)(dppe) ₂]Br	-75.1	-231.5	10	86		dmf	295	t.w.
trans- $[MoI(^{15}N_2H_2)(dppe)_2]I$	- 76.4	-233.7	10	89	_	dmf	295	t.w.
$trans-[Mo(HSO_4)(^{15}N_2H_2)(dppe)_2]HSO_4$	-45.2	-215.3	12	83	_	dmf	205	+ 117
	- 54.1	-224.6		05		unn	295	1
	- 55.8	-229.0	11	92		MeOH	291	t.w.
	- 55.9	- 229.8	9	89		MeOH	270	
trans-[MOBr{ $^{10}N_2H(Me)$ }(dppe) ₂]Br	- 69.2	-227.7	~ 10	92		dmf	293	t.w.
trans-[MOBT{"N2H(Et)}(dppe)2]Br	- /1.8	-215.3	n.r.	95		dmf	297	t.w.
	n.o.	-209.6	~11			thf	298	
trans- $[MoBr{^{15}N^{15}N(CH_2)_3CH_2}(dppe)_3]Br$	- 64.3	-208.8	12			CH.Cl.	208	t w
$[MoCl_2(^{15}N_2H_2)(PMe_2Ph)_3]$	-67.9	-236.2	n.r.	80	_	dmf	295	t w
$[MoI_2(^{15}N_2H_2)(PMe_2Ph)_3]$	n.o.	-221.3	9	n.r.		dmf	298	tw
	- 68.8	-244.9	_		_	thf	298	•••••
$[Mo(HSO_4)_2(^{15}N_2H_2)(PMe_2Ph)_3]$	- 55.2	-233.1				thf	245	11
$[Mo(quin)(^{15}N_2H_2)(PMe_2Ph)_3]Cl^{c}$	- 60.9	-217.4	10			CH ₂ Cl ₂	298	4
$[MoCl(^{15}N_2H_2)(NC_5H_5)(PMe_2Ph)_3]Cl$	- 69.4	-223.6	9.8	83		CH ₂ Cl ₂	298	4
trans- $[WF(^{15}N_2H_2)(dppe)_2]BF_4$	- 98.0	-251.7		_	$\frac{ ^{1}J(NN) + ^{2}J(FN) }{= 62}$	CH ₂ Cl ₂	298	4
	-95.6	-247.5	12	83	$ ^{1}J(NN) + {}^{2}J(FN) $	dmf	298	t.w.
trans-[WC](¹⁵ N ₂ H ₂)(dppe) ₂]C]	- 96.2	-245.0	12	89	- 00	dmf	291	t w
$trans-[WBr(^{15}N_2H_2)(dppe)_2]Br$	-96.5	-246.1	10	87		dmf	270	t w
$trans-[WI(^{15}N_2H_2)(dppe)_2]I$	-97.8	-248.3	10	89	_	dmf	291	t.w.
trans-[W(HSO ₄)($^{15}N_2H_2$)(dppe) ₂]HSO ₄	- 80.2	-242.3	10	88		dmf	293	t.w.
trans-[W(NCPr ⁿ)($^{15}N_2H_2$)(dppe) ₂][HSO ₄] ₂	-63.2	- 229.8	10	n.o. ª		MeOH	291	t.w.
trans-[WBr{ ¹⁵ N ₂ H(Me)}(dppe) ₂]Br	- 88.7	-243.4	~10	95		dmf	295	t.w.
trans-[WBr{ ¹⁵ N ₂ H(Et)}(dppe) ₂]Br	- 92.6	-230.2	~10			thf	298 °	t.w.
	-90.1	-228.8	~10	92	$^{2}J(N_{\alpha}P) = 5$	dmf	293	t.w.
trans-[WBr{ $^{15}N^{15}N(CH_2)_3CH_2$ }(dppe) ₂]Br	- 81.1	-222.3	~10		${}^{2}J(NP) = 5,$ ${}^{1}J(WP) = 122^{g}$	thf	298 ^s	t.w.
$[WCl_2(^{15}N_2H_2)(PMe_2Ph)_3]$	- 86.2	- 249.5	9	80		dmf	295	t.w.
$[WI_2(^{15}N_2H_2)(PMe_2Ph)_3]$	- 87.4	-243.1	10	86	_	dmf	295	t.w.
$[W(HSO_4)_2(^{15}N_2H_2)(PMe_2Ph)_3]$	- 74.8	-239.6				4 L £	245	
	- 83.9	-251.4∫				un	243	11
$[W(quin)(^{15}N_2H_2)(PMe_2Ph)_3]Cl^{c}$	- 78.7	-238.2	9		${}^{1}J(NW) = 114.0$	CH_2Cl_2	298	4
$[WCl(^{15}N_2H_2)(NC_5H_5)(PMe_2Ph)_3]Cl$	- 87.2	-237.2	10.5	83	${}^{1}J(NW) = 124.5,$ ${}^{2}J(NP) = 5$	CH ₂ Cl ₂	298	4

