Variable-temperature NMR study of dynamic exchange in sodium (.mu.-fluoro)bis(triethylaluminate)

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Registry No. 1, 105472-14-8; 2, 105472-94-4; 3, 105472-95-5; 4, 105501-04-0; 5, 105472-92-2; 6, 105472-93-3; (η^5-C_5H_5)Co(CO)$_2$, 12078-25-0; Cr(CO)$_6$, 13007-92-6.

Supplementary Material Available: Tables of structure factors, thermal parameters and calculated mean planes for compounds 3 and 6, a stereo diagram of unit cell packing for 3, and a table of short inter- and intramolecular nonbonded contacts in 3 (9 pages); listings of observed and calculated structure factors for 3 and 6 (34 pages). Ordering information is given on any current masthead page.

Variable-Temperature NMR Study of Dynamic Exchange in Sodium (μ-Fluoro)bis(triethylaluminate)

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Variable-temperature ^{13}C studies and ^1H and ^{27}Al NMR studies have been carried out on mixtures of Na[Al_2Et_6F] and Al_2Et_6. We observe that Na[Al_2Et_6F] undergoes facile exchange of $AlEt_3$ with Al_2Et_6 in contrast to previously published work. The exchange process has been shown to involve a dissociative mechanism. A ΔH^* of 20.4 kcal mol^{-1} (85.4 kJ mol^{-1}) and ΔS^* of 18.7 eu were determined. The value of ΔH^* closely approximates the bond dissociation energy for the Al–F bond in Et_3Al–F–$AlEt_3$. This is the first reported bond dissociation energy for the Al–F bond in this unusual class of compounds.

M[Al_2R_6X] complexes[2] (where M is alkali metal or tetraalkylammonium ion; X is halide, pseudohalide, or oxo anion; and R is an alkyl group) are of interest from the point of view of structure,[3] electronic properties,[4] thermal behavior,[5] and utilization in separating triethylaluminum from α-olefins[6] and as "liquid clathrates".[7] However, little, if any, fundamental thermodynamic bond data or kinetic data are available to aid in understanding the chemistry of these materials.

In this paper, we report the ^1H, ^{13}C, and ^{27}Al NMR characterization of Na[Al_2Et_6F]. Unexpectedly, we find that Na[Al_2Et_6F] exchanges with Al_2Et_6 in toluene solution. The mechanism of exchange has been found to involve dissociation of Na[Al_2Et_6F] to Na[$AlEt_3F$] and $AlEt_3$. Examination of the activation energy for the exchange reaction yields a value for the Et_3Al–F bond dissociation energy for this complex.

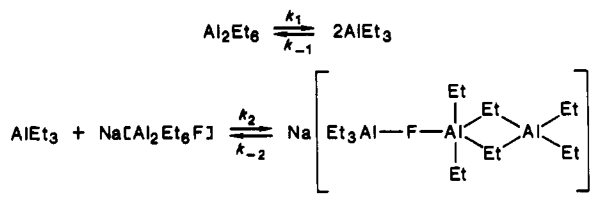
Neat mixtures of Na[Al_2Pr_6F] and Al_2Et_6 show little, if any exchange by ^{27}Al NMR to form Na[Al_2Et_6F] and Al_2Pr_6 at 120 °C.[8] However, in toluene-d_8 at room temperature, we observed by ^1H NMR the characteristic averaging of ethyl resonances, indicative of rapid exchange when Al_2Et_6 was mixed with M[Al_2Et_6X] complexes. Exchange was demonstrated by plotting the ^1H chemical shift of the methyl resonance in mixtures of Al_2Et_6 and Na[Al_2Et_6F] vs. the mole fraction of Na[Al_2Et_6F]. A linear dependence was observed (Figure 1).

