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Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy and Electronic Effects in Dinitrogen Complexes of Molybdenum and Tungsten with *trans* Nitrile and Diphosphine Ligands

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Nitrogen-15 chemical shifts and oxidation potentials are reported for the complexes *trans*-[M($^{15}N_2$)(NCR)(P–P)$_2$] (A) [M = Mo or W; R = Me, Pr^n, or 4-XC$_6$H$_4$ (X = H, MeO, MeCO, or F); P–P = $Ph_2PCH_2CH_2PPh_2$ or $Et_2PCH_2CH_2PEt_2$]. Linear correlations are observed for values of $\delta(^{15}N)$, $E_{\frac{1}{2}}^{ox}$, and Hammett σ_p parameters for the X substituent of the benzonitrile. The shielding of both nitrogens in the $^{15}N_2$ ligand decreases with increase of ($\sigma + \pi$) electron-releasing properties of the *trans* ligand on replacement of one N$_2$ in the complexes *trans*-[M($^{15}N_2$)$_2$(P–P)$_2$] (B) by NCR. The shielding of (only) the ligating nitrogen of $^{15}N_2$ in (A) increases with increase of the σ-donor ability of the *trans* nitrile ligand as the R group is varied.

In studies of the dinitrogen ligand, cross-connections with the extensive literature on electronic properties of related ligands (NCR, CNR, CO) are of value, particularly as these properties correlate with reactivity of these ligands towards electrophilic or nucleophilic attack.[1] We now report *trans* influences of nitrile ligands on the ^{15}N chemical shifts of dinitrogen bonded to molybdenum or tungsten, and their relation to concomitant changes in bond stretching frequencies and oxidation potentials, properties which are relevant to reduction of N$_2$ at metal sites.[1] Our discussion follows on from our examination of other influences, such as change in the metal, on the ^{15}N shielding in the dinitrogen ligand.[2]

Results and Discussion

The Table gives the ^{15}N chemical shifts for the complexes *trans*-[M($^{15}N_2$)(NCR)(P–P)$_2$] (A) (P–P = diphosphine ligand, M = Mo or W) together with values of the stretching frequencies $\nu(N_2)$, the primary oxidation potentials $^1E_{\frac{1}{2}}^{ox}$, and the Hammett σ_p parameter for 4-substituted benzonitriles (NCC$_6$H$_4$X-4). The values for *trans*-[M($^{15}N_2$)$_2$(P–P)$_2$] are included for comparison.

The assignment of the observed two ^{15}N resonances to $^{15}N_\alpha$, the ligating nitrogen, and N$_\beta$, the terminal nitrogen, relies to some extent on the analogy with related complexes in which $^{2,3}J(^{15}N^{31}P)$ couplings are observed.[2] Commonly N$_\alpha$ shows higher shielding than N$_\beta$, but there seems to be a cross-over in molybdenum and tungsten complexes, as for *trans*-[Mo($^{15}N_2$)$_2$(depe)$_2$] [depe = 1,2-bis(diethylphosphino)ethane] in the Table. Other criteria are that a larger change is expected in $\delta(^{15}N_\alpha)$, compared to $\delta(^{15}N_\beta)$, with variation of the *trans* ligand (as in the replacement of N$_2$ by NCR) or with variation of the R group in NCR. Over the wide range of dinitrogen complexes studied, the variation of $\delta(N_\beta)$ is smaller than that of $\delta(N_\alpha)$.[2] Further, a larger change is expected in $\delta(^{15}N_\beta)$ with variation in temperature or solvent, as *e.g.* for the lower-frequency resonance of *trans*-[Mo($^{15}N_2$)(NCC$_6$H$_4$F-4)(dppe)$_2$] (Table). The terminal dinitrogen is in the more exposed environment, as demonstrated for N$_2$O.[3]

