Spectroscopy of Terminal Dinitrogen Complexes: Nitrogen-15 and Phosphorus-31 Nuclear Magnetic Resonance

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Nitrogen-15 chemical shifts and coupling constants are reported for terminal dinitrogen complexes of Mo, W, Re Fe, Ru, Os, and Rh. The nitrogen shielding shows a periodic variation with the central metal, increasing with increasing atomic number of the metal across the transition-metal series, or down a particular group, the increase being steeper for the metal-bound nitrogen N_α than for N_β. For complexes of metals later in the series N_α is more shielded than is N_β, but there appears to be a crossover at molybdenum, and possibly at or near tungsten. The ^{15}N shifts show evidence of interaction of adjacent dinitrogen ligands. The majority of compounds have phosphine co-ligands and their ^{31}P chemical shifts show a smaller sensitivity to change of the central metal (about half to three-quarters of that of the ^{15}N shifts) and also show chelate effects. The preparation, n.m.r. and redox properties of the new complexes *trans*-$[M(N_2)_2(depe)(dppe)]$ (M = Mo or W; depe = $Et_2PCH_2CH_2PEt_2$, dppe = $Ph_2PCH_2CH_2PPh_2$) are reported.

Dinitrogen complexes play a key role in current research into nitrogen fixation because they represent the first stage of the reduction of nitrogen gas, namely its activation towards reaction under mild conditions by co-ordination to a metal.[1] Such a metal–dinitrogen interaction may well occur in the nitrogenase enzyme and may be amenable to detection by spectroscopic methods.

Nitrogen-15 n.m.r. spectroscopy, potentially a powerful technique for nitrogen fixation studies, is becoming more accessible with the advent of high-field multinuclear spectrometers, if high ^{15}N enrichment is possible, and herein we describe a ^{15}N n.m.r. study of a wide range of dinitrogen complexes.

Results and Discussion

^{15}N *Chemical Shifts and Coupling Constants.*—The chemical shifts of the terminal dinitrogen complexes are shown in Table 1, most of the compounds studied being octahedral (d^6) complexes with tertiary phosphine co-ligands. In general for these complexes two resonances are seen, the one at higher field having the larger coupling to phosphorus. In many chemical groups the internuclear spin–spin coupling is larger over three than two bonds, but several lines of evidence support our assignment of the higher-field resonance to the metal-bound nitrogen, N_α. We have already explained [2,3] that we do not expect N_α to have a reduced value of $|^2J(P^{15}N)|$, in contrast to $|^2J(C^{15}N)|$ in pyridine for example, which is unusually small. This is because the nitrogen in pyridine carries an *s*-hybridised lone pair which gives a large contribution to the Fermi contact term that opposes the contribution from the bonding orbitals (the orbital and spin-dipolar contributions being relatively small).[4] It should be noted, moreover, that $|^2J(^{15}N_\alpha H)| > |^3J(^{15}N_\beta H)|$ in ethyl diazoacetate, $EtOC(O)-CHN_2$,[5] in which the one-bond NN coupling is similar to those of the dinitrogen complexes described herein.

As further evidence for assigning the resonance with the larger coupling to phosphorus to N_α, there is the additional coupling to the metal that is observed when this has spin $\frac{1}{2}$, as for ^{183}W and ^{103}Rh, and coupling also to the proton in $[FeH(N_2)(dppe)_2]BPh_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (Table 1). This resonance also shows greater sensitivity to change in the metal, as in the periodic variation described below. On the other hand, the (N_β) line, with the smaller coupling to phosphorus, shows the greater sensitivity to solvent and temperature effects (as does the terminal nitrogen in NNO)[6] and to adduct formation ($MN_2 \longrightarrow MNNM$),[3,7] and sometimes shows larger nuclear Overhauser effects than the N_α resonance.[7]

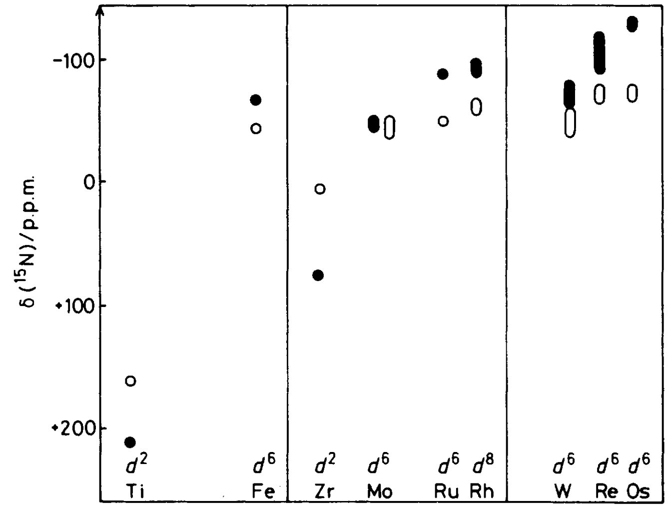

Figure 1. Periodic dependence of ^{15}N chemical shifts; filled symbols correspond to N_α, open symbols to N_β

