The Nitrogen-15 Nuclear Magnetic Resonance Criterion of Bond Angle in Diazenido-complexes

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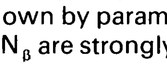
Nitrogen-15 n.m.r. spectroscopy provides a useful criterion of linear or bent geometry, which may differ from solid to solution, at the ligating nitrogen (N_α) of the diazenido (M–N=NR) ligand (as also in nitrosyls M–N=O); as shown by parameters determined for diazenides of Mo, W, Re, Fe, Ru, Rh, Os, Ir, and Pt. Both N_α and N_β are strongly deshielded, sometimes by 400 p.p.m. or more, in the doubly bent compared with the singly bent ligand. The deshielding on bending is linked to low-energy $n(N) \longrightarrow \pi^*$ paramagnetic circulations when there is non-bonding electron density on the nitrogen; thus protonation or alkylation of N_β in a singly bent diazenide to form a hydrazide(2–), or of N_α in a doubly bent diazenide to form a diazene ligand, greatly increases the nitrogen shielding. Coupling constants to the metal, also, are reduced on bending of the α-nitrogen (with development of lone-pair-electron density with *s* character), increasing again on protonation of N_α. The singly bent ligand is particularly responsive to the nature of the co-ordination site, the shielding of both nitrogens decreasing from six-co-ordinate $\{MN_2R\}^6$ to five-co-ordinate $\{MN_2R\}^8$ 18-electron complexes (with increase in back bonding). Both nitrogens are more shielded (and the NN coupling constant reduced) in four-co-ordinate (16-electron) $\{MN_2R\}^8$ complexes, with π donation to the metal. Useful parallels may be drawn with nitrogen n.m.r. parameters in related organic groups: arenediazonium, diazo, and diazene.

In studying the reduction of co-ordinated dinitrogen, of which the first step may be the formation of a diazenido-group MNNH,[1] we have discovered a nitrogen n.m.r. criterion for distinguishing singly bent (**1a**) from doubly bent (**1b**) diazenides. In our work M = Mo, W, Re, Fe, Ru, Os, Rh, Ir, or Pt, and R = H, alkyl, ketyl, or aryl.

(**1a**)



(**1b**)

In (**1a**), with MNN linear, the ligand is formally a three-electron donor N_2R^+,[2–7] comparable to NO^+ in linear nitrosyls.[8] No completely linear diazenido-ligand has been characterized. In (**1b**), with MNN fully bent, the ligand is formally a one-electron donor N_2R^-,[2–7] comparable to NO^- in 120°-bent nitrosyls,[8] with a lone pair on N_α as well as N_β. As with nitrosyls,[8] however, there are intermediate structures with partial bending at N_α.[9] The notation $\{MN_2R\}^n$ (as for nitrosyls[8]) makes no assumption as to the MNN angle as *n* includes electrons in *d*(M) and π*(NN) orbitals, *i.e.* including 'lone pair' electrons on N_α. Bending is favoured in the compounds of the later (more electron-rich) transition metals. The bond angle is important to the reactivity, since nitrogen is susceptible to electrophilic attack at N_α when MNN is bent, and transfer of a *d*-electron pair from the metal to ligating nitrogen may facilitate co-ordination of a base.

Problems have arisen in distinguishing the diazenide bonding mode, which may differ in solution from the solid phase, as described below. The NN stretching frequency is normally lower for the doubly than the singly bent ligand, but (as for nitrosyls[8]) the frequency ranges overlap,[5,10] and there are problems of vibronic couplings.

Nitrogen n.m.r. shifts and coupling constants, however, are peculiarly sensitive to the presence of lone-pair electron density, as two-co-ordinate nitrogen bends.[11] The nitrogen is then deshielded by low-energy $n(N) \longrightarrow \pi^*$ circulations, as observed for nitrosyl complexes:[12–15] ^{15}N shifts in cobalt nitrosyls span a range of over 800 p.p.m., from linear to fully bent,[13] with intermediate values when partially bent.[14] We briefly reported a similar bent–linear criterion for the diazenido-group in a limited range of complexes, with enrichment only of the α-nitrogen.[16,17] The nitrogen shielding increases greatly on protonation, with removal of low-energy $n(N) \longrightarrow \pi^*$ circulations,[11] as described below, on conversion of diazenides into diazene or hydrazido-complexes. Coupling constants to nitrogen are normally reduced in absolute magnitude by the presence of lone-pair electrons with *s* character, as their contribution to the Fermi-contact term is opposite in sign to that of the bonding electrons;[18] thus the coupling constant in the dinitrogen molecule is small, 2.5 Hz for $^{15}N_2$,[19] despite the triple bond.

