Nitrogen-15 Nuclear Magnetic Resonance Relaxation Mechanisms in Dinitrogen Complexes of Molybdenum, Tungsten, Rhenium, and Osmium

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Longitudinal relaxation times T_1 and ^{15}N-{^1H} nuclear Overhauser enhancement (n.O.e.) factors at 2.114 and 9.396 T are reported for ^{15}N in dinitrogen complexes of molybdenum, tungsten, rhenium, and osmium, together with some ancillary ^{31}P and ^{13}C n.m.r. measurements. The n.O.e. factors are more negative for $^{15}N_\beta$ than for $^{15}N_\alpha$ (ligating nitrogen) and nearly all are disadvantageous, because of other mechanisms competing with the dipole–dipole (d.d.) relaxation by protons in the tertiary phosphine coligands and in the tetrahydrofuran solvent. The T_1 values and n.O.e. factors at 9.396 T are smaller by a factor of five or so than those at 2.114 T (*ca.* 30 s). Interpretation of the field dependence in terms of shielding anisotropy (s.a.) relaxation gives rotational correlation times of 40—90 ps, the larger values being for the complexes with bulkier phosphine ligands. At 2.114 T the s.a. and d.d.^1H mechanisms are both important, and d.d.^{15}N relaxation (*i.e.* of ^{15}N by ^{15}N) becomes significant with longer correlation times. In the rhenium complex $^{15}N_\alpha$ is quite strongly relaxed by coupling to quadrupolar $^{185,187}Re$, and d.d.$^{185,187}Re$ relaxation is significant. The ^{14}N linewidths are consistent with the correlation times otherwise derived, as also are the ^{31}P relaxation times; the ^{31}P relaxation appears to be fully dipolar (d.d.^1H).

Nitrogen n.m.r. spectroscopy of metal complexes has been limited by problems of relaxation and low sensitivity,[1–4] since ^{14}N and ^{15}N have relatively small magnetogyric ratios (γ), the abundant nucleus ^{14}N is quadrupolar, and the ^{15}N nucleus (spin $\frac{1}{2}$) has low natural abundance (0.35%) and a negative γ, so that nuclear Overhauser enhancement (n.O.e.) factors ($\eta_{obs.}$) are negative, and signals may be reduced or nulled ($\eta_{obs.} = -1$).[5] Nitrogen-15 therefore shows a greater diversity of relaxation processes than ^{13}C in organic compounds because of the lower efficiency of dipole–dipole relaxation by protons (d.d.^1H), such that other mechanisms supervene. The γ^2 dependence of the d.d.^1H relaxation rate gives a six-fold advantage to ^{13}C (which for directly bonded protons is offset somewhat by the r^{-6} dependence, as bonds to nitrogen are somewhat shorter[1]); the maximum $\eta_{obs.}$ of -4.93 for ^{15}N (under extreme narrowing conditions) is in general found only for amines, amides, and ammonium compounds. Little information is available for nitrogen in metal complexes. In our research on complexes relevant to nitrogen fixation,[6] failure to observe one or both ^{15}N resonances for the dinitrogen ligand led us to perform a series of experiments to optimise the conditions. We now report n.O.e. factors and relaxation behaviour of the dinitrogen ligand in complexes of molybdenum, tungsten, rhenium, and osmium, with tertiary phosphine coligands.

Experimental

The dinitrogen complexes were 95% ^{15}N-enriched, and were made from $^{15}N_2$ or $^{15}N_2H_6SO_4$ (from Prochem Ltd.), as previously.[6] Tetrahydrofuran (thf) solvent was treated with a reducing agent, then KOH, then sodium wire, and distilled from sodium–benzophenone under dry dinitrogen immediately before use. The sample solutions, with concentrations 0.2—0.4 mol dm^{-3}, were made up in rigorously degassed solvent, and sealed in 10-mm n.m.r. tubes under high-purity argon, with a Teflon plug for vortex suppression. To maximise the sample volume, the tube contained no reference/lock capillary.

