# End-to-End Rotation of Rhenium-Bound Dinitrogen

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The singly $^{15}N$-labeled dinitrogen complexes Cp′Re(CO)(L)($^{15}N^{14}N$) (Cp′ = $\eta^5$-$C_5H_5$, L = CO **(1-$^{15}N_\alpha$)** and Cp′ = $\eta^5$-$C_5Me_5$, L = CO **(2-$^{15}N_\alpha$)**, $PMe_3$ **(3-$^{15}N_\alpha$)**, or $P(OMe)_3$ **(4-$^{15}N_\alpha$)**) were synthesized from the corresponding aryldiazenido complex [Cp′Re(CO)(L)($^{15}N^{14}NC_6H_4OMe$)][$BF_4$] by treatment with $Ph_3C$, $Cp_2Co$, Na/Hg, or $NaBH_4$. When these dinitrogen complexes are freshly synthesized, the $^{15}N$ label is exclusively retained in the metal-bound ($N_\alpha$) position irrespective of the reagent used. At 291 K **1-$^{15}N_\alpha$** isomerizes in acetone to give a 1:1 mixture of **1-$^{15}N_\alpha$** and **1-$^{15}N_\beta$**, as indicated by the intensities of the $^{15}N_\alpha$ and $^{15}N_\beta$ resonances in the $^{15}N$ NMR spectra, with rate constant $k_{obs} = (48 \pm 6) \times 10^{-6}$ s$^{-1}$ and $\Delta G^{\ddagger} = 95.3 \pm 0.5$ kJ mol$^{-1}$. For **2-$^{15}N_\alpha$** isomerization occurs similarly, and the temperature dependence over the range 274−291 K yielded $\Delta G^{\ddagger}_{291} = 92.6 \pm 0.4$ kJ mol$^{-1}$, $\Delta H^{\ddagger} = 105.3 \pm 6.0$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = 43.5 \pm 21.2$ J mol$^{-1}$ K$^{-1}$, $E_a = 106.8 \pm 5.4$ kJ mol$^{-1}$, and $A = (2.1 \pm 1.3) \times 10^{-15}$ s$^{-1}$. As a consequence of the linkage isomerization, samples of **1-$^{15}$N** and **2-$^{15}$N** obtained from any of the above syntheses following normal isolation and purification procedures are inevitably 1:1 mixtures of the $^{15}N_\alpha$ and $^{15}N_\beta$ isotopomers. The dinitrogen complexes **3-$^{15}N_\alpha$** and **4-$^{15}N_\alpha$** do not isomerize at ambient temperature, and isolated samples are the pure $^{15}N_\alpha$ isotopomer. However, at higher temperatures both **3-$^{15}N_\alpha$** (at 333 K) and **4-$^{15}N_\alpha$** (at 320 K) isomerize to 1:1 $^{15}N_\alpha$ and $^{15}N_\beta$ mixtures. Neither **1-$^{15}$N** nor **2-$^{15}$N** exchanged with bulk $^{14}N_2$ under pressure at room temperature, nor did **3-$^{15}$N** or **4-$^{15}$N** at 333 or 320 K, respectively, over several half-lives for the isomerization. A mixture of unlabeled **1** and **2-$^{15}$N** showed no evidence of formation of the cross products (unlabeled **2** and **1-$^{15}$N**) at room temperature, and a mixture of unlabeled **4** and **3-$^{15}$N** showed no cross-product formation at 333 K. It is concluded that linkage isomerization of the dinitrogen ligand is nondissociative and intramolecular. The proposed mechanism is end-to-end rotation through the intermediacy of a side-on ($\eta^2$) dinitrogen complex.



## Introduction

The details of the coordination mode and dynamics of ligated dinitrogen are of fundamental interest with regard to its activation, reduction, and chemical transformation.[1−3] Dinitrogen typically binds to a mononuclear metal center in an end-on ($\eta^1$) fashion with a linear or near-linear MNN skeleton. Side-on bonding ($\eta^2$) of dinitrogen in mononuclear metal complexes is uncommon; it has been proposed to occur in a few cases, but there have been no confirmatory structural studies.[4−7] It is, however, well-established for polynuclear systems.[8−12]

Recent developments in nitrogen fixation research have renewed interest into the accessibility of side-on-bonded dinitrogen or dinitrogen hydrides, either in stable complexes or as intermediates. The recent X-ray structure determination of the FeMo component of nitrogenase[13−17] has been interpreted to imply that the active site may function to bind a dinitrogen molecule in a side-on fashion.[18,19] On the basis of the structures observed for a variety of high-oxidation-state tungsten hydrazide and diazene compounds, Schrock has proposed a scheme for reduction of $N_2$ to $NH_3$ in this kind of system that involves side-on-bound intermediates.[20]

In this paper, we report the results of a variable-temperature and time-dependent solution $^{15}N$ NMR study of the rhenium dinitrogen complexes Cp′Re(CO)(L)($^{15}N^{14}N$) (Cp′ = Cp ($\eta^5$-$C_5H_5$); L = CO **(1-$^{15}N_\alpha$)**[21−25] and Cp′ = Cp* ($\eta^5$-$C_5Me_5$); L = CO **(2-$^{15}N_\alpha$)**, $PMe_3$ **(3-**

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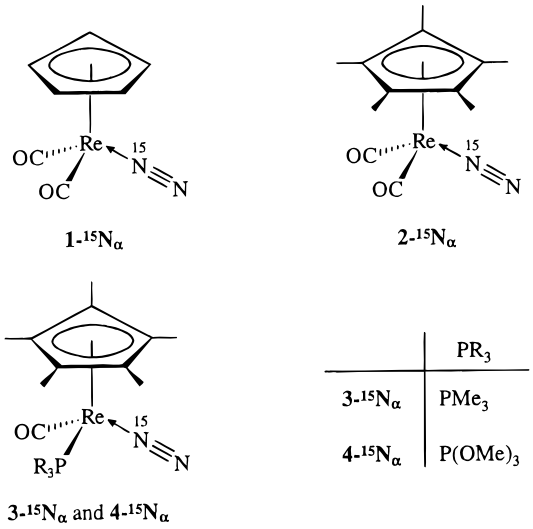
**Chart 1. Structures of 1-$^{15}N_\alpha$–4-$^{15}N_\alpha$**




$^{15}N_\alpha$), or $P(OMe)_3$ (**4-$^{15}N_\alpha$**),[21,26] which were specifically labeled with $^{15}N$ at the rhenium-bound nitrogen atom $N_\alpha$ (Chart 1). The $\eta^1$-dinitrogen ligand in these complexes is shown to undergo linkage isomerization, that is to say an exchange of the coordinated and uncoordinated nitrogen atoms. Of the various possible pathways for this exchange, we conclude that intramolecular end-to-end rotation of the dinitrogen ligand and the intermediacy of an $\eta^2$-bonded dinitrogen species accounts for the experimental results. Some preliminary results of this study have been previously communicated.[27]

