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

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Dinitrogen-bridged complexes of *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$] with NbCl$_5$ and TaCl$_5$ (1 : 1 adducts) and ZrCl$_4$ (2 : 1 adduct) have been characterised and a corresponding complex of HfCl$_4$ 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 (AlMe$_3$), complexes of *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$] with a π acceptor (TiCl$_4$, ZrCl$_4$, HfCl$_4$, NbCl$_5$, or TaCl$_5$), and symmetrical transition-metal complexes, [{W(N$_2$)$_2$(PR$_2$Ph)$_3$}$_2$(μ-N$_2$)] (R = Et or Pr^n), [{Ru(NH$_3$)$_5$}$_2$(μ-N$_2$)]$^{4+}$, *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 AlMe$_3$ [3] or TiCl$_4$ [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 N$_2$H$_4$ 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 Taube [12] 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] Schrock [9] 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 [(Me$_3$P)$_3$CoNNMg(thf)$_4$NNCo(PMe$_3$)$_3$] (thf = tetrahydrofuran),[15] and the K$^+$ ions in crystalline K[Co(N$_2$)(PMe$_3$)$_3$] are simultaneously end-on and edge-on to dinitrogen in (linear) CoNN.[16]

^{15}N 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 $d_\pi \rightarrow \pi^*$ N$_2$ 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 ^{15}N 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 N$_2$ system, and the stretching frequencies in metal complexes may be affected by coupling with co-ligand vibrations. Data for appropriate mononuclear N$_2$ complexes [20,21] are included for comparison.

Adducts of Trimethylaluminium.—The shifts for ligating (N$_\alpha$) and non-ligating nitrogen (N$_\beta$) in N$_2$ complexes of Mo^0, W^0, Re^I, and Os^{II} on co-ordination of AlMe$_3$ are given in Table 1. The N$_\beta$ line is somewhat broadened by proximity to the ^{27}Al quadrupole. Attachment of AlMe$_3$ decreases the ν(N$_2$) frequency by 30—100 cm^{-1}, but increases the N$_\beta$ 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 ^{15}N$_\alpha$ and ^{15}N$_\beta$ 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$_\beta$ shifts on co-ordination to AlMe$_3$ follow the normal periodicity, as in the co-ordination of N$_2$ in the parent compound. The N$_\alpha$ 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$\rightarrow$L charge-transfer band [22,23] increases in parallel, as stronger M–N$_2$ bonding destabilises the unoccupied π^* N$_2$ orbital relative to the (non-bonding) d_{xy}. Thus the deshielding, which depends on the accessibility of magnetic-dipole allowed ($\pi \longleftrightarrow \sigma$) excited states,[24] correlates with electric-dipole-allowed ($\pi \rightarrow \pi$) excitation energies, which are more readily observable in the optical spectrum.

