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

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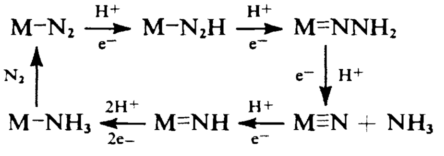
Nitrogen-15 chemical shifts and coupling constants are reported for the range of hydrazido(2−)-complexes $[MX(^{15}N^{15}NR^1R^2)(dppe)_2]^+$ {X = Cl, Br, I, or HSO_4; M = Mo or W; R^1 = H, R^2 = H, Me, or Et [and $^{15}N_2R^1R^2 = {}^{15}N^{15}\overline{N(CH_2)_3C}H_2$]; dppe = $Ph_2PCH_2CH_2PPh_2$}, $[W(NCPr^n)(^{15}N^{15}NH_2)(dppe)_2]HSO_4$, and $[MX_2(^{15}N^{15}NH_2)(PMe_2Ph)_3]$ (X = Cl, I, or HSO_4). 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 = $Et_2PCH_2CH_2PEt_2$) with HBr, and to monitor the reaction of $[MoI_2(^{15}N^{15}NH_2)(PMe_2Ph)_3]$ 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 $[Mo(^{15}N)(S_2CNEt_2)_3]$, $[MX(^{15}N)(dppe)_2]$, $[ReCl_2(^{15}N)(PPr^nPh_2)_2]$, $[ReCl_2(^{15}N)(PMe_2Ph)_3]$, 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 ^{15}N 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 ^{15}N n.m.r. spectroscopy in monitoring reactions of the dinitrogen and hydrazido(2−)-ligands, and in the structural assignment of an imido-complex.



Scheme.

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 $M{=}N_\alpha{-}N_\beta H_2$ the singly bonded, protonated nitrogen (N_β) is more highly shielded than the nitrogen (N_α) doubly bonded to the metal, as expected. The ranges of $\delta(^{15}N)$ are, for N_β, -226 (± 12) p.p.m. in the Mo and -241 (± 12) in the corresponding W complexes, and for N_α, -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 N_2, N_2R, N_2H_2, and N_2HR, both for N_α and N_β. 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 coefficient of 0.996. We notice that the ^{15}N shifts in mononitrosyl $[M(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ and dinitrosyl $[M(\eta^5\text{-}C_5H_5)Cl(NO)_2]$ 'piano-stool' complexes of molybdenum and tungsten are similarly related.[5] The imido-complexes $[MBr(^{15}NH)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (Table 2) diverge slightly from this relationship.

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

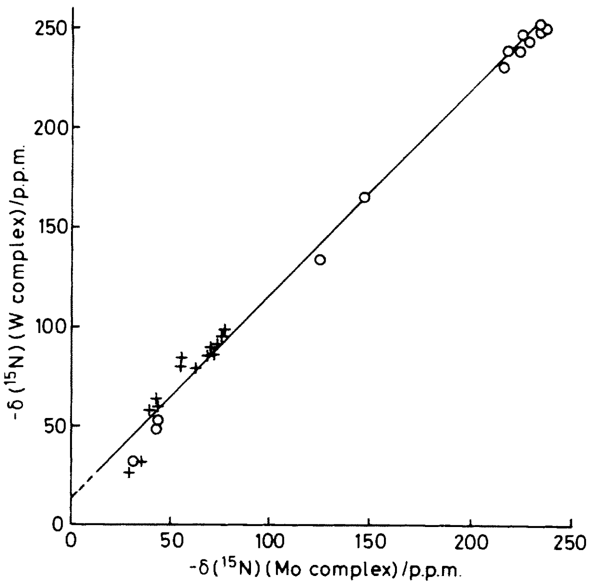


Figure. Graph of $\delta(^{15}N)$ in a molybdenum complex *versus* $\delta(^{15}N)$ for corresponding tungsten complex of the types $ML{-}^{15}N_2$, $ML{-}N_2R$, $ML{-}N_2H_2$, and $ML{-}N_2HR$ (ML = metal + co-ligands): $^{15}N_\alpha$ denoted by + and $^{15}N_\beta$ by ○

In the hydrazido(2−)-complexes, as in diazenido-complexes,[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]