## Experimental Section

**General Methods and Syntheses.** Manipulations, solvent purification, and routine spectroscopic measurements were carried out as described previously.[21] The aryldiazenido complexes [Cp′Re(CO)(L)(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] were prepared by methods already described.[24,26,28] The $^{15}N_\alpha$-enriched aryldiazenido complexes were prepared by using [*p*-$^{15}NNC_6H_4OMe$][$BF_4$] that was in turn synthesized from *p*-anisidine and 99% enriched $Na^{15}NO_2$. High-pressure reactions were performed in a Parr bomb, using oxygen-free nitrogen (Linde Union Carbide). $^{14}N$ and $^{15}N$ NMR chemical shifts (downfield positive) are referenced to external nitromethane. Variable-temperature and time-dependent $^{15}N$ and $^{14}N$ NMR spectra were recorded at 40.6 and 28.9 MHz, respectively, on a Bruker AMX 400 instrument equipped with a B-VT 1000 variable-temperature unit. A Bruker single-frequency probe was used to acquire the $^{14}N$ spectra, and a Bruker tunable broad-band probe was used for the $^{15}N$ spectra. Acetone-$d_6$ (Isotec Inc.), and in some cases $CD_2Cl_2$ (Isotec) or $CD_3CN$ (Isotec), were the solvents for the variable-temperature and time-dependent NMR work and were degassed to remove residual oxygen. Solutions were transferred into NMR tubes contained in Schlenk tubes under a positive pressure of argon at the stated temperatures and then quickly placed in the spectrometer whose temperature unit had been preset to the temperature cited, and equilibrated. Spectrometer temperatures were calibrated by measuring peak separations for a standard Bruker sealed sample of methanol and converting these into temperature values using the quadratic equation of Van Geet[29] for methanol. Temperature gradients within the sample region of the AMX 400 spectrometer are considered to be negligible because of the large distance between the cooling unit and the probe; temperatures are accurate to ±1 K.

**Time-Dependent $^{15}N$ NMR Spectroscopy of Cp*Re(CO)$_2$($^{15}N^{14}N$) (2-$^{15}N_\alpha$) Prepared Using $Ph_3C$.** A solution containing the triphenylmethyl (trityl) radical ($Ph_3C$) was prepared by reduction of $Ph_3CCl$ with zinc dust in THF. A 10-fold stoichiometric excess of the $Ph_3C$ solution was then added by cannula to a solution of [Cp*Re(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4$-OMe)][$BF_4$] in $CD_2Cl_2$ at room temperature. An IR spectrum recorded 15 min after the addition showed the presence of both the starting aryldiazenido complex ($\nu$(NN) 1703 cm$^{-1}$; $\nu$(CO) 2049, 1992 cm$^{-1}$) and the newly formed $^{15}N_\alpha$-labeled dinitrogen complex Cp*Re(CO)$_2$($^{15}N^{14}N$) **(2-$^{15}N_\alpha$)** ($\nu$(NN) 2090 cm$^{-1}$; $\nu$(CO) 1939, 1884 cm$^{-1}$).[21] The solution was then immediately transferred to an NMR tube at 273 K. A sequence of $^{15}N$ NMR spectra was acquired at 293 K over a measured period of time.

**Variable-Temperature and Time-Dependent $^{15}N$ NMR Spectroscopy of CpRe(CO)$_2$($^{15}N^{14}N$) (1-$^{15}N_\alpha$) and Cp*Re(CO)$_2$($^{15}N^{14}N$) (2-$^{15}N_\alpha$) Prepared Using $Cp_2Co$.** A 5-fold stoichiometric excess of $Cp_2Co$ was dissolved in a minimum amount of acetone-$d_6$ and then added by syringe to a solution of [CpRe(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] or [Cp*Re(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] in acetone-$d_6$ at room temperature. An IR spectrum taken immediately after the $Cp_2Co$ addition showed in both cases the complete disappearance of the aryldiazenido complex and the presence of the respective $^{15}N_\alpha$-labeled dinitrogen complex CpRe(CO)$_2$($^{15}N^{14}N$) **(1-$^{15}N_\alpha$)** or Cp*Re(CO)$_2$($^{15}N^{14}N$) **(2-$^{15}N_\alpha$)**.[21] In both cases, the solution was immediately transferred to an NMR tube at 273 K. A sequence of $^{15}N$ NMR spectra was acquired at the following temperatures: 291 K for **1-$^{15}N_\alpha$**; 274, 281, 284, and 291 K in separate experiments for **2-$^{15}N_\alpha$**.

**Time-Dependent $^{15}N$ NMR Spectroscopy of Cp*Re(CO)$_2$($^{15}N^{14}N$) (2-$^{15}N_\alpha$) Prepared Using $NaBH_4$.** A 2-fold stoichiometric excess of $NaBH_4$ was added as a solid to a solution of [Cp*Re(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] in acetone-$d_6$ at room temperature. An IR spectrum of this solution recorded immediately after the $NaBH_4$ addition indicated the total disappearance of the aryldiazenido complex and the presence of minor absorptions corresponding to Cp*Re(CO)$_2$($^{15}N^{14}N$) **(2-$^{15}N_\alpha$)** and major absorptions ($\nu$(CO) 1917, 1852 cm$^{-1}$) due to the aryldiazene complex Cp*Re(CO)$_2$(*p*-$NHNC_6H_4$-OMe).[21] An IR spectrum obtained after 35 min showed only the presence of absorptions attributable to **2-$^{15}N_\alpha$**. The solution was immediately transferred to an NMR tube at 273 K. A sequence of $^{15}N$ NMR spectra was then acquired at 280 K.

**Variable-Temperature and Time-Dependent $^{15}N$ NMR Spectroscopy of Cp*Re(CO){P(OMe)$_3$}($^{15}N^{14}N$) (4-$^{15}N_\alpha$) Prepared Using Na/Hg.** A solution of [Cp*Re(CO){P(OMe)$_3$}(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] in THF was added by syringe to excess sodium amalgam at room temperature, and the mixture was vigorously stirred for 30 min. An IR spectrum showed the complete disappearance of the aryldiazenido complex and the presence of Cp*Re(CO){P(OMe)$_3$}($^{15}N^{14}N$) **(4-$^{15}N_\alpha$)**. The complex **4-$^{15}N_\alpha$** was then purified by following the procedure described previously[21] and subsequently taken up in $CD_3CN$. The solution was transferred to an NMR tube at room temperature. $^{15}N$ NMR spectra acquired at 293 K over 24 h exhibited no change in the $^{15}N$ resonance of **4-$^{15}N_\alpha$**. A change in intensity of this $^{15}N$ resonance was observed at 320 K, and a sequence of $^{15}N$ NMR spectra was acquired over a measured period of time at this temperature.

**Variable-Temperature and Time-Dependent $^{15}N$ NMR Spectroscopy of Cp*Re(CO)(PMe$_3$)$_3$($^{15}N^{14}N$) (3-$^{15}N_\alpha$) Prepared Using Na/Hg.** The $^{15}N_\alpha$-labeled trimethylphosphine

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dinitrogen complex Cp*Re(CO)($PMe_3$)($^{15}N^{14}N$) **(3-$^{15}N_\alpha$)** was synthesized from the corresponding aryldiazenido complex [Cp*Re(CO)($PMe_3$)(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] and subsequently purified following a procedure similar to that described previously.[21] A $CD_3CN$ solution of **3-$^{15}N_\alpha$** was then transferred to an NMR tube. A sequence of $^{15}N$ NMR spectra acquired at 293 K over 24 h exhibited no change in the $^{15}N$ resonance of **3-$^{15}N_\alpha$**. A similar result was obtained at 320 K. A change in intensity of the $^{15}N$ resonance was finally observed at 333 K. A sequence of $^{15}N$ NMR spectra was then acquired over a measured period of time at this temperature.