In the complex *trans*-$[Mo(^{15}N_2)_2(dppe)_2]$ however, the two nitrogen resonances are near-coincident, and in *trans*-$[Mo(^{15}N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) the lower-field signal shows the greater coupling to phosphorus (Table 1). This, and the overall pattern of the periodic variation, suggests that a crossover of the resonance positions is occurring, as has been observed for the N_β and N_γ resonances in azides, $X-N_\alpha N_\beta N_\gamma$, in which X is a more electronegative ligand (such as Cl, ^-CN, or perfluoroaryl), relative to $RN_\alpha N_\beta N_\gamma$ with R = H, alkyl, or aryl *etc.*[8]

It is evident from Figure 1, which shows the periodic dependence of the N_α and N_β shifts, that the N_α resonance is the more sensitive to change in the metal. Both resonances move upfield with increase in atomic number of the metal

Table 1. Nitrogen-15 chemical shifts and coupling constants for dinitrogen complexes [a]

Complex	Solvent	T/K	$\delta(^{15}\mathrm{N}_\alpha)_{\mathrm{corr}}$/ p.p.m.	$\delta(^{15}\mathrm{N}_\beta)_{\mathrm{corr}}$/ p.p.m.	$^1J(^{15}\mathrm{N}^{15}\mathrm{N})$/ Hz	$J(^{15}\mathrm{N}^{31}\mathrm{P})$/Hz	Ref.
$[\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})_2(^{15}\mathrm{N}_2)\}_2\mathrm{N}_2]$ [b]	Toluene	212	+214.4	+165.0	7		15
$[\{\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5Me_5})_2(^{15}\mathrm{N}_2)\}_2\mathrm{N}_2]$ [c]	Toluene	245	+73.5	+4.5	6.2		15
trans-$[\mathrm{Mo}(^{15}\mathrm{N}_2)_2(\mathrm{dppe})_2]$	thf	amb.	−43.1	−42.8	4		2
	Toluene	233	−45.1	−45.1	n.r.		This work
trans-$[\mathrm{Mo}(^{15}\mathrm{N}_2)_2(\mathrm{depe})_2]$	thf	amb.	−42.0	−43.4	5.7 [d]	2.4 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ [d]	This work
	Toluene	288	−42.5	−43.8			This work
	Toluene	243	−43.8	−46.1			This work
cis-$[\mathrm{Mo}(^{15}\mathrm{N}_2)_2(\mathrm{PMe_2Ph})_4]$	thf	amb.	−39.2	−31.5	6	5.2 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})_{trans}]$	2
trans-$[\mathrm{WH}(^{15}\mathrm{N}_2)_2(\mathrm{dppe})_2]\mathrm{HCl}_2$	thf	amb.	−75.3	−49.3	4	n.r.	3, *e*
trans-$[\mathrm{W}(^{15}\mathrm{N}_2)_2(\mathrm{dppe})_2]$	thf	amb.	−60.1	−48.6	5.4	2 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ 0.9 $[^3J(^{15}\mathrm{N}_\beta{}^{31}\mathrm{P})]$	2
	Toluene	233	−66.6	−55.5	n.r.	n.r.	This work
trans-$[\mathrm{W}(^{15}\mathrm{N}_2)_2(\mathrm{depe})_2]$ [f]	thf	291	−63.7	−52.4	6	2 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$	This work
cis-$[\mathrm{W}(^{15}\mathrm{N}_2)_2(\mathrm{PMe_2Ph})_4]$ [g]	thf	amb.	−57.8	−32.5	6.2	16.7 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})_{trans}]$ 1.2 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})_{cis}]$ 0.9 $[^3J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$	2
trans-$[\mathrm{ReCl}(^{15}\mathrm{N}_2)(\mathrm{dppe})_2]$	$\mathrm{CH_2Cl_2}$	amb.	−92.3	n.o.	6	n.r.	This work
trans-$[\mathrm{ReCl}(^{15}\mathrm{N}_2)(\mathrm{dmtpe})_2]$	$\mathrm{CH_2Cl_2}$	298	−91.4	−69.1	6	n.r.	This work
trans-$[\mathrm{ReCl}(^{15}\mathrm{N}_2)(\mathrm{PMe_2Ph})_4]$	thf	298	−85.9	−64.2	4		3, *e*
	thf	298	−86.2	−60.7	6.8 [d]	1.2 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ [d]	This work
	Toluene	233	−87.2	−63.9	6	n.r	This work
	$\mathrm{CH_2Cl_2}$	298	−86.1 [h]	−63.4 [h]	7—8		*i*
	$\mathrm{CH_2Cl_2}$	173	−82.6 [h]	−67.7 [h]			
$[\mathrm{ReCl}(^{15}\mathrm{N}_2)(\mathrm{CO})\{\mathrm{C(OH)Me}\}(\mathrm{PPh_3})_2]$	thf	amb.	−111.2		4	n.r.	*j* and This work
trans-$[\mathrm{FeH}(^{15}\mathrm{N}_2)(\mathrm{dppe})_2]\mathrm{BPh}_4$ [k]	thf	amb.	−61.1	−37.9	4	2 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$	3, *e*
$[\mathrm{Ru(NH_3)_5N_2}]\mathrm{Br}_2$	HCl (10^{-3} mol dm^{-3})	295	−81.3	−43.8			This work
mer-$[\mathrm{OsCl_2}(^{15}\mathrm{N}_2)(\mathrm{PMe_2Ph})_3]$	thf	amb.	−120.2	−65.4	4	n.r.	This work
	Toluene	233	−120.3	−66.8	n.r.	n.r.	This work
mer-$[\mathrm{OsBr_2}(^{15}\mathrm{N}_2)(\mathrm{PMe_2Ph})_3]$	thf	273	−122.6	−63.6	4.5	2 $[^2J(^{15}\mathrm{N}^{31}\mathrm{P})]$	3, *e*
mer-$\{\mathrm{OsHCl}(^{15}\mathrm{N}_2)(\mathrm{PMe_2Ph})_3]$	thf	amb.	−121.0	−67.9	4		This work
mer-$[\mathrm{OsHBr}(^{15}\mathrm{N}_2)(\mathrm{PMe_2Ph})_3]$	thf	amb.	−122.6	−67.3	4	n.r.	This work
mer-$[\mathrm{OsCl_2}(^{15}\mathrm{N}_2)(\mathrm{PEt_2Ph})_3]$	thf	amb.	n.o.	−63.4	n.r.	1 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ [l]	This work
mer-$[\mathrm{OsBr_2}(^{15}\mathrm{N}_2)(\mathrm{PEt_2Ph})_3]$	thf	amb.	n.o.	−62.8	4	1.5 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ [l]	This work
trans-$[\mathrm{RhCl}(^{15}\mathrm{N}_2)(\mathrm{PPr^i_3})_2]$ [m]	Toluene	303	−85 (5) [n]	−52 (5) [n]	4	4 $\{^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$	*o*
trans-$[\mathrm{RhCl}(^{15}\mathrm{N}_2)\{\mathrm{P(C_6H_{11})_3}\}_2]$ [p]	$\mathrm{CH_2Cl_2}$	298	−90.7	−59.2	5	4 $[^2J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ 0.8 $[^3J(^{15}\mathrm{N}_\alpha{}^{31}\mathrm{P})]$ [d]	This work