^{*a*} δ (¹⁵N) (corrected in usual way) relative to nitromethane measured at 18.24 MHz, t.w. = this work, n.o. = not observed, n.r. = not resolved, $|J_{NN}| \leq 12$ Hz. ^{*b*} Signal broad due to unresolved coupling to ¹⁹F. ^{*c*} quin = quinolin-8-olate. ^{*d*} Not observed probably due to exchange with solvent protons. ^{*e*} At 9.04 MHz. ^{*f*} At 36.5 MHz. ^{*e*} From ³¹P n.m.r. spectrum.

The ¹⁵N n.m.r. parameters show clearly that the $-NH_2$ group in the hydrazido(2–)-ligand, which is nearly planar,^{1,4} resembles an imido $-NH_2$ group, which is flat, rather than the pyramidal $-NH_2$ group in hydrazine with a lone pair on nitrogen. Thus N_β in the hydrazido(2–)-ligand is deshielded (relative to hydrazine nitrogen) by $\pi \leftrightarrow \sigma$ circulations, which are of lower energy than the $n(\sigma) \rightarrow \sigma^*$ circulations in hydrazines. Similarly, the $|{}^{1}J({}^{15}N_{B}H)|$ values of 80–95 Hz are closer to those of comparable planar groups (*e.g.* 91.3 Hz in formamide) than to those in hydrazines (*e.g.* 68 Hz for PhNHNH₂). Further, the magnitude of the $|{}^{1}J({}^{15}N{}^{15}N)|$ coupling constants, 10 (±2) Hz, agree with values predicted by Schulman *et al.*⁷ for planar NH₂ groups, as opposed to values *ca.* 3 Hz lower for pyramidal $-NH_2$.

It is interesting that the N_x and N_β shifts vary in the same manner with respect to changes in the *trans* ligand X in the series $[MX(NNH_2)(dppe)_2]^+$. This difference from β - and γ substituent effects in organic compounds $(X^-C_x^-C_\beta^-C_\gamma)$ is no doubt related to the differences in geometry, to which γ effects are very sensitive. The N_x and N_β shielding varies rather little for X = halide, with perhaps a slight deshielding down the group of the halogen. There is stronger deshielding for X = HSO_4^- , which has been suggested to induce a movement of electronic charge towards the *trans*-NNH₂ ligand which is then more susceptible to protonation than with less basic *trans* ligands.^{1,8} Further deshielding occurs for X = NCPrⁿ. This evidence suggests a *trans*-influence series, the N_x and N_p shielding decreasing in the sequence $I^- \ge Br^- \ge CI^- \ge F^- > HSO_4^- > N \equiv CPr^n$. Some comparable results have been reported for the ¹⁵NH₃ shifts in the *d*⁶ complexes [CoX-(¹⁵NH₃)s]ⁿ⁺ (*n* = 2 or 3).⁹

An anomaly is seen in the spectra of the hydrogensulphate complexes in that in dmf or tetrahydrofuran (thf) solution, two sets of NNH_2 resonances are sometimes observed, whereas only one set is seen in methanol (Table 1). This may be due to isomerisation of the hydrogensulphate between monodentate and bidentate forms or some other state of coordination, since variation is often observed in the S-O region of the i.r. spectra of different perparations of these complexes.