**Determination of Rate Constants and Activation Parameters.** The rate constants ($k$) for the isomerization of Cp′Re(CO)$_2$($^{15}N^{14}N$) (Cp′ = Cp **(1-$^{15}N_\alpha$)** or Cp* **(2-$^{15}N_\alpha$)**) to give Cp′Re(CO)$_2$($^{14}N^{15}N$) (Cp′ = Cp **(1-$^{15}N_\beta$)** or Cp* **(2-$^{15}N_\beta$)**) were determined from the sequence of $^{15}N$ NMR spectra obtained over time immediately following the formation of the $^{15}N_\alpha$-labeled complexes by reaction with $Cp_2Co$. The growth of the $^{15}N_\beta$ NMR resonance over time was monitored by integration relative to a $Na^{15}NO_2$ reference of known concentration, which was sealed in a capillary and placed in the NMR tube containing the dinitrogen complex prior to the acquisition of the $^{15}N$ NMR spectra.

Treatment of the observed interconversion between the $^{15}N_\alpha$ and $^{15}N_\beta$ linkage isomers as an "opposing reaction" with identical forward and reverse rate constants $k$ and assuming first-order kinetics (eq 1) leads to the rate constant expression given in eq 2.[30]

$$N_\alpha \underset{k}{\overset{k}{\rightleftharpoons}} N_\beta \quad (1)$$

$$^1/_2 \ln\{N_{\beta^\infty}/(N_{\beta^\infty} - N_\beta)\} = kt \quad (2)$$

In eq 2, $N_{\beta^\infty}$ is the concentration of the $^{15}N_\beta$ isomer at equilibrium and $N_\beta$ is the concentration of the $^{15}N_\beta$ isomer at time $t$. Values for $k$ were obtained from the slope of the straight-line graph obtained by plotting $^1/_2 \ln\{N_{\beta^\infty}/(N_{\beta^\infty} - N_\beta)\}$ against $t$ and using a linear least-squares program.[31] The errors in the rate constants were obtained from the standard deviations derived from the linear least-squares fit. Values for the free energy of activation ($\Delta G^\ddagger$) were determined from the Eyring equation. Errors in $\Delta G^\ddagger$ values were obtained by use of eq 3 for the linearized relative statistical error.[32,33] For

$$(\sigma\Delta G^\ddagger/\Delta G^\ddagger)^2 = [\ln(k_B T/hk)]^{-2}(\sigma_k/k)^2 + \{1 + [\ln(k_B T/hk)]^{-1}\}^2(\sigma_T/T)^2 \quad (3)$$

the dinitrogen complex Cp*Re(CO)$_2$($^{15}N^{14}N$) **(2-$^{15}N_\alpha$)** rate constants $k$ were obtained from the time dependence of the $^{15}N$ NMR spectra at 274, 281, 284, and 291 K. Values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined from the temperature dependence of $k$ obtained by plotting $\ln(k/T)$ versus $1/T$ and using the linear least-squares program. Values for the activation energy ($E_a$) and the frequency factor ($A$) were similarly determined from the Arrhenius equation by plotting $\ln k$ versus $1/T$. Errors in $\Delta H^\ddagger$, $\Delta S^\ddagger$, $E_a$, and $A$ were obtained from the standard deviations derived from the Eyring and Arrhenius plots multiplied by the appropriate statistical factor.[32,33]

**Crossover Experiments.** Subsequent to the kinetic study of the isomerization of **2-$^{15}N_\alpha$** synthesized by using $Cp_2Co$, a sample of the mixture of linkage isomers was isolated by pumping off solvent and purified by extraction with hexane and chromatography on a short column of neutral alumina. To a solution of this mixture of **2-$^{15}N_\alpha$** and **2-$^{15}N_\beta$** in hexane was added an approximately equivalent amount of unlabeled **1**. The solution IR spectrum of the stirred mixture at room temperature was monitored periodically for 2 weeks. A mixture of the unlabeled complex Cp*Re(CO){P(OMe)$_3$}($N_2$) (**4**) and the $^{15}N$-labeled complex Cp*Re(CO)($PMe_3$)($^{15}N^{14}N$) (1:1 mixture of **3-$^{15}N_\alpha$** and **3-$^{15}N_\beta$** resulting from the isomerization study) was stirred in hexane at 333 K for 4 h and monitored by solution IR spectroscopy at room temperature.

**Table 1. $^{15}N$ and $^{14}N$ NMR Data for the Dinitrogen Complexes 1−4**

| | $^{15}N$ NMR[a,b] | | $^{14}N$ NMR[a] | |
|---|---|---|---|---|
| complex | $\delta(^{15}N_\alpha)$ | $\delta(^{15}N_\beta)$ | $\delta(^{14}N_\alpha)$ | $\delta(^{14}N_\beta)$ |
| **1**[c] | −120.9 | −27.3 | −120 | −26 |
| **2**[c] | −110.8 | −28.1 | −110 | −26 |
| **3** | −91.3 | −32.7[d] | −91 | −30 |
| **4** | −99.4 | −32.5[d] | −99 | −29 |

[a] In acetone-$d_6$, referenced to external $MeNO_2$; $\delta$ given in ppm. [b] Samples enriched with $^{15}N$ (99%). [c] Equimolar mixture of $^{15}N_\alpha$ and $^{15}N_\beta$ singly enriched species. [d] $^{15}N_\beta$ resonance was observed only after the corresponding $^{15}N_\alpha$ linkage isomer was maintained at an elevated temperature in $CD_3CN$ for several hours. For **3** $\delta(^{15}N_\alpha)$ in $CD_3CN$ is −93.2; for **4** $\delta(^{15}N_\alpha)$ in $CD_3CN$ is −100.8.

## Results

**Synthesis of the $^{15}N_\alpha$-Labeled Dinitrogen Complexes 1−4.** The synthesis of the dinitrogen compounds **1**−**4** by reduction of the cationic aryldiazenido complexes with a variety of reagents such as $Ph_3C$, $Cp_2Co$, and Na/Hg was reported in a previous publication, together with a discussion of the mechanism involved.[21] Several of these procedures were used to synthesize the samples of **1**−**4** utilized in this study. The $^{14}N$ NMR spectra of **1**−**4** exhibited in each case two broad resonances, as observed before,[21,26] which are assigned to the inequivalent $N_\alpha$ and $N_\beta$ nitrogen atoms for $\eta^1$-bonded dinitrogen. The values observed in this work are given in Table 1. When the $^{15}N$-labeled dinitrogen complexes **1-$^{15}N$**−**4-$^{15}N$** were freshly prepared in situ from the $^{15}N_\alpha$-labeled aryldiazenido complexes, they exhibited a single $^{15}N$ NMR resonance in the same position as one of the $^{14}N$ resonances (Table 1), and this was assigned to the exclusive formation of the dinitrogen complexes **1-$^{15}N_\alpha$**−**4-$^{15}N_\alpha$** with retention of the label in the $N_\alpha$ position (eq 4).

$$[Cp'Re(CO)(L)(p\text{-}^{15}N^{14}NC_6H_4OMe)]^+ \rightarrow Cp'Re(CO)(L)(^{15}N^{14}N) \quad (4)$$
**1-$^{15}N_\alpha$**−**4-$^{15}N_\alpha$**

**Time-Dependent $^{15}N$ NMR Spectroscopy of CpRe(CO)$_2$($^{15}N^{14}N$) (1-$^{15}N_\alpha$) and Cp*Re(CO)$_2$($^{15}N^{14}N$) (2-$^{15}N_\alpha$).** The evolution of the $^{15}N$ NMR spectrum as a function of time was studied subsequent to the synthesis of **1-$^{15}N_\alpha$** or **2-$^{15}N_\alpha$** in situ by more than one method. First, an excess of the triphenylmethyl radical ($Ph_3C$) was added to a solution of [Cp*Re(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4$-OMe)][$BF_4$] in $CD_2Cl_2$ at room temperature. IR spectra of this solution recorded 15 and 33 min, respectively, after the addition showed the slow disappearance of $\nu$(NN) and $\nu$(CO) absorptions of the aryldiazenido complex and the formation of absorptions corresponding to **2-$^{15}N_\alpha$**. A $^{15}N$ NMR spectrum of this solution recorded

