

Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy of Dinitrogen-bridged complexes

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Dinitrogen-bridged complexes of *trans*-[ReCl(N₂)(PMe₂Ph)₄] with NbCl₅ and TaCl₅ (1 : 1 adducts) and ZrCl₄ (2 : 1 adduct) have been characterised and a corresponding complex of HfCl₄ observed in solution. Nitrogen-15 chemical shifts are compared for three types of dinitrogen bridge: complexes of Mo, W, Re, and Os with a main-group acceptor (AlMe₃), complexes of *trans*-[ReCl(N₂)(PMe₂Ph)₄] with a π acceptor (TiCl₄, ZrCl₄, HfCl₄, NbCl₅, or TaCl₅), and symmetrical transition-metal complexes, [{W(N₂)₂(PR₂Ph)₃]₂(μ -N₂)], [Ru(NH₃)₅]₂(μ -N₂)⁴⁺, etc. The variation in the shielding is related by simple molecular orbital arguments to the variation in electronic (charge-transfer) absorption, to the periodicities observed for mononuclear dinitrogen complexes, and to the activation of dinitrogen by co-ordination.

Complexes in which dinitrogen bridges two metals are of interest in several respects, both to nitrogen-fixation studies, and in their own right as delocalised systems.^{1,2} First, the formation of such complexes by co-ordination of a Lewis acid such as AlMe₃³ or TiCl₄^{4,5} to a terminal dinitrogen ligand is a measure of its activation to protonation and other reactions.⁶ Secondly, bridging dinitrogen can be reduced to N₂H₄ under mild conditions in complexes of early or mid-transition metals,⁷⁻¹⁰ and is thought by some workers to be involved in biological nitrogen fixation.¹¹ Thirdly, the versatility of dinitrogen-bridged systems has been shown by the work of Magnusson and Taube¹² and others on mixed-valence (*d*⁶, *d*⁵) complexes of Ru and Os, and of Chatt and others,^{4,5,13,14} and Bercaw,⁸ Schrock⁹ and co-workers with π -acceptor metals which allow push-pull^{4,8} electron delocalisation across the dinitrogen bridge, leading to activation of the dinitrogen towards protic attack in certain cases.

Dinitrogen bridges between two transition metals have so far been found to be effectively linear, but further possibilities arise with non-transition metals. An MNN angle of 159° has been demonstrated at magnesium in [(Me₃P)₃CoNNMg-(thf)₄NNCo(PMe₃)₃](thf = tetrahydrofuran),¹⁵ and the K⁺ ions in crystalline K[Co(N₂)(PMe₃)₃] are simultaneously end-on and edge-on to dinitrogen in (linear) CoNN.¹⁶

¹⁵N N.m.r. spectroscopy is particularly suited to the study of two-co-ordinate nitrogen. The chemical shift is very sensitive to the bond angle, because of strong deshielding associated with low energy $n_N \rightarrow \pi^*$ electronic circulations; thus it affords a criterion of geometry in diazenido and nitrosyl complexes. Depending on the metal and co-ligands, deshieldings up to 350 p.p.m. are observed for strong bending of MNNR,¹⁷ or up to 800 p.p.m. for strong bending of MNO.¹⁸ Even for linear MNNM systems the nitrogen shifts may vary considerably, as witness the 400 p.p.m. range that we now report, for different bond types. Some of the data were included in a preliminary publication.¹⁹

Results and Discussion

It is well established that the co-ordination of terminal or bridging dinitrogen to a π -donor (*e.g.* *d*⁶) metal lengthens the NN bond, and shortens the MN bond compared with the single-bond distance, consistent with $d_{\pi} \rightarrow \pi^*$ N₂ back bonding. Additional co-ordination of terminal N to a π -acceptor (*d*⁰, *d*², etc.) metal further lengthens the NN bond. Table 1 therefore includes NN bond distances (if known) and

stretching frequencies relevant to discussion of the ¹⁵N shifts. Values are included also for NN bonds often taken as standard, the single bond in hydrazine, the double bond in azoethane, and the triple bond in dinitrogen. These, however, are indicative only, since the single and double bonds are lengthened by repulsion of the lone pairs on nitrogen which are not present in the metal complexes, moreover there may be a degree of antibonding in the N₂ system, and the stretching frequencies in metal complexes may be affected by coupling with co-ligand vibrations. Data for appropriate mononuclear N₂ complexes^{20,21} are included for comparison.