Scheme I

$$\mathrm{Na[Al_2Et_6F]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Na[AlEt_3F]} + \mathrm{AlEt_3}$$

$$\mathrm{Al_2Et_6} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{2AlEt_3}$$

Scheme II



The exchange process is of interest from a mechanistic point of view. We have considered two possible mechanisms for the exchange process. The first involves dissociation of M[Al_2Et_6X] to form M[$AlEt_3X$] plus $AlEt_3$ (Scheme I). The second involves a bimolecular associative mechanism to form an alkyl-bridged complex with five-coordinate aluminum (Scheme II). Both mechanisms have precedence in the literature.[9]

A variable-temperature ^{13}C NMR study was carried out by using a mixture of Al_2Et_6 (0.23 g) and Na[Al_2Et_6F] (0.27

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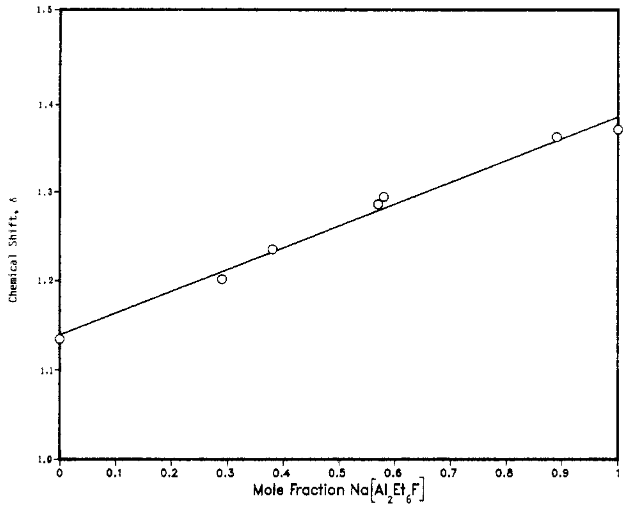

Figure 1. Dependence of ^1H NMR chemical shift of CH_3 resonance on mole fraction of $Na[Al_2Et_6F]$ in $Al_2Et_6/Na[Al_2Et_6F]$ mixture.

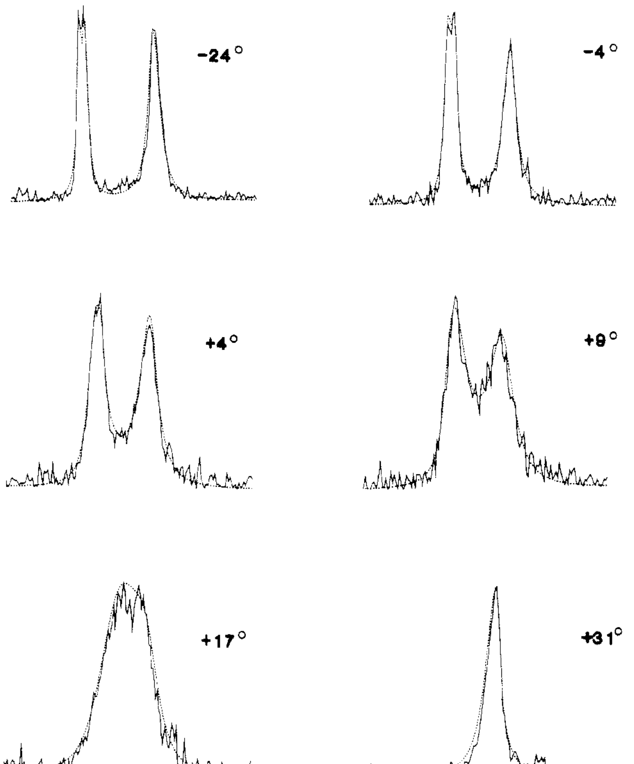

Figure 2. Computer-simulated vs. experimental line-shape analysis of variable-temperature ^{13}C NMR spectra of $Na[Al_2Et_6F]$ plus Al_2Et_6 mixture (CH_3 region of spectra).

g) in 0.94 mL of toluene-d_8. At room temperature a single average resonance was observed for the CH_3 carbon (δ 9.4) and for one CH_2 carbon (δ 0.7). As the temperature was lowered to −40 °C, these peaks broadened and split and separate resonances were observed for Al_2Et_6 [δ 9.2 (s, CH_3), 0.9 (br s, CH_2)] and for $Na[Al_2Et_6F]$ [δ 9.9 (d, $^3J_{CF}$ = 1.8 Hz, CH_3), 0.4 (d, $^2J_{CF}$ = 18 Hz, CH_2)].

