

Direct Comparison of Hydrogenation Catalysis by Intact versus Fragmented Triruthenium Clusters**

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Unraveling the mechanisms by which clusters catalyze reactions is complicated by the variety of reaction pathways available.^[1] It is likely that a greater understanding of these mechanisms will lead to the design and subsequent synthesis of improved cluster catalysts that may compete with mononuclear counterparts. One key issue that is of paramount importance when considering the role of clusters is to separate the impact of fragmentation from that of intact cluster transformation.^[2] Herein we report on the use of parahydrogen-induced polarization (PHIP)^[3] to delineate the pathways involved in the catalytic hydrogenation of alkenes and alkynes by $[\text{Ru}_3(\text{CO})_{12-x}(\text{PPh}_3)_x]$ ($x=1$ or 2) and show that the mechanism is highly dependent on the solvent.

When a sample of $[\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ (**1**) was examined with parahydrogen ($p\text{-H}_2$) in C_6D_6 or CDCl_3 by NMR spectroscopy at 296 K three pairs of enhanced resonances and an emission signal were observed in the hydride region (Figure 1a, C_6D_6). The complexes that yield these resonances have been assigned to species **2**–**5** (Scheme 1), and their NMR spectroscopic data is presented in Table 1. The ratio of the intensities of the hydride resonances of **2**, **3**, and **4** in CDCl_3 at 296 K is 58:9:1. Consequently, if the enhancement factors are the same, K_{23} is 6.4, and **2** corresponds to the dominant form in solution. This suggestion is consistent with the data observed under Boltzmann conditions at 244 K where the species become visible after 10000 scans. The PHIP resonances observed in C_6D_6 at $\delta = -10.2$, -11.2 , and -10.4 (Figure 1a) arise from terminal hydrides (namely **2t**, **3t**, and **4t**, respectively, where *t* indicates a terminal position), while those at $\delta = -17.3$, -17.8 , and -17.5 are due to bridging hydrides (namely **2b**, **3b**, and **4b**, respectively, where *b* indicates bridging).^[4]

