141. Fluxional Behaviour of Isocyanide Derivatives of Dodecacarbonyltetrairidium

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The fluxional behaviour of $[Ir_4(CO)_{11}(t\text{-BuNC})]$ (**1**) and $[Ir_4(CO)_{11}(ArNC)]$ (Ar = 4-methoxyphenyl, 4-tolyl, phenyl, 4-chlorophenyl, 4-nitrophenyl; **2**–**5**) has been investigated by 2D and variable-temperature ^{13}C-NMR. These techniques give new evidence of the processes responsible for CO exchange, namely two successive merry-go-rounds causing *Cotton*-like scrambling and a CO rotation about one metal center.

Introduction. – The synthesis of two series of isocyanide derivatives of $[Ir_4(CO)_{12}]$, namely $[Ir_4(CO)_{12-x}L_x]$ (x = 1–4, L = t-BuNC, MeNC) has been reported by *Stunz* and *Shapley* [1]. Carbonyl scrambling in $[Ir_4(CO)_{11}(t\text{-BuNC})]$ (**1**) has been studied by these authors through variable-temperature ^{13}C-NMR without simulation. Two mechanisms were proposed for the dynamic processes of lowest activation energy, consisting of two merry-go-rounds taking place, simultaneously, on two different faces of the Ir_4 tetrahedron.

We have re-examined the fluxionality of **1**, together with that of five new isocyanide derivatives $[Ir_4(CO)_{11}(ArNC)]$ (Ar = 4-methoxyphenyl, **2**; 4-tolyl, **3**; phenyl, **4**; 4-chlorophenyl, **5**; 4-nitrophenyl, **6**) by ^{13}C-NMR. The distinction between possible mechanisms is now based on dynamic connectivities derived from 2D-NOESY spectra and backed up by simulation of the variable-temperature ^{13}C-NMR spectra up to complete coalescence. The ArNC ligands in **2**–**6** were selected for their different χ parameters [2] to examine a possible effect of ligand basicity on the fluxional processes.

Results and Discussion. – The direct reaction of $[Ir_4(CO)_{12}]$ with RNC (R = t-Bu, Me) in the presence or absence of Me_3NO in THF gives low yields of $[Ir_4(CO)_{12-x}(RNC)_x]$ (x = 1, 2). We have found that the reaction of $[Ir_4(CO)_{11}I][NEt_4]$ with $AgBF_4$ and 1 mol-equiv. of isocyanide in CH_2Cl_2 gives better yields of $[Ir_4(CO)_{11}(RNC)]$ (88–96%) under milder conditions and without need of prep. TLC.

Cluster **1** adopts an unbridged C_s structure in the solid state [3]. This structure is also adopted by compounds **1**–**6** in solution as only IR absorptions in the region (2140–2200 cm^{-1}) appropriate for terminal isocyanide ligands and in the range (2000–2100 cm^{-1}) suitable for terminal CO ligands are observed.

The ^{13}C-NMR spectra of **1**–**6** display in each case one single carbonyl resonance around 310 K. The limiting low-temperature ^{13}C-NMR spectra show five resonances,

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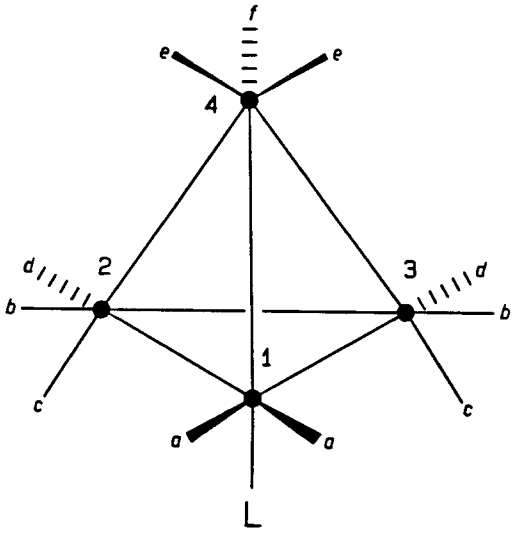


