Nitrogen Nuclear Magnetic Resonance Spectroscopy as a Probe of Bonding, Bending and Fluxionality of the Imido Ligand†

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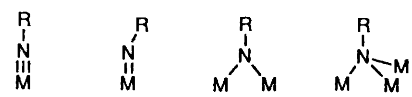
Nitrogen-14 and -15 NMR studies of imido (NR)-ligands have been made for 37 complexes of Ta, Mo, W, Re and Os, including bent NR ligands, with evidence of bent–linear fluxionality in solution, in concert with an OR or a second NR ligand. A striking difference from diazenido (N=NR) or nitrosyl ligands is the small difference in nitrogen shift for linear and bent NR ligands, the latter appearing across the whole range for NR ligands of the metals studied (with R = H, Me, Et, Bu^t, CH_2Bu^t, aryl or $SiMe_3$) in complexes with co-ordination numbers ranging from four to seven, and OR, Cl, F, NHR, NR_2, $N(SiMe_3)_2$, S_2CNEt_2, phosphine, diphosphine or oxo coligands. This range, δ_N −90 to 156, resembles that of linear ligating nitrogen in N_2 and NO ligands; the shielding is higher than in nitrides, with low-energy $n(N) \longrightarrow \pi^*$ paramagnetic circulations, and lower than in bridging imides and amides. The deshielding on bending is much smaller than for N=NR or NO ligands because the imido lowest-unoccupied molecular orbitals (LUMOs), mainly π^*(MN) and σ^*(MN), are higher-lying than the π^*(NN) and π^*(NO) LUMOs. Another difference in the imido ligand is the closer parallelism of the nitrogen and the metal shielding, both of which increase with $(\sigma + \pi)$-acceptor ability of the coligands (increasing the ligand-field splitting). In the $[WCl_4(NC_6H_4X\text{-}4)(thf)]$ (thf = tetrahydrofuran) series, similarly, the nitrogen shielding increases in the sequence X = OMe < Me < H < F < Cl < NO_2, with increase in $(\sigma + \pi)$-acceptor ability of the aromatic group. The overall pattern of imido-nitrogen shielding, including the periodicity of the metal dependence (the shielding increasing down the group of the metal, but decreasing across the row) thus resembles that of other π-donor ligands such as oxo and fluoro but differs from that of π-acceptor nitrogen ligands, such as N_2, N=NR or NO.

Many transition-metal complexes with imido ligands NR (R = H, alkyl, aryl, $SiMe_3$ *etc.*) are now known,[1,2] and the NH ligand may be an intermediate in the reduction of co-ordinated dinitrogen to ammonia.[3] The ligand is sometimes called nitrene by analogy with carbene CR_2. Terminal and bridging bonding modes as in **1a**–**1d**, as well as unsymmetrical bridging modes, are known from the X-ray crystallographic evidence, and nitrogen NMR spectroscopy can play a useful part in their characterization.



1a **1b** **1c** **1d**

The terminal ligand is usually linear as in **1a** and formulated as a four-electron donor, usually with MNC angles of 170–180° in the crystalline state,[4–8] but sometimes as low as 166–168°.[9–11] Occasionally the ligand is bent as in **1b**: it is then formally a two-electron donor with a lone pair on the nitrogen. The first bent ligand characterized[12] and the one with the smallest known MNC angle is in the bis(imido) complex *cis*-$[Mo(NPh)_2(S_2CNMe_2)_2]$, with MNC angles of 139 and 169° in the solid state. Partially bent imides are present in *trans*-$[Re(OEt)(NPh)(S_2CNMe_2)_2]$,[13] with an MNC angle of 155°, and $[Os(NBu^t)_2O_2]$,[8] with MNC angles of 155 and 179°. The ligand bends to maintain an 18-electron count in electron-rich compounds with strongly π-donating and flexible coligands such as NR or OR, and the MN bond length increases with decrease in MNC angle, for a given metal. Bending and reactivity are linked, nucleophilic reactivity being accentuated in the bent NR ligand.

The imido ligand is well suited to study by nitrogen NMR spectroscopy.[14,‡] The linear ligand, because of its axial symmetry, gives acceptable linewidths with the abundant but quadrupolar ^{14}N nucleus,[6,7,15] in relatively small molecules (with fast enough tumbling rates). Some imido complexes have been measured in ^{15}N resonance by sensitivity enhancement *via* NH couplings [with the INEPT (insensitive nuclei enhanced by polarization transfer) pulse sequence],[6,7] and some with 95% ^{15}N-enrichment.[14,16,17] Nitrogen NMR and crystallographic evidence is available also for doubly[18] and triply[19,20] bridging NR ligands, **1c** and **1d**, in which the nitrogen is again formally a four-electron donor.

† *Non-SI unit employed*: cal = 4.184 J.

‡ A chart of nitrogen shift ranges in metal complexes is given on p. 351 of ref. 14 while $^1J(^{15}NH)$ values are given on p. 358.

