# Nitrogen-15 N.M.R. Evidence for Rapid Intramolecular Interconversion of Linear and Bent Nitrosyl Ligands in $[RuCl(NO)_2(PPh_3)_2](BF_4)$, with Observation of a Nitrogen-14,15 Equilibrium Isotope Effect

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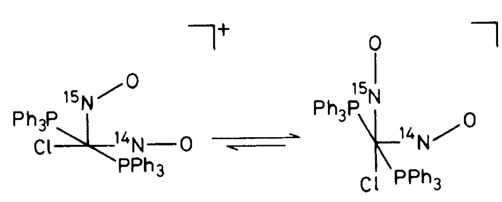
$^{15}$N N.m.r. evidence is presented for rapid intramolecular interconversion of bent and linear nitrosyl ligands in $[RuCl(NO)_2(PPh_3)_2](BF_4)$ in solution, from an $^{14,15}$N equilibrium isotope effect observed with semi-$^{15}$N-enrichment; also for the contribution of more than one co-ordination geometry to the fluxionality, and for slow intermolecular nitrosyl exchange.

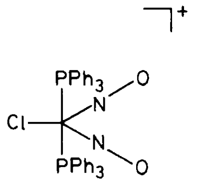
The five-co-ordinate complex $[RuCl(NO)_2(PPh_3)_2](BF_4)$ (**1**) was shown by single crystal *X*-ray crystallography by Eisenberg and co-workers to represent the first example of a complex containing both linear and strongly bent nitrosyl ligands (with MNO angles of 179.5 and 136°).[1] We have recently found that this structure in the solid is clearly demonstrated by $^{15}$N cross-polarization magic-angle-spinning (CP/MAS) n.m.r. spectroscopy, since resonances giving isotropic shifts of 26 and 303 p.p.m. (relative to neat liquid nitromethane) were observed for the linear and bent nitrosyl ligands respectively.[2] The assignments were based on the very large $^{15}$N shielding anisotropy in the bent ligand,[2] and on solution studies which had demonstrated large nitrogen deshieldings in strongly bent nitrosyl groups relative to corresponding linear nitrosyls.[3—6] Smaller deshielding is observed for the slightly bent ligand, as in some dinitrosyls.[6]

The structure of (**1**) in solution is of considerable interest because of Collman *et al.*'s proposal[7] that the nitrosyl ligands undergo the rapid intramolecular fluxional process (**1a**) $\leftrightarrows$ (**1b**). The evidence for this was circumstantial: the i.r. absorption of the solid product of the addition of $NOBF_4$ to a solution of the mononitrosyl $[RuCl(^{15}NO)(PPh_3)_2]$ showed that $^{14,15}$N scrambling had occurred. A trigonal bipyramidal form such as (**2**) was proposed as an intermediate,[1a,7] although exchange between co-ordinated and free $NO^+$ provides another possible mechanism.

In contrast to the two $^{15}$N resonances observed for the solid, $^{15}$N spectra of solutions of $[RuCl(^{15}NO)_2(PPh_3)_2](BF_4)$ (with



**(1a)** **(1b)**



**(2)**

**Table 1.** $^{15}N$ N.m.r. shifts (in p.p.m. relative to neat liquid nitromethane, high frequency positive) for $[RuCl(^{15}NO)_2(PPh_3)_2]^+$ and $[RuCl(^{14}NO)(^{15}NO)(PPh_3)_2]^+$ as a function of solvent and temperature.

| Solvent | Temp./K | $\delta[Ru(^{14}NO)(^{15}NO)]$ | $\delta[Ru(^{15}NO)_2]$ |
|---|---|---|---|
| $(CD_3)_2CO$ | 303 | 130.2 | 131.2 |
|  | 223 | 131.3 | 132.9 |
| $CD_3OD$. | 223 | 125.9 | 127.2 |
| $CD_2Cl_2$ | 293 | 125.6 | 125.9 |
|  | 223 | 121.6 | 122.8 |