The ^{15}N n.m.r. measurements at 2.114 T were made on a JEOL FX90Q spectrometer at 297 K with external (^7Li) lock. Spin–lattice relaxation times (T_1) were measured by the saturation-recovery (homospoil T_1) method,[7] because of the long relaxation times. Gated decoupling was used to suppress the adverse n.O.e. and minimise local heating. Delay times extended to 200 s, and between 1 000 and 2 750 scans per run were required. The n.O.e. factors ($\eta_{obs.}$) were obtained by comparison of the signal-to-noise ratios for the completely proton-decoupled and the gated decoupling modes, with the same computer phase settings. Comparison with the undecoupled mode was not practicable because of the low signal-to-noise ratios. Under our conditions, however, the residual n.O.e. with the gated decoupling is only about 4% for a nucleus with T_1 = 30 s, according to equation (1)[8] where $E_a = \exp(-T_a/T_1)$, T_a = acquisition time = 0.512 s, $E_d = \exp(-T_d/T_1)$, and T_d = delay time = 10 s.

$$\frac{\eta_{obs.}\text{ (gated decoupling)}}{\eta_{obs.}\text{ (continuous decoupling)}} = \frac{E_d(1 - E_a)}{(1 - E_dE_a)} \qquad (1)$$

The ^{14}N and ^{15}N measurements at 9.396 T were made on a Bruker WH400 spectrometer at 297 K with the same samples as at 2.114 T. The 10-mm tubes were placed inside 15-mm tubes containing deuteriated solvent, in the absence of an external locking facility. The inversion recovery sequence[9] was used without proton decoupling for ^{15}N T_1 values, and the n.O.e. factors obtained by comparison of the proton-decoupled and undecoupled spectra. The ^{31}P and ^{13}C T_1 and n.O.e. measurements were made in this way on the JEOL FX90Q spectrometer.

Precautions were taken to exclude paramagnetic impurities as far as possible, since 'exposed' or basic nitrogen is very sensitive to these. Uncertainty limits are *ca.* ±20% for the n.O.e. and T_1 measurements.

Table. Nitrogen-15 spin-lattice relaxation times (T_1) and ^{15}N-{^1H} n.O.e. factors ($\eta_{obs.}$) for terminal dinitrogen complexes in thf solution at 297 K

	$B_0 = 2.114$ T				$B_0 = 9.396$ T			
Complex	$T_1(^{15}N_\alpha)$/s	$T_1(^{15}N_\beta)$/s	$\eta_{obs.}(^{15}N_\alpha)$	$\eta_{obs.}(^{15}N_\beta)$	$T_1(^{15}N_\alpha)$/s	$T_1(^{15}N_\beta)$/s	$\eta_{obs.}(^{15}N_\alpha)$	$\eta_{obs.}(^{15}N_\beta)$
trans-$[Mo(^{15}N_2)_2(depe)_2]$	26	31	−1.2	−1.3	8.3	9.0	—	—
trans-$[W(^{15}N_2)_2(depe)_2]$	<54[a]	<62[a]	−1.5	−1.6	8.9	8.5	−0.26	−0.32
cis-$[W(^{15}N_2)_2(PMe_2Ph)_4]$	33	37	−1.5	−2.0	5.4	7.2	—	—
			−1.4[b]	−1.5[b]				
trans-$[ReCl(^{15}N_2)(PMe_2Ph)_4]$	9	20	−0.3	−2.0	3.8	4.1	—	—
trans-$[OsCl_2(^{15}N_2)(PMe_2Ph)_3]$	23	31	−1.2	−0.9	5.7	4.0	−0.23	−0.35

[a] Value overlong because of a deterioration in resolution during the course of the experiment. [b] In $[^2H_8]$tetrahydrofuran.

Results and Discussion

n.O.e. Observations.—As shown in the Table, the n.O.e. factors ($\eta_{obs.}$) mostly have values between zero and −2, and so are detrimental to the observed intensities. The $^{15}N_2$ ligand thus differs from some others for which more negative n.O.e. factors are observed even though the nitrogen has no directly attached protons. A near-maximum ^{15}N $\eta_{obs.}$ was reported for closed-shell cydta [*trans*-1,2-diaminocyclohexane-*NNN′N′*-tetra-acetate(4−)] complexes of heavy metals,[10] and a sizeable $\eta_{obs.}$ observed for $^{15}N_\beta$ in singly bent diazenido-complexes ($M^{15}N_\alpha{}^{15}N_\beta R$, R = Et or COMe) with phosphine coligands.[11]