This work requires ^{15}N enrichment to 95—99%, since the abundant ^{14}N nuclide is quadrupolar and gives very broad lines for molecules of this size, and the abundance of ^{15}N is too low, even with high-field working for higher sensitivity. The ^{15}N label is more difficult to introduce into side-on or bridging diazenido-ligands, which have not as yet been studied.

Results and Discussion

Singly Bent Diazenides.—The ^{15}N parameters for diazenido-ligands with MNN linear are given in Tables 1—3 for complexes

Table 1. Nitrogen-15 n.m.r. observations for six-co-ordinate singly bent diazenido-complexes, and related compounds[a]

Complex	Solvent	$\delta(N_\alpha)$	$\delta(N_\beta)$	$\lvert{}^1J(N_\alpha N_\beta)\rvert$	Other J	$\nu^{14}(NN)$[b]/ cm^{-1}	Angle MNN/°	Ref.[c]
		p.p.m.		Hz				
$[ReCl_2(^{15}N_2COPh)(py)(PPh_3)_2]$[d]	Toluene	−55.9	−148.6	15		1 530		21
$[RuCl_3(^{15}NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$	CH_2Cl_2	−47.7	—	—		1 858		3
$[RuCl_3(^{15}NNPh)(PPh_3)_2]$	CH_2Cl_2	−46.8	—			1 881	(172)	3
$[RuCl_3(N^{15}NPh)(PPh_3)_2]$	CH_2Cl_2	—	−185.6	—				
$[RuCl_3(^{15}NNC_6H_4Me\text{-}4)(PPh_3)_2]$	CH_2Cl_2	−46.4	—	—		1 895	172	10, 20
$[W(^{15}N_2Ph)(S_2CNMe_2)_3]$	CH_2Cl_2	−38.2	−138.0	16	$^1J(WN_\alpha) = 108$			
$[MoCl(^{15}N_2COMe)(dppe)_2]$	thf[e]	−35.4	−123.7	12				
$[WCl(^{15}N_2COMe)(dppe)_2]$	thf	−32.2	−134.5	12				
$[WBr(^{15}N_2Et)(dppe)_2]$	thf	−28.2	−164.7	12		1 530		22
$[WBr(^{15}N_2H)(dppe)_2]$	thf	−25.9	−187.1	14	$^1J(NH) = 60.5$	1 880		23
$[WF(^{15}N_2H)(dppe)_2]$	thf	−24.6	−182.6	14	$^1J(NH) \approx 6$ $^1J(NH) \approx 60$	1 820		23
$[ReBr_2(^{15}N_2Ph)(^{15}N_2HPh)(PPh_3)_2]$	CH_2Cl_2	−3.7	−124.7	13			172	28
$[MoBr(^{15}N_2Et)(dppe)_2]$	CH_2Cl_2	−2.6	−153.6	12		1 550		22
$[Mo(NCPh)(^{15}N_2Et)(dppe)_2][BPh_4]$	CH_2Cl_2	13.7	−134.2					
Arenediazonium, $RN_\beta N_\alpha^+$		−65 to −15	−160 to −120					31, 32
$[PhN_2(18\text{-crown-}6)][PF_6]$[f]	Acetone	−63.4	−155.8	<0.4				
$[PhN_2][PF_6]$	Acetone	−66.9	−149.7	1.6				
N_2	Acetone	−71.3		2.5[g]				
	CH_2Cl_2	−71.8						

[a] Chemical shifts relative to external neat nitromethane. [b] Solid state measurement of unlabelled compound. [c] Reference to preparative and structural information. [d] py = Pyridine. [e] thf = Tetrahydrofuran. [f] 18-crown-6 = 1,4,7,10,13,16-Hexaoxacyclo-octadecane. [g] Ref. 19.