Adducts of Trimethylaluminium.—The shifts for ligating (N_α) and non-ligating nitrogen (N_β) in N₂ complexes of Mo⁰, W⁰, Re¹, and Os¹¹ on co-ordination of AlMe₃ are given in Table 1. The N_β line is somewhat broadened by proximity to the ²⁷Al quadrupole. Attachment of AlMe₃ decreases the $\nu(N_2)$ frequency by 30–100 cm⁻¹, but increases the N_β shielding, in contrast to the deshielding often observed with transition-metal acceptors. The increase is negligible for the molybdenum complexes, but becomes progressively greater for the complexes of W (27), Re (66), and Os (70 p.p.m.).

The molybdenum compounds are exceptional, in that for the adducts the ¹⁵N_α and ¹⁵N_β resonances could not be resolved. They are near-coincident in the spectra of the parent complexes; there seems to be a cross-over point of these resonances in the periodic scheme of metal–dinitrogen shifts.²¹ It is interesting that the N_β shifts on co-ordination to AlMe₃ follow the normal periodicity, as in the co-ordination of N₂ in the parent compound. The N_α shielding in the parent complexes tends to increase down the Group of the metal (with increased ligand-field splitting, and nephelauxetic effect), and across the transition series.²¹ The energy of the M→L charge-transfer band^{22,23} increases in parallel, as stronger M–N₂ bonding destabilises the unoccupied π^* N₂ orbital relative to the (non-bonding) *d*_{xy}. Thus the deshielding, which depends on the accessibility of magnetic-dipole allowed ($\pi \leftrightarrow \sigma$) excited states,²⁴ correlates with electric-dipole-allowed ($\pi \rightarrow \pi$) excitation energies, which are more readily observable in the optical spectrum.

The N_β shifts on co-ordination to AlMe₃, which has no accessible π -acceptor orbitals, are related to those observed on protonation or alkylation of pyridine, or other nitrogen atoms in a delocalised system.²⁴ Removal of low-energy $n_N \rightarrow \pi^*$ circulations by stabilisation of the $n(\sigma)$ electrons increases the nitrogen shielding in pyridine by over 100 p.p.m.,

