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Preliminary communication

^{15}N NMR SPECTROSCOPY AS A PROBE FOR THE GEOMETRY OF DIAZENIDO LIGANDS

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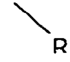
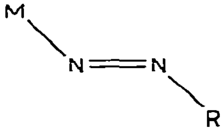
Summary

A useful criterion of linear or bent geometry at N_α of diazenido ($-N_\alpha N_\beta R$) ligands is afforded by ^{15}N NMR. A very large downfield shift (ca. 350 ppm) of the N_α resonance is reported for the "doubly-bent" diazenido ligands in $[RhCl_2(^{15}NNC_6H_4R\text{-}4)(PPh_3)_2]$ (R = H or NO_2) compared with the "singly-bent" diazenido ligands in *trans*-$[MX(^{15}N_2R^1)(dppe)_2]$ (M = Mo or W, X = Cl or Br, R^1 = Et or COMe), $[ReCl_2(^{15}N_2COC_6H_5)(C_5H_5N)(PPh_3)_2]$ and $[RuCl_3(^{15}NNC_6H_5)(PPh_3)_2]$.

Diazenido ligands can adopt the "singly-bent" (A) or "doubly-bent" (B) geometry in their complexes, depending upon the electronic condition of the metal [1]. During the course of our studies of the ^{15}N NMR properties of complexes relevant to nitrogen fixation [2], we have found that ^{15}N NMR provides a means of distinguishing clearly and easily which geometric form of the diazenido ligand is adopted in solution.



(A)



(B)

TABLE 1

^{15}N CHEMICAL SHIFTS OF DIAZENIDO COMPLEXES[a] (dppe = $PPh_2CH_2CH_2PPh_2$

Complex	$\delta(N_\alpha)$	$\delta(N_\beta)$	$J(^{15}N^{15}N)$	Geometry
$[MoBr(^{15}N_2Et)(dppe)_2]$	−29.0 [b]	−146.8 [b,c]	12.0	A
$[WBr(^{15}N_2Et)(dppe)_2]$	−28.2 [b]	−164.7 [b,c]	11.9	A
$[MoCl(^{15}N_2COMe)(dppe)_2]$	−35.4 [b]	−123.7 [b,c]	ca. 12	A
$[WCl(^{15}N_2COMe)(dppe)_2]$	−32.2 [b]	−134.5 [b,c]	12.0	A
$[ReCl_2(^{15}N_2COPh)(C_5H_5N)(PPh_3)_2]$	−55.9 [d]	−148.6 [d]	15.0	A
$[RuCl_3(^{15}NNC_6H_5)(PPh_3)_2]$	−46.8 [e]	—	—	A
$[RhCl_2(^{15}NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$	327.1 [e]	—	—	B
$[RhCl_3(^{15}NHNC_6H_4NO_2\text{-}4)(PPh_3)_2]$	200.1 [c,e]	—	—	
$[RhCl_2(^{15}NNC_6H_5)(PPh_3)_2]$	298.4 [e]			B

[a] Chemical shifts relative to external $C^2H_3NO_2$, ± 0.1 ppm; coupling constants ± 2 Hz. [b] Tetrahydrofuran solution. [c] Inverted signal. [d] Toluene solution. [e] CH_2Cl_2 solution.

We have prepared the series of diazenido complexes shown in Table 1, labelled at N_α or both nitrogen atoms. The doubly-labelled molybdenum [3], tungsten [3] and rhenium [4] complexes contain the (A) form of the diazenido ligand and show two resonances at (−28 to −56 ppm) and (−123 to −165 ppm), to high field of $C^2H_3NO_2$. The complex $[RuCl_3(^{15}NNC_6H_5)(PPh_3)_2]$ also has the (A)-form ligand and $^{15}N_\alpha$ resonates at −46.8 ppm. Thus the lower-field signal in these diazenido complexes is assigned to N_α and that at higher field to N_β.

In proton-decoupled spectra, the higher field resonance shows a Nuclear Overhauser Effect (NOE) which is negative because of the negative gyromagnetic ratio of ^{15}N. Thus for the molybdenum and tungsten complexes, this signal is inverted and is the more intense; for the rhenium complex it is upright, but weaker than the lower-field signal. The lower-field signal is broader for the molybdenum and tungsten complexes, presumably by coupling with ^{31}P nuclei of the phosphine co-ligands, and shows little or no NOE. The observation of NOE is consistent with assignment of the high field resonance to N_β and presumably arises from interaction with nearby, non-bonded protons either from alkyl or acyl substituents or, less probably, solvent or solvent impurities. A similar effect, has, for example, been observed in *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraaceto complexes [5].

The N_α region for the molybdenum, tungsten, rhenium and ruthenium complexes (−28 to −60 ppm) is close to that observed (δ −60 to −100 ppm) for N_α in hydrazido(2−) (=NH_2) complexes [2] and for terminal nitrogen in aryl diazonium salts (−14 to −70 ppm) [6]. Nitrogen bonded to carbon in aryl diazonium ions absorbs in the range −120 to −158 ppm, matching the region observed for our N_β (Table 1).

The singly-labelled (at N_α) rhodium complexes have the (B) geometry [1] and the N_α resonance is dramatically shifted to around 300 ppm downfield of $C^2H_3NO_2$. This very large downfield shift makes the assignment of the (B) geometry obvious. It is presumably associated with the deshielding effect of the high lone pair character at N_α (low-lying ($n \rightarrow \pi^*$) state) and as expected on this basis, protonation of N_α in $[RhCl_2(^{15}NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ to give $[RhCl_3(^{15}NHNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ causes an upfield shift of N_α of 127 ppm (Table 1). A similar upfield shift (150.4 ppm) occurs on protonation of azobenzene [7]. Resonance at low field is observed for bent, conjugated nitrogen in *trans*-aryl diazenes (δ 120—190 ppm) [7] and for the central nitrogen in [tosyl-NNN-tosyl]$^-$, which shows a dramatic downfield shift of 286 ppm relative to the central nitrogen of the linear azide ion [8].

Thus ^{15}N NMR shifts reflect the remarkable electronic lability of NN groups and provide an unambiguous technique for distinguishing the geometry of diazenido ligands in solution. We are extending our studies to a wider range of complexes.

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