The Table shows that the replacement of one N$_2$ ligand in the complexes *trans*-[M(N$_2$)$_2$(P–P)$_2$] (B) by RCN[4] leads to deshielding of $^{15}N_\alpha$ by 11—36 p.p.m. and $^{15}N_\beta$ by 7—12 p.p.m. in the molybdenum complexes, the deshieldings in some corresponding tungsten complexes being up to 50% larger than these. At the same time $^1E_{\frac{1}{2}}^{ox}$ decreases by similar amounts (0.25—0.42 V) for both metals,[5,6] and $\nu(N_2)$ decreases, as does ν(CN) relative to its value in free RCN.[4] Oxidation potential measurements suggest that the ($\sigma + \pi$) electron release to a metal site increases in the order CO < N$_2$ ≪ PPh$_3$ < CNPh < NCPh.[7] Thus the greater ($\sigma + \pi$) release from RCN when it replaces N$_2$ in compounds (B) increases the relative electronic charge on the metal in compounds (A), so that $^1E_{\frac{1}{2}}^{ox}$ is lowered (Table). From σ effects in isolation, increase of the d_σ–d_{σ^*} splitting in compounds (A) relative to compounds (B) would cause an increase of N$_\alpha$ shielding by raising the energy of $\sigma\rightarrow\pi^*$ and $\pi\rightarrow\sigma^*$ circulations close to N$_\alpha$[8] (π refers to h.o.m.o.s of π type which are M–N bonding but N–N antibonding). However, a substantial proportion of the increased metallic charge is π-delocalised onto the RCN and N$_2$ ligands, so that they approach the limiting forms (1) and (2), with decrease in ν(CN) and $\nu(N_2)$.

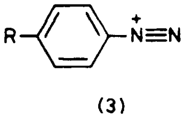
$$\mathrm{M{-}N{\equiv}N} \longrightarrow \mathrm{M{=}\overset{+}{N}{=}\overset{-}{N}} \qquad (1)$$

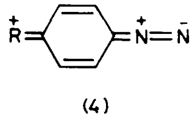
$$\mathrm{M{-}N{\equiv}C{-}R} \longrightarrow \mathrm{M{=}\overset{+}{N}{=}\overset{-}{C}{-}R} \qquad (2)$$

The dominance of the π effects can explain the deshielding of N$_\alpha$ and N$_\beta$. Lowering of ν(CN) of RCN is diagnostic of a strongly π-releasing metal site, as otherwise ν(CN) increases on co-ordination of RCN.[4]

The deshielding of N$_\alpha$ and N$_\beta$ in complexes (A) may be compared with that observed in diazonium salts R–C$_6$H$_4$N≡N$^+$ with increasing electron release from the 4-substituent, R. This deshielding is linked to an increased contribution of the structure (4), which resembles that of diazo-compounds (5), in which both nitrogens are less shielded than in benzenediazonium cations (3).[9] Effects of atomic charge, the shielding decreasing with decrease in electron density on the resonant atom (through decrease in the 2*p* electronic orbital radius) are expected to be relatively small; more important is the deshielding associated with decrease in energy of the $\sigma \longleftrightarrow \pi$ excitations which contribute to the paramagnetic term.

In the isoelectronic carbonyl ligand, similar replacement of


(3)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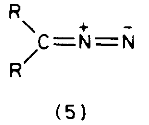
(5)

Table. Nitrogen-15 n.m.r. and i.r. data, oxidation potentials, and Hammett parameters for *trans*-$[M(N_2)(NCR)(P{-}P)_2]$ [a]