The doublet for the CH_2 and CH_3 carbons in $Na[Al_2Et_6F]$ is attributed to long-range C–F coupling through two and three bonds, respectively.[10] As the temperature is lowered still further, the Al_2Et_6 ethyl groups split into bridging and terminal groups as previously reported.[11] The fact that Al_2Et_6 bridging and terminal exchange is frozen out ca. 60 °C lower than the exchange of $Na[Al_2Et_6F]$ and Al_2Et_6 indicates that $k_2 >> k_1$ in Scheme I.

Table I. Rate Data as a Function of Temperature for $Al_2Et_6/Na[Al_2Et_6F]$ Mixture

temp, °C	$1/\tau_A$, s^{-1}	std error[a]
−19	0	
−4	1.5	0.2
0	4.0	0.2
+4	7.5	0.4
+5	7.0	0.3
+6	8.8	0.5
+9	13.2	0.8
+12	19	1.0
+17	30	1.7
+18	40	3.0
+19	42	3.2
+22	49	4.0
+24	87	2.1
+31	199	19.7

[a] DNMR5 program.

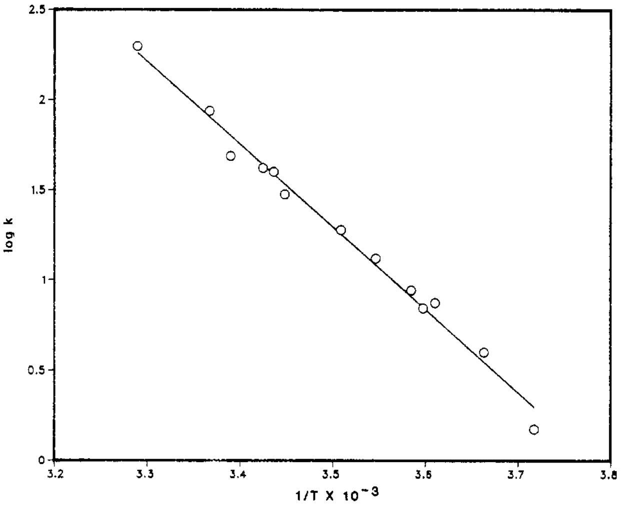

Figure 3. Arrhenius plot for $Al_2Et_6/Na[Al_2Et_6F]$ exchange process.

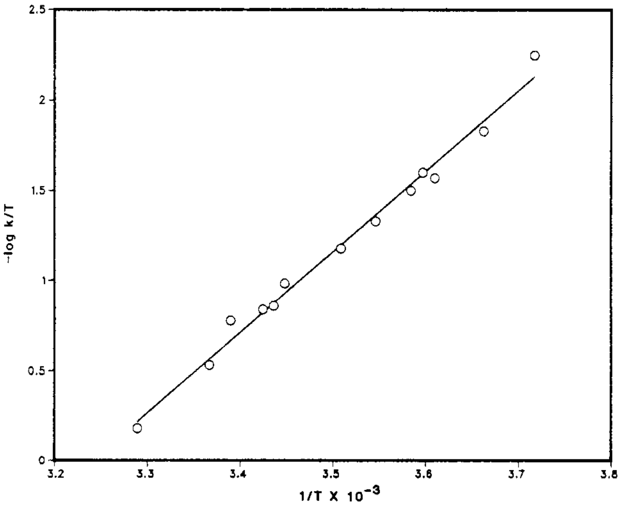

Figure 4. Eyring plot for $Al_2Et_6/Na[Al_2Et_6F]$ exchange process.

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[10] At room temperature, the ^{19}F NMR spectrum of the $Al_2Et_6/Na[Al_2Et_6F]$ mixture consists of a single line at δ −160.6 vs. $CFCl_3$. An unidentified impurity (20%) appears at δ −156. Variable-temperature experiments (up to 130 °C) have shown the absence of exchange between these peaks.

