Figure 2. Schematic illustration of the correlation of the metal-based orbitals of an $[MX_3]_n$ cluster with (a) $n[MX_3]$ fragments and (b) a bare metal M_n cluster. The $(n + 1)$ skeletal electron pairs expected from the polyhedral skeletal electron pair theory are derived predominantly from the metal–metal-bonding orbitals in the s and d bands. The skeletal MO's are stabilized in the actual cluster by mixing in $(n + 1)$ of the $2n$ s/p MO's of M_n (not shown in the figure).

FeX$_3$ in this case] correlate with those of the final cluster, in the context of the isolobal analogy. In particular, Woolley states that the metal physics view would predict two metal–ligand antibonding orbitals with the totally symmetric representation. Woolley suggests that one of these will be derived from the in phase combination of the radial skeletal bonding hybrids of the FeX$_3$ fragments and therefore from the borane analogy would be expected to be strongly metal–metal bonding, but in the metal physics view this orbital may be expected to lie above E_{HOMO}. Such an orbital must clearly be occupied to give a closed-shell configuration for an 86-electron octahedron or a 72-electron trigonal bipyramid. Figure 1 clearly shows however that the "mystery" orbital is simply the central component of the $S_s^\sigma/S_X^\sigma/S_p^\sigma$ three-orbital interaction and is therefore metal–ligand nonbonding but metal–metal bonding, in accord with the isolobal analogy. Woolley is incorrect to imply however that the borane analogy requires that this orbital should be the most strongly bonding of the skeletal electron pairs. Since the energy level ordering of the frontier orbitals of BH (radial below tangential) and M(CO)$_3$ is reversed, it is entirely to be expected that the S^σ skeletal orbital should be the most strongly bonding for B_nH_n and yet the HOMO for $[M(CO)_3]_n$. Thus the confusion arising out of the qualitative metal physics predictions is clearly resolved in the light of EH calculations.

Although the specific EH calculations reported here in detail have been for Fe$_5$ clusters, further calculations on other systems have shown the bonding description given here to be general. Thus for any M_n cluster there will be $(n + 1)$ metal–metal-bonding MO's derived from the p orbitals (one S_p^σ and n L_p^π). Thus there will be $(n + 1)$ three-orbital–four-electron interactions, the central component of each corresponding to the $(n + 1)$ skeletal electron pairs expected from the polyhedral skeletal electron pair theory. It is important to recognize that it is the ligand-induced participation of the $(n + 1)$ *bonding* levels of the p band in such three orbital interactions which dictates the observed number of skeletal electron pairs. For an M_nX_x cluster there will be x M–X bonding MO's [formed from n L_s^σ and $(x − n)$ L_d^π and $\bar{L}_d^\pi$ orbitals], ($6n$

$− x$) d band MO's and $(n + 1)$ skeletal bonding MO's. For the case of an $[MX_3]_n$ cluster, derived from n conical MX$_3$ fragments, the way in which the orbitals of the cluster correlate with those of (a) n MX$_3$ fragments and (b) M$_n$ and X$_{3n}$ fragments is illustrated in Figure 2. There are a total of $(7n + 1)$ occupied MO's. It is the contention of this paper that the arrangement of these levels can be most effectively rationalized in the context of the EH method rather than *qualitative* predictions based on the methodology of metal physics.
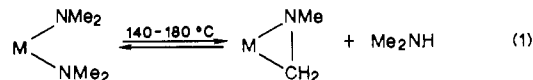

Contribution from the Experimental Station,
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Catalytic H–D Exchange in Deuteriated Alcohols Promoted by Early-Transition-Metal Alkoxides. Insight into a Mechanistic Puzzle[1]

William A. Nugent* and Rosalie M. Zubyk

Several years ago[2] we reported that early-transition-metal dialkylamides catalyze exchange between the N–H and C–H hydrogens of dimethylamine-*N-d*. The reaction was demonstrated to involve the reversible metalation of the dimethylamide ligand (eq 1). Since this observation led to the development of an
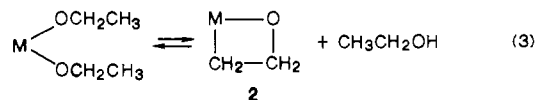
$$M\begin{matrix}\diagup NMe_2 \\ \diagdown NMe_2\end{matrix} \underset{140-180\ ^\circ C}{\rightleftarrows} M\begin{matrix}\diagup NMe \\ \diagdown CH_2\end{matrix} + Me_2NH \qquad (1)$$

unprecedented type of catalytic C–C bond–forming process,[2] we wished to explore the generality of such H–D exchange reactions and in particular whether alcohols might be similarly activated.