The N$_\beta$ shifts on co-ordination to AlMe$_3$, 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	$\delta(^{15}N_{\alpha})^{a}$/ p.p.m.	$\delta(^{15}N_{\beta})^{a}$/ p.p.m.	$\nu(N_2)^{b}$/cm^{-1}	d(NN)/Å	Ref.
trans-$[Mo(^{15}N_2)_2(dppe)_2]$	Orange	Toluene	−45.1		1 979 ^{c}	1.118	6
trans-$[Mo(^{15}N_2AlMe_3)(^{15}N_2)(dppe)_2]$	Dark red	Toluene	−45.4		1 883 ^{c}	—	t.w.
trans-$[Mo(^{15}N_2)_2(depe)_2]$ ^{d}	Orange	Toluene	−43.8	−46.1		—	21, t.w.
trans-$[Mo(^{15}N_2AlMe_3)(^{15}N_2)(depe)_2]$ ^{d}	Red	Toluene	−45.6			—	t.w.
trans-$[W(^{15}N_2)_2(dppe)_2]$	Orange	Toluene	−66.6	−55.5	1 948, 2 015w	—	20,21
trans-$[W(^{15}N_2AlMe_3)(^{15}N_2)(dppe)_2]$	Black	Toluene	−64.3	−82.2	1 869, 2 059w	—	t.w.
trans-$[ReCl(^{15}N_2)(PMe_2Ph)_4]$	Yellow	Toluene	−87.2	−63.9	1 923	1.06	19,21
trans-$[ReCl(^{15}N_2AlMe_3)(PMe_2Ph)_4]$	Yellow	Toluene	−85.4	−129.8	1 894	—	t.w.
trans-$[ReCl(^{15}N_2)(dppe)_2]$	Yellow	CH_2Cl_2	−92.3	n.o.	1 967 ^{e}	—	19,21
trans-$[ReCl(^{15}N_2AlMe_3)(dppe)_2]$	Yellow	Toluene	−88.0	−127.3	1 858	—	t.w.
mer-$[OsCl_2(^{15}N_2)(PMe_2Ph)_3]$	Colourless	Toluene	−120.3	−66.8	2 079	1.112 ^{f}	19,21
mer-$[OsCl_2(^{15}N_2AlMe_3)(PMe_2Ph)_3]$	Colourless	Toluene	−100.6	−136.2	1 979	—	t.w.
$[(thf)Cl_4Ti(^{15}N_2)ReCl(PMe_2Ph)_4]$	Deep red	CH_2Cl_2	−68.1 (br)	−19 (vbr)	1 740	—	t.w.
$[Cl_5Nb(^{15}N_2)ReCl(PMe_2Ph)_4]$	Green	CH_2Cl_2	−74.3	−8.7 (br)	1 630	—	t.w.
$[Cl_5Ta(^{15}N_2)ReCl(PMe_2Ph)_4]$	Brown	CH_2Cl_2	−76.7	−24.2 (br)	1 695	—	t.w.
$[TiCl_4\{(^{15}N_2)ReCl(PMe_2Ph)_4\}_2]$	Deep blue	CH_2Cl_2	−76.7	−53.2	1 812	—	t.w.
$[ZrCl_4\{(^{15}N_2)ReCl(PMe_2Ph)_4\}_2]$	Deep red	CH_2Cl_2	−75.9	−95.0	1 825	—	t.w.
$[HfCl_4\{(^{15}N_2)ReCl(PMe_2Ph)_4\}_2]$ ^{g}	Red	CH_2Cl_2	−75.4	−96.8	1 824	—	t.w.
$[\{Ti(C_5Me_5)_2(N_2)\}_2(\mu\text{-}^{15}N_2)]$	Purple-blue	Toluene	+299 ^{h}		—	—	8
$[\{Zr(C_5Me_5)_2(N_2)\}_2(\mu\text{-}^{15}N_2)]$	Purple-red	Toluene	+179 ^{i}		—	1.182 (μ-N_2), 1.116, 1.114	8
$[\{Ta(CHCMe_3)(PMe_3)_2Cl\}_2(\mu\text{-}^{15}N_2)]$	Yellow	thf	+34 ^{j}		847	1.298 ^{k}	9
$[\{TaCl(C_2H_4)(PMe_3)_3\}_2(\mu\text{-}^{15}N_2)]$	Orange	thf	−6 ^{j}		824	—	9
$[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}^{15}N_2)]$	Red	thf	−21.3		—	—	10
$[\{W(N_2)_2(PPr^n{}_2Ph)_3\}_2(\mu\text{-}^{15}N_2)]$	Red	thf	−25.9		—	—	10
$[\{Ru(NH_3)_5\}_2(\mu\text{-}^{15}N_2)]^{4+}$	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_2H_4	—	Liquid	−334.8		1 098 (i.r.), 1 076 (Raman)	1.45	
PhCH=N−N=CHPh	—	$CDCl_3$	−19.4		—	—	*l*

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 = $Et_2P(CH_2)_2PEt_2$. [e] Chloroform solution. [f] d(NN) for *mer*-$[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$ (D. Cruz-Garritz, J. Leal, R. L. Richards, and H. Torrens, *Transition Met. Chem.*, 1983, **8**, 127). [g] Not isolated, see text. [h] Referenced originally to $[NEt_4]Cl$. [i] Referenced originally to 1 mol dm^{-3} $^{2}HNO_3$. [j] Referenced originally to NH_3 (l). [k] d(NN) for $[\{Ta(CH_2CMe_3)(CHCMe_3)(PMe_3)_2\}_2(\mu\text{-}N_2)]$.[9] [l] 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 $AlMe_3$ might be expected to correlate with increase in basicity of the N_2 complex, and decreased $\nu(N_2)$, with increased back bonding.[3] (No crystal structures have been determined for these binuclear compounds.) This correlation is observed for $[ReCl(N_2)(PMe_2Ph)_4]$, which was found to be more basic than the complexes of Mo and W, but not for $[OsCl_2(N_2)(PMe_2Ph)_3]$, which has a high $\nu(N_2)$ and low basicity towards $AlMe_3$,[3] but the largest upfield shift of N_{β} on adduct formation.