1–4: Ir-atoms;
a–f: CO ligands

1 L = *t*-BuNC
2 L = (4-$MeOC_6H_4$)NC
3 L = (4-MeC_6H_4)NC
4 L = PhNC
5 L = (4-ClC_6H_4)NC
6 L = (4-$NO_2C_6H_4$)NC

each of relative intensity two, and one resonance of unit relative intensity, all of which appear in the terminal CO region (see *Exper. Part*). The signal of relative intensity one is assigned to the unique carbonyl ligand *f* in pseudo-*trans*-position with respect to the isonitrile ligand. Inspection of the COSY ^{13}C-NMR spectra of samples enriched with ^{13}CO (*ca.* 30%; *e.g. Fig. 1* for ^{13}C-enriched **1**) leads to the assignment of the signal of

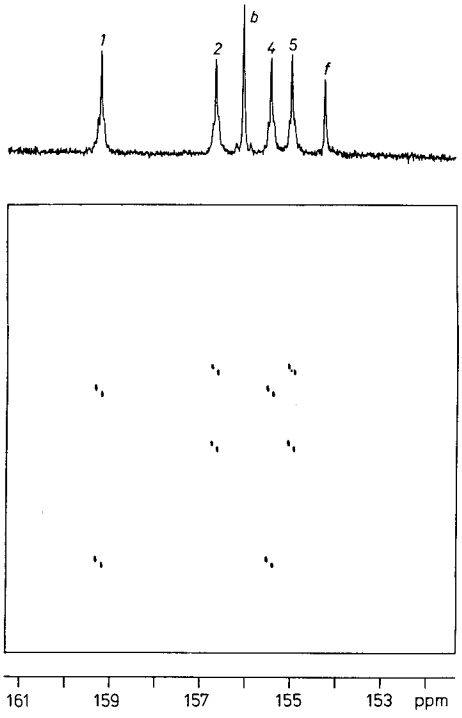


Fig. 1. *COSY ^{13}C-NMR spectrum of ^{13}C-enriched* **1** *in CD_2Cl_2 at 180 K*

relative intensity two, and devoid of couplings to carbonyl ligands *b*. It is indeed well known that in carbonyltetrairidium clusters, the only CO's which couple significantly are in relative pseudo-*trans*-positions (in particular, geminal $^2J(CO,CO)$ are very small) [1]. The remaining four signals with cross peaks have identical vicinal $^3J(CO,CO)$ coupling constants (11.4 ± 0.8 Hz) and cannot be individually assigned; hence they are labelled *1*, *2*, *4*, and *5* in order of decreasing chemical shift. Among the 24 virtually possible assignments, only eight are consistent with the couplings *1,4* and *2,5*.

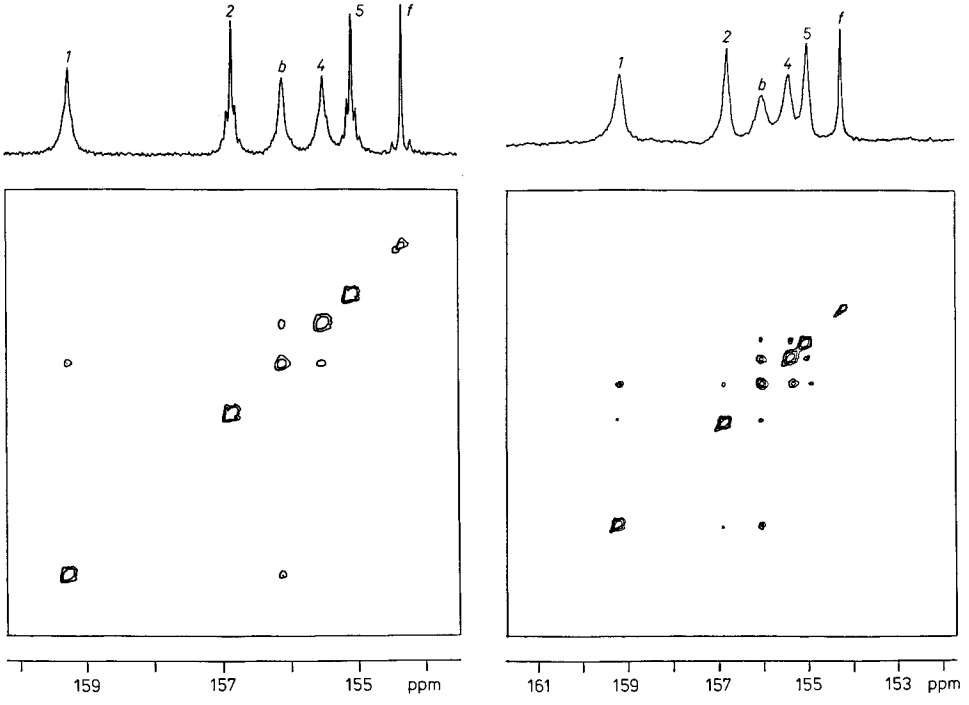
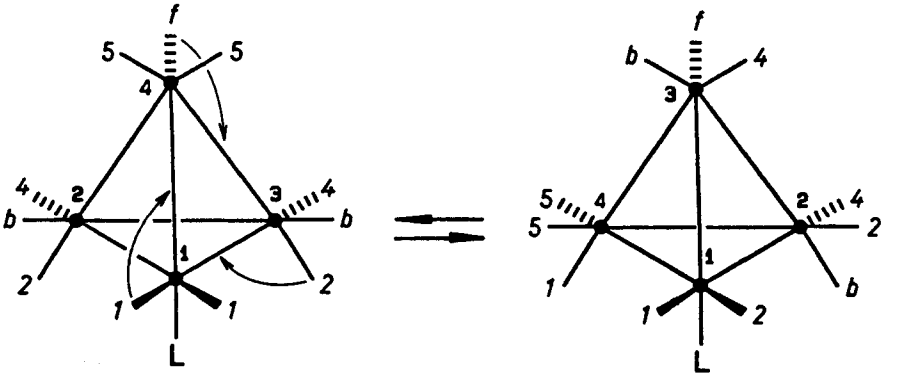