With alkylation of N_{β} in the hydrazido(2-)-group, both N_{α}

Table 2	. Nitro	gen-15 n.m.	r. data for	nitrido- and	imido-comple	exes
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Complex	Solvent	$\delta(^{15}N \text{ corr})/p.p.m.$	¹ J(¹⁵ NH)/Hz	Ref.
[Ta(¹⁵ NPh)(thf) ₂ Cl ₃]	thf	-12.9 °		Ь
[Ta(¹⁵ NPh)(PEt ₃) ₂ Cl ₃]	thf	- 28.9 ª		Ь
[Ta(¹⁵ NPh)(dmpe) ₂ Cl] ^c	C ₆ H ₅ Cl	- 78.9 ª		Ь
[Ta(¹⁵ NPh)(PMe ₁),C[]	thf	- 77.9 °		Ь
$[Mo(^{15}N)(S_2CNEt_2)_3]$	CH ₂ Cl ₂	+ 40.0		2
$trans-[MoC](^{15}N)(dppe)_{2}]$	thf	+ 166.8		t.w.
trans-[MoBr(¹⁵ N)(dppe) ₂]	thf	+ 190.6		t.w.
trans-[MoCl(¹⁵ NH)(dppe) ₂]Cl	CH ₂ Cl ₂	+ 33.3	72	t.w.
trans-[MoBr(¹⁵ NH)(dppe) ₂]Br	thf	+ 10.6	72	t.w.
trans-[Mo(OMe)(¹⁵ NH)(dppe) ₂]BPh ₄ ^d	CH ₂ Cl ₂	- 58.6		t.w.
trans-[MoCl(15NMe)(dppe),]]	CH ₂ Cl ₂	-24.4	75	t.w.
trans-[WBr(¹⁵ NH)(dope),]Br	CH ₂ Cl ₂	-25.2	75	t.w.
trans-[WF ₄ (NMe)(NCMe)]	MeCN	+ 18.8 °		15
trans-[WF.(NMe){MeC(O)(OEt)}]	MeC(O)(OEt)	+ 9.8 °		15
trans-[WF4(NMe){OS(OMe)}]	OS(OMe) ₂	+ 10.1 °		15
$[\operatorname{ReCl}_{2}(^{15}N)(\operatorname{PPr}^{n}\operatorname{Ph}_{2})_{2}]$	CH ₂ Cl ₂	+ 85.8		2
$[\operatorname{ReCl}_{2}(^{15}\mathrm{N})(\operatorname{PMe}_{2}\mathrm{Ph})_{3}]$	CH ₂ Cl ₂	+68.2		2
$[ReCl(^{15}N)(dppe)_2]Cl$	CH ₂ Cl ₂	+ 67.1		2

^a Shifts originally given to liquid NH₃, correction to nitromethane scale = $-381.9 \text{ p.p.m.}^{10}$ b S. M. Rocklage and R. R. Schrock, J. Am. Chem. Soc., 1982, 104, 3077. ^c dmpe = Me₂PCH₂CH₂PMe₂. ^d ²J(¹⁵N³¹P) = 6 Hz. ^e ¹⁴N double-resonance measurement relative to NO₃⁻, conversion factor to nitromethane scale assumed to be -6 p.p.m.

and N_β are deshielded in the sequence NNH₂ > NNHR > NNR₂, where R is Me or Et. This resembles the deshielding by α - or β-alkyl substituents as observed in ¹³C or ¹⁵N resonances in organic molecules, *e.g. ca.* 10 p.p.m. for a β-alkyl substituent.¹⁰

