End-to-end Rotation of Co-ordinated Dinitrogen in $(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)$

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The rate of linkage isomerization of $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{15}N{\equiv}^{14}N)$ to give $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{14}N{\equiv}^{15}N)$ has been measured from ^{15}N NMR intensities, yielding a $\Delta G^{\ddagger}$ value of 90 kJ mol^{-1} for the end-to-end rotation process; this is confirmed to be intramolecular and non-dissociative by a cross-over experiment using $(\eta^5\text{-}C_5H_5)Re(CO)_2(^{14}N{\equiv}^{14}N)$ and $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{15}N{\equiv}^{14}N)$.

We report results that clearly demonstrate the end-to-end rotation of co-ordinated dinitrogen in a mononuclear complex. The details of the co-ordination mode and dynamics of ligated dinitrogen are of fundamental interest with regard to its activation, reduction, or chemical transformation, especially in biological nitrogen fixation. Dinitrogen universally occurs as an end-on (η^1) bonded ligand in all the known isolable mononuclear complexes to date, with one possible exception.[1] Interest therefore centres on the accessibility of the side-on (η^2) bonded form of this ligand, either in stable complexes or as an excited state. Evidence has been presented that it may occur, for example, in a matrix-isolated cobalt system, though this could be binuclear.[2] Side-on dinitrogen is well established for polynuclear systems.[3]

We have reported previously[4] that when the arenediazenide complex (**2**), labelled only at the metal-bound nitrogen N_{α} with ^{15}N, was converted by Bu^{t}Li or $NaBH_4$ to the dinitrogen complex (**1**) the ^{15}N NMR spectrum (acetone/[$^2H_6$]acetone) of the isolated product showed equal intensity resonances in both N_{α} (δ −111) and N_{β} (δ −28) positions demonstrating this to be an equimolar mixture of the linkage isomers (**1**)-$^{15}N_{\alpha}$ and (**1**)-$^{15}N_{\beta}$. This is true also for the cyclopentadienyl analogue $(\eta\text{-}C_5H_5)Re(CO)_2(^{15}N^{14}N)$, the corresponding values being δ −121 (N_{α}) and δ −58 (N_{β}).[4,5]†

We have devised a method by which ^{15}N labelled (**1**) can be generated from (**2**) cleanly, quickly, and in high yield at or below room temperature, so that the process responsible for the scrambling of the ^{15}N label can be determined from ^{15}N NMR spectroscopy.

A slight excess of cobaltocene, $(C_5H_5)_2Co$, was added to (**2**) (*ca.* 100 mg) in acetone (4 ml) at 0 °C. The IR spectrum, recorded immediately, showed the complete disappearance of (**2**) and the only absorptions in the 2200—1600 cm^{-1} region were from (**1**), at 2089 cm^{-1} [ν(NN)] and 1941, 1883 cm^{-1} [ν(CO)]. The ^{15}N NMR spectrum at 287 K, recorded within 27 minutes of the addition (400 scans, 16 min total acquisition time), exhibited only a ^{15}N resonance at δ −110, unambiguously demonstrating that (**1**)-$^{15}N_{\alpha}$ is the initial product. This eliminates the possibility that nitrogen scrambling results from a side-on dinitrogen complex being first formed [as perhaps from a side-bonded intermediate such as (**3**)] in the conversion of (**2**) to (**1**). A sequence of ^{15}N NMR spectra accumulated in the same manner then showed the decay of the δ −110 resonance from (**1**)-$^{15}N_{\alpha}$, and growth of the resonance at δ −27 from (**1**)-$^{15}N_{\beta}$; equilibrium was established in *ca.* 3 h (Figure 1).

A mixture of $(\eta^5\text{-}C_5H_5)Re(CO)_2(^{14}N^{14}N)$ [ν(NN) 2144 cm^{-1}] and $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{15}N^{14}N)$ (**1**) [1 : 1 mixture of (**1**)-$^{15}N_{\alpha}$ and (**1**)-$^{15}N_{\beta}$; ν(NN) coincident at 2091 cm^{-1}][4] in hexane was observed by IR spectroscopy at room temperature

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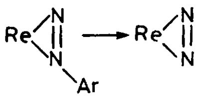
† ^{15}N NMR data are in p.p.m. with respect to external neat $Me^{15}NO_2$.