Table 2. Nitrogen-15 n.m.r. observations for five-co-ordinate singly bent diazenido-complexes, and related compounds[a]

Complex[b]	$\delta(N_\alpha)$	$\delta(N_\beta)$	$\lvert{}^1J(N_\alpha N_\beta)\rvert$	Other J	$\nu^{14}(NN)$[c]/ cm^{-1}	Angle MNN/°	Ref.[d]
	p.p.m.		Hz				
$[Fe(CO)_2(^{15}N_2Ph)(PPh_3)_2][PF_6]$[e]	15.6	−104.2	15	$^2J(PN_\alpha) = 11$	1 723	179	25(*a*)
$[Ir(^{15}N_2Ph)(dppe)_2][PF_6]_2$	46.4	−38.2	14		1 705		
$[Os(CO)_2(^{15}N_2Ph)(PPh_3)_2][PF_6]$[f]	58.5	−21.8	15	$^2J(PN_\alpha) = 7$			
$[IrCl(^{15}N_2Ph)(PPh_3)_3][BF_4]$[g]	59.0	−22.9	14	$^2J(PN_\alpha) = 36{,}5$ $^2J(PN_\alpha) = 8$	1 625		26
$[IrCl(^{15}N_2Ph)(PMePh_2)_3][BF_4]$	64.0	−23.6	15	$^2J(PN_\alpha) = 35{,}6$	1 644	155	9
$[OsH(CO)(^{15}N_2Ph)(PPh_3)_2]$	98.9	−35.5	17		1 543	171	24
$[RhCl(^{15}N_2Ph)(PMePh_2)_3][PF_6]$	109.2	4.8	16	$^2J(RhN_\beta) = 29$ $^2J(RhN_\alpha) \approx 15$ $^2J(P_aN_\alpha) \approx 15$, $^2J(P_bN_\alpha) = 3$	1 653		5
$[Ru(CO)_2(^{15}N_2Ph)(PPh_3)_2][BF_4]$	116.8	−25.2	16		1 666		25(*b*)
Diazo, $R_2C{=}N_\beta N_\alpha$	−40 to 60	−30 to −110					31, 32
Triazenes $R_2N{-}N_\alpha{=}N_\beta R$	70 to 75	−10 to −35	12—13				34

[a] Chemical shifts relative to external neat nitromethane. [b] Measured in CH_2Cl_2. [c] Solid-state measurement of unlabelled compound. [d] Reference to preparative and structural information. [e] Measured at 0 °C. [f] Measured at −10 °C. [g] Measured at −30 °C.

Table 3. Nitrogen-15 n.m.r. observations for four-co-ordinate singly bent diazenido-complexes[a]

Complex	$\delta(N_\alpha)$	$\delta(N_\beta)$	$\lvert{}^1J(N_\alpha N_\beta)\rvert$	Other J	$\nu^{14}(NN)$[b]/ cm^{-1}	Angle MNN/°	Ref.[c]
	p.p.m.		Hz				
trans-$[IrCl(^{15}N_2Ph)(PPh_3)_2][BF_4]$	−92.1	−239.0	8	$^2J(PN_\alpha) = 4$ $^3J(PN) = 2$	1 868		26
cf. trans-$[IrCl(N_2C_5Cl_4)(PPh_3)_2][BF_4]$					1 858	175	27
trans-$[RhCl(^{15}N_2Ph)(PPh_3)_2][PF_6]$[d]	−89.8	−225.7	7	$^1J(RhN_\alpha) = 44$ $^2J(RhN_\beta) = 10$ $^2J(PN_\alpha) = 11$	1 899		5

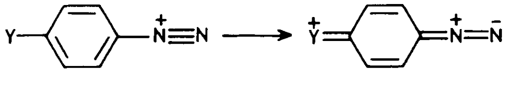
[a–c] See Table 1 for conditions of n.m.r. and i.r. measurements, and applicability of references. [d] Measured at −10 °C.

with co-ordination numbers 6, 5, and 4 respectively; the references[3,9,10,20–28] are to preparative and structural information. The nitrogen shifts, though not the NN stretching frequencies, fall into groups according to the co-ordination geometry. Single-crystal *X*-ray studies have been reported for compounds for which an MNN angle is given: with values of 170° or more the diazenide is essentially linear. The NN distances observed, 1.14—1.24 Å, are intermediate between double-bond (1.24 Å) and triple-bond (1.1 Å) values.