Complex	$\delta(^{15}N_\alpha{}^{corr.})$/ p.p.m.	$\delta(^{15}N_\beta{}^{corr.})$/ p.p.m.	$^1J(^{15}N^{15}N)$/ Hz	$^1J(^{15}N_\beta H)$/ Hz	J_{other}/Hz	Solvent	Temp./K	Ref.
trans-$[MoF(^{15}N_2H_2)(dppe)_2]BF_4$	−79.9	−240.5	10.8	86	$^2J(NP) = 6$	CH_2Cl_2	298	4
					$^2J(FN) = 77$, $^3J(FN) = 12.9$		291	t.w.
	−75.7 [b]	−233.3	n.r.	87	—	dmf	291	t.w.
trans-$[MoBr(^{15}N_2H_2)(dppe)_2]Br$	−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 −54.1	−215.3 −224.6	12	83	—	dmf	295	t.w.
	−55.8	−229.0	11	92	—	MeOH	291	t.w.
	−55.9	−229.8	9	89	—	MeOH	270	
trans-$[MoBr\{^{15}N_2H(Me)\}(dppe)_2]Br$	−69.2	−227.7	~10	92	—	dmf	293	t.w.
trans-$[MoBr\{^{15}N_2H(Et)\}(dppe)_2]Br$	−71.8	−215.3	n.r.	95	—	dmf	297	t.w.
	n.o.	−209.6	~11	—	—	thf	298	
trans-$[MoBr\{^{15}N^{15}\overline{N(CH_2)_3CH_2}\}(dppe)_2]Br$	−64.3	−208.8	12	—	—	CH_2Cl_2	298	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	t.w.
	−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_2Cl_2	298	4
$[MoCl(^{15}N_2H_2)(NC_5H_5)(PMe_2Ph)_3]Cl$	−69.4	−223.6	9.8	83	—	CH_2Cl_2	298	4
trans-$[WF(^{15}N_2H_2)(dppe)_2]BF_4$	−98.0	−251.7		—	$\lvert{}^1J(NN) + {}^2J(FN)\rvert = 62$	CH_2Cl_2	298	4
	−95.6	−247.5	12	83	$\lvert{}^1J(NN) + {}^2J(FN)\rvert = 68$	dmf	298	t.w.
trans-$[WCl(^{15}N_2H_2)(dppe)_2]Cl$	−96.2	−245.0	12	89	—	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. [d]	—	MeOH	291	t.w.
trans-$[WBr\{^{15}N_2H(Me)\}(dppe)_2]Br$	−88.7	−243.4	~10	95	—	dmf	295	t.w.
trans-$[WBr\{^{15}N_2H(Et)\}(dppe)_2]Br$	−92.6	−230.2	~10	—		thf	298 [e]	t.w.
	−90.1	−228.8	~10	92	$^2J(N_\alpha P) = 5$	dmf	293	t.w.
trans-$[WBr\{^{15}N^{15}\overline{N(CH_2)_3CH_2}\}(dppe)_2]Br$	−81.1	−222.3	~10	—	$^2J(NP) = 5$, $^1J(WP) = 122$ [g]	thf	298 [f]	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 −83.9	−239.6 −251.4	—	—	—	thf	245	11
$[W(quin)(^{15}N_2H_2)(PMe_2Ph)_3]Cl$ [c]	−78.7	−238.2	9	—	$^1J(NW) = 114.0$	CH_2Cl_2	298	4
$[WCl(^{15}N_2H_2)(NC_5H_5)(PMe_2Ph)_3]Cl$	−87.2	−237.2	10.5	83	$^1J(NW) = 124.5$, $^2J(NP) = 5$	CH_2Cl_2	298	4

[a] $\delta(^{15}N)$ (corrected in usual way) relative to nitromethane measured at 18.24 MHz, t.w. = this work, n.o. = not observed, n.r. = not resolved, $|J_{NN}| \leqslant 12$ Hz. [b] Signal broad due to unresolved coupling to ^{19}F. [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. [g] From ^{31}P n.m.r. spectrum.

The ^{15}N 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 $\pi \longleftrightarrow \sigma$ circulations, which are of lower energy than the $n(\sigma)\rightarrow\sigma^*$ circulations in hydrazines. Similarly, the $|^1J(^{15}N_\beta H)|$ 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 $PhNHNH_2$). Further, the magnitude of the $|^1J(^{15}N^{15}N)|$ coupling constants, 10 (± 2) Hz, agree with values predicted by Schulman *et al.*[7] for planar NH_2 groups, as opposed to values *ca.* 3 Hz lower for pyramidal $-NH_2$.

It is interesting that the N_α 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 ($X-C_\alpha-C_\beta-C_\gamma$) is no doubt related to the differences in geometry, to which γ effects are very sensitive. The N_α 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*-NNH_2 ligand which is then more susceptible to protonation than with less basic *trans* ligands.[1,8] Further deshielding occurs for X = $NCPr^n$. This evidence suggests a *trans*-influence series, the N_α and N_β shielding decreasing in the sequence $I^- \geqslant Br^- \geqslant Cl^- \geqslant F^- > HSO_4^- > N{\equiv}CPr^n$. Some comparable results have been reported for the $^{15}NH_3$ shifts in the d^6 complexes $[CoX(^{15}NH_3)_5]^{n+}$ (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 co-ordination, 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. Nitrogen-15 n.m.r. data for nitrido- and imido-complexes