Complex	$\delta(^{15}N_{\alpha})$/ p.p.m.	$\delta(^{15}N_{\beta})$/ p.p.m.	$^{1}J(^{15}N^{15}N)$/ Hz	T/K	$\nu(N_2)$/ cm^{-1}	$^{1}E_{\frac{1}{2}}^{\mathrm{ox}}$/V	σ_p
trans-$[Mo(N_2)_2(dppe)_2]$	−43.1	−42.8	n.r.	270	1 976	−0.16 [b]	—
trans-$[Mo(N_2)(NCMe)(dppe)_2]$	−31.2	−34.0	n.r.	270	1 920	−0.58 [b]	—
trans-$[Mo(N_2)(NCPr^n)(dppe)_2]$	−32.2	−35.9	6	270	1 925	−0.57 [b]	—
trans-$[Mo(N_2)(NCPh)(dppe)_2]$	−24.0	−33.0	n.r.	295	1 945	−0.48 [b]	0.0
trans-$[Mo(N_2)(NCC_6H_4OMe\text{-}4)(dppe)_2]$	−28.6	−33.7	n.r.	270	1 935	−0.53	−0.27
trans-$[Mo(N_2)(NCC_6H_4F\text{-}4)(dppe)_2]$	−24.8	−35.1	6	270	1 951	−0.47	+0.06
	−24.7	−33.5		295			
trans-$[Mo(N_2)(NCC_6H_4COMe\text{-}4)(dppe)_2]$	−7.0	−34.8	n.r.	270	1 965	−0.41	+0.5
trans-$[Mo(N_2)_2(depe)_2]$	−42.0	−43.0	5.7	270	1 928	−0.43 [c]	—
trans-$[Mo(N_2)(NCPh)(depe)_2]$	−16.4	−31.0	n.r.	295	—	−0.72 [c]	0.0
trans-$[Mo(N_2)(NCC_6H_4OMe\text{-}4)(depe)_2]$	−24.0	−30.9	n.r.	295	—	—	−0.27
trans-$[Mo(N_2)_2(depe)(dppe)]$	−41.2		n.r.	270	1 945	−0.29	—
trans-$[Mo(N_2)(NCPh)(depe)(dppe)]$	−19.6	−30.3	n.r.	295	—	—	0.0
trans-$[Mo(N_2)(NCC_6H_4OMe\text{-}4)(depe)(dppe)]$	−25.0	−30.2	n.r.	295	—	—	−0.27
trans-$[Mo(N_2)(NCC_6H_4COMe\text{-}4)(depe)(dppe)]$	+3.1	n.o.	n.r.	295	—	—	+0.5
trans-$[W(N_2)_2(dppe)_2]$	−60.1	−48.6	6.2	270	19 53	−0.15	—
trans-$[W(N_2)(NCMe)(dppe)_2]$	−42.3	−55.5	n.r.	270	1 930	−0.57 [b]	—
trans-$[W(N_2)(NCPr^n)(dppe)_2]$	−43.4	−56.3	n.r.	270	1 900	−0.57 [b]	
trans-$[W(N_2)(NCPh)(dppe)_2]$	−28.1	−56.3	6	295	1 920	−0.48 [b]	0.0

[a] $\delta(^{15}N)$ relative to CD_3NO_2 containing tris(pentane-2,4-dionato)chromium(III) (120 mmol dm^{-3}), corrected to neat CD_3NO_2 scale (+3.4 p.p.m.); measured at 18.24 MHz in thf. I.r. data are for Nujol mulls. $^{1}E_{\frac{1}{2}}^{\mathrm{ox}}$ values are relative to a saturated calomel electrode in thf with $[NBu_4][BF_4]$ (0.2 mol dm^{-3}) carrier electrolyte, Pt electrode. n.r. = Not resolved, n.o. = not observed. [b] Ref. 6. [c] J. Chatt, W. Hussain, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. A. Rankin, *J. Chem. Soc., Chem. Commun.*, 1980, 1024.

trans CO ligands by a better (net) electron donor, as in $[MR'(CO)_3]$ or $[M(PR_3)(CO)_5]$ relative to $[M(CO)_6]$ [M = Cr or Mo; R′ = C_6H_4X (X = F, H, Me, NH_2, *etc.*); R = alkyl or aryl),[10,11] decreases the carbon shielding and ν(CO). Indeed, the ^{13}CO and $^{15}N_2$ co-ordination shifts appear to follow a similar pattern. The shifts relative to the free ligand are mostly in the direction of decreased shielding, as in the complexes described here (free N_2 has δ −75 p.p.m.). This shows the importance of $\pi \rightarrow \sigma^*$ (relative to $\sigma \rightarrow \pi^*$) paramagnetic circulations in the co-ordinated relative to the free ligand, since σ bonding and π back-bonding stabilise the σ framework relative to the π system. Measurements of the ^{13}C shielding tensor in transition metal carbonyls have shown that $\sigma_{\parallel}$ is large, as expected for a relatively free circulation about the MCO axis, and the main variation is in $\sigma_{\perp}$, which depends on $\sigma \longleftrightarrow \pi$ circulations.[10]