Table 1 Nitrogen NMR[a] and structural parameters for imido complexes

Complex	δ_N[b]	Angle MNR/°	r(MN)/pm	$\lvert J(^{15}NH)\rvert$/Hz	Ref. NMR	Ref. c
$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}^{15}NH)(CO)_9]$	−297.7			77.5	18	
$[FeRu_3(\mu\text{-}^{15}NH)(CO)_{10}\{P(OMe)_3\}]$	−289.2			72.6	19	
$[\{W(OPr^i)_2(\mu\text{-}OPr^i)\}_3(\mu_3\text{-}^{15}NH)(\mu_3\text{-}OPr^i)]$	−131.6			79.3	20	
trans-$[Re(^{15}NPh)(OEt)(S_2CNEt_2)_2]$	−92.0 (1)[d] −81.1 (3)[d]	155.5	174			13
trans-$[TaCl(^{15}NPh)(dmpe)_2]$[e]	−77.6				16	
trans-$[TaCl(^{15}NPh)(PMe_3)_4]$[f]	−76.6				16	
trans-$[ReCl(^{15}NPh)(S_2CNEt_2)_2]$	−62.2					13
trans-$[Mo(^{15}NH)(OMe)(dppe)_2]BPh_4$	−58.6			68.5	17	
mer-$[WCl_2(NEt)(PMe_3)_3]$	−46.5 (507)					
$[Ta(NCH_2Bu^t)(NHCH_2Bu^t)(OR)_2]$[g]	−29.1 (635)					
trans-$[WBr(^{15}NH)(dppe)_2]Br$	−25.2			75	17	
$[Ta(NEt)(NHEt)(OR)_2]$[g,h]	−25.0 (620)					
trans-$[MoCl(^{15}NMe)(dppe)_2]I$	24.4				17	
mer-$[TaCl_3(^{15}NPh)(PEt_3)_2]$[f]	−24.4 (300)					
$[Ta(NEt)(NHEt)\{N(SiMe_3)_2\}_2]$[h]	−21.5 (208)					
$[Ta(NSiMe_3)\{N(SiMe_3)_2\}(OBu^t)_2]$[h]	−14.5 (52)					
mer-$[TaCl_3(^{15}NPh)(PEt_2Ph)_2]$[i]	−11.8 (290)					
mer-$[TaCl_3(^{15}NPh)(thf)_2]$[f]	−11	(173.3	176)[j]		16	4
$[W(NBu^t)_2(OBu^t)_2]$	−11 (185)					
$[W(NBu^t)(OBu^t)_4]$[h]	−9.8 (160)					
$[WF_5(NMe)]^-$	−6.2				15	
$[Ta(NBu^t)(NHBu^t)(OR)_2]$[g,h]	−3.2 (530)					
$[\{Ta(NSiMe_3)[N(SiMe_3)_2](OMe)(\mu\text{-}OMe)\}_2]$[i]	−0.3 (95)	167.4	177.7			11
$[W(NBu^t)_2(NHBu^t)_2]\cdot C_6H_5Me$	3.7 (185)	*k*				7
$[Ta(NBu^t)(NHEt)\{N(SiMe_3)_2\}_2]$[h]	3.9 (230)					
$[W(NBu^t)_2(OCPh_3)_2]$[i]	6.5 (470)					
trans-$[WF_4(NMe)L](L)$[l]	9 to 19				15	
cis-$[Mo(^{15}NPh)_2(S_2CNEt_2)_2]$	9.6	169.4 139.4	175 179			12
trans-$[MoBr(^{15}NH)(dppe)_2]Br$[f]	10.6			72	17	
$[Ta(NHBu^t)_2(NSiMe_3)\{N(SiMe_3)_2\}]$[h]	12.7 (70)					
$[TaCl(NBu^t)\{N(SiMe_3)_2\}_2]$[h]	19.0 (165)	165.8	176.3			9
trans-$[MoCl(^{15}NH)(dppe)_2]Cl$	33.3			72	17	
$[Mo(^{15}NH)(S_2CNEt_2)_3]Cl$	40.0[m]				17	
$[W(NBu^t)(OBu^t)_2(NH_2Bu^t)O]$[h]	42.0 (88)					
$[WCl_4(NC_6H_4X\text{-}4)(thf)]$[n,o]	43.6–54.3	(177	171)[f]			7
$[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$[i]	45.0	171	173 (av)		6	6
$[WCl(NBu^t)(NHBu^t)(NH_2Bu^t)O]$[h]	47.4 (320)					
$[P(CH_2Ph)Ph_3][WCl_5(NEt)]$[i]	53.9	173.5[p]	171		7	
$[TaCl_2(NSiMe_3)\{N(SiMe_3)_2\}]$[f,h]	54.8 (150)					
trans-$[ReCl(^{15}NH)(dppe)_2]Cl_2$	67.1[m]					
$[\{TaCl(\mu\text{-}Cl)(NSiMe_3)[N(SiMe_3)_2]\}_2]$[h]	67.4 (90)	167.4	175.5			11
mer-$[ReCl_2(^{15}NH)(PMe_2Ph)_3]Cl$	68.2[m]					
$[Os(NBu^t)_2O_2]$	68.8 (90)	178.9 155.1	171 171.9		8	
$[P(CH_2Ph)Ph_3][\{WCl_2(NBu^t)(\mu\text{-}NPh)\}_3(\mu_3\text{-}Cl)]$[n]	70.8 (380)	168	170			10
$[Os(NBu^t)_3O]$	73.0 (300)					
$[WCl_4(NBu^t)(thf)]$	78.1 (145)					
$[WCl_4(NEt)(thf)]$[h]	78.3 (115)				7	
mer-$[WCl_2(^{15}NPh)(PMe_3)_3]$	82.7	179.5	175.5			5
$[ReCl_2(^{15}NH)(PPr^nPh_2)_2]Cl$	85.8[m]					
$[Os(NBu^t)O_3]$	121.5 (30)	171.4[q]	169.7[q]			8
$[Os(NBu^t)O_3\{N(C_2H_4)_3CH\}]$[r]	133.0 (90)					
$[Os(NBu^t)_4]$	155.6[s]					