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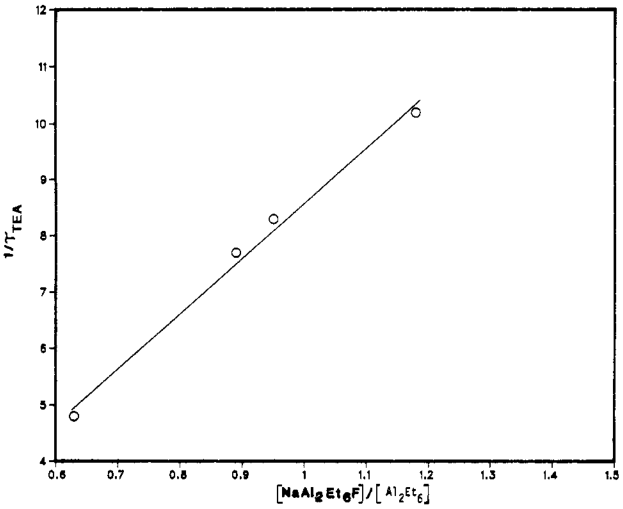

Figure 5. Concentration dependence of reciprocal mean exchange time for Al$_2$Et$_6$ ($1/\tau_{TEA}$) in toluene at +6 °C.

Supporting evidence for the dissociative mechanism was obtained by carrying out complete line-shape analysis of variable-temperature ^{13}C NMR spectra over the temperature range −24 to 31 °C using the DNMR5 program[12] (Figure 2). The Arrhenius plot of log k vs. $1/T$ (Table I), where $k = 1/\tau_A$, was carried out to give an E_a of 21.8 kcal mol^{-1} (91.2 kJ mol^{-1}) and log A of 17.4 eu (Figure 3). The Eyring plot (log (k/T) vs. $1/T$) gave a $\Delta H^\ddagger$ of 20.4 kcal mol^{-1} (85.4 kJ mol^{-1}) and a $\Delta S^\ddagger$ of 18.7 eu (Figure 4). Since $\Delta H^\ddagger$ for the exchange was greater than $\Delta H^\ddagger$ for bridge–terminal exchange of Al$_2$Et$_6$ in toluene solution ($\Delta H^\ddagger$ = 15.0 kcal mol^{-1} (62.8 kJ mol^{-1})),[11] our assignment of a dissociative mechanism seems justified.

Examination of $\Delta S^\ddagger$ for related exchange processes[9,13] indicates that a negative $\Delta S^\ddagger$ is evidence for a bimolecular associative mechanism such as Scheme II and a positive $\Delta S^\ddagger$ is evidence for a dissociative mechanism. The observed $\Delta S^\ddagger$ of 18.7 eu supports the dissociative mechanism.

A satisfactory kinetic expression for the observed exchange rates can be obtained by using the approach of Matteson.[14] Using this procedure, one obtains for the dissociative mechanism

$$\frac{1}{\tau_A} = \frac{k_2 Q[\mathrm{Al_2Et_6}]}{[\mathrm{NaAl_2Et_6F}]} \tag{1}$$

$$\frac{1}{\tau_{TEA}} = k_2 Q \tag{2}$$

where $1/\tau_A$ and $1/\tau_{TEA}$ are the reciprocal mean exchange times for Na[Al$_2$Et$_6$F] and Al$_2$Et$_6$, respectively, and where Q is represented by the expression

$$Q = \frac{[\mathrm{NaAl_2Et_6F}]}{(k_2/k_1)[\mathrm{Al_2Et_6}] + [\mathrm{NaAl_2Et_6F}]} \tag{3}$$

See Appendix for further information relating to derivation of eq 1–3.

Since Al$_2$Et$_6$ bridge–terminal exchange is rapid compared to exchange between Na[Al$_2$Et$_6$F] and Al$_2$Et$_6$ ($k_2 >> k_1$), Q approaches k_1[NaAl$_2$Et$_6$F]/k_2[Al$_2$Et$_6$]. Therefore, $1/\tau_{TEA}$ approaches k_1[NaAl$_2$Et$_6$F]/[Al$_2$Et$_6$] for the dissociative mechanism.

