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# $^{15}N$ NMR Spectra of Metal Complexes Relevant to Nitrogen Fixation

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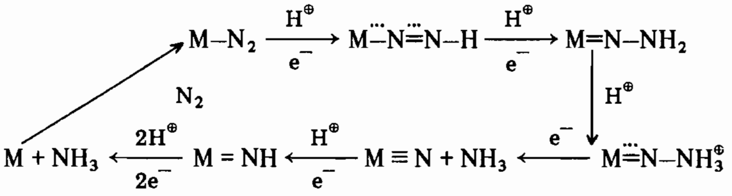
Following studies of the reactions of dinitrogen complexes leading to the formation of ammonia, a mechanism for the reductive degradation of ligating dinitrogen to ammonia has been proposed [1] (Scheme).



Scheme

This mechanism, which involves dinitrogen, diazenido-, nitrene and nitrido-complex intermediates, is based upon the isolation of stable complexes and may relate to the mode of action of nitrogenase at the atomic level.

$^{15}N$ NMR spectroscopy provides a means of observing the behaviour of such species in solution and we are determining the $^{15}N$ parameters of a range of examples of these complexes so that we may apply this technique to the study of reactions which lead to the reduction of dinitrogen. The appearance of a brief report of a $^{15}N$ NMR study of dinitrogen and related complexes [2] prompts us to present here our observations on a wide range of complexes, the $^{15}N$ parameters of which are shown in Tables I and II.

Our preliminary conclusions concerning these and related [3, 4] data are as follows:

(a) The regions of chemical shift observed for the various ligands allow them to be distinguished one

TABLE I. $^{15}N$ NMR Parameters for Dinitrogen Complexes.[a]

| Complex | $\delta\,^{15}N_\alpha$, ppm (±0.1) | $\delta\,^{15}N_\beta$, ppm (±0.1) | $^1J(^{15}N^{15}N)$, Hz (±1) | J(other), Hz (±1) | Solvent |
|---|---|---|---|---|---|
| $[WH(^{15}N_2)_2(dppe)_2]HCl_2$ | −78.7 | −52.7 | 4 | | thf |
| *trans*-$[ReCl(^{15}N_2)(PMe_2Ph)_4]$ | −89.3 | −67.6 | 4 | $^2J(^{15}N_\alpha{}^{31}P)$, 5 | thf |
| | −91.2 | −67.3 | 4 | | toluene (−40 °C) |
| | $-86.1^b$ | $-63.4^b$ | $3-5^b$ | | $CH_2Cl_2{}^b$ |
| *trans*-$[FeH(^{15}N_2)(dppe)_2]BPh_4$ | −64.5 | −41.3 | 4 | $^2J(^{15}N_\alpha{}^{31}P)$, 2<br>$^3J(^{15}N_\alpha H)$, 3 | thf |
| *mer*-$[OsCl_2(^{15}N_2)(PMe_2Ph)_3]$ | −118.5 | −63.7 | 4 | | thf |
| *mer*-$[OsHCl(^{15}N_2)(PMe_2Ph)_3]^c$ | −119.2 | −65.9 | 4 | | thf |
| *mer*-$[OsBr_2(^{15}N_2)(PMe_2Ph)_3]$ | −126.0 | −67.0 | 4.5 | $^2J(^{15}N_\alpha{}^{31}P)$, $2^d$ | thf |
| *mer*-$[OsHBr(^{15}N_2)(PMe_2Ph)_3]^c$ | −120.9 | −65.6 | 4 | | thf |
| *mer*-$[OsCl_2(^{15}N_2)(PEt_2Ph)_3]^c$ | n.o. | −61.7 | n.o. | $^2J(^{15}N_\alpha{}^{31}P)$, $1^d$ | thf |
| *mer*-$[OsBr_2(^{15}N_2)(PEt_2Ph)_3]$ | n.o. | −61.1 | 4 | $^2J(^{15}N_\alpha{}^{31}P)$, $1.5^d$ | thf |
| *trans*-$[RhCl(^{15}N_2)\{P(C_6H_{11})_3\}_2]^c$ | −94.0 | −62.5 | 5 | $^1J(^{103}Rh^{15}N_\alpha)$, 30<br>$^2J(^{15}N_\alpha{}^{31}P)$, 4<br>$^3J(^{15}N_\beta{}^{31}P)$, 0.8 | $CH_2Cl_2$ |
| $[\{Ru(NH_3)_5\}_2{}^{15}N_2][BF_4]$ | $+210.8^e$ | | | | $H_2O$ |
| *trans*-$[ReCl(^{15}N_2AlMe_3)(PMe_2Ph)_4]$ | −88.8 | −133.2 | n.o. | | toluene (−40 °C) |
| *mer*-$[OsCl_2)(^{15}N_2AlMe_3)(PMe_2Ph)_3]$ | −104.0 | −139.6 | n.o. | | toluene (−40 °C) |

[a] Chemical shifts relative to $C^2H_3NO_2$, Bruker WP180 or JEOL FX900 instruments, approx. $10^{-3}$ *M* solutions, 25 °C. [b] Taken from ref. 2. [c] $Cr(acetylacetonate)_3$ (~1 mg/ml) added. [d] Determined from $^{31}P$ spectrum. [e] Bridging $^{15}N_2$; n.o. = not observed.