Fig. 2. *NOESY ^{13}C-NMR spectrum of ^{13}C-enriched* **1** *in CD_2Cl_2* a) *at 215 K* (mixing time 50 ms); *and* b) *at 225 K* (mixing time 65.5 ms)

The NOESY ^{13}C-NMR spectrum of **1** at 215 K (*Fig. 2a*) gives the dynamic connectivities *1* ↔ *b* ↔ *4* and corresponds to the exchange matrix of a first merry-go-round of 6 CO's around either the Ir(1)-Ir(2)-Ir(3) face (for 4 of the 8 possible assignments) or the Ir(2)-Ir(3)-Ir(4) (for the remaining ones). The NOESY spectrum at 225 K (*Fig. 2b*) shows 4 additional cross peaks which lead to the dynamic connectivities *1* ↔ *2* ↔ *b* ↔ *5* ↔ *4* which corresponds to a second merry-go-round taking place on any of the equivalent Ir(1)-Ir(3)-Ir(4) or Ir(1)-Ir(2)-Ir(4) faces. The eight possible assignments are in agreement with such a mechanism. A merry-go-round of 5 CO's has never been observed when the ground state of the Ir_4 cluster contains a face bearing a radial L ligand, 3 edge-bridging, and two terminal CO's [4]. The proposed *Scheme* shows that the intermediate of the second merry-go-round in $[Ir_4(CO)_{11}(RNC)]$ contains a radial RNC ligand. However, as

Scheme



the ground state has here all terminal ligands, the only condition to be satisfied in the fluxional process is to end up with a state of equal energy with the same pseudo-*trans* relationship between RNC and carbonyl ligand *f* and without constrains on the choice of the face for the merry-go-round. This condition doesn't necessarily imply the participation of the RNC ligand in the CO site exchanges.

At *ca.* 270 K, a third process involving carbonyl ligand *f* in a 3 CO's exchange around one metal center (Ir(4)) is taking place.

Line-shape analysis [5] of the variable-temperature ^{13}C-NMR spectra was carried out using the following *Kubo-Sack* matrix elements: $(1,1) = (4,4) = -k_1/2 \; -k_2/2$, $(1,2) = (2,b) = (b,5) = (4,5) = k_2/2$, $(1,b) = (b,4) = k_1/2$, $(2,2) = -k_2$, $(b,b) = -k_1 \; -k_2$, $(5,5) = -k_2 \; -k_3/2$, $(5,f) = k_3/2$, $(f,f) = -k_3$, $(f,5) = k_3$, with k_1, k_2, k_3 = rate constant in s^{-1} of the first and the second merry-go-round processes and of the rotation of 3 CO's at one metal center, respectively. An example of the obtained and simulated spectra is given in *Fig. 3*.