Table II. Concentration Dependencies of the Reciprocal Mean Exchange Times for CH$_3$ Group Exchange for Na[Al$_2$Et$_6$F] and Al$_2$Et$_6$ in Toluene at +6 °C

concn of A, M (Na[Al$_2$Et$_6$F])	concn of TEA, M (Al$_2$Et$_6$)	$1/\tau_A$, s^{-1}	std error[a]	$1/\tau_{TEA}$, s^{-1}
1.10	1.24	8.7	0.5	7.7
0.98	1.56	7.6	0.4	4.8
1.06	1.12	8.8	0.5	8.3
1.04	0.88	8.6	0.5	10.2

[a] DNMR5 program.

Table III. Concentration Dependencies of the Reciprocal Mean Exchange Times for CH$_3$ Group Exchange for Na[Al$_2$Et$_6$F] and Al$_2$Et$_6$ in Toluene at +18 °C

concn of A, M (Na[Al$_2$Et$_6$F])	concn of TEA, M (Al$_2$Et$_6$)	$1/\tau_A$, s^{-1}	std error[a]	$1/\tau_{TEA}$, s^{-1}
1.06	1.12	27	1.4	26
1.04	0.88	28	3.3	33
2.10	0.63	83	35.4	276
1.29	0.97	50	5.7	67

[a] DNMR5 program.

Table IV. ^{27}Al NMR Line Widths ($w_{1/2}$)

sample	$w_{1/2}$, Hz
TEA	2900
Na[Al$_2$Et$_6$F]	7600
mixture TEA plus Na[Al$_2$Et$_6$F]	4600

A plot of $1/\tau_{TEA}$ vs. [NaAl$_2$Et$_6$F]/[Al$_2$Et$_6$] for various concentrations at +6 °C (Table II) gives the expected straight line with zero intercept (intercept = −1.2 ± 1.2) in support of a dissociative mechanism (Figure 5).

The slope of the curve in Figure 5 (9.9 ± 1.3 s^{-1}) is k_1 and is reasonably close to $1/\tau_A$ (average 8.4 s^{-1}) from Table II, which approaches k_1 as Q approaches k_1[NaAl$_2$Et$_6$F]/k_2[Al$_2$Et$_6$] (eq 1). Additional experiments that were carried out at 18 °C by using a wider concentration range for [NaAl$_2$Et$_6$F] also support these conclusions (Table III).

The value of 85.4 kJ mol^{-1} for $\Delta H^\ddagger$ for the exchange reaction approximates the bond dissociation energy for the Al–F bond in Et$_3$Al–F–AlEt$_3$. This value is the first reported bond dissociation energy for an Al–F bond in this class of compounds.

Aromatic solvents such as toluene have been shown to lower the heat of dissociation of trialkylaluminum compounds[15] due to complex formation of the aromatic with the organoaluminum. Toluene was shown to have a $\Delta H_{\mathrm{complex}}$ = −3.8 kcal mol^{-1} (−15.9 kJ mol^{-1}).[14] It is not known if there is an appreciable solvent effect due to toluene in the Na[Al$_2$Et$_6$F] system.

An ^{27}Al NMR study of Al$_2$Et$_6$, Na[Al$_2$Et$_6$F], and the mixture at 20 °C was performed. This study indicated (Table IV) that in the mixture, a single resonance with a line width (4600 Hz) intermediate between the line width of Al$_2$Et$_6$ (2900 Hz) and Na[Al$_2$Et$_6$F] (7600 Hz) was observed.

At +19 °C, we observed a rate of exchange $1/\tau_A$ = 42 s^{-1} (Table I). Since this corresponds to a contribution of about 132 Hz to the line width at half-height, it is unlikely that exchange would have been detected via ^{27}Al NMR, as reported earlier.[8b] Thus exchange may have occurred in Na[Al$_2$Pr$_6$F] and Al$_2$Et$_6$ mixtures but was undetected by ^{27}Al NMR.

Examination of exchange reactions of other members of the class M[Al$_2$Et$_6$X] via ^{13}C NMR may yield important thermodynamic and kinetic information, useful in un-

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derstanding the chemistry and properties of these materials.

Experimental Section

^{13}C NMR spectra were obtained on a Varian FT-80A instrument equipped with a 10-mm ^{13}C–^{1}H switchable probe and the standard temperature controller. Samples in sealed tubes with toluene-d_8 as lock solvent were excited with a 45° pulse every second with full proton decoupling. Only 512 points were taken at a spectral width of 500 Hz in most cases. The free induction decays were zero filled to 1024 points before Fourier transformation with no additional line broadening added in the data processing. Each sample required 2000–4000 pulses to accumulate sufficient signal to noise for further data analysis.