For each compound the resonance at lower frequency (higher shielding) is assigned to the β-nitrogen on the evidence of the spin–spin coupling patterns, selective labelling at N_α in the $[RuCl_3(N_2R)(PPh_3)_2]$ (R = aryl) series, and the greater nuclear Overhauser effects (n.O.e.s) on proton decoupling. The n.O.e. is due to dipolar relaxation by nearby protons, mainly those on the phosphine coligands,[29] the solvents being deuteriated. Little or no n.O.e. is observed for the α-nitrogen because of the greater proton distance.

As shown in Table 1, the six-co-ordinate complexes $\{MN_2R\}^6$ of Mo, W, Re, or Ru (effectively d^6 octahedral) have nitrogen shift ranges (relative to nitromethane) of -60 to 15 p.p.m. for $\delta(N_\alpha)$ and -190 to -120 p.p.m. for $\delta(N_\beta)$. The nitrogen shifts in the seven-co-ordinate compound $[W(^{15}N_2Ph)(S_2CNMe_2)_3]$, with $n = 4$, fall in these ranges.

Since co-ordination shifts (between the free and the co-ordinated ligand) are usually small, a few tens of p.p.m. (unless the ligand is greatly changed on co-ordination),[30] it is interesting that the ranges for N_α and N_β in these diazenido-complexes resemble those observed for N_α and N_β in arene diazonium cations $RN_\beta N_\alpha{}^+$, in which $CN_\beta N_\alpha$ is linear. With a range of ring substituents these have values of -65 to -15 p.p.m. for N_α and -160 to -120 p.p.m. for N_β.[31,32] Further, effects of substituents in the benzene ring appear to be similar in aryldiazenido-ligands and in diazonium cations (4-Y)-$C_6H_4N_2{}^+$, in which the shielding of both nitrogens decreases with increase in π-electron donor ability of the 4 substituent, *e.g.* from NO_2 to H and to Me. Small shifts in this sense are observed in the series $[RuCl_3(N_2R)(PPh_3)_2]$ ($R = C_6H_5Y$-4; Y = Me, H, or NO_2), but the compounds could be labelled at N_β as well as N_α only for Y = H. The deshielding is related to the extension of the delocalized system to the Y substituent, reducing the energy of the paramagnetic circulation, and strongest deshielding is observed with π-electron-donor substituents that increase the diazo-character of the diazonium group, as in (1). Thus diazo-compounds $R_2C{=}N_\beta N_\alpha$ have $\delta(N_\alpha)$ -40 to 60 p.p.m. and $\delta(N_\beta)$ -110 to -30.[31,32]


(1)

In the parent MN_2H ligand the replacement of hydrogen by ethyl, or of ethyl by ketyl, deshields N_β by about 20 p.p.m., as observed in organic molecules, but N_α is slightly shielded. The diazenido-proton is strongly deshielded, with $\delta(^1H)$ *ca.* 10 p.p.m. compared with 4—5 p.p.m. for protons in the hydrazido(2−)-group.

Small *trans* influences are evident and their effects, also, are opposite for the two nitrogens. The N_α shielding decreases (and the N_β shielding increases) in the sequence Cl > Br > F in the tungsten complexes, and similarly for molybdenum. Periodic effects of the metal on the N_α and N_β shielding resemble those observed for dinitrogen complexes[33] (and correspondingly for related ligands such as CO, CN, *etc.*), namely increased shielding across the transition-metal series or down the Group, in comparable complexes.[30]

Lower shielding is observed, as shown in Table 2, for the five-co-ordinate $\{MN_2Ph\}^8$ complexes with MNN linear; these are likely to have the trigonal-bipyramidal co-ordination geometry observed in the compounds so far measured.[9,24,25] The ranges of 15—120 p.p.m. for N_α and -104 to 5 for N_β thus resemble those observed for diazo-compounds $R_2C{=}N_\beta N_\alpha$ [$\delta(N_\alpha)$ -40 to 60, $\delta(N_\beta)$ -110 to -30 p.p.m.][31,32] or for triazenes $R_2N{-}N_\alpha{=}N_\beta R'$ (R' = aryl) [$\delta(N_\alpha)$ *ca.* 70 to 75, $\delta(N_\beta)$ -35 to -10 p.p.m.].[34] The lower shielding is therefore consistent with greater π donation from the (d^8) metal than in the $\{MN_2R\}^6$ diazenides. It may also indicate partial bending in solution, or lengthening of the M–N bond indicative of greater ease of bending.[24] Deshielding may also reflect lower ligand-field splittings than in the octahedral complexes of Table 1; in bent nitrosyl complexes of cobalt the overlap of the $n(N) \longrightarrow \pi^*$ and *d–d* circulations leads to some correlation of the nitrogen and cobalt shifts.[13]