Table 1. Dinitrogen-bridged complexes and related molecules

Compound	Colour	Solvent	$\delta(^{15}\text{N}_\alpha)^a/$ p.p.m.	$\delta(^{15}\text{N}_\beta)^a/$ p.p.m.	$\nu(\text{N}_2)^b/\text{cm}^{-1}$	$d(\text{NN})/\text{\AA}$	Ref.
<i>trans</i> -[Mo($^{15}\text{N}_2$) ₂ (dppe) ₂]	Orange	Toluene	—45.1	—	1 979 ^c	1.118	6
<i>trans</i> -[Mo($^{15}\text{N}_2$ AlMe ₃)($^{15}\text{N}_2$)(dppe) ₂]	Dark red	Toluene	—45.4	—	1 883 ^c	—	t.w.
<i>trans</i> -[Mo($^{15}\text{N}_2$) ₂ (depe) ₂] ^d	Orange	Toluene	—43.8	—46.1	—	—	21, t.w.
<i>trans</i> -[Mo($^{15}\text{N}_2$ AlMe ₃)($^{15}\text{N}_2$)(depe) ₂] ^d	Red	Toluene	—	—45.6	—	—	t.w.
<i>trans</i> -[W($^{15}\text{N}_2$) ₂ (dppe) ₂]	Orange	Toluene	—66.6	—55.5	1 948, 2 015w	—	20,21
<i>trans</i> -[W($^{15}\text{N}_2$ AlMe ₃)($^{15}\text{N}_2$)(dppe) ₂]	Black	Toluene	—64.3	—82.2	1 869, 2 059w	—	t.w.
<i>trans</i> -[ReCl($^{15}\text{N}_2$)(PMe ₂ Ph) ₄]	Yellow	Toluene	—87.2	—63.9	1 923	1.06	19,21
<i>trans</i> -[ReCl($^{15}\text{N}_2$ AlMe ₃)(PMe ₂ Ph) ₄]	Yellow	Toluene	—85.4	—129.8	1 894	—	t.w.
<i>trans</i> -[ReCl($^{15}\text{N}_2$)(dppe) ₂]	Yellow	CH ₂ Cl ₂	—92.3	n.o.	1 967 ^e	—	19,21
<i>trans</i> -[ReCl($^{15}\text{N}_2$ AlMe ₃)(dppe) ₂]	Yellow	Toluene	—88.0	—127.3	1 858	—	t.w.
<i>mer</i> -[OsCl ₂ ($^{15}\text{N}_2$)(PMe ₂ Ph) ₃]	Colourless	Toluene	—120.3	—66.8	2 079	1.112 ^f	19,21
<i>mer</i> -[OsCl ₂ ($^{15}\text{N}_2$ AlMe ₃)(PMe ₂ Ph) ₃]	Colourless	Toluene	—100.6	—136.2	1 979	—	t.w.
[(thf)Cl ₂ Ti($^{15}\text{N}_2$)ReCl(PMe ₂ Ph) ₄]	Deep red	CH ₂ Cl ₂	—68.1 (br)	—19 (vbr)	1 740	—	t.w.
[Cl ₃ Nb($^{15}\text{N}_2$)ReCl(PMe ₂ Ph) ₄]	Green	CH ₂ Cl ₂	—74.3	—8.7 (br)	1 630	—	t.w.
[Cl ₃ Ta($^{15}\text{N}_2$)ReCl(PMe ₂ Ph) ₄]	Brown	CH ₂ Cl ₂	—76.7	—24.2 (br)	1 695	—	t.w.
[TiCl ₄ {($^{15}\text{N}_2$)ReCl(PMe ₂ Ph) ₄ }] ₂	Deep blue	CH ₂ Cl ₂	—76.7	—53.2	1 812	—	t.w.
[ZrCl ₄ {($^{15}\text{N}_2$)ReCl(PMe ₂ Ph) ₄ }] ₂	Deep red	CH ₂ Cl ₂	—75.9	—95.0	1 825	—	t.w.
[HfCl ₄ {($^{15}\text{N}_2$)ReCl(PMe ₂ Ph) ₄ }] ₂ ^g	Red	CH ₂ Cl ₂	—75.4	—96.8	1 824	—	t.w.
[(Ti(C ₅ Me ₅) ₂ (N ₂)) ₂ (μ- $^{15}\text{N}_2$)]	Purple-blue	Toluene	—	+299 ^h	—	—	8
[(Zr(C ₅ Me ₅) ₂ (N ₂)) ₂ (μ- $^{15}\text{N}_2$)]	Purple-red	Toluene	—	+179 ⁱ	—	1.182 (μ-N ₂), 1.116, 1.114	8
[(Ta(CHCMe ₃)(PMe ₃) ₂ Cl) ₂ (μ- $^{15}\text{N}_2$)]	Yellow	thf	+34 ^j	—	847	1.298 ^k	9
[(TaCl(C ₂ H ₄)(PMe ₃) ₃) ₂ (μ- $^{15}\text{N}_2$)]	Orange	thf	—6 ^j	—	824	—	9
[(W(N ₂) ₂ (PEt ₂ Ph) ₃) ₂ (μ- $^{15}\text{N}_2$)]	Red	thf	—21.3	—	—	—	10
[(W(N ₂) ₂ (PPr ⁿ Ph) ₃) ₂ (μ- $^{15}\text{N}_2$)]	Red	thf	—25.9	—	—	—	10
[(Ru(NH ₃) ₃) ₂ (μ- $^{15}\text{N}_2$)] ⁺	Pale yellow	Water	+209.1	—	2 100	1.12	t.w., 2
N≡N	—	Gas	—75.3	—	2 330	1.095	20
EtN=NEt	—	Liquid	+146	—	1 576	1.23	20
N ₂ H ₄	—	Liquid	—334.8	—	1 098 (i.r.), 1 076 (Raman)	1.45	—
PhCH=N=N=CHPh	—	CDCl ₃	—19.4	—	—	—	1

w = Weak, br = broad, v = very, t.w. = this work, and n.o. = not observed.