[a] Chemical shifts relative to neat nitromethane (external) and corrected for $[\mathrm{Cr(pd)_3}]$ in reference (see Experimental Section); amb. = ambient, n.r. = not resolved, n.o. = not observed. [b] Referenced originally to $[\mathrm{NEt_4}]\mathrm{Cl}$ (11 mol dm^{-3} in $\mathrm{H_2O}$), converted to neat nitromethane scale. [c] Referenced originally to $\mathrm{HNO_3}$, converted to neat nitromethane scale. [d] Coupling constant measured at $\nu_0 = 40.5$ MHz (this work). [e] C. T. Kan, Ph.D. Thesis, University of Sussex, 1979. [f] $^1J(^{183}\mathrm{W}^{15}\mathrm{N}) = 48$ Hz (see also footnote *d*). [g] $^1J(^{183}\mathrm{W}^{15}\mathrm{N}) = 66.9$ Hz (see also footnote *d*). [h] Referenced originally to 1 mol dm^{-3} $\mathrm{DNO_3}$, correction to nitromethane scale = −4.4 p.p.m. [i] A. L. Blumenfeld, V. C. Lenenko, B. Lorentz, I. Mobius, M. Nahrea, V. B. Shur, and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, 1980, **251**, 611. [j] D. R. Stanley, unpublished work. [k] $^2J(^{15}\mathrm{N}_\alpha{}^1\mathrm{H}) = 3$ Hz. [l] Determined from ^{31}P spectrum. [m] $^1J(^{103}\mathrm{Rh}^{15}\mathrm{N}_\alpha) = 28$, $^2J(^{103}\mathrm{Rh}^{15}\mathrm{N}_\beta) = 4$ Hz. [n] Referenced originally to $^{15}\mathrm{NH_4}^+$, concentration not stated. [o] D. L. Thorn, T. H. Tulip, and J. A. Ibers, *J. Chem. Soc., Dalton Trans.*, 1979, 2022. [p] $^1J(^{103}\mathrm{Rh}^{15}\mathrm{N}_\alpha) = 30$ Hz.