$(\eta^5\text{—}C_5Me_5)Re(CO)_2(^{15}N^{14}N)$ $(\eta^5\text{—}C_5Me_5)Re(CO)_2(^{14}N^{15}N)$

(**1**)—$^{15}N_\alpha$ (**1**)—$^{15}N_\beta$

$[(\eta^5\text{—}C_5Me_5)Re(CO)_2(^{15}NNAr)][BF_4]$

(**2**)—$^{15}N_\alpha$ (Ar = p-C_6H_4OMe)



(**3**)

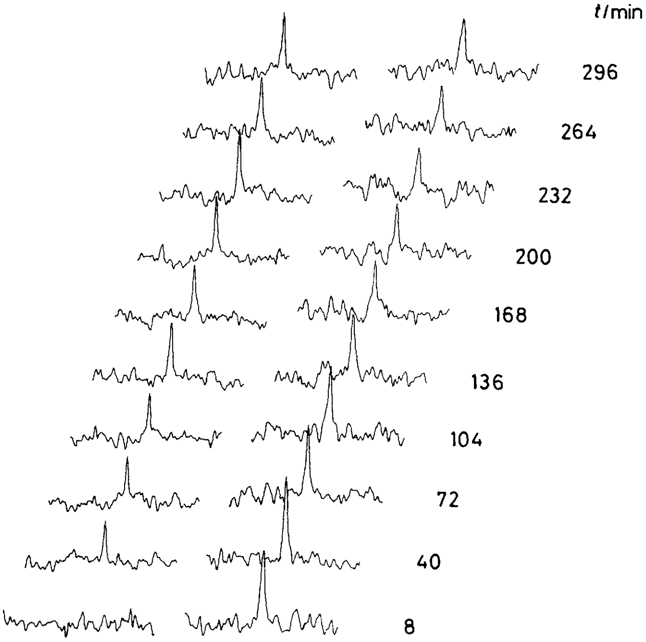
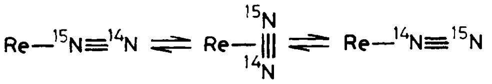


Figure 1. Time dependence of the $^{15}N_\alpha$ (right; δ −110) and $^{15}N_\beta$ (left; δ −27) resonances in the 40.56 MHz ^{15}N NMR spectrum of $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{15}N{\equiv}^{14}N)$ (**1**).

over a period of 3 weeks. The ν(NN) absorptions of the ^{15}N and ^{14}N isotopomers of these two complexes (C_5H_5 or C_5Me_5) are sharp in hexane, are quite characteristic, and would readily indicate if any cross products were formed. We observed no change; specifically, no absorptions attributable to $(\eta^5\text{-}C_5H_5)Re(CO)_2(^{15}N^{14}N)$ [ν(NN) 2110 cm^{-1}] or $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{14}N^{14}N)$ [ν(NN) 2124 cm^{-1}]. Also, no exchange of (**1**) with external $^{14}N_2$ at atmospheric pressure occurs.[4] Therefore, the scrambling of the label in (**1**) is intramolecular and non-dissociative (Scheme 1).



$$Re\text{—}^{15}N{\equiv}^{14}N \rightleftharpoons Re\text{—}\overset{^{15}N}{\underset{^{14}N}{|||}} \rightleftharpoons Re\text{—}^{14}N{\equiv}^{15}N$$

Scheme 1

The first order rate constant at 287 K was found to be 1.45 (±0.05) × 10^{-2} min^{-1}, providing a $\Delta G^\ddagger$ value of 90.1 (±0.1) kJ mol^{-1} for the barrier to rotation at this temperature. This is similar to the barrier estimated from IR spectroscopy for $[Ru(NH_3)_5(N_2)]^{2+}$, which is the only other example that we are aware of for which the barrier for linkage isomerization of co-ordinated N_2 has been estimated;[6] isomerization of N_2 was observed in related Ru complexes.[7] The observed relatively slow rate of exchange in (**1**) accounts for the inability to observe this exchange previously by magnetization transfer in ^{15}N NMR.[4] Replacement of one CO group by PMe_3 raises the barrier to the point where no exchange of $^{15}N_\alpha$-labelled $(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)(N_2)$ is observed.[4] Thus, this system provides an opportunity to examine how the relative energies of end-on and side-on bound N_2 are affected by ligand substitution.

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