^a N_α = Atom adjacent to metal of starting complexes and their adducts, N_β = distal nitrogen. ^b Nujol mulls unless otherwise stated. ^c Benzene solution. ^d depe = Et₂P(CH₂)₂PEt₂. ^e Chloroform solution. ^f $d(\text{NN})$ for *mer*-[OsCl(SC₆F₅)(N₂)(PMe₂Ph)₃] (D. Cruz-Garriz, J. Leal, R. L. Richards, and H. Torrens, *Transition Met. Chem.*, 1983, **8**, 127). ^g Not isolated, see text. ^h Referenced originally to [NEt₄]Cl. ⁱ Referenced originally to 1 mol dm⁻³ HNO₃. ^j Referenced originally to NH₃ (l). ^k $d(\text{NN})$ for [(Ta(CH₂CMe₃)(CHCMe₃)(PMe₃)₂(μ-N₂))]. ⁹ G. P. Journard and G. J. Martin, *Org. Magn. Reson.*, 1979, **12**, 263.

and there are large increases also on protonation of N_β in ligating dinitrogen to form the hydrazido(2-)-ligand.²⁵

This removal of $n_N \rightarrow \pi^*$ circulations (increase in N_β shielding) on co-ordination of AlMe₃ might be expected to correlate with increase in basicity of the N₂ complex, and decreased $\nu(\text{N}_2)$, with increased back bonding.³ (No crystal structures have been determined for these binuclear compounds.) This correlation is observed for [ReCl(N₂)(PMe₂Ph)₄], which was found to be more basic than the complexes of Mo and W, but not for [OsCl₂(N₂)(PMe₂Ph)₃], which has a high $\nu(\text{N}_2)$ and low basicity towards AlMe₃,³ but the largest upfield shift of N_β on adduct formation.

The increase in N_β shielding on co-ordination of AlMe₃ is consistent with the shifts of the electronic absorption to lower energies, the molybdenum complexes changing from orange to red and the tungsten complex from orange to black. Formation of the adduct stabilises the σ - and π -nitrogen orbital manifolds (the σ effects being the greater), lowering the lowest unoccupied molecular orbital (l.u.m.o.) for M→L charge-transfer ($d_{xy} \rightarrow \pi^*$ N₂) excitations and reducing the interaction with the metal. Thus the ligating nitrogen (N_α) is slightly deshielded upon co-ordination of AlMe₃ (increasingly as N_β becomes more shielded), as expected, since $\pi \rightarrow \sigma^*$

paramagnetic circulations are thought to be dominant for ligating nitrogen.²¹

Adducts with π -Acceptor Molecules.—A second series of N₂-bridged complexes is composed of binuclear and trinuclear adducts of *trans*-[ReCl($^{15}\text{N}_2$)(PMe₂Ph)₄] with the transition-metal π acceptors TiCl₄, ZrCl₄, HfCl₄, NbCl₅, and TaCl₅.^{4,5} The N_β resonance is broadened by interaction with the ⁹³Nb and ¹⁸¹Ta quadrupoles; other assignments rely on the small co-ordination shift expected for N_α. Both resonances of the 1:1 adduct with TiCl₄ are very broad, probably because of its substitution lability in solution. Attempts to isolate the HfCl₄ adduct were frustrated by the low solubility of HfCl₄ and side reactions involving loss of ¹⁵N₂, but signals were observed (Table 1) which differ from those of the parent complex, and are in the appropriate region for the trinuclear Re-N-N-Hf-N-N-Re complex, analogous to the one formed by Ti.⁵ Attempts to measure the spectrum of the corresponding complex with MoCl₄¹⁴ (for which electronic and resonance-Raman spectra have been recorded²⁶) were unsuccessful because of the build-up of paramagnetic products during the measurement.

The co-ordination shifts in this series are shown in Figure 1.