The increase in N_{β} shielding on co-ordination of $AlMe_3$ 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 ($d_{xy} \rightarrow \pi^*$ N_2) excitations and reducing the interaction with the metal. Thus the ligating nitrogen (N_{α}) is slightly deshielded upon co-ordination of $AlMe_3$ (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 N_2-bridged complexes is composed of binuclear and trinuclear adducts of *trans*-$[ReCl(^{15}N_2)(PMe_2Ph)_4]$ with the transition-metal π acceptors $TiCl_4$, $ZrCl_4$, $HfCl_4$, $NbCl_5$, and $TaCl_5$.[4,5] The N_{β} resonance is broadened by interaction with the ^{93}Nb and ^{181}Ta quadrupoles; other assignments rely on the small co-ordination shift expected for N_{α}. Both resonances of the 1 : 1 adduct with $TiCl_4$ are very broad, probably because of its substitution lability in solution. Attempts to isolate the $HfCl_4$ adduct were frustrated by the low solubility of $HfCl_4$ and side reactions involving loss of $^{15}N_2$, 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 $MoCl_4$ [14] (for which electronic and resonance-Raman spectra have been recorded [26]) 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.

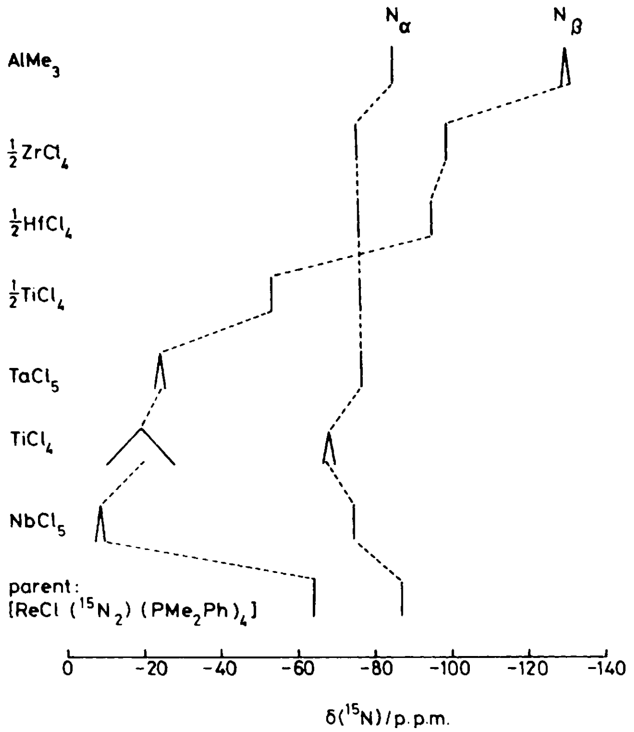

Figure 1. Chart of ^{15}N resonances of *trans*-$[ReCl(^{15}N_2)(PMe_2Ph)_4]$ and some of its adducts with acceptor molecules

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 1*e* and 2*e* 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 Re→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 $[\{M(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ 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 proposed [21]) 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 ReNNM′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_2,b_1) acceptor orbitals, while d_π-electron density from the Zr 1*a* orbital delocalises into a π^* 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 π N_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 ν(NN) less than 850 cm^{-1}, that the bridge has been formulated as di-imido Ta=N–N=Ta, with ligating N_2^{4-}.[9] Comparison was made with related imido-(Ta=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 M=N–N=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 *trans*-$[MoX(NR)(dppe)_2]^+$ complexes [25] where R is H or Me and dppe = $Ph_2P(CH_2)_2PPh_2$. Similarly the shielding of bridging dinitrogen in $[\{W(N_2)_2(PR_2Ph)_3\}_2(\mu\text{-}N_2)]$ is close to that in *trans*-$[WBr(NH)(dppe)_2]^+$ (−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 $[\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+}$, 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 $[Ru(NH_3)_5(N_2)]^{2+}$. 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 3*e* level which is NN bonding, cancelling part of the antibonding effect of the 2*e* 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 M→L charge-transfer absorption, 38 000 cm^{-1} for the binuclear as against 45 200 cm^{-1} for the mononuclear complex.[1] The higher-energy band of the latter complex was explained [2] 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.