[a] Measured in CD_2Cl_2 unless stated; all solvents were deuteriated. [b] Nitrogen shifts relative to neat liquid nitromethane, high frequency positive. Liquid NH_3 has δ_N −380.2, NH_4^+ ion in 5 mol dm^{-3} NH_4NO_3 in 2 mol dm^{-3} HNO_3 has δ_N −359.0; ^{15}N-enriched compounds were measured in ^{15}N resonance, the rest in ^{14}N resonance, in which case the linewidth, $W_{\frac{1}{2}}$ (Hz), is given in parentheses. The shifts in compounds without ^{15}N enrichment for which no linewidth is given were measured by ^{15}N INEPT experiments using values of ^1J(NH) values obtained from the ^1H NMR spectrum. [c] Structural and (or) preparative information. [d] Relative intensities; see discussion. [e] In PhCl; dmpe = 1,2-bis(dimethylphosphino)ethane. [f] In thf. [g] R = $C_6H_2Bu^t_2$-2,6-Me-4. [h] In C_6D_6. [i] In $CDCl_3$. [j] *mer*-$[TaCl_3(NPh)(PEt_3)(thf)]$. [k] Mononuclear, disordered structure. [l] The nitrogen shielding increases in the sequence of L, NCMe < OS(OMe)$_2$ ≤ CH_3CO_2Et < OPMe(OMe)$_2$ < F < OMe (ref. 15). [m] Resonance previously attributed[27] to the parent nitride. [n] In $CDCl_3$–CD_2Cl_2. [o] X = NO_2, Cl, F, H, Me or OMe. [p] In $[WCl_5(NC_6H_4Me\text{-}4)]^-$. [q] In tris(adamantan-1-ylimido)trioxoosmium. [r] $N(C_2H_4)_3CH$ = quinuclidine. [s] Ref. 28.

Nitrogen NMR spectroscopy has been useful in distinguishing bent and linear bonding modes of nitrogen in π-acceptor ligands, N=NR[21] and N=O[22–26] in particular. There is strong deshielding in the bent ligand, arising from low-energy n(N) ⟶ π* paramagnetic circulations. Differences between the solid and solution phases have been observed, including fluxionality in a complex containing one bent and one linear N=O.[25,26] With the NR ligand, therefore,

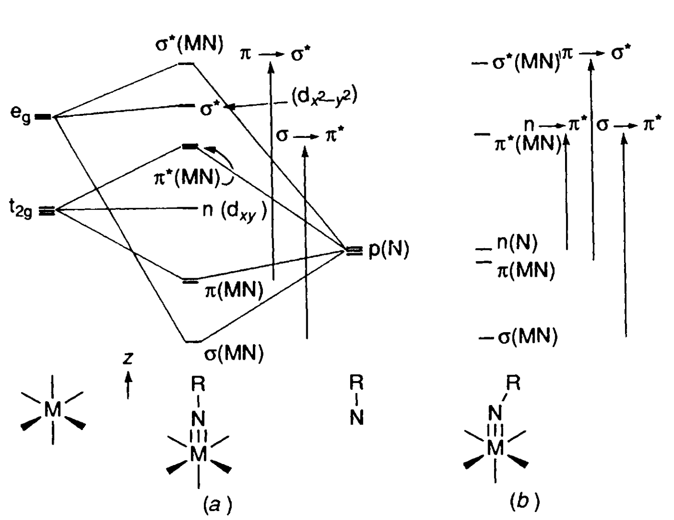


Fig. 1 Orbital energy diagrams for (*a*) the linear and (*b*) the bent imido ligand (in an octahedral complex), showing the major magnetic-dipole-allowed excitations

corresponding opportunities might be expected in the π-donor regime.

Results and Discussion

Imido Shift Range.—Table 1 gives nitrogen shifts, ^{14}N linewidths, and $|^1J(^{15}N^1H)|$ coupling constants for NR ligands, and the imido geometry if available. Unexpectedly, in contrast to N=NR and N=O ligands, deshielding on bending is small and the nitrogen shift ranges are not distinct for bent and linear NR ligands. The shift range for the terminal NR ligand, δ −92 to +155.6, shows an increase in nitrogen shielding of 130–200 ppm compared with nitrido complexes,[17,27,29] which corresponds to a protonation, alkylation or arylation shift. For a second-row element the paramagnetic term (σ^P), which dominates the chemical shift, is given approximately by equation (1)

$$\sigma^P = -(\mu_0/4\pi)(e^2/m^2) < 0|L^2|0 > < r^{-3} >_{2p} (\Delta E)^{-1} \quad (1)$$

that is, the local paramagnetic circulation is the greater the closer to the nucleus (*i.e.* the larger is the radial factor $< r^{-3} >_{2p}$, where r is the valence p-electron radius), the smaller the excitation energies (ΔE), and the larger the angular momentum factor $< 0|L^2|0 >$ which generates the circulation, arising from imbalance of charge in the valence shell. The increase in shielding from nitrido- to imido-nitrogen can thus be attributed to increase in effective excitation energies ΔE on stabilisation of the nitride lone pair highest-occupied-molecular orbital (HOMO) by bond formation, removing lower-energy n(N) ⟶ π* and σ ⟷ π (that is, σ ⟶ π* and π ⟶ σ*) paramagnetic circulations.[14,30]