We have also used ¹⁵N n.m.r. spectroscopy to monitor two classes of reaction involving hydrazido(2-)-complexes, in order to search for transient intermediates. In the first, we treated trans- $[Mo(^{15}N_2)_2(dppe)_2]$ or trans- $[Mo(^{15}N_2)_2(dppe)_2]$ (depe)] $(depe = Et_2PCH_2CH_2PEt_2)$ with HBr in thf and observed the nitrogen-containing species produced. The technique used was as described elsewhere for similar reactions of $cis-[M(N_2)_2(PMe_2Ph)_4]^{11}$ (see Experimental section). For trans- $[Mo(^{15}N_2)_2(dppe)_2]$ only the hydrazido(2-)-product $[\delta(N_x) - 72.5, \delta(N_\beta) - 226.2 \text{ p.p.m}, {}^1J(^{15}N^{15}N) = 9 \text{ Hz}]$ and free ¹⁵N₂ were observed (see Experimental section). For the 'mixed-diphosphine' complex [Mo(15N2)2(dppe)(depe)], however, in addition to free ${}^{15}N_2$ and the hydrazido(2-)-product $[\delta(^{15}N_x) - 69.7, \delta(^{15}N_\beta) - 224.1 \text{ p.p.m., } {}^1J(^{15}N^{15}N) \sim 10 \text{ Hz}],$ a smaller doublet (J \sim 10 Hz) at -210.6 p.p.m. was observed after ca. 1 min reaction time, which subsequently disappeared when the solution was left to stand for a further 2 h. This observation is consistent with the formation of a diazenidotype intermediate 6 which was subsequently completely converted to the hydrazido(2-)-product. No ammonia or hydrazine is formed in these reactions.

In the second application, we monitored the reaction of $[MoI_2(^{15}NH_2)(PMe_2Ph)_3]^{11}$ with HI in thf. This reaction follows the stoicheiometry shown in reaction (2). {The

$$[MoI_{2}(NNH_{2})(PMe_{2}Ph)_{3}] \xrightarrow{HI}_{thf}$$
$$NH_{3} + \frac{1}{2}N_{2} + [MoI_{3}(PMe_{2}Ph)_{3}] \quad (2)$$

 $[MoI_3(PMe_2Ph)_3]$ reacts further with the excess of HI to give other iodide complexes.) ¹²

Although we were unsuccessful in observing any intermediates between NNH_2 and the final products, a rate constant for the reaction was derived from the variation of signal intensities (1) with time, the N_{β} signal being used because of its high relative intensity due to favourable n.O.e. under the conditions of proton decoupling. A plot of log $I_{N_{\beta}}$ against time leads to a pseudo-first-order rate constant of $7 \times 10^{-5} \text{ s}^{-1}$, which is close to the values of $5(\pm 2) \times 10^{-5} \text{ s}^{-1}$ derived from N₂ evolution and NH₃ formation measurement.¹³ Further investigations of the kinetics of this and related reactions will be discussed elsewhere.

Imido- and Nitrido-complexes .--- Chemical shifts and coupling constants are given in Table 2, together with the (rather few) literature values for comparison. It is interesting that the nitride shifts span a wide range, $\delta + 40$ to ± 190 for the molybdenum complexes alone. We should expect the shielding of a ligating atom as close to the metal as triply bonded nitrogen to be particularly sensitive to changes in the coordination sphere of the metal. Thus the large increase in nitrogen shielding from trans-[MoX(15N)(dppe)2] to [Mo- $(^{15}N)(S_2CNEt_2)_3$] runs parallel to the increase in metal shielding that is commonly observed 14 with increase in coordination number. The range of $\delta(^{15}N)$ for the imidocomplexes is ca. 110 p.p.m. There is a large upfield shift on protonation of a nitride, e.g. ~180 p.p.m. from trans- $[MoBr(^{15}N)(dppe)_2]$ to trans- $[MoBr(^{15}NH)(dppe)_2]^+$, or on alkylation, e.g. 190 p.p.m. from trans-[MoCl(¹⁵N)(dppe)₂] to trans-[MoCl(¹⁵NMe)(dppe)₂]⁺. These may be compared with the upfield shift of 127 p.p.m. observed on the protonation of N_{α} in the 'doubly bent' diazenido group in $[RhCl_2(^{15}NNC_6-$ H₄NO₂-4)(PPh₃)₂].⁶ Upfield shifts on protonation of π bonded nitrogen may be explained in terms of the removal of the low-energy $n(N) \rightarrow \pi^*$ circulation, as the lone-pair electrons are stabilised by bonding to hydrogen, and it is interesting to regard the nitride ligand in this way. There is an upfield shift of 300-400 p.p.m. from imido to ammine ligands.14

trans-Ligand influences on the ¹⁵N shifts were observed in the imido-complexes. In the series ¹⁵ trans-[MoX(NH)-(dppe)₂]⁺ the nitrogen shielding decreases in the sequence X = OMe > Br > Cl, compared to the series [WL(NMe)F₄] in which the order of L is MeC(O)(OEt) > OS(OMe)₂ > MeCN.¹⁶ Thus some regularities are beginning to emerge.