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at 293 K, 27 min after the $Ph_3C$ addition, displayed resonances at $\delta$ −7.3, −110.6, and −66.2 corresponding respectively to $N_\alpha$ of the unreacted aryldiazenido complex, to **2-$^{15}N_\alpha$**, and to free $^{15}N$-labeled diazonium ion.[34] No resonance near $\delta$ −28 was observed, indicating the absence of the $^{15}N_\beta$ linkage isomer **2-$^{15}N_\beta$**. A sequence of $^{15}N$ NMR spectra over time showed the eventual disappearance of the resonances for the aryldiazenido complex and the diazonium ion and the growth of a new resonance at $\delta$ −28.4 assigned to **2-$^{15}N_\beta$**. After 202 min, the $^{15}N$ NMR spectrum showed two equally intense resonances for **2-$^{15}N_\alpha$** and **2-$^{15}N_\beta$**. An IR spectrum of this solution exhibited a single absorption for $\nu$(NN) at 2092 $cm^{-1}$, indicating that $\nu$(NN) absorptions for the individual isomers, while expected in principle to be different, are not resolved. The unexpected presence of the free diazonium salt coupled with poor signal to noise in the $^{15}N$ NMR spectra precluded the use of the spectra for extraction of reliable kinetic data.

The addition of excess $Cp_2Co$ to a solution of [Cp*Re(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] in acetone-$d_6$ at room temperature proved to be a much more efficient route to **2-$^{15}N_\alpha$**. An IR spectrum of the solution, recorded immediately after the $Cp_2Co$ addition, showed the total disappearance of the aryldiazenido complex and the presence of absorptions corresponding exclusively to the dinitrogen complex. A $^{15}N$ NMR spectrum of this solution at 284 K, acquired 25 min after the $Cp_2Co$ addition, exhibited a single resonance at $\delta$ −110.8 assigned to the presence of only **2-$^{15}N_\alpha$** (Figure 1). A sequence of $^{15}N$ NMR spectra then demonstrated the slow, gradual decay of this resonance and the concomitant growth of a second resonance at $\delta$ −28.1 due to **2-$^{15}N_\beta$**. The resonances reached effectively equal intensity in *ca.* 7 h. The observed rate constants $k_{obs}$ ($10^{-6}$ $s^{-1}$) determined at the temperatures cited (K) were 9.5 ± 1.1 (274), 27 ± 3 (281), 47 ± 3 (284), and 142 ± 11 (291). The resulting values of the activation parameters for the reversible isomerization of **2-$^{15}N_\alpha$** to **2-$^{15}N_\beta$** are $\Delta G^\ddagger = 92.6 \pm 0.4$ kJ $mol^{-1}$ at 291 K, $\Delta H^\ddagger = 105.3 \pm 6.0$ kJ $mol^{-1}$; $\Delta S^\ddagger = 43.5 \pm 21.2$ J $mol^{-1}$ $K^{-1}$, $E_a = 106.8 \pm 5.4$ kJ $mol^{-1}$, $A = (2.1 \pm 1.3) \times 10^{-15}$ $s^{-1}$.

Corresponding results were obtained for the $^{15}N_\alpha$-labeled Cp analog **1-$^{15}N_\alpha$** when it was synthesized from the corresponding $^{15}N_\alpha$-labeled aryldiazenido complex [CpRe(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] by reaction with $Cp_2Co$ in acetone-$d_6$ at room temperature. A sequence of $^{15}N$ NMR spectra of this solution recorded at 291 K showed that **1-$^{15}N_\alpha$** ($\delta$ −120.9) decayed, and **1-$^{15}N_\beta$** ($\delta$ −27.3) grew in, until essentially equal intensity resonances for these isomers was obtained (Figure 2).[35] For **1-$^{15}N_\alpha$**, $k_{obs} = (48 \pm 6) \times 10^{-6}$ $s^{-1}$, giving $\Delta G^\ddagger = 95.3 \pm 0.5$ kJ $mol^{-1}$ at 291 K for the cyclopentadienyl complex. Attempts were made to obtain kinetic data for **1-$^{15}N_\alpha$** at other temperatures. At 284 K no significant change was observed over 6 h, but at 300 K equilibration occurred so fast that only two spectra could be accumulated. Therefore, reliable temperature dependence data for a sufficiently wide temperature range were unobtainable for **1-$^{15}N_\alpha$**.

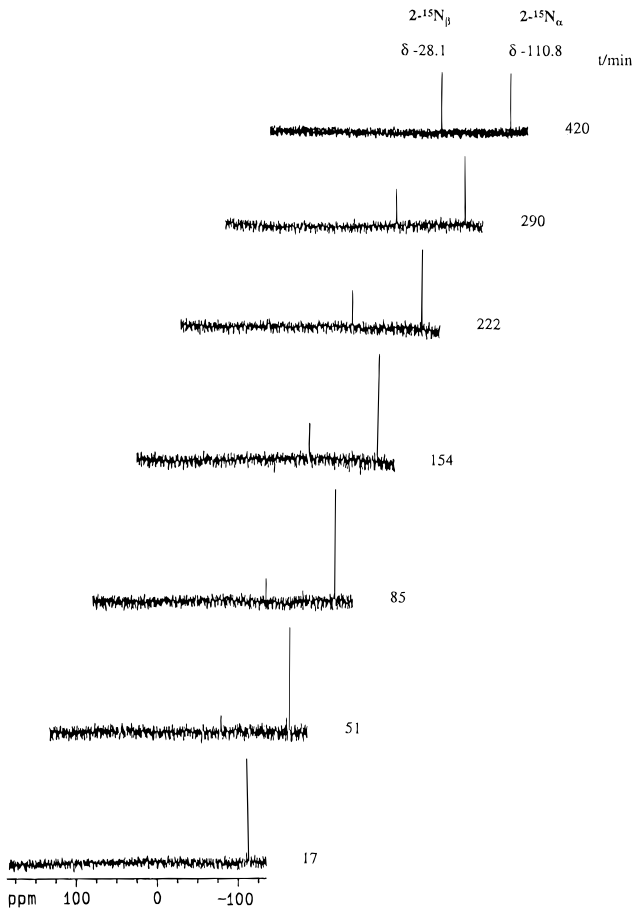



**Figure 1.** Time-dependent $^{15}N$ NMR spectra (40.6 MHz) for the $^{15}N_\alpha$ linkage isomer Cp*Re(CO)$_2$($^{15}N^{14}N$) **(2-$^{15}N_\alpha$)** in acetone-$d_6$ at 284 K.

As expected from previous work, an IR spectrum taken immediately following addition of $NaBH_4$ to [Cp*Re(CO)$_2$(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] showed the formation of the aryldiazene complex Cp*Re(CO)$_2$(*p*-$^{15}NH^{14}NC_6H_4OMe$) and some dinitrogen complex.[21] The aryldiazene complex converted completely to give additional dinitrogen complex in 35 min. A $^{15}N$ NMR spectrum of this solution at 280 K, acquired 40 min after the borohydride addition, demonstrated that only **2-$^{15}N_\alpha$** was formed ($\delta$ −110.8). However, a $^{15}N$ NMR spectrum obtained *ca.* 8 h after warming to 293 K now showed the presence of an equimolar mixture of **2-$^{15}N_\alpha$** and the newly formed **2-$^{15}N_\beta$** ($\delta$ −28.1).