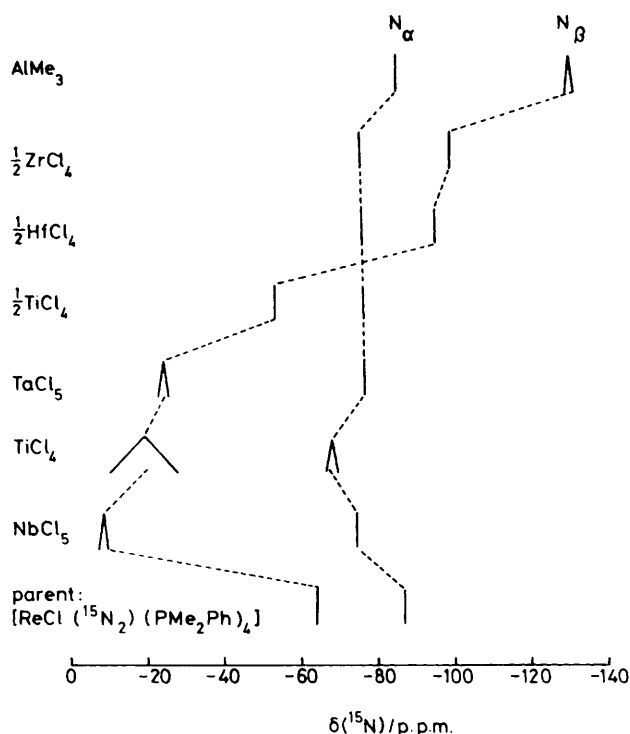


Figure 1. Chart of ^{15}N resonances of $\text{trans-}[\text{ReCl}(^{15}\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ and some of its adducts with acceptor molecules

Both N_β and N_α are now deshielded on adduct formation, except for the trinuclear complexes of ZrCl_4 and HfCl_4 , in which the N_β shielding is increased. The N_α and N_β shieldings in this series show the normal periodic dependence on the metal.²¹ The $n(\sigma)$ electrons are stabilised on co-ordination, but d_{σ^*} l.u.m.o.s are now available for paramagnetic circulations of nitrogen π electrons.

Figure 2 is a diagram of valence orbitals for a binuclear system with bridging N_2 , following earlier proposals;^{2,12,13} a corresponding diagram can be drawn for trinuclear systems.²⁶ In the ReNNM' adducts of d^0 metals the $(d^6 + p^4)$ π electrons fill the $1e$ and $2e$ orbitals and the non-bonding d_{xy} orbital on rhenium. Table 2 shows the electronic spectral data. The strong bands in the visible spectrum now represent $\text{Re} \rightarrow \text{M}'$ charge transfer,⁵ but the band energy again increases in parallel with the nitrogen shielding.

Symmetric MNNM Bridges.—Compared with the unsymmetrical NN bridges so far discussed, the symmetric (formally d^2) titanium and zirconium $[\{\text{M}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{N}_2)\}_2(\mu\text{-N}_2)]$ complexes are characterised by low nitrogen shielding.⁸ Indeed, the bridging nitrogen in the titanium complex is deshielded by over 300 p.p.m. compared to nitrogen bonded to Ti in a TiNNRe bridge, although the deshielding relative to N_α of the terminal N_2 ligand (if assigned as proposed²¹) is much less, only 85 p.p.m. Corresponding data for the zirconium complex are *ca.* 200 and 105 p.p.m., respectively. The substantial difference in the ReNNM' systems, therefore, is the larger splitting of the nitrogen orbitals of π type (this being larger still in the corresponding $\text{ReNNM}'\text{NNRe}$ complex) for the third-row, Group 7, d^6 metal. The increased shielding from the Ti_2 to the Zr_2 complex reflects the increase in orbital splittings from the first to the second transition series.

The deshielding of bridging nitrogen relative to N_α of the

terminal N_2 ligand, which is larger for the Zr_2 than for the Ti_2 compound, is a measure of the electron delocalisation across the bridge, as is the lengthening of the NN bond (1.18 Å in the ZrNNZr bridge compared with 1.115 Å for terminal NN) and shortening of the ZrN bond (2.08 Å in the bridge, 2.19 Å terminal).^{8b} Opposing push–pull interactions are now possible, with $\mu\text{-N}_2$ π -electron density delocalised into Zr d_π (a_{2g}, b_{1g}) acceptor orbitals, while d_π -electron density from the Zr $1a$ orbital delocalises into a $\pi^* \text{N}_2$ orbital.⁸ Both processes weaken the NN bond and strengthen the ZrN bond, and correspond to higher nitrogen shielding (larger splitting of the frontier orbitals for rotation of charge). They may be expected to occur to a greater extent in the zirconium than the titanium complex because of the better match of the d_π and πN_2 orbital energies for the second-row metal, and to still greater extent in the tantalum complexes included in Table 1, as observed.⁹ The nitrogen shielding is slightly greater in the tantalum(III) than in the tantalum(V) compound (the N_2 is regarded as N_2^{4-} in these compounds, see below).⁹