The $^{15}N_{\alpha}$ and ^{13}C shieldings also have similar periodicities in N_2– and CO–metal complexes, tending to increase with atomic number across the transition series (and down the group), in parallel with increase in the ligand-field splitting (Δ) for a given *d*-electron configuration, and with filling of the *d* shell, as from d^6 to d^8.[2] Strong deshielding of N_{α} and N_{β} is observed for N_2 bonded to metals early in the series, as in the (formally d^2) complexes of titanium and zirconium,[12] and this may be associated with paramagnetic circulations of N(π) electrons in low-lying *d* orbitals. Particularly strong deshielding is often observed for ligands bridging two metals, as in M–NN–M or M–C(O)–M. It has been pointed out [13] that ^{13}C shielding normally increases with π donation to organic carbonyl groups, because of destabilisation of the π^* l.u.m.o., as is also the case for nitrogen in hydrazones, and similar ligands.[14] Thus deshielding with increase in back-bonding in metal carbonyls is related to the availability of the $d\sigma^*$ l.u.m.o., giving the correlation with Δ.[13] In the isoelectronic CN^- ligand the ^{13}C shielding was found to decrease with decrease in *d-d* transition energy (from electronic spectroscopy), and with increase in the Mössbauer isomer shift (which also reflects the ligand-field strength), in a range of $[Fe^{II}(CN)_5L]^{q-}$ (L = CO, CN, NO, or nitrogen base; q = 2, 3, or 4) complexes.[15] The larger deshielding of N_{α} and N_{β} (on replacement of *trans* N_2 by *trans* NCR) in the tungsten than in the molybdenum complexes accords with an interpretation in terms of stronger π-acceptor properties of the N_2 ligand, the back-bonding tending to increase from the 4*d* to the 5*d* metal.

Electron release from the nitrile ligand can be varied by variation of the R group. In the complexes *trans*-$[Mo(^{15}N_2)(NCR)(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane], for example, the Table shows that $^{1}E_{\frac{1}{2}}^{\mathrm{ox}}$ decreases, as expected, with increased donor ability of the R group, and with decrease in the Hammett σ_p parameter for the 4-substituent in the benzonitriles. At the same time $\nu(N_2)$ decreases but ν(CN) increases (that is, the reduction of the free-ligand stretching frequency on complexation diminishes); there is a near-linear negative correlation of the two frequencies for a large range of these complexes.[4] Concomitantly the N_{α} shielding increases over a range of 24 p.p.m., although the N_{β} shift stays much the same; comparable shifts are observed in each of the series of complexes (A) [$(P{-}P)_2$ = $(dppe)_2$, $(depe)_2$, or (dppe)(depe)]. Again, the effect on the N_{α} shielding is larger in the tungsten than in the molybdenum series of complexes.

Thus increased electron release from the R group in the nitrile runs parallel with increase in the CN bond order and in electron density at the metal. Similarly in the isonitrile ligand, electron release from the R group appears to decrease the oxidation potential, increase ν(CN),[16] and increase the ^{13}C shielding.[17] These observations are consistent with a greater importance of σ- than π-donor effects at the metal, with these variations of the R group. The result in compounds (A) is then to reduce the $\pi \rightarrow \sigma^*$ and the $\sigma \rightarrow \pi^*$ contributions to the deshielding of N_{α}, more so in the tungsten than in the molybdenum compounds, but with little effect at N_{β}. Interestingly, ^{13}CO is deshielded on replacement of *trans* CO by PPh_3, which is a less electron-withdrawing ligand, and further deshielded on replacement of PPh_3 by the more electron-releasing ligand $P(C_6H_{11})_3$.[11]

Conclusions.—The shielding of both nitrogens in the N_2 ligand decreases with decrease in the ligand-field strength of the *trans* ligand from N_2 to RCN in parallel with the better π-acceptor properties of N_2 than RCN.[1,6,7] The N_α shielding in the N_2 ligand also increases with increase in 'ligand-field strength' of a *trans* nitrile ligand as its σ-donor ability increases, either with electron release from a 4-substituent in benzonitriles, or from an aryl to an alkyl R group. Thus the ^{15}N shifts provide useful supplementary data to those obtained by i.r. and electrochemical means as to electronic effects transmitted across the metal.