across the transition-metal series, and down a particular group, the changes being greater for N_α than for N_β. Similar periodicities are observed in the ^{13}C resonance for transition-metal carbonyl [9,10] and some cyanide [11] complexes, in the ^{15}N resonance in the same cyanides,[11] in the ^{15}N resonance in linear nitrosyls,[12,13] and in the ^{17}O resonance in carbonyl complexes.[14] The trends for the metals of Groups 6—8 suggest a crossover of N_α and N_β resonances at molybdenum and perhaps a corresponding crossover in the third transition series, and it is on this basis that we have (very tentatively) assigned the nitrogen resonances reported by Bercaw and co-workers [15] for titanium and zirconium complexes to N_α and N_β in Table 1. As yet there is no other evidence for their assignment, and we hope that future work with early and middle transition-metal complexes will clarify the position.

The tendency for ligand nuclear magnetic shielding to increase down a given group of the transition elements is more readily demonstrated than the trend across the series because of the greater ease of observing strictly comparable compounds in the same group. Indeed, in corresponding complexes of molybdenum and tungsten the ^{15}N shifts of N_α and N_β in dinitrogen, diazenido, and hydrazido(2−) ligands show a linear correlation (with correlation coefficient 0.996) [equation (i)].[7]

$$\delta(^{15}\mathrm{N})(\mathrm{W\ complex}) = \delta(^{15}\mathrm{N})(\mathrm{Mo\ complex}) + 14(\pm 5) \quad \text{(i)}$$

This group trend for a transition element as neighbour resembles that observed for a main-group element as neighbour.[16] The increase in shielding may be related to the tendency for polarisability to increase down the group with concomitant increase in radius of paramagnetic circulations (increased nephelauxetic effect), and to the tendency for the ligand-field splitting to increase down the group.[17] The trend across the transition-metal series, interestingly, is opposite to the trend to *decreased* shielding across the row of a main-group element as neighbour. This deshielding is particularly large in fluorinated compounds, and seems to be related to a decrease in radius of the paramagnetic circulation with increase in ($-I$) electron-withdrawing inductive effect of the neighbour, despite the increase in the relevant excitation energies across the row.[18] Across the transition-metal series, however, electronegativity changes are smaller, and the dominant influence seems to be the tendency for ligand-field splittings (and $\sigma \longleftrightarrow \pi$ excitation energies) to increase (for corresponding compounds).[18]

The importance of ($\sigma \longleftrightarrow \pi$) excitation energies to ^{15}N shielding in the (linear) nitrosyl group is evident from the sizeable deshielding, by 50—150 p.p.m., observed for *cis*-dinitrosyl complexes compared with corresponding mononitrosyls (of Mo or W,[19] Co, Ru, Rh, or Os [13]). The solid-state structures provide some evidence for the interaction of adjacent nitrosyls as the NMN angle is often enlarged, and the MNO group slightly bent with angles of 159—180°. In 120°-bent nitrosyls the nitrogen is strongly deshielded, by 350—700 p.p.m., compared with corresponding linear mononitrosyls.[12,13] As in organic nitroso-compounds,[16] the deshielding is linked to low-energy $n(N) \longrightarrow \pi^*$ circulations; the lone-pair highest occupied molecular orbital (h.o.m.o.), though linked to the σ framework, is high-lying, and the π^* lowest unoccupied molecular orbital (l.u.m.o.) is low-lying because of the electronegativity of oxygen. The ^{17}O nucleus shows similar deshieldings.[20]

With the example of the nitrosyl group in mind, we may compare the nitrogen shieldings (measured under the same conditions) in the *cis*- and *trans*-bis(dinitrogen) complexes of molybdenum and tungsten in Table 1. The *cis*-$(N_2)_2$ compounds have monophosphine (PMe_2Ph) co-ligands and the *trans* compounds have diphosphine (dppe or depe) co-ligands, but the N_α shifts are little affected by exchange of depe for dppe, or of N_2 for phosphine as *trans* ligand. There is, however, a significant deshielding of N_β in the *cis* compared with the *trans*-$(N_2)_2$ complexes, by 12 p.p.m. in the Mo compounds and by 17—20 p.p.m. in the W compounds. [N_α is deshielded by 2—6 p.p.m. in the *cis* compared to the *trans*-$(N_2)_2$ compounds, but this small change could be attributable to *trans* effects as well as to *cis* interactions.] Thus the chemical shift may be a sensitive detector of interactions between *cis* ligands which are not evident from the geometry in the solid state.