The temperature was measured by the exchange method: an open 10-mm NMR tube containing about 2 mL of cooking oil and an immersed copper constantan thermocouple was allowed to equilibrate in the spectrometer with the decoupler on before measurement of the thermocouple voltage with a potentiometer sensitive to ±0.001 mV. Temperatures were read from standard tables. The samples were also allowed to equilibrate for 15 min before any data acquisition.

^{1}H NMR spectra were obtained on a Varian T60 NMR spectrometer. ^{27}Al NMR spectra were obtained on a Varian XL200 spectrometer using resonance frequency at (4.7 T) 52.128 MHz. Since we were interested only in peak width, the chemical shifts were not obtained.

Samples of Al_2Et_6 were obtained from Texas Alkyls and used as received. $Na[Al_2Et_6F]$ was prepared[2] by heating Al_2Et_6 (2.0 mol) with anhydrous NaF (1.0 mol) under rigorously purified inert atmosphere.

Appendix

The derivation follows Matteson.[14]

$$Na[Al_2Et_6F] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Na[AlEt_3F] + AlEt_3$$

$$Al_2Et_6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2[AlEt_3]$$

Let Q = the fraction of ethyl groups on $AlEt_3$ that have come from $Na[Al_2Et_6F]$. As $AlEt_3$ dimerizes, $-d[Et_{2:1}]/dt = 6Qk_2[Al_2Et_6]$. Also, $-d[Et_{TEA}]/dt = 6(1 - Q)k_1[Na[Al_2Et_6F]]$. But, $-d[Et_{2:1}]/dt = -d[Et_{TEA}]/dt$. So, $6Qk_2[Al_2Et_6] = 6(1 - Q)k_1[Na[Al_2Et_6F]]$.

$$Q = \frac{[Na[Al_2Et_6F]]}{(k_2/k_1)[Al_2Et_6] + [Na[Al_2Et_6F]]} \qquad (3)$$

The lifetimes are

$$1/\tau_{2:1} = \frac{-d[Et_{2:1}]}{6dt[Na[Al_2Et_6F]]} = \frac{k_2Q[Al_2Et_6]}{[Na[Al_2Et_6F]]} \qquad (1)$$

$$1/\tau_{TEA} = \frac{-d[Et_{TEA}]}{6dt[Al_2Et_6]} = k_2Q \qquad (2)$$

Gas-Phase Reactions of Yttrium and Lanthanum Ions with Alkanes by Fourier Transform Mass Spectrometry

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The gas-phase reactions of Y^+ and La^+ with linear, branched, and cyclic alkanes are reported. Dehydrogenation is predominant for ethane and propane while dehydrogenation and carbon–carbon bond cleavage occur for linear and branched alkanes larger than C_3. As was observed for the other group 3 metal ion, Sc^+, both Y^+ and La^+ form characteristic dialkyl ions. Evidence is given for two different $YC_4H_6^+$ and $LaC_4H_6^+$ isomeric structures. Reaction with cyclopropane gives predominant dehydrogenation products. The observation of $LaCH_2^+$ from cyclopropane implies $D°(La^+–CH_2) > 93$ kcal/mol. Only dehydrogenation products are observed for cyclopentane and cyclohexane. In general, the primary reactions of Y^+ and La^+ are found to be similar to those of Sc^+. The secondary reactions of La^+, however, are found to be considerably slower than those for Sc^+ and Y^+.

Introduction

In recent years, a number of laboratories have demonstrated that transition-metal ions are highly reactive with organics in the gas phase.[1-16] There has been considerable interest in these reactions from both the standpoint of the fundamental chemistry involved as well as the practical applications of transition-metal ions as selective chemical ionization reagents for analytical mass spectrometry.[1,13,14] Thus far, most of the attention has focussed on the interactions of first-row groups 8–10 transition-metal ions Fe^+, Co^+, and Ni^+ with simple hydrocarbons[4-6,8,11-14] and has resulted in a good understanding of the processes and

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