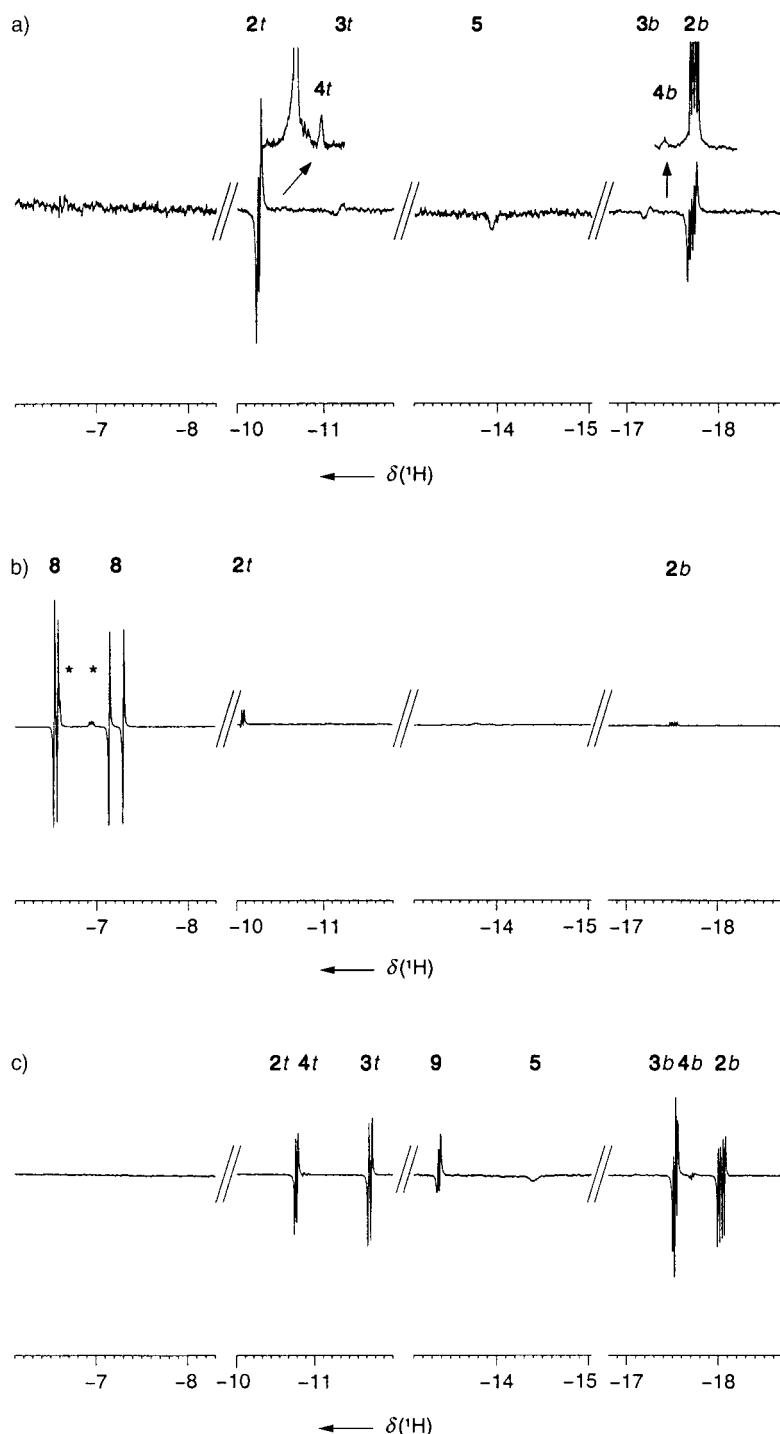


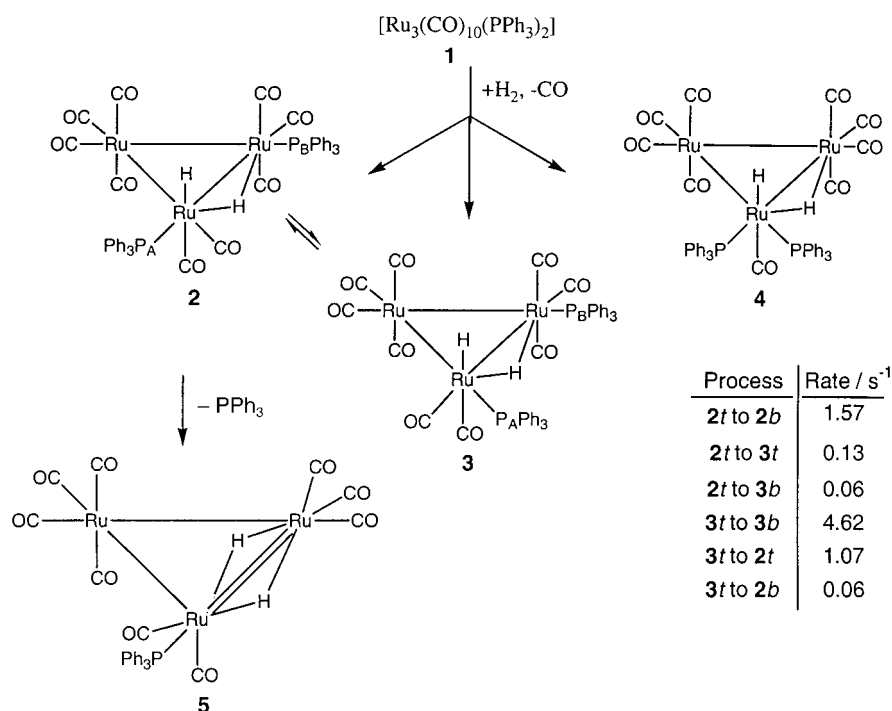
Figure 1. ^1H NMR spectra (256 scans) at constant vertical expansion showing selected parts of the hydride region of a series of samples of **1** obtained during reaction with $p\text{-H}_2$ at 296 K: a) In C_6D_6 , with insets showing very weak signals due to species **4**, detected after 10000 scans at 244 K in $[\text{D}_8]\text{toluene}$. b) In C_6D_6 in the presence of a 100-fold excess of styrene. Enhanced resonances due to the *cis,trans* isomer of **8** are clearly visible. The peaks marked (*) are due to the corresponding *cis,cis* isomer of **8**.^[4] c) In CDCl_3 in the presence of a 100-fold excess of diphenylacetylene.