Complex	Solvent	$\delta(^{15}N^{\text{corr.}})$/p.p.m.	$^{1}J(^{15}NH)$/Hz	Ref.
$[Ta(^{15}NPh)(thf)_2Cl_3]$	thf	-12.9^{a}	—	*b*
$[Ta(^{15}NPh)(PEt_3)_2Cl_3]$	thf	-28.9^{a}	—	*b*
$[Ta(^{15}NPh)(dmpe)_2Cl]^{c}$	C_6H_5Cl	-78.9^{a}	—	*b*
$[Ta(^{15}NPh)(PMe_3)_4Cl]$	thf	-77.9^{a}	—	*b*
$[Mo(^{15}N)(S_2CNEt_2)_3]$	CH_2Cl_2	+40.0	—	2
trans-$[MoCl(^{15}N)(dppe)_2]$	thf	+166.8		t.w.
trans-$[MoBr(^{15}N)(dppe)_2]$	thf	+190.6		t.w.
trans-$[MoCl(^{15}NH)(dppe)_2]Cl$	CH_2Cl_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_2Cl_2	−58.6		t.w.
trans-$[MoCl(^{15}NMe)(dppe)_2]I$	CH_2Cl_2	−24.4	75	t.w.
trans-$[WBr(^{15}NH)(dppe)_2]Br$	CH_2Cl_2	−25.2	75	t.w.
trans-$[WF_4(NMe)(NCMe)]$	MeCN	$+18.8^{e}$	—	15
trans-$[WF_4(NMe)\{MeC(O)(OEt)\}]$	MeC(O)(OEt)	$+9.8^{e}$		15
trans-$[WF_4(NMe)\{OS(OMe)_2\}]$	$OS(OMe)_2$	$+10.1^{e}$		15
$[ReCl_2(^{15}N)(PPr^{n}Ph_2)_2]$	CH_2Cl_2	+85.8	—	2
$[ReCl_2(^{15}N)(PMe_2Ph)_3]$	CH_2Cl_2	+68.2	—	2
$[ReCl(^{15}N)(dppe)_2]Cl$	CH_2Cl_2	+67.1	—	2

[a] Shifts originally given to liquid NH_3, correction to nitromethane scale = −381.9 p.p.m.[10] [b] S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 3077. [c] dmpe = $Me_2PCH_2CH_2PMe_2$. [d] $^{2}J(^{15}N^{31}P)$ = 6 Hz. [e] ^{14}N double-resonance measurement relative to NO_3^-, conversion factor to nitromethane scale assumed to be −6 p.p.m.

and N_β are deshielded in the sequence $NNH_2 > NNHR > NNR_2$, where R is Me or Et. This resembles the deshielding by α- or β-alkyl substituents as observed in ^{13}C or ^{15}N resonances in organic molecules, *e.g. ca.* 10 p.p.m. for a β-alkyl substituent.[10]

We have also used ^{15}N 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*-$[Mo(^{15}N_2)_2(dppe)(depe)]$ (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 [$\delta(N_\alpha)$ − 72.5, $\delta(N_\beta)$ − 226.2 p.p.m, $^{1}J(^{15}N^{15}N)$ = 9 Hz] and free $^{15}N_2$ were observed (see Experimental section). For the 'mixed-diphosphine' complex $[Mo(^{15}N_2)_2(dppe)(depe)]$, however, in addition to free $^{15}N_2$ and the hydrazido(2−)-product [$\delta(^{15}N_\alpha)$ −69.7, $\delta(^{15}N_\beta)$ −224.1 p.p.m., $^{1}J(^{15}N^{15}N)$ ~10 Hz], a smaller doublet (J ~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 diazenido-type 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 $[MoI_2(^{15}N^{15}NH_2)(PMe_2Ph)_3]$[11] with HI in thf. This reaction follows the stoicheiometry shown in reaction (2). {The

$$[MoI_2(NNH_2)(PMe_2Ph)_3] \xrightarrow[\text{thf}]{\text{HI}} NH_3 + \tfrac{1}{2}N_2 + [MoI_3(PMe_2Ph)_3] \quad (2)$$

$[MoI_3(PMe_2Ph)_3]$ 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 (I) 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_β} against time leads to a pseudo-first-order rate constant of $7 \times 10^{-5}\ s^{-1}$, which is close to the values of $5(\pm 2) \times 10^{-5}\ s^{-1}$ derived from N_2 evolution and NH_3 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, δ + 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 co-ordination sphere of the metal. Thus the large increase in nitrogen shielding from *trans*-$[MoX(^{15}N)(dppe)_2]$ to $[Mo(^{15}N)(S_2CNEt_2)_3]$ runs parallel to the increase in metal shielding that is commonly observed[14] with increase in co-ordination number. The range of $\delta(^{15}N)$ for the imido-complexes 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*-$[MoCl(^{15}N)(dppe)_2]$ to *trans*-$[MoCl(^{15}NMe)(dppe)_2]^+$. 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 $[RhCl_2(^{15}NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$.[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 ^{15}N 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 $[WL(NMe)F_4]$ 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*-$[Mo(OMe)(^{15}NH)(dppe)_2]BPh_4$ has also resolved a problem of assignment of structure for this complex. Observation of a doublet $[|^1J(^{15}NH)| = 68.5$ 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 $|^1J(^{15}NH)|$ values (*ca.* 70 Hz) of the imido-complexes are intermediate between those observed in diazenido-complexes (*ca.* 65 Hz)[5] and those of hydrazido(2−)-complexes noted above.

Conclusions

The regions of ^{15}N chemical shifts for the ligands NNH_2, 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 CD_3NO_2 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 super-conducting 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 CH_3NO_2 resonates 0.1 p.p.m. upfield of CD_3NO_2.

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 ^{15}N 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 cm^3) 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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