Lowest N_α shielding is observed for $[Ru(^{15}N_2Ph)(CO)_2(PPh_3)_2][BF_4]$, some 18 p.p.m. lower than that of the osmium complex $[OsH(^{15}N_2Ph)(CO)(PPh_3)_2]$ (despite the loss of cationic charge), exemplifying the periodicity described. The M–N distance is rather long in the osmium complex (in which the co-ordination sphere is distorted by the presence of the small hydride ligand)[24] and this may be related to the relatively low N_α shielding.

In $[RhCl(^{15}N_2Ph)(PMePh_2)_3][PF_6]$, $|^1J(RhN)| < |^2J(RhN)|$, which is unusual for a linear ligand; in $[W(^{15}N_2Ph)(S_2CNMe_2)_3]$ $^1J(WN) = 108$ Hz was observed but not $^2J(WN)$, and in dinitrogen complexes $|^1J(RhN)| \gg |^2J(RhN)|$. The low value of $|^1J(RhN)|$, together with the low shielding of N_α, suggest the possibility of partial bending in solution.

The iridium complexes $[IrCl(N_2Ph)(phosphine)_3]^+$ (phosphine = PMe_2Ph or PPh_3) have similar nitrogen shifts and NN coupling constants to those of the other compounds in Table 2, and are likely to have the same singly bent bonding mode in solution, corresponding to an 18-electron configuration. Interestingly, the *X*-ray structure[9] of the PMe_2Ph complex indicates an intermediate geometry of the diazenide in the solid state, with an $MN_\alpha N_\beta$ angle of 150° and a distorted co-ordination sphere, between square pyramidal and trigonal bipyramidal. No structure has been determined for the PPh_3 complex, but the linear bonding mode is to be expected in solution in view of the bulk of the PPh_3 ligand, so the intermediate structure of the diazenide ligand in the PMe_2Ph compound could be a requirement of the crystal packing.

The $|^1J(^{15}N^{15}N)|$ values of 12—17 Hz are similar in Tables 1 and 2. They are slightly smaller than those observed for aryldiazenes (17 Hz for *trans* and 21 Hz for *cis* compounds),[35] and resemble those observed for triazenes $RN{=}N{-}NR'_2$[34] and pyrazoles (12—13 Hz).[36]

Table 3 contains two four-co-ordinate $\{MN_2R\}^8$ complexes with rather similar nitrogen n.m.r. parameters: *trans*-$[IrCl(^{15}N_2Ph)(PPh_3)_2]^+$ {derived from Vaska's compound $[IrCl(CO)(PPh_3)_2]$} and its rhodium analogue. Both nitrogens are more highly shielded, and the $|^1J(^{15}N^{15}N)|$ values smaller, in these 16-electron compounds, than in the 18-electron $\{MN_2R\}^6$ or $\{MN_2R\}^8$ complexes: indeed, the shifts and coupling constants closely resemble those of linear hydrazido(2—)-complexes ($M{=}N{-}NR_2$), as shown in Table 5, rather than of the other diazenides.

In the solid state the $\nu^{14}(NN)$ stretching frequencies for the complexes of Ir and Rh are 1 868 and 1 899 cm^{-1}, as for linear MNN.[26] There is no full account of an *X*-ray crystallographic determination, but the crystal structure of $[IrCl(^{15}N_2Ph)(PPh_3)_2]^+$ is reported to resemble that of the corresponding compound *trans*-$[IrCl(N_2C_5Cl_4)(PPh_3)_2]^+$ in which the tetrachlorocyclopentadienyldiazenide ligand replaces phenyldiazenide and $\nu(NN)$ is 1 858 cm^{-1}.[27] The two iridium complexes both have square planar geometry, with IrNN angle 175—176°, and the aromatic diazenide ligand perpendicular to the P–P vector. They also have similar Ir–N and NN distances, and both complexes readily add a phosphine ligand to form a five-co-ordinate complex in which the NN stretching frequency is reduced by 200 cm^{-1}.[27]