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Notably, **2t** and **3t** couple to a single ^{31}P nucleus that is *cis* to each hydride ($J(\text{P}_\text{A},\text{H})$ values are 11 and 8 Hz, respectively). In contrast, **2b** and **3b** couple to two phosphorus nuclei. Since the resonance for **2b** appears as a doublet ($J(\text{P}_\text{A},\text{H}) = 20$ Hz) of doublets ($J(\text{P}_\text{B},\text{H}) = 10$ Hz) of antiphase doublets, and that for **3b** appears as a triplet ($J(\text{P},\text{H}) = 9$ Hz) of antiphase



Scheme 1. Structure and observed reaction pathways connecting products formed by *p*-H₂ addition to **1**. Rate constants for hydride interchange between **2** and **3** obtained in CDCl₃ at 301 K are tabulated.

Table 1. ¹H and ³¹P NMR data at 296 K for **2**–**9** with labeling according to Scheme 1 (400 MHz, CDCl₃, **7** at 233 K, **8** in C₆D₆).

	δ (hydride)	δ (PPh ₃)
2	–10.84, dd, <i>J</i> (P _A ,H) = 11 Hz, <i>J</i> (H,H) = –4.5 Hz, (2t)	44.60, s (P _A)
	–17.57, ddd, <i>J</i> (P _B ,H) = 10 Hz, <i>J</i> (P _A ,H) = 20 Hz, <i>J</i> (H,H) = –4.5 Hz, (2b)	31.25, s (P _B)
3	–11.68, dd, <i>J</i> (P _A ,H) = 8 Hz, <i>J</i> (H,H) = –4.5 Hz, (3t)	22.91, s (P _A)
	–17.76, ddd, <i>J</i> (P _B ,H) = 9 Hz, <i>J</i> (P _A ,H) = 9 Hz, <i>J</i> (H,H) = –4.5 Hz, (3b)	30.13, s (P _B)
4	–10.87, td, <i>J</i> (P,H) = 15.0 Hz, <i>J</i> (H,H) = –4.5 Hz, (4t)	41.1, s
	–17.47, dd, <i>J</i> (P,H) = 10 Hz, <i>J</i> (H,H) = –4.5 Hz, (4b)	
5	–14.35, br s	32.1, s
7	–11.43, s (7t)	30.7, s
	–18.34, d, <i>J</i> (P,H) = 10 Hz, (7b)	
8	–6.54, dd, <i>J</i> (P,H) = 16 Hz, <i>J</i> (H,H) = –5.5 Hz	44.91, s
	–7.22, dd, <i>J</i> (P,H) = 62 Hz, <i>J</i> (H,H) = –5.5 Hz	
9	–13.32, dd, <i>J</i> (P,H) = 10 Hz, <i>J</i> (H,H) = –4.5 Hz	36.6, s
	7.5, d, <i>J</i> (H,H) = –4.5 Hz	

doublets, **2b** is *trans* to one phosphane and *cis* to a second, while **3b** is *cis* to both phosphanes. The appearance of the hydride resonances for complex **4** differ significantly from those observed for **2** and **3** because both **4t** and **4b** couple to two ³¹P nuclei in accordance with both phosphanes being coordinated to the same Ru center. COSY and HMQC measurements are consistent with all these assignments.

The remaining signal at δ = –13.7 failed to show resolvable fine structure even at 233 K. Since this hydride resonance was initially observed as an emission signal, it must be formed by a cluster with inequivalent hydrides in an analogous manner to that described by Aime et al.^[5] The identity of this species, namely **5** (Scheme 1), is supported by the kinetic behavior described later.

Examination of the related mono-phosphane cluster [Ru₃(CO)₁₁(PPh₃)] (**6**) with *p*-H₂ in CDCl₃ at 296 K revealed a new species (**7**) with two broad hydride resonances (see Table 1). Since the signal at δ = –11.43 due to **7t** does not couple to ³¹P, while that at δ = –18.34 due to **7b** couples to a single ³¹P nucleus, the structure of the product is analogous to that for **2** (Scheme 1) but with phosphane P_APh₃ replaced by CO.