In the Ta_2 compounds the NN bonds are so long, in the region of 1.30 Å (as measured for a related compound), with $\nu(\text{NN})$ less than 850 cm^{-1} , that the bridge has been formulated as di-imido $\text{Ta}=\text{N}-\text{N}=\text{Ta}$, with ligating N_2^{4-} .⁹ Comparison was made with related imido- $(\text{Ta}=\text{NPh})$ -compounds with rather similar nitrogen shielding, again slightly higher (–76 p.p.m.) in tantalum(III) than tantalum(V) compounds (–11 to –27 p.p.m.).⁹ However, the nitrogen shielding appears to be much the same in $\text{M}=\text{N}-\text{N}=\text{M}$ bridges and in related imido-complexes. Thus the shifts of bridging (and terminal) dinitrogen in the molybdenum compounds in Table 1 fall within the range (–59 to +33 p.p.m.) observed for $\text{trans-}[\text{MoX}(\text{NR})(\text{dppe})_2]^+$ complexes²⁵ where R is H or Me and $\text{dppe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$. Similarly the shielding of bridging dinitrogen in $[\{\text{W}(\text{N}_2)_2(\text{PR}_2\text{Ph})_3\}_2(\mu\text{-N}_2)]$ is close to that in $\text{trans-}[\text{WBr}(\text{NH})(\text{dppe})_2]^+$ (–25.2 p.p.m.),²⁵ although somewhat less (by 35 p.p.m.) than that of N_α in corresponding terminal dinitrogen groups.²¹

It is interesting that the shifts of bridging nitrogen in the symmetrical complexes of Ti, Zr, Ta, and W follow the normal periodicity, despite the differences in the co-ordination sphere. In $[\{\text{Ru}(\text{NH}_3)_5(\mu\text{-N}_2)\}^{4+}]$, however, the shielding of the bridging nitrogen is lower than the periodic sequence would suggest, and 290 p.p.m. lower than that of N_α in ²¹ the mononuclear compound $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$. The bridging NN bond is relatively short (1.12 Å) because the $(d^6 + p^4 + d^6)$ π electrons are now sufficient to fill the $3e$ level which is NN bonding, cancelling part of the antibonding effect of the $2e$ level (Figure 2). Thus the deshielding may now be attributed to the relatively high π h.o.m.o. (highest occupied molecular orbital), as well as a relatively low σ^* l.u.m.o. Again, the deshielding correlates with lower energy of the $\text{M} \rightarrow \text{L}$ charge-transfer absorption, $38\,000 \text{ cm}^{-1}$ for the binuclear as against $45\,200 \text{ cm}^{-1}$ for the mononuclear complex.¹ The higher-energy band of the latter complex was explained² in terms of the higher effective nuclear charge on Ru (stabilising the d_π orbitals) in the RuN_2 compared with the RuNNRu system, since both systems supply four π electrons in back bonding to dinitrogen.

Conclusions

The pattern of nitrogen shielding in bridging and terminal dinitrogen complexes of a range of metals can be interpreted by a simple model of frontier orbitals for paramagnetic circulations, in terms of delocalised π orbitals, and by periodicities in the transition series which are well known from optical spectroscopy. The chemical shifts thus reflect the bonding and to some extent the reactivity of the dinitrogen.