Fig. 1(*a*) is a partial molecular-orbital diagram for a linear imido ligand (NR^{2-}) in an octahedral complex, showing the major paramagnetic circulations of MN electrons, σ ⟶ π* and π ⟶ σ*, perpendicular to the MN axis (z). The HOMOs are the π(MN) orbitals in d^0 and d^2 complexes (in the latter, the d_{xy} orbital is the HOMO for the metal but not the nitrogen shielding). In tetrahedral complexes similar considerations apply *locally* to the MNR group, the nitrogen shielding being mediated by σ ⟷ π circulations perpendicular to the bond axis (even though σ and π electrons are not distinguished overall).

The (σ ⟷ π) excitation energies which mediate the nitrogen shielding depend directly on the ligand-field splitting, so this should influence the shielding of the nitrogen (as well as that of the metal),[30] and this is influenced also by σ ⟷ π circulations of the N–R bonding electrons, not shown in Fig. 1. The nitrogen shift, therefore, depends on a multiplicity of factors: the nature of the metal and of the coligands, the symmetry of the complex, and the nature of the R group. Thus, if we compare like with like in Table 1, it is evident that the nitrogen shielding is greater in octahedral than in tetrahedral complexes (with smaller ligand-field splitting).

The imido shift range is comparable with those of ligating nitrogen in some other ligands with linear MNX groups, N_2, N=NR, or N=O, for example.[14] These shieldings are much higher than in *bent* nitrosyls or diazenides, in which there are low n ⟶ π* excitation energies involving low-lying π*(NO) and π*(NN) lowest-unoccupied molecular orbitals (LUMOs). In the linear ligands the higher nitrogen shielding reflects the free diamagnetic circulation about the MNX bond axis, *cf.* the higher carbon shielding in linear relative to bent alkyne or carbyne groups.[14]

Given the large variation in the types of complex in Table 1, the overall shift range of 250 ppm is smaller than those observed for bent and linear N=NR (400 ppm) or N=O ligands (900 ppm). The smaller range reflects the smaller effect of variations in larger ΔE values, and less deshielding on bending; and is no doubt reduced by fluxional averaging in solution of the shifts in electron-rich complexes with two or more flexible ligands, NR or OR.

Effects of the Metal.—Table 1 shows that the nitrogen shielding increases down the group of the metal, as in $[MBr(NH)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane], from δ 10.6 (Mo) to δ −25.2 (W), as increase in the ligand-field splitting increases the σ ⟷ π excitation energies. Across the transition series, however, the nitrogen shielding tends to decrease, as the d levels stabilize relative to the p(N) level, decreasing the σ ⟷ π excitation energies. This pattern resembles that observed for other π-donor ligands (with the metal in a high oxidation state), such as oxide[31] or fluoride.[32] In π-acceptor ligands, such as CO or N_2, the shielding of the ligating atom increases down the group of the transition metal, but tends to increase across the transition series also, with increase in the ligand-field splitting and decrease in back bonding.[30]

Effects of trans- *and Other Coligands.*—The nitrogen shielding is strongly dependent on the nature of the coligands in the tetrahedral complexes, and on the *trans* ligand in particular in octahedral complexes. *trans*-Influence series can be discerned in closely related compounds: *e.g.* in *trans*-$[WF_4(NMe)L]$ compounds the nitrogen shielding increases as L = NCMe < $OS(OMe)_2$ ⩽ CH_3CO_2Et < $OPMe(OMe)_2$ < F < OMe;[15] further series *e.g.* tetrahydrofuran (thf) < Cl < Br ≈ S ligands < OR are evident also. The nitrogen shielding increases with increase in π-donor and σ-acceptor ability of X,[33] increasing the ligand-field splitting. Related observations are the movement of the long-wavelength bands in the visible spectrum of $[MX(NH)(dppe)_2]^+$ complexes (M = Mo or W) to higher energies as X = I < Br < Cl < F < OMe,[34] and the increase in basicity of the nitrido group in $[MN(dppe)_2X]$ as X = Br, I < Cl < F < OMe. The imido pattern differs from the one observed for π-acceptor ligands, in which the ligating atom is *deshielded* by π donation from a *trans* ligand (with increase in back bonding).