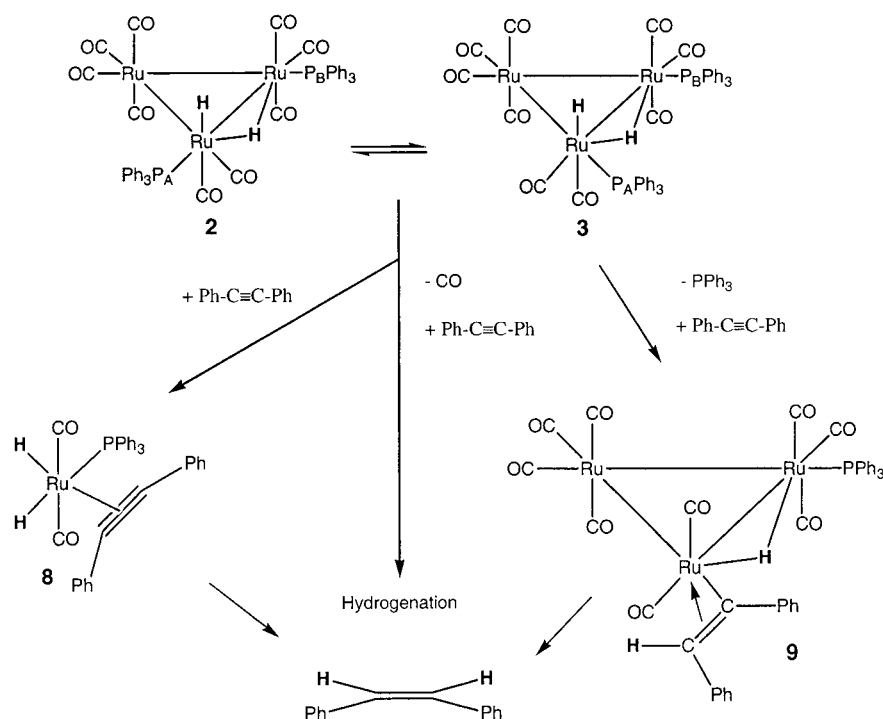
When a sample of **1** was monitored in C₆D₆ with *p*-H₂ in the presence of a 100-fold excess of styrene, in addition to signals described above, two new PHP-enhanced resonances were observed at δ = –6.54 (doublet of anti-phase doublets (*dad*), *J*(P,H) = 16 Hz) and δ = –7.22 (*dad*, *J*(P,H) = 62 Hz) as shown in Figure 1b. This species (**8**) has signals which have similar characteristics to those reported for [Ru(H)₂(CO)₃PPh₃].^[4] When the same experiments were repeated with 3-nitrostyrene as the substrate, the cor-

responding product resonances moved to δ = –6.65 and –7.35, whilst with phenylacetylene they moved to δ = –8.57 and –9.46. The associated species therefore contains the substrate, namely [Ru(H)₂(CO)₂(L)PPh₃] (L = styrene, 3-nitrostyrene and phenylacetylene). Surprisingly, when **1** was treated with *p*-H₂ and styrene in CDCl₃, the resonances for [Ru(H)₂(CO)₂(styrene)PPh₃] were five times less intense than those observed in C₆D₆, while the resonance for **2t** was 25 % larger and that for **3t** remained unchanged.

When a sample of **1** was examined in CDCl₃ with *p*-H₂ in the presence of a 100-fold excess of diphenylacetylene the spectrum shown in Figure 1c was obtained. Enhanced hydride resonances matching those described for **2**–**5** were present with similar initial intensities to those seen in the absence of substrate. However, the signal intensities associated with **2** and **3** rapidly increase in size (by a factor of 5 for **2** and a factor of 32 for **3**) until after 1 min they have the same relative intensity. Since hydrogenation is evident in these spectra as enhanced signals for PhH¹³C≡¹²CHPh,^[6] this effect can be explained by promotion of the rate of hydrogen cycling by sacrificial hydrogenation.^[7] Since the hydride signals associated with **4** show only minor enhancement this species is a poor hydrogenation catalyst.

Surprisingly, a new signal due to a bridging hydride that coupled to a single phosphorus center was now observed at δ = –13.32 (*dad*, *J*(P,H) = 10 Hz; Figure 1c). Since the associated coupling partner surprisingly appears at δ = 7.5, the new species (**9**) contains a pendant vinyl unit (*μ*-η²) and bridging hydride (see Scheme 2).^[8] When **6** was used as the precursor, the signals for **9** were substantially larger requiring **9** to contain only one phosphane.