Coupling Constants.—(*a*) $|^1J(^{15}N_\alpha{}^{15}N_\beta)|$ *values.* These values in the dinitrogen complexes span the range 4—7 Hz and, within the limits of precision of measurement, are close to the value for ethyl diazoacetate [$^1J(^{15}N^{15}N) = 5.6$ Hz].[5] Their relatively small magnitude has been discussed [2,3] in terms of the one-bond effect of the *s*-hybridised lone pair on nitrogen making a large contribution to the Fermi contact term, which tends to cancel the contribution from the bonding electrons.[4]

(*b*) $|^1J(^{15}N_\alpha M)|$ *values.* These values have been observed for dinitrogen complexes of rhodium and tungsten (Table 1). The $^1J(^{15}N_\alpha{}^{183}W)$ values are obtained from the high-field resonance of the tungsten complexes, coupling to the lower-field resonance being too small to be resolved, as expected for the assignment of this resonance to N_β. The ^1J values (48 and 67 Hz) are smaller than those observed in hydrazido(2−) complexes (114—125 Hz)[2,3] and imido-complexes (98—140 Hz)[7] in

Table 2. Phosphorus-31 chemical shifts and coupling constants for dinitrogen complexes [a]

Complex	Solvent	$\delta(^{31}P)$/p.p.m.	J/Hz	Ref.
trans-$[Mo(N_2)_2(dppe)_2]$	thf thf	−75.3 −84.5		2 *b* and This work
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	thf	−132.3		*c*
trans-$[W(N_2)_2(dppe)_2]$	thf thf	−95.0 −104.2	322 [$^1J(^{183}W^{31}P)$] 303 [$^1J(^{183}W^{31}P)$]	*c* *b* and This work
cis-$[W(N_2)_2(PMe_2Ph)_4]$	thf	−155.8 −156.1	5 [$^2J(^{31}P^{31}P)$] 313 [$^1J(^{183}W^{31}P)$] 309 [$^1J(^{183}W^{31}P)$]	*c*
trans-$[ReCl(N_2)(dppe)_2]$	CH_2Cl_2	−113.1		*b* and This work
trans-$[ReCl(N_2)(dmtpe)_2]$	CH_2Cl_2	−112.5		This work
trans-$[ReCl(N_2)(PMe_2Ph)_4]$	thf	−172.2 −172.6		This work
mer-$[OsCl_2(N_2)(PMe_2Ph)_3]$	thf	−175 [d,e]	14.7 [$^2J(^{31}P^{31}P)$]	2, 4, and This work
mer-$[OsBr_2(N_2)(PMe_2Ph)_3]$	thf	−183.5 (d) −179.7 (t)	14.7 [$^2J(^{31}P^{31}P)$]	This work
mer-$[OsHCl(N_2)(PMe_2Ph)_3]$	thf	−172.9 (d) −181.1 (t)	14.7 [$^2J(^{31}P^{31}P)$]	This work
mer-$[OsHBr(N_2)(PMe_2Ph)_3]$	thf	−176.4 (d) −186.3 (t)	14.7 [$^2J(^{31}P^{31}P)$]	This work
mer-$[OsCl_2(N_2)(PEt_2Ph)_3]$	thf	−168.1 (d) −163.8 (t)	14.7 [$^2J(^{31}P^{31}P)$]	This work
mer-$[OsBr_2(N_2)(PEt_2Ph)_3]$	thf	−176.1 (d) −166.6 (t)	14.7 [$^2J(^{31}P^{31}P)$]	This work
trans-$[RhCl(N_2)\{P(C_6H_{11})_3\}_2]$	CH_2Cl_2	−101.1	120 [$^1J(^{103}Rh^{31}P)$]	This work
trans-$[RhCl(N_2)(PPr^i{}_3)_2]$	Toluene	−99.2	122 [$^1J(^{103}Rh^{31}P)$]	*f*

[a] Chemical shifts relative to trimethyl phosphite (tmp)/C_6D_6 (external, which has δ −140.4 relative to 85% H_3PO_4; measured on a JEOL FX90Q spectrometer at 36.2 MHz [$\delta(^{31}P)$ for free phosphines relative to tmp: $P(C_6H_{11})_3$ −130.9 (benzene); PMe_2Ph −183.1 (thf); PEt_2Ph −156.6 (thf); dppe −153.0 (CH_2Cl_2); depe −159.7 (thf); dmtpe −153.1 (thf)] [b] W. Hussain, G. J. Leigh, and D. Rankin, unpublished work. [c] M. E. Fakley, Ph.D. Thesis, University of Sussex, 1979. [d] Doublet and triplet are overlapping; previously observed [24] as a broad singlet at 148.5 relative to P_4O_6 (internal). [e] Originally referenced to 85% H_3PO_4, corrected to tmp scale. [f] D. L. Thorn, T. H. Tulip, and J. A. Ibers, *J. Chem. Soc., Dalton Trans.*, 1979, 2022.