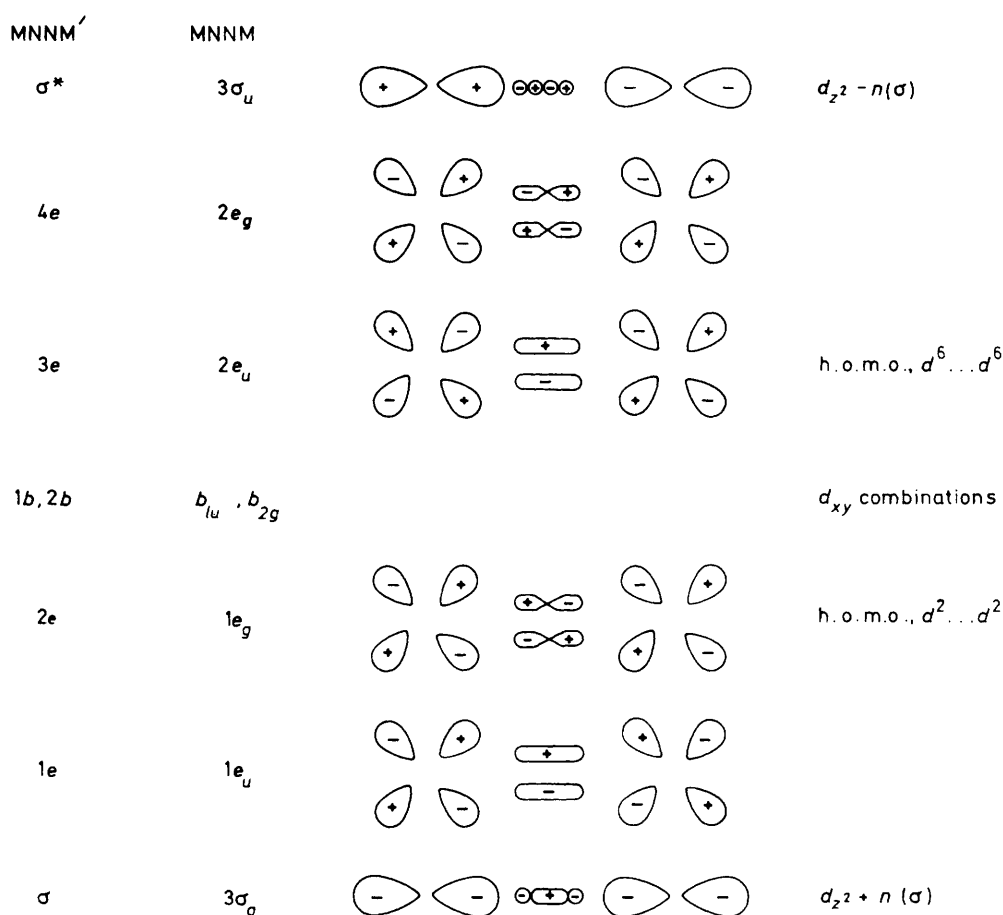


Figure 2. Valence-orbital scheme for a complex with bridging dinitrogen and eclipsed C_{4v} structure. The $d_{xz,yz}$ orbitals interact mainly with the π^* N_2 orbitals. The ordering of the orbitals (e.g. σ^* and $4e$, or $1b$, $2b$, and $2e$) may vary in different complexes

Table 2. Electronic spectral data for dinitrogen complexes

Compound	$\nu_{\max.}^a/10^3 \text{ cm}^{-1}$	$\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. ^b
$\{[\text{Zr}(\text{C}_5\text{Me}_5)(\text{N}_2)]_2(\mu\text{-N}_2)\}$	25.5 18.4 13.0	'intense'	8b
<i>trans</i> - $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$	43.0 38.0 32.0	>30 12.0 4.8	t.w.
$[\text{TiCl}_4(\text{thf})\{(\text{N}_2)\text{Re}\}]^c$	39.5 19.8	>30 21.1	5, t.w.
$[\text{NbCl}_5\{(\text{N}_2)\text{Re}\}]^{c,d}$	42.0 37.0 (sh) 21.5 17.2	>30 ca. 8.9 15 27	t.w.
$[\text{TaCl}_5\{(\text{N}_2)\text{Re}\}]^c$	38.4 25.6 20.8 (sh)	>30 20.7 3.4	t.w.
$[\text{TiCl}_4\{(\text{N}_2)\text{Re}\}_2]^c$	40.0 19.8 15.7	>30 4.2 5.5	5, t.w.
$[\text{ZrCl}_4\{(\text{N}_2)\text{Re}\}_2]^c$	42.4 37.0 (sh) 27.8 24.1	>30 ca. 9.4 9.7 25	t.w.
$[\text{Ru}(\text{N}_2)(\text{NH}_3)_5]^{2+}$	45.2	130	1,2
$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-N}_2)]^{4+}$	38.0	48	1,2

^a In CH_2Cl_2 solution. ^b t.w. = this work. ^c $(\text{N}_2)\text{Re} = \text{trans-ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4$. ^d Green in solid state, blue in solution.

The shifts with transition metal compared to main-group acceptors support the view that $\pi \rightarrow \sigma^*$ excitations are important for ligating nitrogen, and $n(\sigma) \rightarrow \pi^*$ excitations for non-ligating nitrogen in mononuclear complexes.