It has previously been demonstrated that the dynamic behavior of *p*-H₂ enhanced hydride ligands can be explored by



Scheme 2. Intermediates derived from **2** and **3** during the hydrogenation of Ph-C≡C-Ph.

exchange spectroscopy (EXSY).^[7,9] This technique allows chemical reactions to be monitored by examining magnetization exchange as a function of the reaction time as illustrated in Figure 2 for **3**.^[10] Notably, for mixing times in

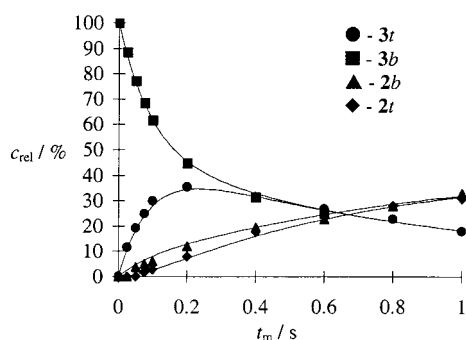


Figure 2. Simulation/experimental trace showing exchange processes starting from site **3b** of **3** in CDCl₃ at 301 K in the presence of a 100-fold excess of alkyne. The points corresponding to sites **3t**, **3b**, **2b**, and **2t**, defined according to the inset key, represent experimental data, while the solid line indicates the simulated values (t_m = mixing time).

excess of 500 ms, transfer of magnetization from **3b** into **4**, **5**, **9**, and the hydrogenation product *cis*-stilbene was observed in accordance with Figure 3a and b. The associated rate constants are tabulated in Scheme 1.

Experiments involving varying the concentrations of CO, PPh₃, and alkyne at constant [H₂] revealed that 1) the rate of interconversion of **2** and **3** into **5** and **9** is reduced as the concentration of PPh₃ increases, 2) the interconversion between **2** and **3** and the rate of hydrogenation decrease with increase in CO concentration, and 3) increasing the alkyne

concentration has no visible effect. However, since **2** and **3** correspond to minor reaction products the relative excess of alkyne is always substantial.

Collectively, these data suggest that *interchange* between **2** and **3** involves CO loss. The ratio $(k_{3t \rightarrow 2t} + k_{3t \rightarrow 2b}) / (k_{2t \rightarrow 3t} + k_{2t \rightarrow 3b})$ deduced from the exchange data collected in the presence of alkyne equates to a sixfold preference for **2** and matches that determined in the absence of substrate. This confirms that the hydride signal intensities of **2** and **3** become comparable because **3** is the more active hydrogenation catalyst. Compound **3** converts directly into **9**, and **2** into **5**, with rates that decrease with increase in [PPh₃]. It can therefore be concluded that both **5** and **9** are formed by PPh₃ loss with complex **5** corresponding to the coordinatively unsaturated 46-electron species [Ru₃(μ-H)₂(CO)₉-PPh₃] with equivalent hydrides. Interestingly, the vinyl hydride **9** was observed to eliminate PhCH=CHPh at longer mixing times.

The mechanism of hydrogenation can be deduced from these data (Scheme 2). First, in polar solvents products **2** and **3** undergo rapid CO loss to yield a vacant coordination site that reacts with PhC≡CPh. Rapid hydride transfer within the associated cluster-based intermediate subsequently generates *cis*-stilbene. Loss of PPh₃ from **2** and **3** competes with CO loss and leads to the formation of less active **5** and **9** (see also Scheme 1). Interestingly, it is the minor isomer **3** that proves to be the dominant hydrogenation catalyst in polar solvents. Second, in nonpolar solvents such as C₆D₆ catalyst fragmentation to [Ru(H)₂(CO)₂(PPh₃)(substrate)] (e.g., **8** in Scheme 2) is observed. Subsequent mononuclear-based hydrogenation then competes with that by the intact clusters **2** and **3**. The solvent therefore plays a central role in controlling the reaction selectivity shown by triruthenium clusters with the overall rate of hydrogenation increasing as the solvent polarity increases.

Experimental Section

The clusters [Ru₃(CO)₁₀(PPh₃)₂] and [Ru₃(CO)₁₁(PPh₃)] were prepared according to literature methods.^[11] For the PHIP experiments, *p*-H₂ was prepared as described previously.^[12] NMR spectra were recorded on a Bruker DRX-400 spectrometer with ¹H at 400.13 and ³¹P at 161.9 MHz and ¹H NMR chemical shifts are reported relative to [D₅]benzene (δ = 7.13) and CHCl₃ (δ = 7.27), while ³¹P NMR shifts are relative to external phosphoric acid. Hydride exchange pathways were examined by magnetization transfer experiments based on the EXSY approach.^[7,9] The sum of the integrals of the primary resonance and the corresponding exchange peaks were first normalized to 100%. A kinetic model was then constructed in Excel that allowed the peak intensities to be explicitly calculated as a function of the exchange rate constant and reaction time. The calculated peak intensities were then compared to the experimental values, noting the squares of the differences.^[13] Rate constants were varied to minimize the