The values of *ca.* −1.5 at lower field (2.1 T) correspond to 30% or so of the relaxation being of d.d.^1H type. A particularly small value (−0.3) is observed for ligating nitrogen ($^{15}N_\alpha$) in the rhenium complex, together with a particularly short relaxation time, and these can be attributed to quadrupolar and dipolar effects of the rhenium, as discussed below. Slightly smaller n.O.e. values for the osmium complex compared with those for molybdenum and tungsten may be related to the smaller number of phosphine ligands. In the other complexes the n.O.e. factors are greater for $^{15}N_\beta$ than for $^{15}N_\alpha$, which is the more protected from interaction with protons. That the interaction is partly with the solvent is shown by the n.O.e. factors observed on substitution of a fully deuteriated solvent, $[^2H_8]$tetrahydrofuran, in measurements on *cis*-$[W(^{15}N_2)_2(PMe_2Ph)_4]$: the n.O.e. factor for $^{15}N_\alpha$ is slightly reduced, from −1.5 to −1.4, but for $^{15}N_\beta$ it falls significantly, from −2.0 to −1.5.

For ligating nitrogen, therefore, the interactions with protons may be largely intramolecular, whereas for $^{15}N_\beta$ the interaction is probably intra- and inter-molecular (with solvent and solute molecules). Similarly, larger solvent effects on the chemical shifts are observed for $^{15}N_\beta$ than for $^{15}N_\alpha$.[6] The Figure, drawn from a photograph of a space-filling model of *trans*-$[Mo(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$), gives some idea of the exposure of the nitrogens to intermolecular influences. In the *cis*- compared with the *trans*-$(^{15}N_2)_2$ (or mono-$^{15}N_2$) complexes the intramolecular interaction with phosphine protons is presumably reduced (in principle by 25%), with compensation by improved intermolecular access.

The smaller n.O.e. factors observed at higher field (9.396 T) clearly implicate the shielding anisotropy (s.a.) relaxation mechanism. Interestingly, ^{31}P shows maximum n.O.e. factors (theoretically 1.24) at 2.114 T for the complexes *trans*-$[M(^{15}N_2)_2(dppe)_2]$ (M = Mo or W) in thf solution. Thus the ^{31}P relaxation is likely to be fully dipolar (^1H), and competing mechanisms may be preventing this for $^{15}N_2$ at lower as well as higher field. Carbon-13 in the methyl group in $[ReCl(^{15}N_2)(PMe_2Ph)_4]$ also shows a near-maximum $\eta_{obs.}$.

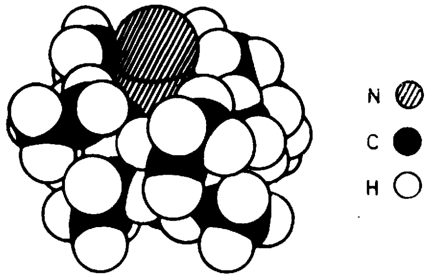

Figure. Space-filling model of *trans*-$[Mo(N_2)_2(depe)_2]$

Shielding Anisotropy (s.a.) Relaxation.—The most striking feature of the Table is the diminution in relaxation times and n.O.e. factors for the measurements at higher field. This shows the importance of the s.a. mechanism of relaxation, for which the rate is proportional to the square of the field B_0 and of the shielding anisotropy $\Delta\sigma$, *cf.* the $\Delta\sigma$ values 654,[12] 603,[13] and 590[14] p.p.m. reported for the N_2 molecule. The rate (for extreme narrowing) is given by equation (2)[15] on the assumption of cylindrical symmetry, and a single correlation time τ_c for the molecular tumbling. This mechanism is important also for ^{13}C in carbonyl[16] and in cyano[17] complexes, and solid-state[18,19] and solution[16] studies have shown that the shielding anisotropy is similar in free and ligating CO both for ^{13}C[16,18] and for ^{17}O.[19] The N_2 ligand may be more pliable, so that $^{15}N_\beta$ may perhaps have a slightly larger shielding anisotropy and s.a. relaxation rate than $^{15}N_\alpha$: but there is no obvious reflection, in the ^{15}N relaxation times, of the observation for carbonyl complexes that $\Delta\sigma$ (for ^{13}C or ^{17}O) decreases slightly down the group Cr, Mo, W.[18]

$$T_{1(s.a.)}{}^{-1} = \frac{2}{15}\gamma_{^{15}N}{}^2 B_0{}^2(\Delta\sigma)^2\tau_c \qquad (2)$$