A simulation using matrix elements derived from the mechanism proposed by *Stunz et al.* [1] failed to reproduce variable-temperature ^{13}C-NMR spectra of **1**. However, other possible CO site exchange mechanisms should also be considered. First, one should take into account a process involving bridging of the isocyanide ligand, since edge-bridging RNC geometries have been observed in di- and trinuclear complexes [6]. Bridging of RNC on the Ir(1)-Ir(2) or Ir(1)-Ir(3) edge involved in merry-go-rounds around the Ir(1)-Ir(2)-Ir(4) or Ir(1)-Ir(3)-Ir(4) faces, respectively, gives an exchange matrix different from that corresponding to the observed connectivities of the second merry-go-round (*Fig. 2b*). This hypothetical matrix failed to reproduce experimental spectra.

Second, we have seen that the mechanism proposed for the lowest-energy process (*Fig. 2a*) is a merry-go-round through a CO-bridged intermediate having RNC either in axial or in apical position. When the ground state of Ir_4 clusters has 3 edge-bridging CO's defining a basal plane, as in $[Ir_4(CO)_{11}(PEt_3)]$ [7], the relative energies of the 3 possible isomers follow the sequence L(axial) > L(radial) > L(apical). If we assume that the same sequence of energy levels is applicable to the postulated intermediates of the first merry-go-round in $[Ir_4(CO)_{11}(t\text{-BuNC})]$ (**1**), this same process could be due to a merry-go-round on the Ir(1)-Ir(2)-Ir(3) face, followed by another on the Ir(2)-Ir(3)-Ir(4) face. This alterna-

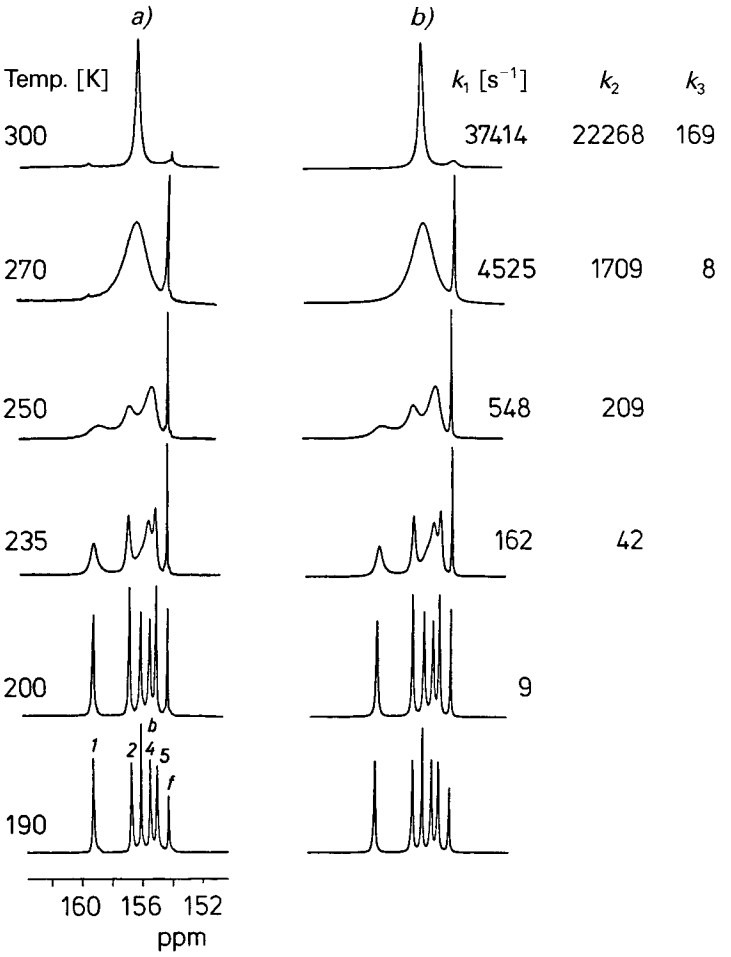


Fig. 3. a) *Experimental and* b) *simulated variable-temperature* ^{13}*C-NMR spectra of* ^{13}*C-enriched* **1** *in* CD_2Cl_2