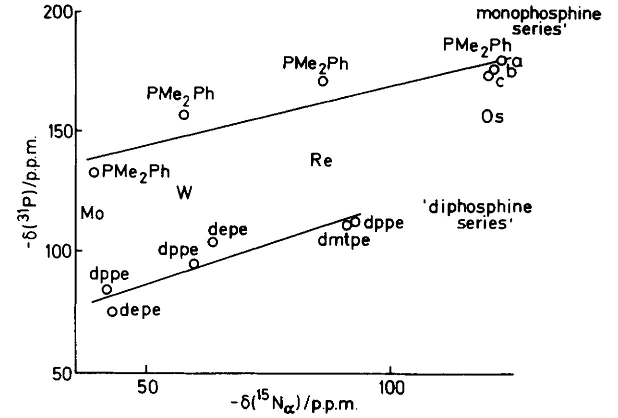

Figure 2. Correlation between ^{31}P chemical shift and $^{15}N_\alpha$ chemical shift in d^6 octahedral terminal dinitrogen complexes with tertiary phosphine co-ligands. *mer*-[OsXY(N$_2$)(PMe$_2$Ph)$_3$]: (a) X = Y = Br; (b) X = H, Y = Cl; (c) X = Y = Cl

parallel with the higher W–N bond order in the latter complexes.

(*c*) $|^2J(^{15}N_\alpha{}^{31}P)|$ *values.* These are generally small, being of the order of 1–2 Hz for *cis*-^{31}P and 5—16 Hz for *trans*-^{31}P. $|^3J(^{15}N_\alpha{}^{31}P)|$ values, where observed, are somewhat less than 1 Hz (Table 1). The higher coupling is generally to the higher-field resonance of the dinitrogen ligand which is assigned to $^{15}N_\alpha$ as discussed above and elsewhere.[2,3]

Effect of Solvent and Temperature on $\delta(^{15}N)$.—In those complexes for which a temperature or solvent dependence is observed, *i.e.* *trans*-[M($^{15}N_2$)$_2$(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$] (M = Mo or W, R = Ph or Et) and *trans*-[ReCl($^{15}N_2$)(PMe$_2$Ph)$_4$] (Table 1), $\delta(^{15}N_\beta)$ is found to be slightly more sensitive to these effects than is $^{15}N_\alpha$. This may be a consequence of $^{15}N_\beta$ being in a less protected environment than is $^{15}N_\alpha$, as indicated by space-filling models. This interpretation is consistent with the observation that the shielding of the more exposed terminal nitrogen in N_2O is more sensitive to the presence of other molecules and is more temperature dependent than is the central nitrogen atom.[6]

^{31}P *Chemical Shifts and their Correlation with* ^{15}N *Shifts.*—The theme of periodicity of chemical shifts is continued in the $\delta(^{31}P)$ values for dinitrogen complexes shown in Table 2. The variation of $\delta(^{31}P)$ with metal is the same as for $\delta(^{15}N)$ and for the phosphine complexes studied falls into two distinct series depending upon whether the phosphines are monodentate or bidentate as is illustrated in Figure 2.

The reduction in phosphorus shielding by 50—65 p.p.m. in the bidentate-phosphine complexes as compared with the monodentate-phosphine complexes resembles the ring contribution for a five-membered metallocycle, as documented by Garrou.[21]

In Figure 2 the plot of $\delta(^{31}P)$ *versus* $\delta(^{15}N)$ is linear for the two series of complexes: *trans*-[M($^{15}N_2$)$_2$(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$] (M = Mo or W, R = Et or Ph) and *trans*-[ReCl($^{15}N_2$)(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$] [R = C$_6$H$_4$Me-*m* (dmtpe) or Ph] and *cis*-[M($^{15}N_2$)$_2$(PMe$_2$Ph)$_4$] (M = Mo or W), *trans*-[ReCl($^{15}N_2$)(PMe$_2$Ph)$_4$], and *mer*-[OsXY($^{15}N_2$)(PMe$_2$Ph)$_3$] (X = Cl, Br, or H; Y = Cl or Br). The metal influence is clearly evident.

As expected, the ^{31}P shifts are the more sensitive to changes in the phosphine ligands and the lines in Figure 2 corresponding to the two series of complexes are close to parallel, *i.e.* both nuclei appear to be experiencing effects in the same direction.

Linear relationships between ^{15}N and ^{31}P chemical shifts have been found for aminophosphines[22] and correlations between $\delta(^{15}N)$ and shifts for other nuclei (X) (X = ^1H, ^{13}C, ^{19}F, *etc.*) have been expressed in the form $\delta(^{15}N) = a\delta(X) + b$,[23] but no data for metal complexes were included. It was proposed[23] that where the slope (*a*) of a plot of $\delta(^{15}N)$ *versus* $\delta(X)$ is positive, the two nuclei under consideration are in equivalent positions in the molecule in the sense that electronic effects are transmitted in the same direction for both, as appears to be the case for $\delta(^{15}N)$ and $\delta(^{31}P)$ in these dinitrogen complexes. The magnitude of *a* (1.5—1.8 in Figure 2) is considered to be a measure of the relative sensitivities of the two nuclei to electronic effects (from the central metal in our case). Thus the ^{15}N chemical shifts of these dinitrogen complexes are some 1.5 to 2 times more sensitive to changes in the metal than are their ^{31}P chemical shifts.