The n.O.e. factors show that the d.d.^1H mechanism contributes 4.7—7.1% of the relaxation at 9.396 T. If we make a small allowance for other relaxation mechanisms and take $T_{1(s.a.)}$ as 4.3—9.5 s at 9.396 T, with $\Delta\sigma$ = 600 or 550 p.p.m., equation (2) gives correlation times τ_c of 34—74 or 40—90 ps respectively. These and other correlation times that can be derived for the solutions studied justify the assumption of the extreme (motional) narrowing condition, $\omega^2\tau^2 \ll 1$. They may be compared with the value of 22 ps observed in ^{17}O resonance for the small cluster $[Os_3H_2(CO)_{10}]$ in $CDCl_3$, and with the smaller values, 4—16 ps, measured in ^{13}C resonance for organic groups attached to bi- and mono-nuclear carbonyl complexes.[16]

The Debye–Stokes–Einstein hard-sphere friction model gives equation (3) where V is the molecular volume, η' the solution viscosity, and f a microviscosity factor usually found to be *ca.*

$$\tau_c = V\eta' f/kT \qquad (3)$$

0.16 for neat liquids. Values of $\eta' = 1$ cP, $f = 1$, $T = 300$ K, and a molecular radius of 100 pm give $\tau_c = 1$ ps.[20] Our $(depe)_2$ complexes are near-spherical with radius *ca.* 400 pm, so that equation (3) gives τ_c in the region of 65 ps (with uncertainties of ±25% or so), if $f = 1$. This seems to be a limiting value of f for solutions in which the molecule of interest has about 100 times the radius of a molecule of solvent, so that frictional resistance to the motion is large.[20] Interestingly, with $\Delta\sigma$ taken as 550—600 p.p.m., equation (2) gives τ_c values of 35—45 ps for the $(depe)_2$ complexes, and 45—90 ps for the bulkier $(PMe_2Ph)_4$ complexes.

According to the field dependence, $T_{1(s.a.)}$ values of 4.3—9.5 s at 9.396 T correspond to values of 85—190 s at 2.114 T. If additivity of the relaxation rates is assumed, the s.a. mechanism may then account for up to 30% of the relaxation at the lower field.

Dipole–Dipole Relaxation by Triply Bonded ^{15}N.—This mechanism might be indicated by the similarity of the T_1 values observed for $^{15}N_\alpha$ and $^{15}N_\beta$ (except for the rhenium complex). It is favoured by the close N≡N approach (r_{NN}), about 110 pm, although disfavoured because of the small magnetogyric ratio of ^{15}N. The equation for directly bonded like spins, with extreme narrowing, gives expression (4)[15] where μ_0 is the

$$[T_{1(d.d.^{15}N)}]^{-1} = 2\left(\frac{\mu_0}{4\pi}\right)^2 \cdot \frac{\gamma_{^{15}N}{}^4\hbar^2 I(I+1)}{r_{NN}{}^6} \cdot \tau_c$$
$$= 5.1 \times 10^7 \tau_c \qquad (4)$$

permeability of free space. Putting $\tau_c = 50$—65 ps gives T_1 values of 400—300 ps, so this process plays some part in the relaxation at lower field, particularly for the longer correlation times. Similar relaxation of ^{15}N by ^{14}N has been demonstrated in liquid azoxybenzene, $Ph^{15}N^{14}N(O)Ph$, with $T_{1(d.d.^{14}N)} = 200$ s at 11 °C ($\tau_q \approx 10$ ps),[21] and of ^{13}C by ^{14}N in cyano-complexes such as $[Ni(CN)_4]^{2-}$ in D_2O, with $T_{1(d.d.^{14}N)} \approx 316$ s and $\tau_{eff.} \approx 13$ ps.[17] Dipolar relaxation of unprotonated ^{13}C by attached ^{14}N is important also in adenosine and guanosine 5′-monophosphates in water, with τ_c *ca.* 320 ps.[22]

Dipole–Dipole Relaxation of $^{15}N_\alpha$ *by the Metal Nuclei*.—The 'most magnetic' of the metal nuclei are those of rhenium, since ^{185}Re is 37% abundant and ^{187}Re 63% abundant, and both have spin $\frac{5}{2}$ and relatively large magnetogyric ratios. It is likely that the faster relaxation and smaller n.O.e. factor for $^{15}N_\alpha$ compared to $^{15}N_\beta$ in the rhenium complex at 2.114 T, or compared to the other ligating nitrogen, can be explained by interactions with the $^{185,187}Re$ magnetic dipoles, or with the electric quadrupoles, or both. The equation for d.d. relaxation of a nucleus A by a nucleus X bonded to it (under extreme narrowing conditions) is (5).[15] With $S = \frac{5}{2}$ and $r_{ReN} = 197$ pm,[23] this relaxation rate becomes $6.1 \times 10^7\ \tau_c\ s^{-1}$ in the rhenium complex. Putting τ_c equal to 50—65 ps gives relaxation times of 330—250 s, so this mechanism can account for a small part only of the increased relaxation rate for $Re-N_\alpha$. The magnetic nuclei of the other metals have lower natural abundances by a factor of 4 or more, and smaller magnetogyric ratios by a factor of 3 or more (and ^{183}W and ^{189}Os have smaller spin quantum numbers), so this mechanism must be much less effective for them.