The pattern in the tetrahedral complexes is similar: the nitrogen shielding increases on replacement of an amido coligand NHR by OR, as in $[W(NBu^t)_2(NHBu^t)_2]$ (δ_N 3.7) and $[W(NBu^t)_2(OBu^t)_2]$ (δ_N −11), or $[Ta(NHBu^t)_2(NSiMe_3)\{N(SiMe_3)_2\}]$ (δ_N 12.7) and $[Ta(NSiMe_3)\{N(SiMe_3)_2\}(OBu^t)_2]$ (δ_N −14.5). Strong deshielding is observed in complexes with oxo coligands, as in $[Os(NBu^t)O_3]$ (δ_N 121.5), in which the NR ligand is linear. The irregular sequence of the nitrogen shifts in the $[Os(NBu^t)_nO_{4-n}]$ series is due to partial bending when more than one NR ligand is present, and averaging of the shifts by bent–linear fluxionality, as discussed below.

Table 1 shows that steric effects are important also. As well as partial bending, these include angle distortion and bond lengthening in the co-ordination sphere, with bulky ligands. Significant effects on the metal shifts have been reported with departures from orthoaxiality of chelate ligands, in octahedral complexes.[35]

Effects of Oxidation State and Charge on the Complex.—In agreement with the observed increase in nitrogen shielding with π donation from the coligands, increases are observed from d^0 (octahedral) to analogous d^2 complexes. These are responsible for the highest shielding in terminal NR ligands in Table 1, in the range δ_N −46 to −92. (A comparable observation is the marked increase in ^{19}F shielding from d^0 to d^6 complexes.[32]) Some d^2 complexes have low nitrogen shielding, *mer*-[$WCl_2(^{15}NPh)(PMe_3)_3$] (δ_N 82) and [$ReCl_2(^{15}NH)(PPrPh_2)_2$]$^+$ (δ_N 85.8), for example; these have weak as well as strong ligands in the *xy* plane (reducing the ligand-field splitting), also the latter complex is five-co-ordinate, and positively charged. The nitrogen shielding increases with reduction in positive charge on the complex, as illustrated in the d^2 species *trans*-[$ReCl(^{15}NH)(dppe)_2$]Cl_2 (δ_N +67) and *trans*-[$ReCl(^{15}NPh)(S_2CNEt_2)_2$] ($\delta_N$ −62); and with increase in negative charge on the complex, as from *trans*-[$WF_4(NMe)L$]L (δ_N 9–19 for a range of ligands L, Table 1, footnote *l*) to [$WF_5(NMe)$]$^-$ (δ_N −6.2). Again, this pattern differs from the one observed for π-acceptor ligands, in which the ligating atom is deshielded with increase in negative charge on the complex (with increase in back bonding).

Effects of the Organic Group attached to Nitrogen.—To explore electronic influences of the organic group we prepared the 4-substituted phenylimido complexes [$WCl_4(NC_6H_4X\text{-}4)(thf)$] (X = NO_2, Cl, F, H, Me or OMe) listed in Table 2. The nitrogen shift range is relatively small, 10.7 ppm, but the increase in nitrogen shielding, in the sequence X = OMe < H < F < Cl < NO_2, clearly follows the increase in the sum of substituent constants ($\sigma_p + \sigma_I$), where σ_p expresses the π-acceptor ability of the 4- (*i.e. para*-) substituent and σ_I its σ-acceptor ability.[33] Here strengthening the N–aryl bonding, increasing the σ–π splittings, increases the nitrogen shielding, the major influence being the decrease in shielding as better π donation from the aromatic group raises the π-MN levels.

Nitrogen shieldings are somewhat lower with larger R groups such as Bu^t and $SiMe_3$ (as observed also in amines): *cf.* the increase by 25.4 ppm from NBu^t to NEt in [$Ta(NR)(NHEt)\{N(SiMe_3)_2\}$]; although the nitrogen shielding increases by 57 ppm from R = H to Me in [$MoCl(NR)(dppe)_2$]$^+$.

Parallelisms in the Nitrogen and the Metal Shielding.—Since the shielding of a transition metal nucleus is mediated by d–d, that is, ML($\sigma \longleftrightarrow \pi$) circulations,[30] the imido nitrogen and the metal shifts should move in parallel. This can be tested in vanadium resonance, because of the high NMR accessibility of ^{51}V and the range of imidovanadium complexes studied.[36] In [$VCl_3(NC_6H_4X\text{-}4)$] compounds the ^{51}V shielding increases over a range of 221 ppm in the sequence X = OMe < Me < F < Cl < Br < CF_3, with increase in ($\sigma + \pi$)-acceptor ability of the aromatic group, in parallel with our observations of the [$WCl_4(NC_6H_4X\text{-}4)(thf)$] sequence. In [$V(NC_6H_4Me\text{-}4)X_3$] the ^{51}V shieldings increase in the sequence X = CH_2SiMe_3 < Cl < $OC_6H_3Me_2$-2,6 < OBu^t over a range of 1700 ppm, with increase in the ligand-field splitting. Addition of a fifth ligand decreases the vanadium shielding somewhat, as from [$V(NC_6H_4Me\text{-}4)Cl_3$] ($\delta_V$ 305) to [$V(NC_6H_4Me\text{-}4)Cl_3(thf)$] ($\delta_V$ 374) and [$V(NC_6H_4Me\text{-}4)Cl_3(PPh_3)$] ($\delta_V$ 392), paralleling observations in nitrogen resonance, from [$Os(NBu^t)O_3$] (δ_N 121.5) to [$Os(NBu^t)O_3\{N(C_2H_4)_3CH\}$] (imido δ_N 133.0).