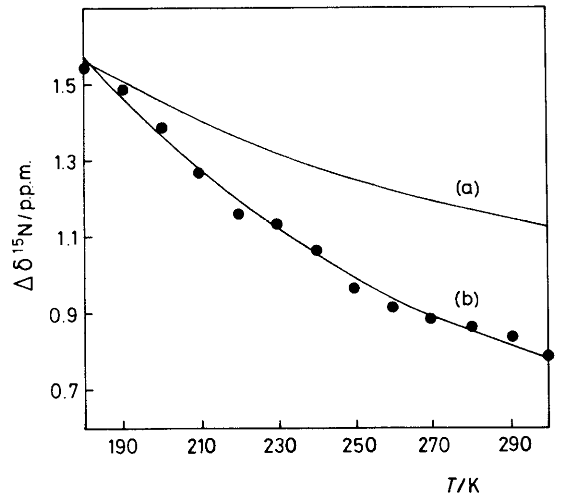


**Figure 1.** Temperature-dependence of the $^{14,15}N$ equilibrium isotope effect shown by semi-$^{15}N$-enriched $[RuCl(NO)_2(PPh_3)_2](BF_4)$. $\Delta\delta$ is the difference in $^{15}N$ shift from the $(^{15}NO)_2$ to the $(^{15}NO)(^{14}NO)$ complex, high frequency positive. ● experimental. (a) Calculated $\Delta\delta$ for the equilibrium system (**1a**) $\leftrightarrows$ (**1b**) with $\Delta_{zp}$ = 20 J mol$^{-1}$ and $(\delta_b - \delta_l)$ = 277 p.p.m. (see text). (b) Calculated $\Delta\delta$ for the equilibrium system (**1a**) $\leftrightarrows$ (**1b**) $\leftrightarrows$ (**2**) with $\Delta_{zp}$ = 42 J mol$^{-1}$, $\delta_b - \delta_l$ = 277 p.p.m. in (**1**), $\delta^{15}N$ = 30 p.p.m. in (**2**), and an average free energy difference between (**1**) and (**2**) of 2.58 kJ mol$^{-1}$.

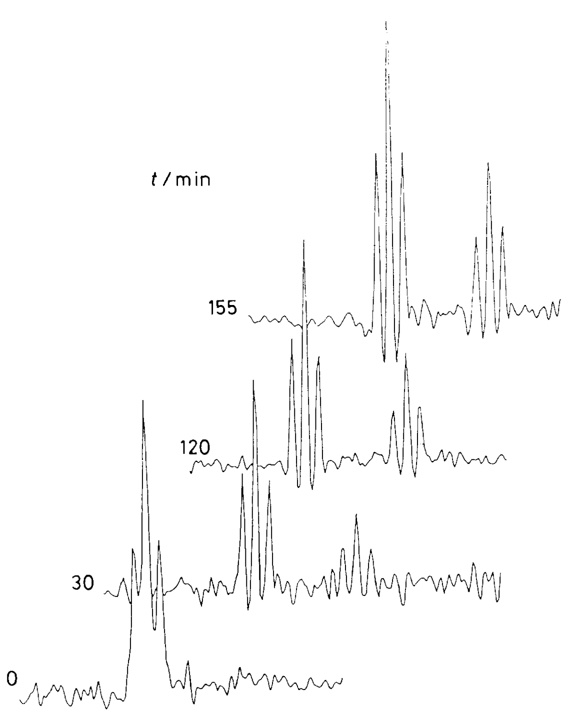


**Figure 2.** Evolution of two $^{15}N$ resonances with time after the mixing of $CD_2Cl_2$ solutions of $[RuCl(^{15}NO)_2(PPh_3)_2](BF_4)$ and $[RuCl(NO)_2(PPh_3)_2](BF_4)$ at room temperature. Equilibrium was attained after approx. 3 h.

99% $^{15}N$-enrichment) show a single resonance only, a triplet with $\delta^{15}N$ *ca.* 130 p.p.m. and $^2J(^{31}P^{15}N)$ 2.5 Hz. This was observed over the temperature range 183—300 K with little line-broadening even at low temperatures ($w_{\frac{1}{2}}$ *ca.* 7 Hz). The shift is both solvent- and temperature-dependent; examples are given in Table 1. These spectra might be consistent with rapid (**1a**)–(**1b**) fluxionality, which must be intramolecular as the coupling is preserved, or with an alternative structure in solution such as (**2**), with equivalent nitrosyls.