$$[T^{\text{intra}}_{1(d.d.X)}]^{-1} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \cdot \frac{\gamma_A{}^2\gamma_X{}^2\hbar^2 S(S+1)}{r_{AX}{}^6} \cdot \tau_c \qquad (5)$$

Scalar Relaxation of the Second Kind.[15]—Both ^{185}Re and ^{187}Re have rather large electric quadrupole moments, 2.36 $\times 10^{-24}$ and 2.24×10^{-24} cm^2 respectively, so the ligating nitrogen is likely to be relaxed by modulation of the spin–spin coupling to these fast relaxing nuclei. The equation, for extreme narrowing conditions, is (6)[15] which reduces to (7) where S and T_q are the spin and relaxation time of the quadrupolar neighbour, J the (unresolved) $Re-^{15}N$ coupling constant, and $\Delta\omega$ the difference between the Larmor frequencies. The $(\Delta\omega)^2$ term makes this mechanism more efficient at lower field, and it is noticeable that there is a much smaller difference in the relaxation behaviour of the two nitrogens at higher field in the rhenium complex. For rhenium, T_q can be estimated very approximately from ^{95}Mo linewidths of *ca.* 40 Hz (corresponding to T_q *ca.* 8 ms) observed for molybdenum complexes analogous to the rhenium complexes, in thf solution. From the $(n.q.c.c.)^2$ dependence of the relaxation rate [equation (9)], ^{95}Mo having $I = \frac{5}{2}$ and quadrupole moment -1.1×10^{-26} cm^2, a T_q of *ca.* 0.2 μs can be estimated for rhenium in *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$. The value of $^1J(^{183}W-^{15}N) = 67$ Hz observed for *cis*-$[W(^{15}N_2)_2(PMe_2Ph)_4]$[6] affords an estimate of $^1J(Re-^{15}N)$, if allowance is made for the γ dependence, and some increase in magnitude across the row of the Periodic Table and with a *trans*-Cl ligand (with increase in *s*-electron density at the nucleus). Equation (7) with $T_q = 0.2$ μs and $^1J(Re-^{15}N)$ couplings of 300—350 Hz gives $T_{1(s.c.)}(^{15}N_\alpha)$ values of 32—44 s at 2.114 T, so the presence of this mechanism is likely. It was found to dominate the methyl ^{13}C relaxation in $[Re(^{13}CH_3)(CO)_5]$, despite the efficiency of the d.d.^1H and internal spin-rotation relaxation processes.[24] The other quadrupolar metal nuclei, $^{95,97}Mo$ and ^{189}Os, have Larmor frequencies that are quite close to that of ^{15}N, but their smaller quadrupole moments and natural abundance (compared to $^{185,187}Re$) make their scalar contribution negligible.

$$T_{1(s.c.)}{}^{-1} = 8\pi^2 J^2 S(S+1)\ T_q/3[1 + (\Delta\omega T_q)^2] \qquad (6)$$

$$T_{1(s.c.)}{}^{-1} = 8\pi^2 J^2 S(S+1)/3(\Delta\omega)^2\ T_q \qquad (7)$$

Some relaxation of ^{15}N by ^{14}N by this mechanism is conceivable, since up to 10% of $^{14}N^{15}N$ could be present in 95 atom % ^{15}N-enriched dinitrogen. Equation (7) with $^1J(^{14}N-^{15}N) = 4.3$ Hz, and T_q values of 80—160 ms for ^{14}N, gives $T_{1(s.c.)}$ values of the order of 10^8 s at 2.114 T; this mechanism is insignificant because of the small spin–spin coupling constant.