**Time-Dependent $^{15}N$ NMR Spectroscopy of Cp*Re(CO)(PMe$_3$)($^{15}N^{14}N$) (3-$^{15}N_\alpha$) and Cp*Re(CO){P(OMe)$_3$}($^{15}N^{14}N$) (4-$^{15}N_\alpha$).** Notably, by comparison with complexes **1** or **2**, the $^{15}N$ NMR spectrum of **4-$^{15}N_\alpha$** formed by Na/Hg reduction of [Cp*Re(CO){P(OMe)$_3$}(*p*-$^{15}N^{14}NC_6H_4OMe$)][$BF_4$] was unchanged after 24 h; no $^{15}N$ resonance corresponding to the formation of **4-$^{15}N_\beta$** was observed. At 320 K the $^{15}N$ NMR spectrum showed initially a single resonance due to **4-$^{15}N_\alpha$** at $\delta$ −100.8, which then began to decay to produce a second resonance at $\delta$ −32.5, assigned to **4-$^{15}N_\beta$**. The resonances attained equal intensity in *ca.* 3 h (Figure 3). Likewise, **3-$^{15}N_\alpha$**, which was synthesized similarly to **4-$^{15}N_\alpha$**, gave a single $^{15}N$ NMR resonance at $\delta$ −93.2 corresponding to **3-$^{15}N_\alpha$** and the spectrum remained the same after 24 h. However, at 333 K there was slow decay of this

(34) The $^{15}N$ NMR spectrum of [*p*-$^{15}N^{14}NC_6H_4OMe$][$BF_4$] in THF/$CD_2Cl_2$ (1:1) exhibited a single resonance at $\delta$ −66. The free diazonium ion is most likely present as an impurity arising from the synthesis of **2-$^{15}N_\alpha$**, since a subsequent IR spectrum of the sample of **2-$^{15}N_\alpha$** used exhibited an impurity absorption at 2224 $cm^{-1}$ assigned to $\nu$(NN) of [*p*-$^{15}N^{14}NC_6H_4OMe$][$BF_4$].

(35) The $^{15}N_\beta$ resonance for **1** was previously[26] stated in error to occur at $\delta$ −58.18, and this value was unfortunately quoted in the preliminary communication.[27]

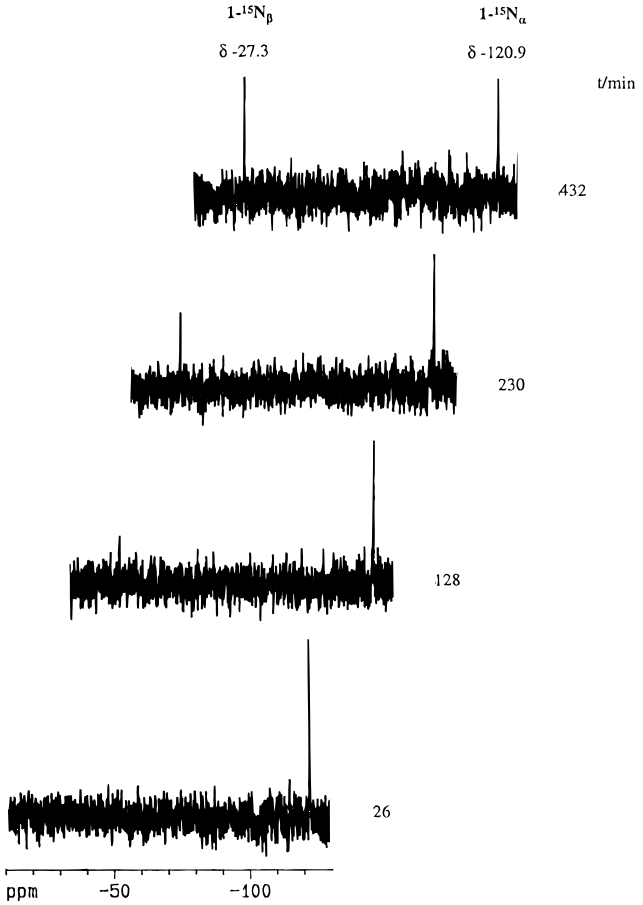



**Figure 2.** Time-dependent $^{15}N$ NMR spectra (40.6 MHz) for the $^{15}N_\alpha$ linkage isomer $CpRe(CO)_2(^{15}N^{14}N)$ **(1-$^{15}N_\alpha$)** in acetone-$d_6$ at 291 K.

resonance and the concomitant growth of a second resonance at $\delta$ −32.7 corresponding to **3-$^{15}N_\beta$** until, after *ca.* 3 h, the resonances had equal intensities (Figure 4). Because it was possible to accumulate only a small number of individual spectra before equilibrium was effectively established in both of these cases, no reliable estimate of the rate constant or activation free energy could be extracted (see Discussion).

To verify that the reducing agent was not responsible for the observed differences between the $^{15}N$ NMR spectra of the dicarbonyl dinitrogen complexes and those of the carbonyl phosphorus-ligand complexes, **4-$^{15}N_\alpha$** was prepared again using $Cp_2Co$ (the same reagent used for the preparation of **1-$^{15}N_\alpha$** and **2-$^{15}N_\alpha$**) instead of Na/Hg and gave identical $^{15}N$ NMR results.

**Test for $N_2$ Dissociation.** An equimolar mixture of **2-$^{15}N_\alpha$** and **2-$^{15}N_\beta$** in hexane was examined for dissociative exchange with $^{14}N_2$. After 24 h under 1500 psi of $^{14}N_2$, the IR spectrum of the $^{15}N$-labeled complex ($\nu(^{15}N^{14}N)$ 2092 $cm^{-1}$) showed no observable incorporation of $^{14}N_2$, as indicated by the lack of $\nu(^{14}N^{14}N)$ absorption expected at 2125 $cm^{-1}$ for **2**. Similarly, a hexane solution of equimolar **1-$^{15}N_\alpha$** and **1-$^{15}N_\beta$** ($\nu(^{15}N^{14}N)$ 2110 $cm^{-1}$) also showed no observable IR absorption for **1** ($\nu(^{14}N^{14}N)$ 2145 $cm^{-1}$) when pressurized with $^{14}N_2$ at 1500 psi over 18 h. These observations corroborate ones made earlier.[26] An equimolar mixture of **4-$^{15}N_\alpha$** and **4-$^{15}N_\beta$** in hexane was similarly examined for dissociative exchange with $^{14}N_2$. After 4 h under 1000 psi of $^{14}N_2$, at a temperature of 320 K in hexane, the IR spectrum of the $^{15}N$-labeled complex ($\nu(^{15}NN)$ 2033, 2045 $cm^{-1}$) exhibited negligible incorporation of $^{14}N_2$ ($\nu(NN)$ for **4** 2066, 2078 $cm^{-1}$).[21] An acetonitrile