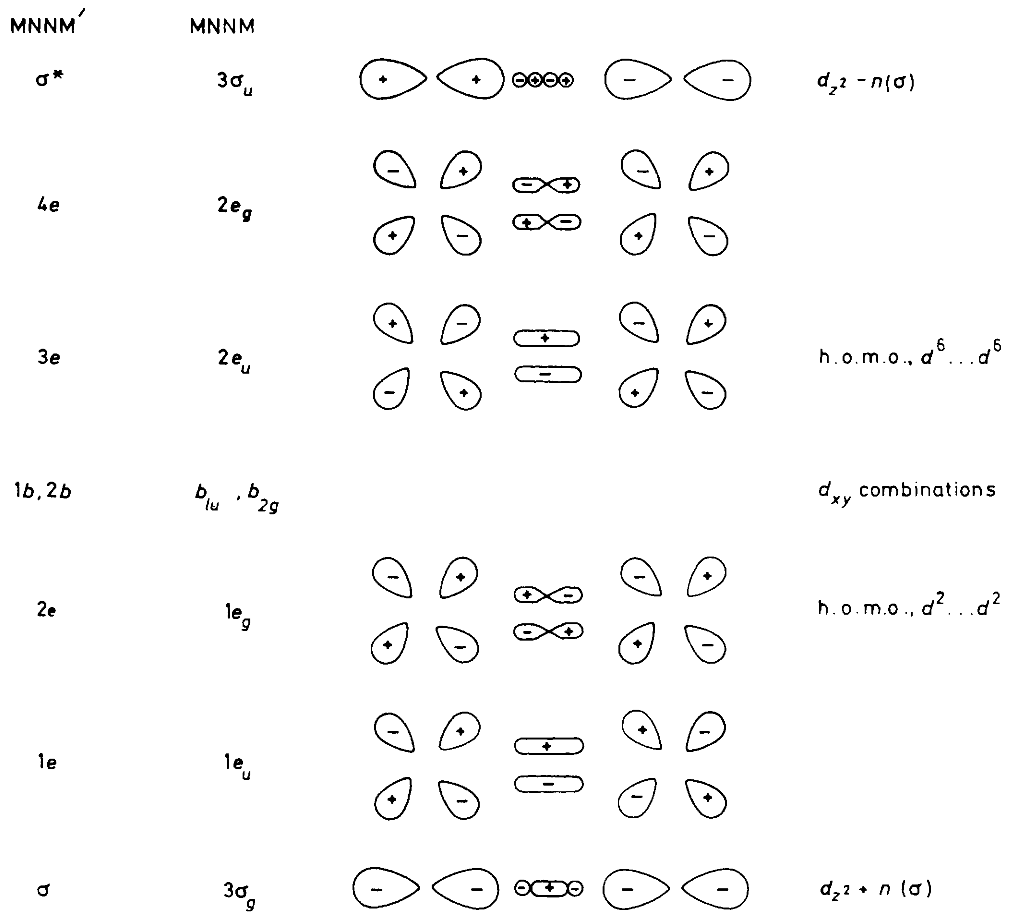

Figure 2. Valence-orbital scheme for a complex with bridging dinitrogen and eclipsed C_{4v} structure. The $d_{xz,yz}$ orbitals interact mainly with the π^* N_2 orbitals. The ordering of the orbitals (*e.g.* σ^* and 4*e*, or 1*b*, 2*b*, and 2*e*) may vary in different complexes

Table 2. Electronic spectral data for dinitrogen complexes

Compound	$\nu_{max.}$[a]/10^3 cm^{-1}	ε/10^3 dm^3 mol^{-1} cm^{-1}	Ref.[b]
$[\{Zr(C_5Me_5)(N_2)\}_2(\mu\text{-}N_2)]$	25.5	'intense'	8*b*
	18.4		
	13.0		
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	43.0	>30	t.w.
	38.0	12.0	
	32.0	4.8	
$[TiCl_4(thf)\{(N_2)Re\}]$[c]	39.5	>30	5, t.w.
	19.8	21.1	
$[NbCl_5\{(N_2)Re\}]$[c,d]	42.0	>30	t.w.
	37.0 (sh)	*ca.* 8.9	
	21.5	15	
	17.2	27	
$[TaCl_5\{(N_2)Re\}]$[c]	38.4	>30	t.w.
	25.6	20.7	
	20.8 (sh)	3.4	
$[TiCl_4\{(N_2)Re\}_2]$[c]	40.0	>30	5, t.w.
	19.8	4.2	
	15.7	5.5	
$[ZrCl_4\{(N_2)Re\}_2]$[c]	42.4	>30	t.w.
	37.0 (sh)	*ca.* 9.4	
	27.8	9.7	
	24.1	25	
$[Ru(N_2)(NH_3)_5]^{2+}$	45.2	130	1,2
$[\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+}$	38.0	48	1,2