Spin-rotation Relaxation of the $^{15}N_2$ *Ligand*.—Liquid and solid $^{15}N_2$ relax by the spin-rotation (s.r.) mechanism,[13] which contributes also to ^{13}C and ^{15}N relaxation in aqueous cyanide ion.[25] This is less effective for larger molecules in the liquid phase as the rotation is more frequently interrupted, but was found to be important for $C_6H_5C^{15}N$, with $T_{1(s.r.)} = T_{1(d.d.)} = 1\,150$ s at 50 °C.[20] This means of relaxation, uniquely, is favoured by higher temperatures, but long relaxation times precluded variable-temperature studies of the dinitrogen complexes. This mechanism (and scalar relaxation of the first kind) should be significant for complexes in which the $^{15}N_2$ ligand is rotating end over end;[26] but any such process is very slow in the complexes under study (as shown by the resolution of the $^{15}N_{\alpha,\beta}$ resonances, which are only 1 p.p.m. apart in the molybdenum complex[6]).

Quadrupolar Relaxation of the $^{14}N_2$ *Ligand*.—For comparison with the correlation times for molecular reorientation, the ^{14}N spectrum was measured for the complex *trans*-$[ReCl(^{14}N_2)(PMe_2Ph)_4]$ in thf solution. A broad asymmetric band of width at half-height ($W_{\frac{1}{2}}$) 2 600 Hz was obtained. From the chemical shifts obtained for $^{15}N_\alpha$ and $^{15}N_\beta$, −86 and −64 p.p.m., respectively,[6] two lines can be fitted to the envelope with widths at their half-height of perhaps 2 000—3 800 Hz. Since the ^{14}N relaxation is wholly quadrupolar the relaxation time $T_1 = T_2 = T_q$ (in the extreme narrowing region) is given by equation (8) and for isotropic motions by equation (9)[15] where

$$T_q = 1/\pi W_{\frac{1}{2}} \qquad (8)$$

$$T_q^{-1} = \frac{3}{8}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1 + \frac{a^2}{3}\right)\tau_c \qquad (9)$$

τ_q is the correlation time for reorientation of the electric field gradient (e.f.g., eq) at the ^{14}N nucleus, e^2qQ/h the nuclear quadrupole coupling constant (n.q.c.c.), in radians, and a the asymmetry parameter, which is zero for axial symmetry.

Equation (8) gives T_q values of 80—160 μs for the two nitrogens in the rhenium complex. Some n.q.c.c. values for related molecules are 5.4 MHz for liquid N_2,[13] and 4.98, 4.70 MHz respectively for the outer and inner nitrogen in the weakly bonded linear molecule $N_2 \cdots HF$ in the gas phase,[27] with slightly smaller values 4.6, 4.3 MHz for $NC–CN \cdots HF$, the more negatively charged nitrogen having the lower value;[28] *cf.* also 4.6 MHz for HCN.[29] Cyano-complexes have ^{14}N n.q.c.c. of 4—4.2 MHz for d^{10} metals, or 3.5—4 MHz for d^6 or d^8 ions, in which there is more back bonding;[30] similarly in metal carbonyls the ^{17}O n.q.c.c. values are reduced to 1.3—3 MHz compared with 4.43 MHz in the free ligand.[16] Electric field gradients may be greater for terminal than for the two-coordinate nitrogen, which usually has the more equal charge distribution: thus S-bonded thiocyanato-complexes have ^{14}N n.q.c.c. in the range 2.9—3.4 MHz, whereas with N-ligation (MNCS being near-linear) the range is 0.4—1.5 MHz (the values being lower for d^8 than d^{10} ions, as before).[31] Interestingly, n.q.c.c. values of 2.5—4 MHz for the nitrogens in the rhenium complex give correlation times [by equation (9)] of 50—65 ps, in agreement with the estimates from s.a. relaxation in the high-field studies. This may indicate a lesser role for other contributions to modulation of the ^{14}N e.f.g., such as molecular vibrations, which are important in the relaxation of ^{59}Co in symmetrical cobalt(III) complexes in water.[32]

Dipole–Dipole Relaxation by Protons.—Maximum n.O.e. factors were observed for ^{31}P in *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$), and T_1 values of 5.6 and 6.6 s respectively. The phosphorus is therefore wholly proton-relaxed and this is likely also for the complexes in the Table, since there are more protons close to phosphorus in the depe and PMe_2Ph ligands than in dppe (even though shorter correlation times reduce the efficiency of the relaxation). Very few ^{31}P relaxation measurements have been published for transition-metal complexes, but near-maximum n.O.e. factors have been reported for $[PdCl_2(phosphine)_2]$ complexes. The $T_1(^{31}P)$ values are *ca.* 12 s for the *trans*-$(PEt_3)_2$ complex and 15—18 s for *trans*- and *cis*-$(PMe_2Ph)_2$ complexes,[33] *cf.* values of 4—10 s reported for diphenylphosphinite or dimethyl phosphite ligands in complexes of Pt^{II} and Ru^{II}[34] (all in deuteriated solvents).