Bending of the Imido Ligand.—The absence of a clear differentiation in nitrogen shift ranges for linear and bent imido ligands can be interpreted in terms of their molecular-orbital diagrams in Fig. 1(*a*) and 1(*b*). Bending replaces one of the π(MN) orbitals by a lone-pair n(N), so that a lower-energy $n(N) \longrightarrow \pi^*$ circulation replaces part of the $\pi \longrightarrow \sigma^*$ circulation. The decrease in ΔE acts to reduce the nitrogen shielding, as does the lowering of the local symmetry (through the angular momentum term $<0|L^2|0>$) as observed for N=NR and nitrosyl ligands. In these ligands, however, the π^*(NN) or π^*(NO) LUMOs are low-lying (because of the electronegativity of nitrogen and oxygen), whereas the only type of π^* LUMO available to the imido group is π^*(MN), present in all three ligands. This can explain the relatively small reduction in shielding on separation of the n(N) level in the imido ligand. Further, factors promoting metal-imido bending may act to increase the shielding: thus, strongly π-donating coligands, increasing the (MN) π–π^* splitting, increase all the excitation energies shown in Fig. 1(*b*), $n \longrightarrow \pi^*$, $\pi \longrightarrow \sigma^*$ and $\pi \longrightarrow \sigma^*$ (although if σ-acceptance increases also, this acts to increase the $\pi \longrightarrow \sigma^*$ and $\sigma \longrightarrow \pi^*$ energies).

A balance of opposing influences, together with bent-linear fluxionality, can thus account for the absence of a clear distinction between the shift ranges for linear and bent NR ligands. Deshielding on bending can, however, be discerned in comparisons of closely related compounds, as in the [$Os(NBu^t)_nO_{4-n}$] series.

Fluxionality and Bending in Bis(imido) and Related Complexes.—The singlet imido nitrogen resonances observed in solution for the bis(imido) complexes which contain bent and linear NR ligands in the solid state are consistent with bent–linear fluxionality in solution. This applies to *cis*-[$Mo(^{15}NPh)_2(S_2CNEt)_2$] (MNC 139 and 169°)[12] and [$Os(NBu^t)_2O_2$] (MNC 155 and 179).[8] Such fluxionality has been demonstrated for [$RuCl(NO)_2(PPh_3)_2$]$^+$,[26] which contains one bent and one linear nitrosyl in the solid state,[37] by the observation of an $^{14,15}N$ equilibrium isotope effect in the semi-^{15}N-enriched compound in solution, persisting at low temperatures.[25] Potential barriers to fluxionality appear to be low {some preparations of [$RuCl(NO)_2(PPh_3)_2$]$^+$ have yielded modifications with two semi-bent ligands[38]} and the angles observed in the solid phase may be strongly influenced by crystal forces.

The [$Os(NBu^t)_nO_{4-n}$] series shows strong deshielding compared with other imido complexes, and a curious sequence of shifts. A solid-state structure[8] for an analogue of [$Os(NBu^t)O_3$] shows MNR to be linear (Table 1). Modified extended-Hückel calculations for the bis(imido) complex suggest a very shallow potential well, less than 1 kcal mol^{-1}, for OsNC angle deformation, separately or in concert, whereas the structure with both imides linear has maximal energy, and deformation of the linear imide in [$Os(NMe)O_3$] to a 120° angle requires 5 kcal mol^{-1}.[8] The bending is related to an insufficiency of d orbitals for π bonding with the nitrogen,[1,8] and progressively more bending is expected in the tris- and tetrakis-imido compounds.

The sequence, where (lin) and (bent) stand for the linear and bent NBu^t ligands, is then [$Os(lin)O_3$] (δ_N 121.5), [$Os(lin)(bent)O_2$] (δ_N 69.8), [$Os(lin)(bent)_2O$] (δ_N 73), and [$Os(lin)(bent)_3$] (δ_N 155.6), with fluxional averaging. Clearly the nitrogen is strongly deshielded by the presence of oxo coligands, and comparison of the shifts for [$Os(NBu^t)O_3$] and [$Os(NBu^t)_4$] shows that the nitrogen is deshielded, though less strongly, on bending. The shift sequence is 'hill-shaped', with higher shielding for the two middle members.

Additivity of substituent contributions to chemical shifts is often found for transition-metal as well as main-group nuclei.[39] The ^{51}V NMR shifts are near-linear in the sequences of [$VCl_n(NC_6H_4Me\text{-}4)(OBu^t)_{3-n}$] or [$VCl_n(NC_6H_4Me\text{-}4)(CH_2SiMe_3)_{3-n}$] complexes, for n = 0–3.[36] Deviations from additivity are common (particularly when π interactions are strong) leading to U-shaped (sagging) or hill-shaped curves; thus hill-shaped curves of ^{59}Co shielding in octahedral complexes with NH_3, NO_2^- or CN^- ligands have been explained by increase in

Table 2 Nitrogen and proton NMR parameters for $[WCl_4(NC_6H_4X\text{-}4)(thf)]$ complexes in $CDCl_3$–CD_2Cl_2 solution, and substituent parameters for the X group