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TABLE II. $^{15}N$ NMR Parameters for Diazenido-, Nitrene and Nitrido-complexes.[a]

| Complex | $^{15}N_\alpha$, ppm | $^{15}N_\beta$, ppm | $J(^{15}N^{15}N)$, Hz | J(other), Hz | Solvent |
|---|---|---|---|---|---|
| *trans*-$[WF(^{15}N_2H)(dppe)_2]$ | −24.6 | −182.6[b] | 14(2) | $J(^{15}N_\beta H)$, ~60<br>$J(^{15}N_\alpha{}^{19}F)$, ~60 | thf |
| *trans*-$[WBr(^{15}N_2H)(dppe)_2]$ | −25.9 | −187.1[b] | 14(2) | $J(^{15}N_\beta H)$, 60.5(2) | thf (−40 °C) |
| $[ReCl_2(^{15}N)(PPr^nPh_2)_2]$ | 82.4 | | | | $CH_2Cl_2$ |
| $[ReCl_2(^{15}N)(PMe_2Ph)_3]$ | 64.8 | | | | $CH_2Cl_2$ |
| $[ReCl(^{15}N)(dppe)_2]Cl$ | 63.7 | | | | $CH_2Cl_2$ |
| $[Mo^{15}N(S_2CNEt_2)_3]$ | 36.7 | | | | $CH_2Cl_2$ |
| *trans*-$[MoCl(^{15}NH)(dppe)_2]Cl$ | 29.9 | | | $J(^{15}NH)$, 72(1) | $CH_2Cl_2$ |

[a]Chemical shifts relative to $C^2H_3NO_2$. [b]Inverted due to NOE in noise decoupled spectrum.

from another in a mixture and from hydrazido (2−) complexes [3] [$\delta(^{15}N_\alpha)$ −64 to −101 ppm, $\delta(^{15}N_\beta)$ −220 to −260 ppm] which are also intermediates in the Scheme.

(*b*) Provisional assignment of the $^{15}N_\alpha$ and $^{15}N_\beta$ dinitrogen resonances in the mononuclear complexes follows our earlier proposal based on the expected greater coupling of $^{15}N_\alpha$ to phosphorus [4]. On coordination of $AlMe_3$ to $^{15}N_\beta$, giving the adducts [5] shown in Table I, the resonance assigned to $^{15}N_\alpha$ is little affected, moving slightly downfield, but the $N_\beta$ resonance, which is broadened by the $^{27}Al$ quadrupole, moves upfield by about 70 ppm. Such a coordination shift is consistent with stabilisation of the $n_N(\sigma)$ lone pair electrons (relative to the $\pi^*$ LUMO) by formation of the bond to aluminium. Thus the $^{15}N_\beta$ shifts of the adducts are comparable to those of 'singly-bent' $(M{-}N{-}N\diagdown_{R})$ diazenido-ligands (*e.g.* $[ReCl(N_2CoPh)(C_5H_5)(PPh_3)_2]$ (−148.6) [6] and $[WBr(N_2H)(dppe)_2]$ (Table II)).

In strong contrast are the resonances some 250–450 ppm downfield for dinitrogen bridging two transition metals in $[\{Ru(NH_3)_5\}_2(N_2)]^{4+}$ (Table I) and $[\{M(C_5Me_5)_2(N_2)\}_2(N_2)]$ (M = Ti or Zr) [4, 7]. In these complexes the dinitrogen is part of an extensive delocalised system and it is reasonable that the deshielding should correlate with low-lying $\sigma \leftrightarrow \pi$ states.

(*c*) In general there is a shift to higher field of $^{15}N_\alpha$ (and to a lesser extent $^{15}N_\beta$) resonances of dinitrogen complexes on passing to the heavier members of the groups and along the periods of the transition metal series. Comparable behaviour is observed for CO ligands in $^{13}C$ resonance [8].

These data are now being extended and also applied to study of protonation of dinitrogen complexes in solution, where hydrazido (2−) complex intermediates have been clearly observed [9] and to other reactions which lead to the degradation or substitution of dinitrogen.

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