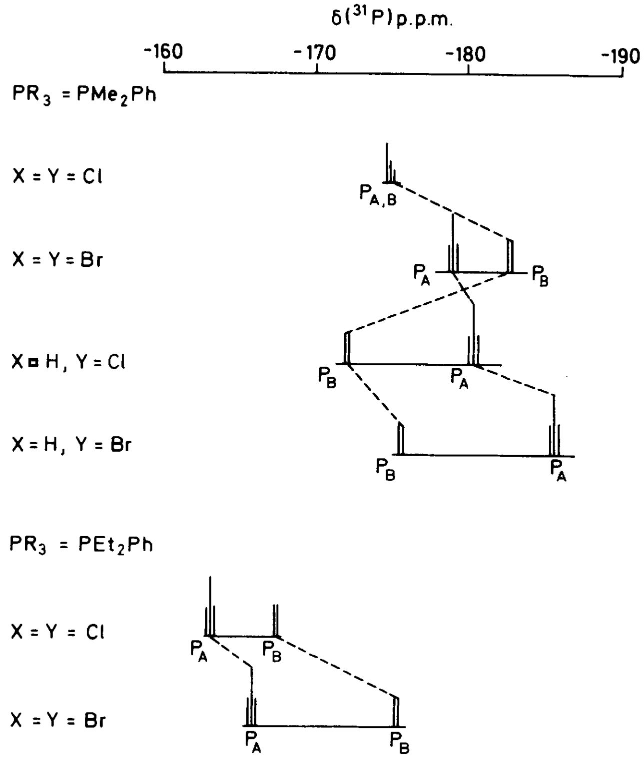

Figure 3. Phosphorus-31 n.m.r. spectra (schematic) for *mer*-[OsXY(N$_2$)(PR$_3$)$_3$] (PR$_3$ = PMe$_2$Ph or PEt$_2$Ph)

^{31}P *N.M.R. Spectra of mer*-[OsXY(N$_2$)(PR$_3$)$_3$] (X = Cl, Br, or H; Y = Cl *or* Br; PR$_3$ = PMe$_2$Ph *or* PEt$_2$Ph).—These complexes (whose geometry is shown below) show a characteristic ^{31}P pattern for the meridional phosphine array consisting of a doublet for the *trans* pair (P$_B$) and a triplet for the unique phosphine (P$_A$).[24]

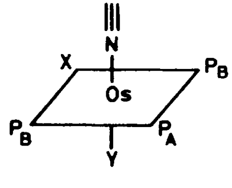

Figure 3 shows differing *cis*- and *trans*-influences of co-ligands X and Y. Replacing X = halide *trans* to P$_A$ by H

Table 3. Data of $\nu(N_2)$, $^{1}E_{\frac{1}{2}}^{ox}$, and n.m.r. for *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ and *trans*-$[M(N_2)_2$(depe)(dppe)] (M = Mo or W; R = Et or Ph) [a]

Complex	$\delta(^{15}N_\alpha)$/ p.p.m.	$\delta(^{15}N_\beta)$/ p.p.m.	$\delta(^{31}P)$/p.p.m.	$\delta(^{95}Mo)$/ p.p.m.	$^{1}E_{\frac{1}{2}}^{ox}$/V (*vs.* s.c.e.)	$\nu(^{14}N_2)/cm^{-1}$ (Nujol)
trans-$[Mo(N_2)_2(depe)_2]$	−42.0	−43.4	−84.5	−1 022	−0.43 [b]	1 928
trans-$[Mo(N_2)_2$(depe)(dppe)]	−41.2		AA′BB′ pattern, centred at −87.8, −72.9	−899	−0.28	1 945
trans-$[Mo(N_2)_2(dppe)_2]$	−43.1	−42.8	−75.3	−787	−0.16 [b]	1 976
trans-$[W(N_2)_2(depe)_2]$	−63.7	−52.4	−104.2		−0.45 [b]	1 891
trans-$[W(N_2)_2$(depe)(dppe)]	−59.4	−47.4	AA′BB pattern, centred at −92.4, −108.2		−0.29	1 929
trans-$[W(N_2)_2(dppe)_2]$	−60.1	−48.6	−95.0		−0.15 [b]	1 946

[a] ^{15}N N.m.r. shifts relative to neat nitromethane (external) at 18.25 MHz, ^{31}P n.m.r. shifts relative to tmp–C_6D_6 (external), and ^{95}Mo n.m.r. shifts relative to $Na_2[MoO_4]$ (2 mol dm^{-3}), pH = 11.5 (external); for all downfield is positive (thf solution). [b] Ref. 26.

increases the shielding of P_A but deshields P_B, whereas replacing X or Y = chloride by bromide increases the shielding of both *cis*- and *trans*-phosphorus.