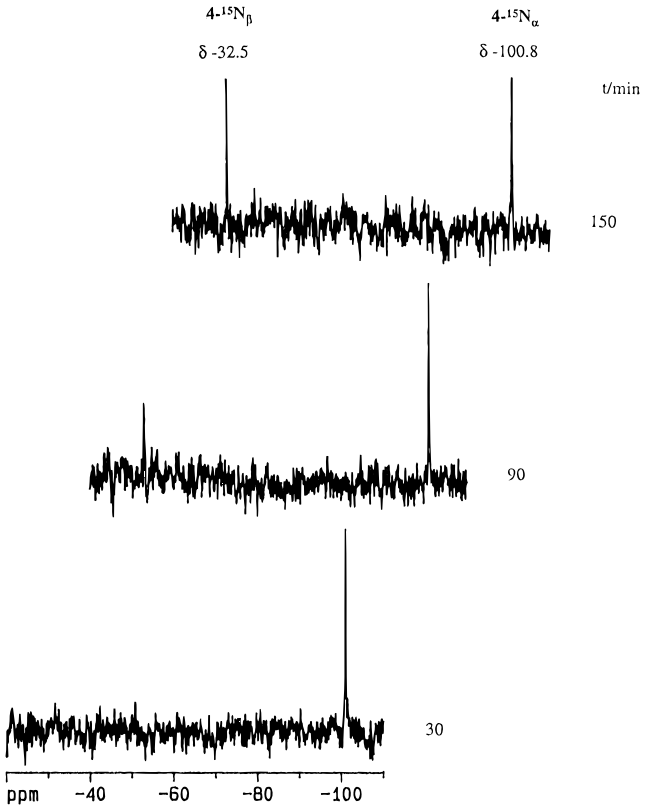



**Figure 3.** Time-dependent $^{15}N$ NMR spectra (40.6 MHz) for the $^{15}N_\alpha$ linkage isomer $CpRe(CO)\{P(OMe)_3\}(^{15}N^{14}N)$ **(4-$^{15}N_\alpha$)** in $CD_3CN$ at 320 K.

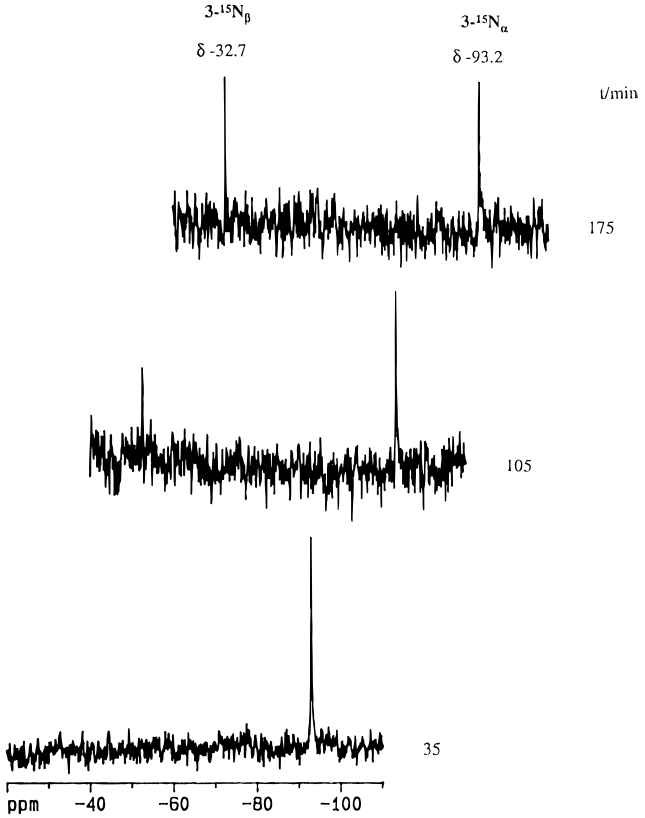



**Figure 4.** Time-dependent $^{15}N$ NMR spectra (40.6 MHz) for the $^{15}N_\alpha$ linkage isomer $CpRe(CO)(PMe_3)(^{15}N^{14}N)$ **(3-$^{15}N_\alpha$)** in $CD_3CN$ at 333 K.

solution of **3-$^{15}N_\alpha$** and **3-$^{15}N_\beta$** ($\nu(^{15}NN)$ 1995 $cm^{-1}$) also showed no observable IR absorptions for $\nu(^{14}N^{14}N)$ when pressurized with $^{14}N_2$ at 1000 psi over 4 h at 343 or 358 K, and the $^1H$ NMR confirmed that **3-$^{15}N$** was still present, accompanied by some $Cp^*ReO_3$[36] presumably resulting from reaction with residual oxygen present in the nitrogen.

**Test for Intermolecular Exchange.** A mixture of unlabeled **1** ($\nu$(NN) 2145 $cm^{-1}$) and $^{15}N$-labeled **2** (1:1 molar mixture of **2-$^{15}N_\alpha$** and **2-$^{15}N_\beta$**; $\nu$(NN) coincident at 2092 $cm^{-1}$) in hexane was observed by IR spectroscopy at room temperature over a period of 3 weeks. The $\nu$(NN) absorptions of the $^{15}N^{14}N$ and $^{14}N^{14}N$ isotopomers of these two complexes (Cp or Cp*) are characteristically sharp in hexane and would readily indicate if any cross products were formed. No change was observed; specifically, there were no absorptions attributable to $^{15}N$-labeled **1** ($\nu(^{15}N^{14}N)$ and $\nu(^{14}N^{15}N)$ are coincident at 2110 $cm^{-1}$) or unlabeled **2** ($\nu$(NN) 2125 $cm^{-1}$). Similarly, a crossover experiment involving unlabeled **4** ($\nu$(NN) 2078, 2066 $cm^{-1}$) and $^{15}N$-labeled **3** (1:1 molar mixture of **3-$^{15}N_\alpha$** and **3-$^{15}N_\beta$**; $\nu(^{15}N^{14}N)$ and $\nu(^{14}N^{15}N)$ are coincident at 2011 $cm^{-1}$) in hexane at 333 K indicated no cross products were formed after 4 h.

## Discussion

$CpRe(CO)_2(N_2)$ (**1**) was first synthesized by oxidation of the hydrazine complex or by reaction of $CpRe(CO)_2$(THF) with dinitrogen or $N_2O$.[22,23] Among more recent syntheses, its direct formation (along with $CpRe(CO)(N_2)_2$ and $CpRe(N_2)_3$) from irradiation of the tricarbonyl in supercritical xenon may be noted.[37,38] $Cp^*Re(CO)_2(N_2)$ (**2**) may also be synthesized from the corresponding THF complex and dinitrogen.[39] It was observed some time ago that the Cp dinitrogen complex **1** was accessible by treatment of an aryldiazenido complex with a number of reagents, including $NaBH_4$ and iodide.[24,25,40] The Cp* complex **2** could also be obtained from the aryldiazenido complex by using $NaBH_4$[39] or *t*-BuLi.[26] The latter reagent was effective in the formation of phosphorus-substituted Cp* complexes such as **3** and **4** from the corresponding aryldiazenido complexes, but in general, *t*-BuLi suffered from the disadvantage that for a reasonable yield the reactions needed temperatures above ambient.[26] More recently, high-yield syntheses of **1**−**4** from the aryldiazenido complexes by using $Cp_2Co$ or Na/Hg, for example, have been developed in this laboratory, allowing the preparation of these compounds under mild conditions.[21] This study also demonstrated that with these reagents the syntheses proceed by reduction, followed by C−N bond homolysis (eq 5).

$$[Cp'Re(CO)(L)(p\text{-}^{15}NNC_6H_4OMe)][BF_4] \xrightarrow{1e^- \text{ reduction}} [Cp'Re(CO)(L)(p\text{-}^{15}NNC_6H_4OMe)] \xrightarrow{C-N \text{ homolysis}} Cp'Re(CO)(L)(^{15}NN) + C_6H_4OMe^\bullet \quad (5)$$

These mild synthetic methods have thus allowed the preparation of **1**−**4** (in particular the ones that are more kinetically labile with respect to linkage isomerization, i.e. **1** and **2**) in situ prior to linkage isomerization of the $N_2$ ligand occurring.[21] As a result, this has made it possible subsequently to follow the isomerization kinetically.