Experimental

The preparation and manipulation of air-sensitive materials entailed standard vacuum, Schlenk, or glove-box techniques. Unless stated otherwise, the preparation of dinitrogen complexes followed the procedures described in the literature.¹⁻¹⁰ [¹⁵N₂]Dinitrogen (95% enriched) was purchased from Prochem Ltd. and used as supplied.

Solutions for n.m.r. measurement were made up under argon and concentrations were typically ca. 10⁻² mol dm⁻³. The ³¹P and ¹H n.m.r. spectra were recorded on a JEOL FX90Q spectrometer, and ¹⁵N spectra using the FX90Q spectrometer, Bruker WH180 (P.C.M.U., Harwell), or Bruker WH360 spectrometers. Analyses were by Mr. C. Macdonald of the A.F.R.C. Unit of Nitrogen Fixation.

Preparation of [Cl₅Nb(μ-N₂)ReCl(PMe₂Ph)₄].—Dry CH₂Cl₂ (30 cm³) was distilled at -196 °C in a vacuum on to a mixture of *trans*-[ReCl(N₂)(PMe₂Ph)₄] (1.0 g) and NbCl₅ (0.34 g, 1 mol equiv.), then the mixture was allowed to warm to 20 °C and stirred for 18 h to give a green solution. The solution was filtered under argon, concentrated to ca. 10 cm³ volume under reduced pressure, then hexane was added to give dark green *microcrystals* (1.1 g, 82%) (Found: C, 35.6; H, 4.1; N, 2.6. C₃₂H₄₄Cl₆N₂NbP₄Re requires C, 35.8; H, 4.1; N, 2.6%). N.m.r. (C²HCl₃ solution): ¹H, δ 1.82 (br s, PMe₂) relative to SiMe₄; ³¹P, δ -178.4 (s) p.p.m. relative to P(OMe)₃. I.r. (Nujol): ν(N₂) 1 630, ν(¹⁵N₂) 1 585 cm⁻¹. The complex is water sensitive and it and its TaCl₅ analogue are assumed to be monomeric by analogy with their analogues of known structure.¹⁴ The ¹⁵N-labelled compound was similarly prepared.

The compound [Cl₅Ta(μ-N₂)ReCl(PMe₂Ph)₄] was prepared by the same technique as its NbCl₅ analogue from *trans*-[ReCl(N₂)(PMe₂Ph)₄] (0.3 g) and TaCl₅ (0.2 g, 1.2 mol equiv.) in 95% yield as brown *microcrystals* (Found: C, 28.9; H, 3.6; N, 2.2. C₃₂H₄₄Cl₆N₂P₄ReTa requires C, 33.1; H, 3.8; N, 2.4%). N.m.r. (C²HCl₃ solution): ¹H, δ 1.79 (br s, PMe₂) relative to SiMe₄; ³¹P, δ -176.0 p.p.m. relative to P(OMe)₃. I.r. (Nujol): ν(N₂) 1 695, ν(¹⁵N₂) 1 635 cm⁻¹. The ¹⁵N analogue was similarly prepared.

The compound [ZrCl₄{(μ-N₂)ReCl(PMe₂Ph)₄]₂·C₆H₁₄ and its ¹⁵N analogue were also prepared by the above technique from *trans*-[ReCl(N₂)(PMe₂Ph)₄] (0.8 g) and ZrCl₄ (0.1 g, 0.5 mol equiv.) as red *crystals* of the hexane solvate (Found: C, 44.3; H, 5.3; N, 3.0. C₇₀H₁₀₂Cl₆N₄P₈Re₂Zr requires C, 43.7; H, 5.3; N, 2.9%). N.m.r. (C²HCl₃ solution): ¹H, δ 1.73 (s, PMe₂) relative to SiMe₄; ³¹P, δ -172.8 (s) p.p.m. relative to P(OMe)₃. I.r. (Nujol): ν(N₂) 1 825, ν(¹⁵N₂) 1 760 cm⁻¹.

The adducts of AlMe₃ were not isolated, but prepared directly in the n.m.r. tube by addition of AlMe₃ (1 mol equiv.) in toluene solution to the dinitrogen complex in toluene under argon.

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