The ${}^{15}N$ n.m.r. spectrum of *trans*-[Mo(OMe)(${}^{15}NH$)-(dppe)₂]BPh₄ has also resolved a problem of assignment

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of structure for this complex. Observation of a doublet $[|^{1}J(^{15}NH)| = 68.5 \text{ Hz}]$ for this compound unequivocally confirms that in solution the location of the proton is at the nitrogen atom, a fact not clear from other physical measurements.¹⁵ The $|^{1}J(^{15}NH)|$ values (*ca*. 70 Hz) of the imidocomplexes are intermediate between those observed in diazenido-complexes (*ca*. 65 Hz)⁵ and those of hydrazido(2-)-complexes noted above.

Conclusions

The regions of ¹⁵N chemical shifts for the ligands NNH₂, NH, and N are defined and the technique can be successfully used to probe reaction solutions for these and related ligands as reaction intermediates and to derive kinetic data for their degradation. Some *trans*-influence series of ligands are apparent, which correlate to some extent with the known properties of given series of complexes but perhaps not between series for different metals.

Experimental

The complexes were prepared by published methods $^{1.5,15,17,18}$ and were generally 95% 15 N enriched. Solvents were dried and degassed before use by standard techniques. 15 N-Labelled chemicals were used as purchased from Prochem Ltd.

Solutions for n.m.r. spectroscopy were made up under purified argon, concentrations being typically about 10⁻² mol dm⁻³. Nitrogen-15 n.m.r. spectra were recorded on a JEOL FX90Q spectrometer with 10-mm tubes, or a Bruker WH180 spectrometer (at P.C.M.U., Harwell) with 25-mm tubes. In each case the reference standard in a coaxial tube was CD₃NO₂ containing $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) as relaxation agent. Different susceptibility corrections were necessary for the different instruments since the field of the superconducting magnet is parallel to the sample tube; 10 the correction to $\delta_{obs.}$ is $-\Delta\chi/6$ or -1.7 p.p.m. for the electromagnet (JEOL FX90Q), and $+\Delta\chi/3$ or 3.4 p.p.m. for the super-conducting magnet (Bruker WH180), where $\Delta \chi =$ $\chi_{reference} - \chi_{sample}$, and χ is the magnetic susceptibility. A further correction was made for the deuterium isotope effect as CH₃NO₂ resonates 0.1 p.p.m. upfield of CD₃NO₂.

Reaction of $[Mo(^{15}N_2)_2(dppe)_2]$ or $[Mo(^{15}N_2)_2(dppe)(depe)]$ with HBr.—In an attempt to detect transient intermediates in the reaction, concentrated HBr (10 molar excess) was added to a thf solution of the dinitrogen complex in the n.m.r. tube (25 mm) at -5 °C. The ¹⁵N spectral accumulation at 18.25 MHz was commenced about 1 min later at -30 °C. After a suitable period of accumulation (*ca.* 2 h, acquisition time 0.333 s, pulse angle 30°) the reaction solution was allowed to warm to room temperature, then recooled and accumulation recommenced after an appropriate time.

Reaction of $[MoI_2(^{15}N^{15}NH_2)(PMe_2Ph)_3]$ with HI.—Fresh, colourless concentrated HI (0.2 cm³) was added to $[MoI_2-(^{15}N^{15}NH_2)(PMe_2Ph)_3]$ (0.1 g, 1.26×10^{-4} mol) in thf in the

n.m.r. tube (25 mm) at 245 K. Spectra (with proton decoupling) were accumulated at intervals of 30 min.

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