It is of interest to compare our ^{15}N n.m.r. results with those from ^{95}Mo n.m.r. spectroscopy of similar compounds.[18] The ^{95}Mo shielding decreases in the sequence of (triply bonded) ligands as CO > MeCN > N_2 > NO^+, which is one of decreasing nephelauxetic effect, as well as showing the influence of the spectrochemical series (decrease in ligand-field splitting).

Applications of ^{15}N *N.M.R. to Reactions of* RCN *with Dinitrogen Complexes*.—The correlations discussed above were derived mainly for complexes of molybdenum because these compounds could be obtained in highest purity and covered the largest range of ligands. The tungsten analogues are formed more slowly because of the lower rate of loss of N_2 from *trans*-$[M(N_2)_2(dppe)_2]$ for M = W as compared to M = Mo,[19] which can lead to problems of contamination of products with starting materials.

Loss of dinitrogen from complexes of series (A) [M = Mo, $(P^-P)_2$ = $(depe)_2$ or (depe)(dppe)] is also slower than from *trans*-$[Mo(N_2)_2(dppe)_2]$ because of the greater release of electrons to N_2 induced by the more basic depe ligand. However, substitution of N_2 by NCR does occur under irradiation of complexes (A) with NCR in the n.m.r. tube and the resonances of the products as well as those of the starting material could be observed, although it was not possible to obtain the pure compounds. The chemical shifts for these species are shown in the Table and clearly show the same trend as do complexes (A) (M = Mo, P^-P = dppe), *i.e.* deshielding of $^{15}N_\alpha$ on replacement of N_2 with NCR or with decreasing electron release from R.

Experimental

Solvents were purified before use by standard methods and manipulations of air-sensitive materials entailed standard Schlenk, vacuum, or glove-box techniques. $^{15}N_2$ gas (95% enriched) was used as purchased from Prochem Ltd. ^{15}N-labelled compounds were prepared by published methods [1,2] except as noted below.

Nitrogen-15 n.m.r. spectra of *ca.* 10^{-2} mol dm^{-3} solutions under argon were recorded at 18.24 MHz in sealed 25-mm tubes using a Bruker WH180 spectrometer and chemical shifts are corrected to neat CD_3NO_2 as reference. I.r. spectra were determined on Unicam SP2000 or SP200 spectrometers and electrochemical measurements were carried out by as described in the literature.[5] Microanalyses were by Mrs. G. Olney of Sussex University.

Preparation of trans-$[Mo(N_2)(NCC_6H_4F\text{-}4)(dppe)_2]$.—*trans*-$[Mo(N_2)_2(dppe)_2]$ (0.2 g) and 4-fluorobenzonitrile (76.6 mg, 3 mol equiv.) were stirred in tetrahydrofuran (thf) (*ca.* 40 cm^3) under argon for 18 h. The resultant dark green solution was concentrated to low volume *in vacuo*; the *green product* was precipitated by addition of hexane and recrystallised from thf–hexane. Yield 0.3 g, 59% (Found: C, 67.8; H, 5.1; N, 3.7. $C_{59}H_{52}FMoN_3P_4$ requires C, 68.0; H, 5.0; N, 4.0%). $\nu(N_2)$ (Nujol), 1 951 cm^{-1}; $\nu(^{15}N_2)$ (Nujol), 1 886 cm^{-1}; $\nu(CN)$ (Nujol), 2 118 cm^{-1}.

Reactions of trans-$[M(^{15}N_2)_2(P^-P)_2]$ *with* RCN [$(P^-P)_2$ = $(depe)_2$ *or* (depe)(dppe)].—These reactions were carried out in the n.m.r. tube containing a *ca.* 10^{-2} mol dm^{-3} solution of the dinitrogen complex and 1 mol equiv. of the nitrile. The tube was then irradiated with a 150-W tungsten filament lamp for *ca.* 10—16 h, to give an intense green solution. The ^{15}N spectrum of the solution showed the presence of $^{15}N_2$, starting material, and the product *trans*-$[M(^{15}N_2)(NCR)(P^-P)_2]$. Assignments of the ^{15}N resonances are in the Table.

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