In keeping with the overwhelming majority of structurally determined mononuclear dinitrogen complexes, it is reasonable to assume that dinitrogen is coordinated as an end-on ($\eta^1$) ligand in the rhenium half-sandwich complexes **1**−**4** in this study. However, since there are no reported crystal structure determinations for these complexes, it is important to review the supporting evidence. In the IR spectra, the $\nu$(NN) absorption is strong and occurs in a region typical of structurally determined $\eta^1$ dinitrogen complexes when allowance is made for the substitution of CO by phosphorus ligands in **3** and **4**.[21,26] Furthermore, the expected isotopic shift in $\nu$(NN) is observed when one or both of the nitrogen atoms is labeled with $^{15}N$. For the dicarbonyl complex **1** and its $^{15}N_2$ isotopomer in $N_2$ matrices, the IR spectra closely match theoretically calculated spectra.[38]

For **1** and **2** the nitrogen atoms are inequivalent in a static $\eta^1$ structure but are expected to be equivalent in a static side-on structure in which the N−N axis is normal to the molecular plane of symmetry. The $^{14}N$ NMR spectra of **1**−**4** (Table 1) all show two distinct resonances,[21,26] which indicates inequivalent nitrogen sites in all four cases and is consistent with end-on coordination. There is, therefore, little doubt that the dinitrogen ligand is coordinated end-on in these dinitrogen complexes.

The synthesis of the rhenium dinitrogen complexes from the aryldiazenido complexes is crucial to the introduction and monitoring of the labeled nitrogen atom in this work. It is simple to selectively label the nitrogens of an arenediazonium ion and, hence, specifically label the metal-bound nitrogen in the rhenium aryldiazenido complexes (eq 5). Therefore, the fate of the specifically labeled nitrogen atom during the conversion of the aryldiazenido complex to the $N_2$ complex and any subsequent rearrangement can, in principle, be followed by $^{15}N$ NMR. Note that this would not be possible merely by synthesizing the dinitrogen complex with use of singly labeled dinitrogen ($^{15}N^{14}N$) gas, because this will, of course, always give a 1:1 mixture of isotopomers.

For the complexes **1-$^{15}N$**−**4-$^{15}N$** that were freshly prepared in situ from the corresponding cationic aryldiazenido complexes, which had been specifically labeled with $^{15}N$ at the rhenium-bound nitrogen atom ($N_\alpha$), the $^{15}N$ NMR spectra, in all cases, exhibited a single resonance at a position similar to one of the $^{14}N$ resonances (Table 1), allowing this resonance to be assigned unambiguously to $N_\alpha$ and the other to $N_\beta$. This assignment, of course, relies on the assumption that the metal−nitrogen bond remains intact during the transformation at the temperatures utilized. The relative positions of the $N_\alpha$ and $N_\beta$ resonances resulting from this assignment (with $N_\beta$ downfield from $N_\alpha$) is consistent with the assignment of the relative shifts for $N_\alpha$ and $N_\beta$ in other rhenium dinitrogen complexes.[41]



(36) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313.
(37) Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804.
(38) Howdle, S. M.; Grebenik, P.; Perutz, R. N.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1517.
(39) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.
(40) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.
(41) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 469.

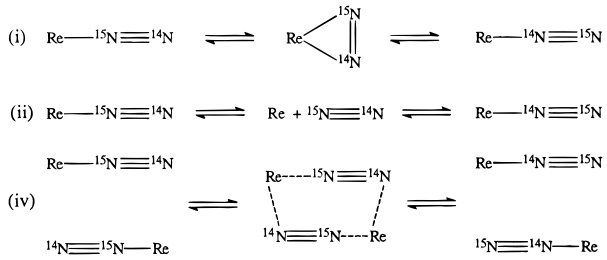
By way of contrast, it had been noted previously, and was observed again here, that the singly $^{15}$N-labeled dicarbonyl dinitrogen compounds **1-$^{15}$N** and **2-$^{15}$N** (but not **3-$^{15}$N** or **4-$^{15}$N**), when not quickly formed and isolated at a temperature near or below ambient, exhibited *two* equal-intensity $^{15}$N resonances in positions similar to the $^{14}$N resonances.[26] Equal amounts of the isotopomers **1-$^{15}$N$_\alpha$** and **1-$^{15}$N$_\beta$**, and similarly **2-$^{15}$N$_\alpha$** and **2-$^{15}$N$_\beta$**, were proposed to be formed.[26] In order to account for this result, three possibilities had been considered: (i) an intramolecular exchange process *via* an $\eta^2$-dinitrogen intermediate, (ii) dissociation−recombination of the $N_2$, or (iii) scrambling of the $^{15}$N label at some point in the transformation of the aryldiazenido complex to the dinitrogen complex, as, for example, might possibly occur if a side-on aryldiazenido ligand were to be present in an intermediate (e.g., the neutral aryldiazenido complex shown in eq 5) or an $\eta^2$-aryldiazene intermediate were involved in the case of $NaBH_4$ reactions, and either one collapses to the nitrogen complex.[26] To these processes should be added a further possibility: (iv) a four-center intermolecular exchange via a doubly bridged intermediate (Scheme 1). The lack of significant exchange of labeled **2** with unlabeled molecular dinitrogen did not support mechanism ii. There was no observed $^{15}$N NMR magnetization transfer between the $^{15}$N resonances of the $^{15}N_\alpha$ and $^{15}N_\beta$ isotopomers, but this did not necessarily invalidate mechanism i if exchange occurs at a slower rate than the time scale of this experiment, which was of the order of seconds.[26] At that time, therefore, no clear conclusion could be drawn as to the true mechanism operating.

The synthesis of the dinitrogen complexes from the aryldiazenido complexes by the reduction methods used here also leads to scrambling of the coordinated and uncoordinated nitrogen atoms in the *isolated* complexes in the case of **1** and **2**, but not **3** and **4**, in agreement with the previous observations.[26] The properties of the isolated dinitrogen complexes are thus seen to be independent of the method of synthesis from the aryldiazenido complex.

More importantly, in this work we have demonstrated that *when formed in situ* from reactions involving $Cp_2$-Co, Na/Hg, $Ph_3C$, or $NaBH_4$ the $^{15}$N label is wholly retained in the metal-bound position for **1** and **2**, just as it is for **3** and **4**. This therefore eliminates possibility iii. In the case of $NaBH_4$ the reaction initially affords the aryldiazene complex Cp′Re(CO)$_2$(*p*-$^{15}$NH$^{14}$NC$_6$H$_4$-OMe), which eliminates anisole to give the dinitrogen complex.[21,24,26] The observation of an equimolar mixture of $^{15}N_\alpha$ and $^{15}N_\beta$ isotopomers in the *isolated* labeled dinitrogen complex could be accounted for if anisole were eliminated from an $\eta^2$-aryldiazene intermediate. However, as with the other methods of synthesis, it is found that $NaBH_4$ *also* gives exclusively the $^{15}N_\alpha$ isotopomer initially. So, while the mechanism of elimination of the arene from the aryldiazene complex has not yet been established, we do know that it does *not* result in scrambling of the $^{15}$N isotope. This occurs only after the dinitrogen complex has been formed.

Also, we have demonstrated that the $N_2$ ligand isomerizes in all four of the dinitrogen complexes examined. The only difference is the rates. Compounds **1** and **2** isomerize fairly rapidly at ambient temperature; thus, understandably, the labeled material isolated after the time taken for usual chemical workup is a mixture of isotopomers. But, once it is appreciated that isomerization can occur, the $^{15}N_\alpha$ isotopomers of **1** and **2** can readily be obtained by controlling the temperature and employing rapid isolation.[21] Furthermore, **3** and **4**, which are isolated as the $^{15}N_\alpha$ isotopomers, are seen also to undergo isomerization at the appropriate higher temperature.