In these compounds, therefore, it is likely that the diazenido-ligand adjusts to maximize donation to the 16-electron metal centre at the expense of the NN multiple bonding, this adjustment being unnecessary with the addition of a third phosphine ligand. The increase in shielding from the five- to the four-co-ordinate iridium complex of 151 p.p.m. for N_α and 216 p.p.m. for N_β, with reduction in the $^{15}N^{15}N$ coupling constant from 14 to 8 Hz, and increase from 4 to 36 Hz in the two-bond coupling constant to phosphorus, is a remarkable illustration

Table 4. Nitrogen-15 n.m.r. observations for doubly bent diazenido-complexes and related compounds[a]

Complex	$\delta(N_\alpha)$ p.p.m.	$\delta(N_\beta)$ p.p.m.	$\lvert ^1J(N_\alpha N_\beta)\rvert$ Hz	Other J Hz	$\nu^{14}(NN)$[b]/ cm^{-1}	Angle MNN/°	Ref.[c]
$[RhCl(^{15}N_2Ph)\{PhP(CH_2CH_2CH_2PPh_2)_2\}][PF_6]$[d]	137.9	40.2	14		1 627, 1 751	125	4
minor isomer	84.6	−26.8	15				
$[ReCl_2(^{15}N_2COPh)(PPh_3)_2]$	157.4	−72.0	23	$^2J(PN_\alpha) = 23$			21
$[IrBr(^{15}N_2Ph)(dppe)_2][PF_6]$	220.5	158.3	18	$^3J(PN) = 6$	1 470		
$[RhCl(^{15}N_2Ph)(dppe)_2][PF_6]$[d]	224.6	135.3	18	$^1J(RhN_\alpha) = 9$ $^3J(PN_\beta) = 8$	1 466, 1 493		5
$[IrCl_2(CO)(^{15}N_2Ph)(PPh_3)_2]$[e]	241.4	150.2	18	$^3J(PN_\beta) = 4$	1 470		37
$[RhCl_2(^{15}N_2Ph)(PEtPh_2)_2]$	241.0	n.o.	16	$^1J(RhN) = 8$			
$[PtCl(^{15}N_2Ph)(PEt_3)_2]$[f]	285.0	162.0	19	$^1J(PtN) = 157$ $^3J(PN_\alpha) = 5$	1 440		38
cf. trans-$[PtCl(NNC_6H_4F\text{-}4)(PEt_3)_2]$						118	39
$[PtCl(N^{15}NPh)(PEt_3)_2]$[f]	—	162.0	19	$^2J(PtN_\beta) = 70$			
$[RhCl_2(^{15}NNPh)(PPh_3)_2]$	298.4	—			1 545, 1 610		3
$[RhCl_2(^{15}NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$	327.1	—			1 553		3
trans-RN=NR (R = aryl)	120—170		17				35

[a–c] See Table 1 for conditions of n.m.r. and i.r. measurements, and applicability of references. [d] Measured at 0 °C. [e] Measured at −10 °C. [f] thf solvent.

of the versatility of the singly bent diazenido-ligand and the sensitivity of the nitrogen n.m.r. spectroscopic parameters to changes in it.

Doubly Bent Diazenides.—As shown for the compounds in Table 4,[4,5,37–39] bending at N_α is accompanied by a dramatic deshielding of up to 400 p.p.m. or more for N_α, and quite strong deshielding for N_β also. The assignments were secured by selective labelling of N_α and N_β. The shift ranges are 138—330 p.p.m. for $\delta(N_\alpha)$ and 40—165 p.p.m. for $\delta(N_\beta)$, the latter resembling that found for *trans* alkyl- or aryl-diazenes R–N=N–R, 120—170 p.p.m.[35] A parallel in main-group chemistry is the large decrease in shielding from the linear azide ion NNN^- to the 1,3-ditosyltriazene anion $tsNNNts^-$, of 286 p.p.m. for the central nitrogen and 247 p.p.m. for the others. The importance of low-lying π lowest unoccupied molecular orbitals (l.u.m.o.s) is shown by the much higher shielding of nitrogen in the $tsNts^-$ anion, which has δ −218 p.p.m.[40]

Resonances in this region are observed also for some complexes with bridging dinitrogen.[41] In the diazenes X–N=N–X the resonances cover the range from 0 to 600 p.p.m.[35,42,43] As also in nitrosyls NOX, the nitrogen shielding decreases markedly with increase in electropositivity of X, with highest shielding for X = F, and low shielding for X = R or $SiMe_3$, as the $n(N) \longrightarrow \pi^*$ absorption goes to longer wavelengths ($Me_3SiN{=}NSiMe_3$ is deep blue, like alkylnitroso compounds); $Me_3SiN{=}NMe$ has δ(N) 302 and 271 p.p.m.[42] The lower shielding of N_α than N_β in the fully bent diazenido-complexes follows this pattern.