The relevant equation for the relaxation of a nucleus A by protons in the same molecule, under extreme narrowing conditions, is (10). Each ith proton, at P–H distance r_i, has a

$$[T^{\text{intra}}_{1(\text{d.d.})}]^{-1} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_A{}^2\gamma_{^1H}{}^2\hbar^2 I(I+1)\sum_i n_i\tau_i r_i{}^{-6} \qquad (10)$$

correlation time τ_i which is appropriate to the reorientation of the P–H^i vector, and is shortened (compared with the molecular τ_c) by internal motions such as rotations of methyl and phenyl groups, or pseudorotations of methylene groups. [A rather long relaxation time, $T_1(^{13}C)$ = 36 s, corresponding to a very short correlation time, was in fact measured for methyl carbon in the rhenium complex.] Estimates of r_i values from the X-ray crystallographic measurements are 240 pm for alkyl β-H, 390 pm for alkyl γ-H, and 354 pm for aryl β-H. For want of better information, a common $\tau_{\text{eff.}}$ must be assumed. With $T_1(^{31}P)$ = 6 s, equation (10) gives $\tau_{\text{eff.}}$ values of 50 ps for the depe ligand (with six β-H and eight γ-H) and 56 ps for PMe_2Ph (with six β-H and two aryl γ-H). These are maximum values in the sense that relaxation by protons in the coligands or in neighbouring molecules has not been allowed for, and $T_1(^{31}P)$ may be shorter in the depe or PMe_2Ph complexes than in the dppe complexes.

d.d.^{1}H Relaxation times for nitrogen were obtained from the n.O.e. factors, as $T_{1(\text{d.d.}^1\text{H})} = -4.93\ T_1{}^{\text{obs.}}/\eta_{\text{obs.}}$. For ligating nitrogen ($^{15}N_\alpha$) most of this relaxation is mediated by protons in the phosphine ligands, since the use of a deuteriated solvent only slightly reduces the n.O.e. factor. The intramolecular contribution to the relaxation rate, for n protons at a van der Waals distance of 260 pm, is given by equation (10) as $1.89n \times 10^7\ \tau_{\text{eff.}}\ s^{-1}$. The average $T_{1(\text{d.d.}^1\text{H})}$ value observed for $^{15}N_\alpha$, 121 s, gives a value of n = 8 for $\tau_{\text{eff.}}$ = 55 ps, consistent with the ^{31}P results.

For $^{15}N_\beta$ there are more unknowns. The reduction in n.O.e. when the solvent is deuteriated corresponds to about a quarter of the d.d.^{1}H relaxation being mediated by solvent protons, and protons in other solute molecules must be effective also. The average $T_{1(\text{d.d.}^1\text{H})}$ value observed for $^{15}N_\beta$ is 120 s (with larger variations than for $^{15}N_\alpha$): if this corresponds to say 180 s for the intramolecular portion it gives n = 6 for $\tau_{\text{eff.}}$ = 55 ps. Again, this is consistent with the numbers estimated for the phosphorus relaxation, since the M–P bond distance, about 250 pm, is midway between the M–N_α and the M–N_β distances. The consistency as between values for the same complex at different field strengths is reasonable in view of the experimental uncertainties; it is less good for N_β in the osmium complex, for which slight decomposition to form Os^{III}, in long runs, is a possibility.

Conclusions

Our studies have shown the importance of s.a. relaxation for the $^{15}N_2$ ligand at higher magnetic fields (9 T or so), and its presence with d.d. and possibly other mechanisms at lower fields (say below 2.25 T). They emphasise the value of working at higher fields, since the n.O.e. becomes much more disadvantageous at lower fields. They have shown also that the shielding anisotropy must be similar in free and ligating N_2, as found for CO.[16] More light will be shed on the complex balance of mechanisms at lower field if experiments can be performed in which the temperature is varied.