**Scheme 1. Possible Pathways (i), (ii), and (iv) for the Isomerization of the $^{15}$N-Labeled Rhenium-Bound Dinitrogen Ligand in 1−4 (See Text): (i) Intramolecular Nondissociative, End-to-End Rotation; (ii) Dissociation−Recombination; (iv) Intermolecular Exchange**




We are therefore left only with distinguishing between pathways i, ii, and iv for linkage isomerization of the dinitrogen complexes. Pathway ii is eliminated by the failure of either **1-$^{15}$N$_\alpha$** or **2-$^{15}$N$_\alpha$** to exchange with unlabeled $N_2$ at room temperature over a period of much longer than the time for essentially complete scrambling of the label within the complexes, as mentioned above and confirmed independently here. Similarly, no exchange was observed for labeled **3** or **4** with unlabeled $N_2$ at the higher temperatures at which scrambling of the label internally is observed.

Because **1** and **2** each readily undergoes isomerization, it is possible to test for the four-center mechanism iv by the crossover experiment in which labeled **1** and unlabeled **2** are mixed. Intramolecular exchange by mechanism i should lead to no formation of the crossover products labeled **1** and unlabeled **2**, but these should result from mechanism iv. Since the $\nu$(NN) values for all four permutations are well separated, the result is quite conclusive. No crossover products were evident, eliminating mechanism iv. Incidentally this also provides additional evidence against the dissociative mechanism ii. Similarly, no cross products were formed from a mixture of **3** and **4** at the temperature at which internal exchange for these complexes is observed.

In conclusion, therefore, the evidence supports only intramolecular exchange as the mechanism, and we envisage that the dinitrogen undergoes end-to-end rotation as illustrated in Scheme 1(i).

The extraction of kinetic data for the linkage isomerization of **1**−**4** from the $^{15}$N NMR spectra proved to be severely limited by the nature of the technique. The $^{15}$N nucleus ($I = {}^1/_2$) has a natural abundance of only 0.37%, a receptivity 1/100 times that of $^{13}$C, and a very long spin−lattice relaxation time (e.g., 9.8 s for **2-$^{15}$N$_\alpha$**). Despite using highly concentrated, 99% $^{15}$N-enriched samples for the $^{15}$N NMR experiments, the acquisition of spectra with acceptable signal/noise still required a lengthy time (*ca.* 40−60 min per spectrum at each temperature, depending on the complex being investi-

gated). As a result of this time factor, the temperature range over which meangingful $^{15}N$ NMR data could be acquired was limited. For example, the conversion of **2-$^{15}N_\alpha$** to **2-$^{15}N_\beta$** was too fast to be measured above 291 K, yet no isomerization was detected below 274 K. For the isomerization of **1-$^{15}N_\alpha$** to **1-$^{15}N_\beta$** the temperature range was even smaller and only a single reliable rate constant could be obtained, at 291 K. Note also that each $^{15}N$ NMR run required a fresh sample of $^{15}N$ isotopically labeled aryldiazenido complex so as to furnish a fresh sample of $^{15}N_\alpha$-labeled dinitrogen complex in situ. Furthermore, no reliable estimate of the rates of isomerization could be obtained for the carbonyl phosphine and phosphite dinitrogen complexes **3-$^{15}N_\alpha$** and **4-$^{15}N_\alpha$**, because too few spectra could be accumulated before intensities became equal.

As a result, we have only incomplete kinetic and thermodynamic data, but a comparison of the $\Delta G^\ddagger$ values obtained for the two dicarbonyl dinitrogen complexes **1** (Cp) and **2** (Cp*) indicates that the free energy of activation for the isomerization is somewhat lowered when the Cp ligand is replaced by its methylated analog Cp*. These $\Delta G^\ddagger$ values are similar to the energy of activation estimated from IR spectroscopy by Taube et al. for $[Ru(NH_3)_5(N_2)]^{2+}$ (*ca.* 88 kJ mol$^{-1}$), which is the only other example that we are aware of for which the energy of activation for linkage isomerization of metal-bound dinitrogen has been estimated.[42] From measurements of the rate of aquation of $[Ru(NH_3)_5(N_2)]^{2+}$, Taube et al. also obtained a value of *ca.* 117 kJ mol$^{-1}$ for the enthalpy of activation for the dissociation of the $N_2$ ligand.[43] For **2-$^{15}N_\alpha$**, $\Delta H^\ddagger$ was calculated to be 105.3 ± 6.0 kJ mol$^{-1}$; this value is significantly smaller than the one obtained by Taube for $N_2$ dissociation and thus is consistent with an intramolecular, nondissociative process for the isomerization of the rhenium-bound $N_2$ ligand. The isomerization of $N_2$ was also reported to have been detected in other related ruthenium complexes.[44]

The observed, relatively slow, rate of exchange in **1-$^{15}N_\alpha$** and **2-$^{15}N_\alpha$** and the large chemical shift separation between the $N_\alpha$ and $N_\beta$ resonances in the $^{14}N$ and $^{15}N$ NMR spectra of these dinitrogen complexes made it impossible to use the technique of variable-temperature NMR line shape analysis to calculate the rate constant for this interconversion in the 1:1 mixture of isotopomers. Therefore, the only viable method that we could devise to monitor the isomerization is the one described here. The isomerization of **3-$^{15}N_\alpha$** and **4-$^{15}N_\alpha$** was detected only at elevated temperature. As described earlier, the results did not allow the accumulation of reliable kinetic data, and line shape analysis could not be used either because at these temperatures there was significant thermal decomposition or reaction with residual oxygen, and again the resonances are well separated. From the temperatures of the onset of isomerization, however, it appears in a qualitative comparison that the barrier to isomerization for the rhenium-bound $^{15}N$-labeled dinitrogen ligand must be raised significantly by replacing a CO group in Cp*Re(CO)$_2$($^{15}N^{14}N$) **(2-$^{15}N_\alpha$)** by $P(OMe)_3$ and raised further when the CO is substituted by $PMe_3$. Whether these changes result principally from perturbation of the energies of the end-on or side-on configurations upon substitution with the phosphorus ligands is not clear.

## Conclusion

In this paper we have demonstrated by $^{15}N$ labeling that the synthesis of the dinitrogen complexes **1**−**4** from the corresponding aryldiazenido complexes proceeds with full retention of the labeled rhenium-bound nitrogen in the dinitrogen products. Subsequent to this, scrambling of the $^{15}N$ label equally between the $N_\alpha$ and $N_\beta$ sites occurs at room temperature in the case of Cp′Re(CO)$_2$($^{15}N^{14}N$) (Cp′ = Cp **(1-$^{15}N_\alpha$)** or Cp* **(2-$^{15}N_\alpha$)**), but only at elevated temperatures in the case of Cp*Re(CO)($PR_3$)($^{15}N^{14}N$) ($PR_3$ = $PMe_3$ **(3-$^{15}N_\alpha$)** or $P(OMe)_3$ **(4-$^{15}N_\alpha$)**), with the result that equimolar amounts of the $^{15}N_\alpha$- and $^{15}N_\beta$-labeled molecules ultimately occur. For all the complexes examined, the scrambling of the $^{15}N$ label was shown to proceed by an intramolecular, nondissociative process considered to be an end-to-end rotation of the rhenium-bound dinitrogen ligand *via* the elusive side-on-bonded ($\eta^2$) configuration. The barrier for this linkage isomerization is evidently increased in the phosphorus ligand complexes.

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