	$\delta(^{14}N)^a$		$\delta(^1H)$ aromatic		$\delta(^1H)$ thf				
X	Imido	$W_{\frac{1}{2}}$/Hz	AA	BB	α	β	$\sigma_I(X)^b$	$\sigma_p(X)^c$	$\sigma_I + \sigma_p$
NO_2	43.6	85	8.62	7.50	4.84	2.20	0.68	0.81	1.49
Cl	48.9	160	7.75	7.30	4.82	2.22	0.50	0.24	0.74
F	49.5	130	7.40	7.32	4.77	2.18	0.54	0.15	0.69
H	53.2	180					0.0	0.0	0.0
Me	54.2	125	7.56	7.20	4.79	2.19	0.02	−0.14	−0.12
OMe	54.3	153	7.20	7.17	4.75	2.16	0.34	−0.27	0.07

[a] See footnote *b* in Table 1. [b] σ-inductive parameter.[33] [c] Conjugative parameter for aromatic 4 substituents.[33]

ligand-field splitting with removal of t_{2g} and e_g degeneracies.[40] Deviations from additivity are expected also with sizeable perturbations to the structure, as in substitution of a bulky bent imido for an oxo ligand.

Bending of the imido group is observed also in *trans*-$[Re(^{15}NPh)(OEt)(S_2CNEt_2)_2]$, with an MNC angle of 155° in the solid state. This complex, however, gives two singlets in the ^{15}N NMR solution spectrum, separated by only 11 ppm, with intensities in the ratio 3:1. The same multiplicity is observed in proton resonance,[13] with lower sensitivity, two sets of peaks with intensity ratios ranging from 6:1 to 1:3 being shown by the complexes *trans*-$[Re(NR')(OR)(S_2CNR''_2)_2]$ (R = Me, Et; R′ = Me, C_6H_4Me-4; R″ = Me, Et). When R″ = Et both isomers are present in appreciable amounts, but with R″ = Me one isomer predominates. In solid *trans*-$[Re(^{15}NPh)(OEt)(S_2CNEt_2)_2]$ the cisoid NPh and OEt ligands bend towards each other in the same plane (with ReNC, ReOC and NReO angles of 155, 132 and 167°, respectively) to maintain the 18-electron count, which could rise to 20 if both were linear. In solution, therefore, the cisoid–transoid isomerism about the ReNC and ReOC bonds is thought to persist (rather than the two singlets being explained by *cis–trans* isomerism at the metal, or bent–linear isomerism of the imido ligand).[13]

Bent–linear fluxionality of the imido ligand in *trans*-$[Re(^{15}NPh)(OEt)(S_2CNEt_2)_2]$ is supported by the comparison with $[ReCl(^{15}NPh)(S_2CNEt_2)_2]$,[13] in which Cl replaces OR, the imido ligand is expected to be linear, and no isomerism of the chloride is detected in solution. The imido nitrogen in the chloride (δ_N −62.2) is deshielded by only 20 or 30 ppm relative to the isomers of the alkoxy analogue, compared with 92 ppm from *trans*-$[MoCl(^{15}NH)(dppe)_2]^+$ (δ_N 33.3) to *trans*-$[Mo(^{15}NH)(OMe)(dppe)_2]^+$ (δ_N −58.6). This can be explained by bent–linear fluxionality in the alkoxy compound, with deshielding of the nitrogen on bending. Table 1 contains other electron-rich complexes in which fluxional averaging may be present, such as the bis(imido) complex $[W(NBu^t)_2(NHBu^t)_2]$, which is disordered in the solid.[7]

Bridging Imido Ligands.—Nitrogen-14 resonances were not observed for bridging organoimido ligands in the compounds in Table 1, presumably because of the contribution of a sizeable electric field gradient at nitrogen to the linewidth (already increased in the larger molecule). The ^{15}N shifts reported for doubly- and triply-bridging NH in small clusters of Fe, Ru and W,[17–19] shown in Table 1, resemble those in amido or ammine ligands[14] in showing an increase in shielding, relative to the terminal NH ligand, comparable to protonation or alkylation shifts. This again differs from the pattern observed for the ligating atom in back-bonding ligands, such as NO or CO, or shielding *decreasing* with increase in the number of metals to which the ligand is bound, that is, with increase in back bonding.[30]

Coupling Constants in Imido Ligands.—Coupling constants to nitrogen are sensitive to the presence of lone-pair electron density on the nitrogen, being decreased algebraically to an extent that depends on the s character of the lone pair.[14] Bending, therefore, should decrease the coupling constant: thus in the *trans*-$[MX(^{15}NH)(dppe)_2]^+$ compounds (M = Mo or W) the reduction to 68.5 Hz in the complex with *trans*-OMe, compared to 72–75 Hz with *trans*-Br,Cl, suggests some bending.

Nitrogen-14 Linewidths.—There may be some contribution to the ^{14}N linewidths from unresolved spin-spin coupling, but in general they reflect the bulk (more precisely, the correlation time) of the complex as a whole. Particularly broad lines ($W_{\frac{1}{2}}$ 530–635 Hz) are observed for the complexes with two $OC_6H_2Bu^t_2$-2,6-Me-4 coligands. Other things being equal, the linewidth can be a sensitive indicator of lone-pair electron density on the nitrogen, increasing the electric field gradient at the nucleus. Thus linewidths appear to be smaller in the $SiMe_3$ than in the *tert*-butylimido complexes, with the availability of back bonding to silicon.