X-Ray crystallographic study of $[RhCl(N_2Ph)\{PhP(CH_2CH_2CH_2PPh_2)_2\}][PF_6]$ shows this compound to have a square pyramidal co-ordination sphere, in which the diazenide is apical, with MNN angle 125° and NN distance 1.17 Å;[3,4] the other five-co-ordinate rhodium complexes are expected to have the same co-ordination geometry. These are all analogues of five-co-ordinate (d^6) rhodium complexes with a bent apical nitrosyl, in which the nitrogen is strongly deshielded compared to linear nitrosyls.[15] The lower $^1J(RhN)$ value of 8 Hz for the doubly bent rhodium diazenide compared with 16 Hz for the singly bent complex $[RhCl(^{15}N_2Ph)(PMePh_2)_3]^+$ in Table 2 reflects the lone-pair-electron density at N_α in the doubly bent ligand;[18] protonation at N_α restores the higher coupling constant,[44] as described below.

Similar relationships can be followed in the platinum complexes. *X*-Ray crystallographic study[39] of $[PtCl(NNC_6H_4F\text{-}4)(PEt_3)_2]$ has shown this compound to have a *trans* square planar geometry with MNN angle 118° and NN distance 1.17 Å. The value of $\lvert ^1J(^{195}Pt^{15}N)\rvert$ in *trans*-$[PtCl(^{15}N_2Ph)(PEt_3)_2]$ is relatively low, 157 Hz, and increases to 518 Hz with protonation of N_α to give the diazene complex.[44]

The deshielding of N_β as well as N_α in the doubly bent compared with the singly bent diazenides arises from the presence of adjacent lone pairs (on the two nitrogens) of similar energy. These overlap to give bonding and antibonding combinations, reducing the frontier-orbital gap for the paramagnetic circulation at both nitrogens. Similarly, protonation of one nitrogen increases the shielding also at the other, as described below.[15]

Table 4 includes the chelate complex $[ReCl_2(N_2COPh)(PPh_3)_2]$ which is in a class of its own, since the α-nitrogen can be formulated as a two-electron donor, and is bent with lone-pair electrons in the plane of the chelate ring, The shielding is somewhat higher than for the bent diazenides, as might be expected for a cyclic delocalized system; the β-nitrogen shift of −72 p.p.m. resembles those observed for two-co-ordinate nitrogen attached to nitrogen in other five-membered rings, as in pyrazoles.[36] The (*cis*) $\lvert ^2J(^{15}N^{31}P)\rvert$ coupling constants of 23 Hz are large compared with those in the diazenido-complexes, which are often unresolved, or in dinitrogen–phosphine complexes;[33] $\lvert ^3J(^{15}N^{31}P)\rvert$ values are normally very small.

Protonation of Diazenides.—Effects of protonation are summarized in Table 5. Protonation of the singly bent diazenido-ligand in $[MX(N_2R)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) complexes, with M = Mo or W, X = halogen, and R = H or alkyl, occurs at the β-nitrogen to give the hydrazido(2−)-ligand, the shielding increasing by 60—75 p.p.m.[44,45] The N_α shielding increases also, to a smaller extent. Similarly, the N_β shielding in the dinitrogen ligand increases by about 100 p.p.m. with protonation of N_β to give the diazenide, but N_α is then deshielded slightly.