References

1 G. C. Levy and R. L. Lichter, 'Nitrogen-15 NMR Spectroscopy,' Wiley-Interscience, New York, 1979.
2 M. Witanowski, L. Stefaniak, and G. A. Webb, *Annu. Rep. NMR Spectrosc., Sect. B*, 1981, **11**.
3 G. J. Martin, M. L. Martin, and J. P. Gouesnard, in 'NMR Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer, Berlin, 1981, vol. 18.
4 J. Mason, *Chem. Rev.*, 1981, **81**, 205; *Chem. Br.*, 1983, 654.
5 G. E. Hawkes, W. M. Litchman, and E. W. Randall, *J. Magn. Reson.*, 1975, **19**, 255.
6 S. Donovan-Mtunzi, J. Mason, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1984, 469 and refs. therein.
7 G. G. McDonald and J. S. Leigh, *J. Magn. Reson.*, 1973, **9**, 358.
8 D. Shaw, 'Fourier Transform NMR Spectroscopy,' Elsevier, Amsterdam, 1976.
9 R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, 1968, **48**, 3821.

10 E. H. Curzon, N. Herron, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 721.

11 J. R. Dilworth, C-T. Kan, J. Mason, R. L. Richards, and I. A. Stenhouse, *J. Organomet. Chem.*, 1980, **201**, C24.

12 S. I. Chan, M. R. Baker, and N. F. Ramsey, *Phys. Rev. A*, 1964, **136**, 1224; M. R. Baker, C. H. Anderson, and N. F. Ramsey, *ibid.*, **133**, 1533.

13 L. M. Ishol and T. A. Scott, *J. Magn. Reson.*, 1977, **27**, 23; L. M. Ishol, T. A. Scott, and M. Goldblatt, *ibid.*, 1976, **23**, 313.

14 E. E. Burnell and C. A. de Lange, *Chem. Phys. Lett.*, 1984, **106**, 413.

15 A. Abragam, 'The Principles of Nuclear Magnetism,' Clarendon Press, Oxford, reprinted 1978.

16 G. E. Hawkes, E. W. Randall, S. Aime, D. Osella, and J. E. Elliott, *J. Chem. Soc., Dalton Trans.*, 1984, 279; S. Aime, R. Gobetto, D. Osella, G. E. Hawkes, and E. W. Randall, *ibid.*, p. 1863.

17 R. E. Wasylishen, G. L. Neufeld, and K. J. Friesen, *Inorg. Chem.*, 1981, **20**, 638.

18 J. W. Gleeson and R. W. Vaughan, *J. Chem. Phys.*, 1983, **78**, 5384.

19 E. Oldfield, M. A. Keniry, S. Shinoda, S. Schramm, T. L. Brown, and H. S. Gutowsky, *J. Chem. Soc., Chem. Commun.*, 1985, 791.

20 R. T. Boeré and R. G. Kidd, *Annu. Rep. NMR Spectrosc.*, 1982, **13**, 319.

21 E. Lippmaa, T. Saluvere, and S. Laisaar, *Chem. Phys. Lett.*, 1971, **11**, 120.

22 R. S. Norton and A. Allerhand, *J. Am. Chem. Soc.*, 1976, **98**, 1007.

23 B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 578.

24 R. F. Jordan and J. R. Norton, *J. Am. Chem. Soc.*, 1979, **101**, 4853.

25 P. Loftus, W. H. Bearden, and J. D. Roberts, *Nouv. J. Chim.*, 1977, **1**, 283.

26 J. N. Armor and H. Taube, *J. Am. Chem. Soc.*, 1970, **92**, 2560.

27 P. D. Soper, A. C. Legon, W. G. Read, and W. H. Flygare, *J. Chem. Phys.*, 1982, **76**, 292.

28 A. C. Legon, P. D. Soper, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 4936.

29 R. M. Garvey and F. C. De Lucia, *J. Mol. Spectrosc.*, 1974, **50**, 38; *cf.* also J. M. Lehn and J. P. Kintzinger, in 'Nitrogen NMR,' eds. M. Witanowski and G. A. Webb, Plenum, New York and London, 1973, ch. 3.

30 R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, 1968, **72**, 2982.

31 W. C. Fultz, J. L. Burmeister, C. P. Cheng, and T. L. Brown, *Inorg. Chem.*, 1981, **20**, 1734.

32 V. P. Chacko and R. G. Bryant, *J. Magn. Reson.*, 1984, **57**, 79.

33 W. Bosch and P. S. Pregosin, *Helv. Chim. Acta*, 1979, **62**, 838.

34 D. M. Appel, A. S. F. Boyd, I. W. Robertson, D. M. Roundhill, and T. A. Stephenson, *Inorg. Chem.*, 1982, **21**, 449.

Received 29*th January* 1985; *Paper* 5/159