Preparation of trans-$[M(N_2)_2$(depe)(dppe)] (A).—During the course of this work the two new 'mixed phosphine' complexes (A) were prepared from dinitrogen gas ($^{14}N_2$ or $^{15}N_2$) according to reaction (ii). They are characterised by the

$$[MCl_4(\text{depe})] + \text{dppe} \xrightarrow[N_2]{Mg,\ thf} [M(N_2)_2(\text{depe})(\text{dppe})] \quad \text{(ii)}$$

physical properties shown in Table 3 which includes data for *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ (M = Mo or W, R = Et or Ph) for comparison. The $^{1}E_{\frac{1}{2}}^{OX}$, $\nu(N_2)$, and $\delta(^{95}Mo)$ values for (A) are mid-way between those of the parent *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ species, but the $\delta(^{15}N)$ values of (A) are slightly to lower field of those of the parents.

The ^{31}P n.m.r. spectra of compounds (A) consist of an AA′BB′ pattern which in the case of (A; M = W) was analysed by computer simulation to yield the coupling constants: $^{2}J(PP)_{trans}$ = 106.7, $^{2}J(PP)_{cis}$ = 20, and $^{3}J(PP)$ = −10 Hz.

Conclusions

The region of ^{15}N chemical shift for terminal dinitrogen complexes has been defined and the dependence of $\delta(^{15}N)$ for ligating $^{15}N_2$ upon the central metal atom demonstrated. $\delta(^{15}N)$ Chemical shifts in metal complexes appear to be more sensitive to change of the central metal atom than do ^{31}P chemical shifts. Chemical shifts of both nuclei show some dependence upon co-ligand which is small in comparison to the dependence upon the central metal atom.

Experimental

Solvents were dried and distilled under dinitrogen or argon as appropriate before use. Manipulations of air-sensitive materials entailed standard vacuum, Schlenk-tube, or glove-box techniques. Except where described below, the preparation of dinitrogen complexes followed published procedures.[2,3,24,25] 95% Enriched $^{15}N_2$ was purchased from Prochem Ltd. and used as supplied.

Solutions for n.m.r. measurements were made up under argon and concentrations were typically *ca.* 10^{-2} mol dm^{-3}. ^{31}P Spectra were recorded at 36.2 MHz on a JEOL FX90Q spectrometer. ^{15}N Spectra were recorded on the FX90Q spectrometer at 9.04 MHz, on a Bruker WH180 spectrometer at 18.24 MHz at P.C.M.U. (Harwell) in 25-mm tubes, or at 40.5 MHz on a Bruker WH400 spectrometer at Queen Mary College, London. Susceptibility corrections were applied to allow for differences in concentration of the $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) relaxation agent in the reference standard ($MeNO_2$) and the sample. Cyclic voltammetry was carried out using the published technique.[26]

Preparation of trans-$[ReCl(N_2)$(dmtpe)] [dmtpe = (*m*-$MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me$-*m*$)_2$].—This complex was prepared by a published method [27] as yellow crystals but could not be obtained analytically pure (Found: C, 60.7; H, 5.9; N, 1.9. $C_{60}H_{64}ClN_2P_4Re$ requires C, 58.0; H, 4.7; N, 2.4%), $\nu(N_2)$ (Nujol) = 1 955 cm^{-1}; $\nu(^{15}N_2)$ = 1 889 cm^{-1}.

Preparation of trans-$[M(N_2)$(depe)(dppe)] (A; M = Mo or W).—(*i*) (A; M = W). $[WCl_4$(depe)] (1.2 g) and dppe (0.9 g) in tetrahydrofuran (thf) (50 cm^3) were stirred with magnesium (*ca.* 3 g) for 18 h under dinitrogen. The resulting orange-brown solution was filtered through Celite, concentrated in a vacuum to low volume and the *orange-brown product* isolated by addition of methanol (50 cm^3) and recrystallised from thf–methanol. Yield 0.7 g (37%) (Found: C, 51.0; H, 5.6; N, 6.4. $C_{36}H_{48}N_4P_4W$ requires C, 51.2; H, 5.7; N, 6.6%).

(*ii*) (A; M = Mo). This was similarly prepared from $[MoCl_4$(depe)] as an orange product which always contained about 25% of *trans*-$[Mo(N_2)_2(depe)_2]$ as impurity, which could be clearly distinguished from *trans*-$[Mo(N_2)_2$(depe)(dppe)] in all physical measurements (Table 3).

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