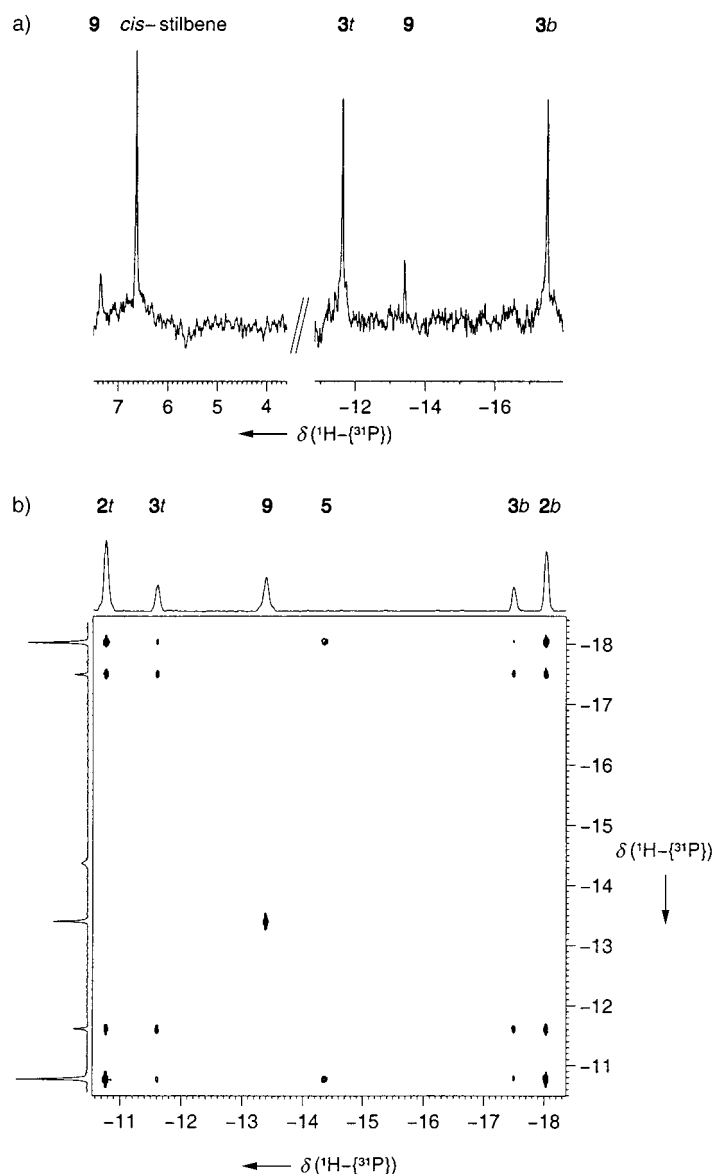


Figure 3. a) 1D $^1\text{H}\{-^{31}\text{P}\}$ EXSY NMR spectrum recorded in CDCl_3 at 301 K on a sample containing **1**, $p\text{-H}_2$, and a 100-fold excess of diphenylacetylene. The resonance for **3t** was selectively excited and the results for a reaction time of 700 ms are displayed. Exchange into **3b**, **9**, and *cis*-stilbene is indicated; b) 2D $^1\text{H}\{-^{31}\text{P}\}$ EXSY spectrum (positive contours) of an identical sample employing a mixing time of 400 ms. Off-diagonal peaks arise due to chemical exchange.

sum of the squares of the differences. The rate constants obtained in this way were multiplied by two.^[14]

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Samarium-Catalyzed Tandem Semipinacol Rearrangement/Tishchenko Reaction of α -Hydroxy Epoxides: A Novel Approach to Highly Stereoselective Construction of 2-Quaternary 1,3-Diol Units**

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Diastereoselective constructions of 1,3-diol units have always been in high demand in synthetic organic chemistry, and preparation of 2-quaternary 1,3-diol units is of major importance for the synthesis of many biologically significant molecules, such as the Furaquinocins,^[1] and chiral ligands.^[2] However, the quaternary carbon atom is generally difficult to construct with high diastereoselectivity, because a simple aldol reaction of carbonyl compounds is not efficient in this situation. Several procedures for construction of 2-quaternary 1,3-diol units have already been developed on the basis of the Lewis acid mediated semipinacol rearrangement of α -hydroxy epoxides. However, they generally need one equivalent or an excess of a promoter and produce only the β -

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