Protonation of the doubly bent diazenido-ligand occurs at the α-nitrogen[46] to give the diazene ligand, and this is accompanied by sizeable increases in shielding, of more than 200 p.p.m. (Table 5). This compares with the increase of 150 p.p.m. reported for protonation of diphenyldiazene PhN=NPh, the shifts in the cation being averaged by proton exchange.[47] That the increase in shielding is linked to the removal of low-energy $n(N) \longrightarrow \pi^*$ circulations is supported by the increase in protonation shift with increase in the chemical shift of the

Table 5. Protonation shifts, and comparison of ^{15}N n.m.r. parameters for terminal hydrazido(2−)-, dinitrogen, diazene, and diazenido-complexes

	$\delta(N_\alpha)$	$\delta(N_\beta)$		
Complex*	p.p.m.		$\vert{}^1J(N_\alpha N_\beta)\vert$/Hz	Ref.
Hydrazido(2−) M=N-NH_2 (M = Mo or W)	−100 to −45	−255 to −205	9—12	44
Dinitrogen M-N≡N (M = Mo, W, Re, Ru, Rh, or Os)	−125 to −40	−70 to −30	4—8	33
Diazene M-NH=NPh (M = Re, Os, Rh, Ir, or Pt)	−81 to 10	44 to 126	15—17	45
Diazenido M-N=NR				t.w.
Singly bent:				
c.n. 6 (M = Mo, W, Re, or Ru)	−56 to 14	−190 to −120	12—16	
c.n. 5 (M = Ru, Rh, Os, or Ir)	15 to 120	−104 to 5	14—17	
c.n. 4 (M = Rh or Ir)	−92 to −90	−239 to −226	7—8	
Doubly bent (M = Rh, Ir, or Pt)	137 to 330	40 to 162	14—19	

* c.n. = Co-ordination number; t.w. = this work.

nitrogen before protonation, and by the increase in shielding also at N_β.

Rather similar NN coupling constants of 12—20 Hz are observed for the diazenide and diazene complexes. These resemble those for organic diazenes,[11] and are larger than those in hydrazido(2−)-complexes, in which the NN bond has lower multiplicity. The lower values in dinitrogen complexes (shown in Table 3) can be explained by the large negative contribution to the Fermi-contact term of lone-pair electrons with considerable *s* character,[18] *cf.* the low coupling constant (2.5 Hz) for the dinitrogen molecule.[19]

Conclusions

Tables 1—4 show the clear differentiation of doubly from singly bent diazenides by the deshielding of both nitrogens (as well as the unreliability of the NN stretching frequency as a criterion). Of particular interest also is the variation in the response of the singly bent diazenide ligand to the demands of the co-ordination site, as shown by the lower shielding of both nitrogens in the five-co-ordinate as compared with the six-co-ordinate (18-electron) diazenides, and the high shielding of both nitrogens in the four-co-ordinate (16-electron) diazenides. The non-ligating nitrogen is at least as responsive as the ligating nitrogen: in the 'singly bent' ligand the shifts cover a range of 210 p.p.m. for N_α and 244 p.p.m. for N_β, *cf.* total ranges of 420 and 400 p.p.m. respectively for all the diazenides.

In the singly bent diazenides the nitrogen shift ranges for the six-co-ordinate complexes resemble those in arenediazonium cations (as do the aryl substituent effects), while in the five-co-ordinate complexes the lower nitrogen shieldings are closer to those in diazo-compounds (although the NN coupling constants are small, as in N_2, in the organic compounds with one of the nitrogens singly co-ordinated). For the doubly bent diazenides the N_β shifts and NN coupling constants resemble those for aryldiazenes, as might be expected, while the ligating nitrogen may be more deshielded.

Protonation of the singly bent diazenido-ligand at N_β [to form a hydrazido(2−)-ligand] and the doubly bent ligand at N_α (to form a diazene) is accompanied, in each case, by a large increase in nitrogen shielding, as also for alkylation, arylation, *etc.* of the nitrogen. This increase, on formation of a bond to hydrogen or carbon by quasi-lone-pair electrons on the bent nitrogen, illustrates the importance of low-lying $n(N) \longrightarrow \pi^*$ excitations to the deshielding. By contrast there is little difference in N_α shift from a singly bent diazenido-ligand to a diazene ligand, in similar complexes.

Experimental

Vacuum, Schlenk, or glove-box techniques were used for the manipulation of air-sensitive materials. The compounds were prepared by literature methods (as referenced), typically from $[Ph^{15}N_2][BF_4]$, which was made from $^{15}NH_2Ph$ and $Na^{15}NO_2$ by standard methods.

The ^{15}N n.m.r. spectra were run on a Bruker WM360 or WH180 spectrometer, and referenced to CD_3NO_2 with added $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) to facilitate relaxation (the shifts being corrected for differences in magnetic susceptibility).

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