[a] In CH_2Cl_2 solution. [b] t.w. = this work. [c] $(N_2)Re$ = *trans*-$ReCl(N_2)(PMe_2Ph)_4$. [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] [$^{15}N_2$]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 ^{31}P and ^{1}H n.m.r. spectra were recorded on a JEOL FX90Q spectrometer, and ^{15}N 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 [$Cl_5Nb(\mu-N_2)ReCl(PMe_2Ph)_4$].—Dry CH_2Cl_2 (30 cm^3) was distilled at −196 °C in a vacuum on to a mixture of *trans*-[$ReCl(N_2)(PMe_2Ph)_4$] (1.0 g) and $NbCl_5$ (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 cm^3 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. $C_{32}H_{44}Cl_6N_2NbP_4Re$ requires C, 35.8; H, 4.1; N, 2.6%). N.m.r. (C^2HCl_3 solution): ^1H, δ 1.82 (br s, PMe_2) relative to $SiMe_4$; ^{31}P, δ −178.4 (s) p.p.m. relative to $P(OMe)_3$. I.r. (Nujol): $\nu(N_2)$ 1 630, $\nu(^{15}N_2)$ 1 585 cm^{-1}. The complex is water sensitive and it and its $TaCl_5$ analogue are assumed to be monomeric by analogy with their analogues of known structure.[14] The ^{15}N-labelled compound was similarly prepared.

The compound [$Cl_5Ta(\mu-N_2)ReCl(PMe_2Ph)_4$] was prepared by the same technique as its $NbCl_5$ analogue from *trans*-[$ReCl(N_2)(PMe_2Ph)_4$] (0.3 g) and $TaCl_5$ (0.2 g, 1.2 mol equiv.) in 95% yield as brown *microcrystals* (Found: C, 28.9; H, 3.6; N, 2.2. $C_{32}H_{44}Cl_6N_2P_4ReTa$ requires C, 33.1; H, 3.8; N, 2.4%). N.m.r. (C^2HCl_3 solution): ^1H, δ 1.79 (br s, PMe_2) relative to $SiMe_4$; ^{31}P, δ −176.0 p.p.m. relative to $P(OMe)_3$. I.r. (Nujol): $\nu(N_2)$ 1 695, $\nu(^{15}N_2)$ 1 635 cm^{-1}. The ^{15}N analogue was similarly prepared.

The compound [$ZrCl_4\{(\mu-N_2)ReCl(PMe_2Ph)_4\}_2$]$\cdot C_6H_{14}$ and its ^{15}N analogue were also prepared by the above technique from *trans*-[$ReCl(N_2)(PMe_2Ph)_4$] (0.8 g) and $ZrCl_4$ (0.1 g, 0.5 mol equiv.) as red *crystals* of the hexane solvate (Found: C, 44.3; H, 5.3; N, 3.0. $C_{70}H_{102}Cl_6N_4P_8Re_2Zr$ requires C, 43.7; H, 5.3; N, 2.9%). N.m.r. (C^2HCl_3 solution): ^1H, δ 1.73 (s, PMe_2) relative to $SiMe_4$; ^{31}P, δ −172.8 (s) p.p.m. relative to $P(OMe)_3$. I.r. (Nujol): $\nu(N_2)$ 1 825, $\nu(^{15}N_2)$ 1 760 cm^{-1}.

The adducts of $AlMe_3$ were not isolated, but prepared directly in the n.m.r. tube by addition of $AlMe_3$ (1 mol equiv.) in toluene solution to the dinitrogen complex in toluene under argon.

Acknowledgements

We thank Mr. M. Cooper, P.C.M.U. Harwell, for ^{15}N n.m.r. measurements (Bruker WH180), the S.E.R.C. for provision of this spectrometer, and Mr. C. Macdonald for other n.m.r. measurements.

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Received 10*th February* 1984; *Paper* 4/238