Interestingly, the $^{15}N$ n.m.r. spectrum with 50% enrichment shows a doubling of the $^{15}N$ resonance. Whether synthesized by the addition of $NOBF_4$ to $[RuCl(^{15}NO)(PPh_3)_2]$ or by the equilibration of the $(^{14}NO)_2$ with the $(^{15}NO)_2$ species of complex (**1**) for several hours, the semi-$^{15}N$-enriched material shows two triplet resonances, each with $^2J(^{31}P^{15}N)$ 2.5 Hz as before, separated by *ca.* 1.0 p.p.m. at 300 K and 1.6 p.p.m. at 183 K (Figure 1). The equilibration process was followed by $^{15}N$ n.m.r., as shown in Figure 2.

We attribute this doubling to an equilibrium isotope effect.[8,9] For rapid (**1a**) $\leftrightarrows$ (**1b**) fluxionality this is associated with a small difference in averaged shielding for the $(^{15}NO)_2$ and $(^{14}NO)(^{15}NO)$ species present in statistical proportion. Since the NO stretching frequency is about 200 cm$^{-1}$ lower for a nitrosyl when strongly bent than when linear, with a lower zero-point energy for the heavier nucleus, $^{15}NO$ is very slightly favoured in the linear geometry in the $(^{14}NO)(^{15}NO)$ species. This therefore shows a higher averaged shielding than the $(^{15}NO)_2$ species and gives a second resonance. In general zero-point energy differences are small for nuclei heavier than $^{1,2}H$. This $^{14,15}N$ equilibrium isotope effect for bent and linear nitrosyls is observable because of the large differences in NO stretching frequencies and chemical shifts.

However, greater complexity is present in this system than is represented by fluxionality involving only the square pyramidal structure, as shown in the averaged shifts, and in their dependence on temperature. The $^{15}N$ shift in solution of *ca.* 130 p.p.m. represents an increase in shielding of 34.5 p.p.m. compared with the average of the isotropic shifts in the solid, 164.5 p.p.m. For the four-co-ordinate dinitrosyl $[Ru(NO)_2(PPh_3)_2]$, however, the shift in solution (50.7 p.p.m.

in benzene)[6] shows a *de*crease in shielding of 12 p.p.m. relative to the solid,[2] which is comparable in magnitude with known solvent effects for nitrogen. The increase in the averaged shielding on dissolution of (**1**) suggests that an alternative structure such as (**2**) with two linear nitrosyls may be present as well in the solution.

Figure 1 compares the observed temperature-dependence of the difference in shift ($\Delta\delta$) for the two isotopomers in $CD_2Cl_2$ solution with two calculated curves (a) and (b). Curve (a) was calculated for the isotope effect in the (**1a**) $\leftrightharpoons$ (**1b**) equilibrium, with the bent-linear difference in shift ($\delta_b - \delta_l$) taken as 277 p.p.m. as in the solid state, and a zero-point energy difference ($\Delta_{zp}$) of 20 J mol$^{-1}$. Curve (a) shows that the observed effect has the expected order of magnitude but has an anomalous temperature-dependence. This discrepancy, also, is consistent with the participation in the equilibrium of a structure such as (**2**). A full analysis of the problem in terms of two isolated systems with six levels by statistical mechanics requires five independent parameters, so an exact solution lies outside our scope. Reasonable estimates of these parameters, as shown in Figure 1(b), give a good fit with the experimental points. The nitrogen shift in the bipyramidal structure (**2**) of 30 p.p.m. was estimated from those reported for the related compounds $[Ru(NO)_2(PPh_3)_2]$ and $[RuCl_3(NO)(PPh_3)_2]$.[6] This analysis suggests the presence of 27% of (**2**) and 73% of (**1**) at room temperature. The presence of an additional structure in solution was confirmed by the observation of $\nu(^{14}NO)$ bands at 1828, 1778, 1739(sh.), and 1722 cm$^{-1}$ in methanol as compared with 1845, 1687 cm$^{-1}$ in the solid.

The $^{15}N$ spectra were obtained on the Bruker AM 250 spectrometer in the Dyson-Perrins Laboratory, University of Oxford. We thank David Tew, Dominic Evans, and Drs. Eirian Curzon and Oliver Howarth for preliminary measurements on the S.E.R.C.-funded WH 400 spectrometer at the University of Warwick.

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