Conclusion.—Axial symmetry in the linear NR ligand allows it to be studied in ^{14}N resonance without undue line broadening, and this may not be excessive even with bending of the ligand and a quite bulky R group, as in the $[Os(NBu^t)_nO_{4-n}]$ series. Nitrogen-15 NMR spectroscopy provides additional information, as in the resolution of coupling constants which may reflect partial bending, and of multiplicities due to isomeric forms resulting from partial bending of NR and other flexible ligands, OR in particular. The pattern of nitrogen shielding in the imido ligand (the effects of the coligands and the metal, and co-ordination shifts) resembles that of other π-donor ligands. There is no great deshielding on bending (in contrast to the π-acceptor ligands, N=NR and N=O) and the presence of the NR or OR coligand which allows the bending also allows bent–linear fluxionality in solution.

Experimental

References to the preparative methods are given in Table 1. The $[WCl_4(NC_6H_4X\text{-}4)(thf)]$ complexes (X = NO_2, Cl, F, H, Me or OMe) were prepared by the reaction of $WOCl_4$ with the appropriate isocyanate RNCO to give $[WCl_4(NR)]$ compounds, which were then treated with thf. The preparation of $[WCl_4(NC_6H_4F\text{-}4)(thf)]$ is a typical example: $OCNC_6H_4F$-4 (0.85 cm^3, 7.47 mmol) was added to a suspension of $WOCl_4$ (2.55 g, 7.46 mmol) in benzene (60 cm^3) and then refluxed for 18 h with evolution of CO_2, and a colour change from deep orange-red to dark brown-green. After filtration of the hot solution dark green crystals of $[WCl_4(NC_6H_4F)]$ were separated, washed with pentane and dried *in vacuo*, a further batch being obtained by concentration of the mother-liquor, the product after recrystallization from toluene (2.45 g) amounting to a 76% yield (Found: C, 16.7; H, 1.0; N, 3.2. $[WCl_4(NC_6H_4F)]$ requires C, 16.6; H, 0.9; N, 3.2%.) IR spectrum: 1580s, 1480s, 1352m, 1290m, 1235m, 1145s, 1092w, 1015m, 840s, 807m, 640w, 595m, 460m, 402m, 380(sh), 375vs, 338s, 280w, 270w and 245w cm^{-1}. Mass spectrum: Found m/z 432.859 220. $^{12}C_6{}^{1}H_4{}^{35}Cl_3{}^{37}Cl^{19}F^{14}N^{183}W$ requires 432.858 970. Major fragment ions: 396 (P − Cl); 287 (WCl_3); 111 ($FC_6H_4NH_2$); 95 (C_6H_4F); 75 (C_6H_3). The thf complex was obtained by dissolving [$WCl_4(NC_6H_4X)$] in thf, evaporating off the excess of ligand *in vacuo*, washing the residue with pentane, followed by drying *in vacuo*. The proton shifts for complexes [$WCl_4(NC_6H_4X)$(thf)] are given in Table 2.

The osmium complexes [Os(NBu^t)O_3], [Os(NBu^t)-O_3{N(C_2H_4)$_3$CH}], [Os(NBu^t)$_2O_2$], and [Os(NBu^t)$_3$O] were synthesised by literature methods.[8,41] Attempts to prepare other organoimido complexes of osmium by reactions of (*i*) OsO_4 with $H_2NC_6H_4$Me-4, (*ii*) [Os(NBu^t)O_3] with $C_6F_5NPPh_3$, (*iii*) [$OsO_2Cl_2(PPh_3)_2$] with Bu^{t}NPPh$_3$, PhNCO or Bu^{t}NH(SiMe$_3$), (*iv*) [$OsCl_4(PPh_3)_2$] or [$OsCl_2(PPh_3)_3$] with LiNHBu^t, (*v*) [$Os(CO)_3(PPh_3)_2$] with $C_6F_5N_3$ or Me_3SiN_3 were all unsuccessful. Since our work was completed Wilkinson and co-workers[28] have reported the synthesis of [Os(NBu^t)$_4$] from the reaction of OsO_4 with Bu^{t}NH(SiMe$_3$).

NMR Spectroscopy.—For ^{14}N NMR spectroscopy, samples were dissolved in dry outgassed solvents and sealed under N_2 in 10 mm tubes. Vacuum, Schlenk or glove-box techniques were used for the manipulation of air-sensitive materials. The rapid ^{14}N relaxation rates allowed moderately fast spectrum acquisition with pulse rates of *ca.* 3 s^{-1}. The NH_4^+ ion in 5 mol dm^{-3} NH_4NO_3 in 2 mol dm^{-3} HNO_3 (D_2O solvent) was used as reference, with δ_N −359 relative to neat liquid nitromethane.

Some ^{15}N NMR spectra were measured in natural abundance by use of the INEPT technique, with coupling constants obtained from the proton spectrum. Those measured with 95% ^{15}N-enrichment were 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.

The spectra were run on Bruker WH400, WN360 and WH180 spectrometers.

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