tive mechanism agrees with the observed NOESY ^{13}C-NMR spectra of **1** at 225 K (*Fig. 2b*), if second-order peaks are taken into account. Therefore, a quantitative treatment of the 2D spectrum was needed. Recently, *Orrell* and coworkers [8] have proposed a general method for evaluating rate constants in complex exchange networks from two-dimensional NOESY NMR spectra. We have used their D2DNMR computer program capable of performing signal intensity to exchange rate calculation to distinguish between first- and second-order peaks. Including, as input data, the number of exchanging sites (6), their relative populations, and the experimental 2D signal intensities based on integration of all 2D peaks, a kinetic matrix was derived (see *Supplementary Material*) whose elements are the rate constants of the first-order exchange process. This matrix was equivalent to that of the proposed second merry-go-round, but not to that of the above alternative mechanism.

Table. *Free Enthalpies of Activation* $\Delta G^{\neq}$ ($\pm$ 0.4 kJ mol^{-1}) *of the 3 Fluxional Processes in* $[Ir_4(CO)_{11}(RNC)]$ *at 298 K*

	R	$\Delta G_1^{\neq}$	$\Delta G_2^{\neq}$	$\Delta G_3^{\neq}$		R	$\Delta G_1^{\neq}$	$\Delta G_2^{\neq}$	$\Delta G_3^{\neq}$
1	*t*-Bu	47.5	48.6	60.7	**4**	phenyl	49.4	49.9	60.8
2	4-methoxyphenyl	48.8	49.8	59.3	**5**	4-chlorophenyl	50.6	51.6	60.6
3	4-tolyl	49.0	50.4	59.9	**6**	4-nitrophenyl	49.8	53.2	62.4

The observed fluxional behaviour of cluster compounds **2**–**6** is the same as that of **1**, and can be viewed as a CO site exchange through two consecutive merry-go-rounds, followed by the rotation of 3 CO's around one metal center. The energy barriers are given in the *Table*.

The basicity of the non-CO ligand has no significant effect on the $\Delta G^{\neq}_{298}$ of the exchange processes, as also observed in $[Ir_4(CO)_{11}X]^-$ (X = Br, I) and $[Ir_4(CO)_{11}(PAr_3)]$ systems [9]. The rotation of apical CO's is also the highest activation energy process in the halogeno and phosphine clusters which have a different ground-state geometry.

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Experimental Part

1. *General.* IR spectra: *Perkin-Elmer 880* spectrophotometer equipped with a data station; 0.1-mm CaF_2 cells previously purged with N_2. ^{13}C-NMR spectra: *Bruker WH 360* (90.55 MHz); in CD_2Cl_2 at normal atmospheric pressure; δ in ppm, J(C,C) in Hz from COSY spectra. 2D ^{13}C-NMR spectra: COSY experiment in CD_2Cl_2 at 180 K, 256 t_1 increments with 2-K transients, spectral width 900.90 Hz in the F_2 domain and 450.45 Hz in the F_1 domain; NOESY experimets in CD_2Cl_2 at 215 and 225 K, mixing time 50 and 65.5 ms, resp., 512 increments with 2-K transients, spectral width 1199.0 Hz in the F_2 domain and 599.52 Hz in the F_1 domain; a squared sine bell was applied in both domains prior to *Fourier* transformation.

2. *Isocyanide Ligands.* Commercially available *t*-BuNC was used (*Merck*) without further purification. The other ligands were synthesised starting from the corresponding formamides and following the method proposed by *Ugi* and coworkers [10]. When formamides were not commercially available (4-chloro-, 4-nitro-, and 4-methoxyphenyl-substituted ones), they were obtained from the corresponding amines according to [11].

3. *Monosubstituted Complexes.* A soln. of $[Ir_4(CO)_{11}I][NEt_4]$ [12] (200 mg, 0.15 mmol) and the isocyanide ligand (0.15 mmol) was vigorously stirred, after addition of $AgBF_4$ (32.1 mg, 0.165 mmol) for 1 h at 263 K. The mixture containing solid AgI was filtered through a 15 × 3 cm column packed with silica gel (70–230 mesh) and eluted with cold CH_2Cl_2. The yellow filtrate was evaporated and the residue crystallised from CH_2Cl_2/hexane 1:1 at 248 K.

*(*tert*-Butyl isocyanide)undecacarbonyltetrairidium* ($[Ir_4(CO)_{11}(t\text{-BuNC})]$; **1**): For spectral characteristics, see [1].

Undecacarbonyl(4-methoxyphenyl isocyanide)tetrairidium ($Ir_4(CO)_{11}(4\text{-MeOC}_6H_4NC)$]; **2**): IR ($CH_2Cl_2$, 298 K): 2091*m*, 2060*vs*, 2038*s*, 2018*s*, 2009*m* (CO); 2149*m* (CN). ^{13}C-NMR (CD_2Cl_2, 190 K): 158.7 (J = 11.4, *1*); 156.9 (J = 11.2, *2*); 155.7 (*b*); 155.3 (J = 11.4, *4*); 155.0 (J = 11.6, *5*); 154.4 (*f*). Anal. calc. for $C_{19}H_7Ir_4NO_{12}$ (1210.14): C 18.86, H 0.58, N 1.16; found: C 19.20, H 0.59, N 1.17.

Undecacarbonyl(4-tolyl isocyanide)tetrairidium ($[Ir_4(CO)_{11}(4\text{-MeC}_6H_4NC)]$; **3**): IR ($CH_2Cl_2$, 298 K): 2092*m*, 2058*vs*, 2037*s*, 2016*s*, 2007*m* (CO); 2165*m* (CN). ^{13}C-NMR (CD_2Cl_2, 190 K): 158.6 (*1*); 156.9 (*2*); 155.7 (*b*); 155.3 (*4*); 154.9 (*5*); 154.3 (*f*); same J's as in **2**. Anal. calc. for $C_{19}H_7Ir_4NO_{11}$ (1194.1): C 19.11, H 0.59, N 1.17; found: C 19.34, H 0.6, N 1.18.

Undecacarbonyl(phenyl isocyanide)tetrairidium ($[Ir_4(CO)_{11}(PhNC)]$; **4**): IR (CH_2Cl_2, 298 K): 2092*m*, 2058*vs*, 2037*s*, 2016*s*, 2008*m* (CO); 2164*m* (CN). ^{13}C-NMR (CD_2Cl_2, 190 K): 158.5 (*1*); 156.9 (*2*); 155.7 (*b*); 155.3 (*4*);154.9

(*5*); 154.4 (*f*); same *J*'s as in **2**. Anal calc. for $C_{18}H_5Ir_4NO_{11}$ (1180.1): C 18.32, H 0.43, N 1.19; found: C 18.70, H 0.44, N 1.19.

Undecacarbonyl(4-chlorophenyl isocyanide)tetrairidium ($[Ir_4(CO)_{11}(4\text{-}ClC_6H_4NC)]$; **5**): IR ($CH_2Cl_2$, 298 K): 2092*m*, 2059v*s*, 2038*s*, 2016*m* (CO); 2161*s*, 2008*m* (CN). ^{13}C-NMR (CD_2Cl_2, 190 K): 158.3 (*1*); 156.9 (*2*); 155.6 (*b*); 155.1 (*4*); 154.9 (*5*); 154.3 (*f*); same *J*'s as in **2**. Anal calc. for $C_{18}H_4ClIr_4NO_{11}$ (1214.6): C 17.8, H 0.33, N 1.16; found: C 18.5, H 0.34, N 1.16.

Undecacarbonyl(4-nitrophenyl isocyanide)tetrairidium ($[Ir_4(CO)_{11}(4\text{-}NO_2C_6H_4NC)]$; **6**): IR ($CH_2Cl_2$, 298 K): 2093*m*, 2059v*s*, 2036*s*, 2014*s*, 2006*m* (CO); 2183*m* (CN). ^{13}C-NMR (CD_2Cl_2, 190 K): 157.8 (*1*); 156.9 (*2*); 155.4 (*b*); 155 (*4*); 154.8 (*5*); 154.4 (*f*); same *J*'s as in **2**. Anal calc. for $C_{18}H_4Ir_4N_2O_{13}$ (1225.1): C 17.65, H 0.33, N 2.29; found: C 17.88, H 0.34, N 2.27.

Supplementary Material. – The kinetic matrices for the D2DNMR program is available from *R. Roulet* upon request.

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