Catalytic H–D exchange in alcohols required elevated temperatures (180–220 °C). Nevertheless, heating ethanol-*d* in the presence of 1 mol % of the ethoxides of Nb, Ta, or Zr did result in exchange as indicated by the appearance of the OH resonance in the ^{1}H NMR spectrum. To our surprise, the deuterium was not scrambled into the α-position of the ethanol by analogy to eq 1. Instead, ^{2}H NMR showed exclusive incorporation of deuterium into the methyl group[3] (eq 2). By taking advantage of

$$CH_3CH_2OD \xrightarrow[M = Zr,\ Nb,\ Ta]{M(OEt)_m} CD_nH_{3-n}CH_2OH(D) \qquad (2)$$
$$\textbf{1}$$
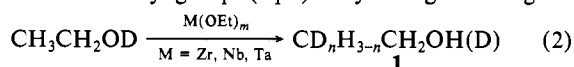
the isotopic shift effect in the ^{2}H NMR, it was possible to distinguish between deuterated products containing one, two, or three ^{2}H atoms in the methyl group. As summarized in Table I, even at low conversions, much of the product consisted of di- and trideuteriated ethanols (**1**; $n = 2$ or 3).

This observation complicates the mechanistic interpretation of eq 2. Although reversible cyclometallation according to eq 3 would explain the exclusive activation of the methyl hydrogen, it is not

$$M\begin{matrix}\diagup OCH_2CH_3 \\ \diagdown OCH_2CH_3\end{matrix} \rightleftharpoons \begin{matrix}M——O \\ |\quad\quad| \\ CH_2—CH_2\end{matrix} + CH_3CH_2OH \qquad (3)$$
$$\textbf{2}$$

apparent why such a process would result in predominant multiple deuteration. (Alkoxide exchange with free alcohol is known to be rapid.[2]) Moreover, oxametalacycle **2** is expected to decompose
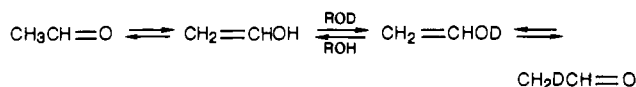
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(1) Contribution No. 4012.

(2) Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161–162.

(3) This situation represents a striking contrast with the scrambling of deuterium of CH$_3$CH$_2$OD exclusively onto the methylene carbon, which is promoted by low-valent group 8 catalysts: Regan, S. L. *J. Org. Chem.* **1974**, *39*, 260–261. Sasson, Y.; Blum, J. *J. Chem. Soc., , Chem. Commun.* **1974**, 309–310.

**Table I.** H–D Exchange in CH_3CH_2OD Catalyzed by Transition-Metal Ethoxides[a]

catalyst	temp, °C	% H–D exchange[c]	distribn of ^2H label,[b] %		
			CH_2D	CD_2H	CD_3
$Ti(OEt)_4$	180	0[e]			
$Zr(OEt)_4$	200	14	5	25	70
$Nb_2(OEt)_{10}$	200	18	27	41	32
$Ta_2(OEt)_{10}$	180	9			
$Ta_2(OEt)_{10}$	200	23	28	39	33
$Ta_2(OEt)_{10}$	220	47			
$Ta_2(OEt)_{10} + C_6H_5N^d$	200	55	38	39	23
$Ta_2(OEt)_{10} + Et_3N^d$	200	50			
$W(OEt)_6$	200	0[e,f]			

[a] All runs involved 0.5 mmol of catalyst in 50 mmol of ethanol-*d* for 14 h in evacuated glass tubes. [b] Relative areas of mono-, di-, and trideuteriated resonances, see Experimental Section. [c] Percent of starting OD incorporated into methyl group determined by area of OH NMR resonance. [d] Run additionally contains 2.0 mmol of amine additive. [e] Catalyst decomposed to white insolubles; no exchange detected under conditions where 1% exchange could be observed. [f] Ethanol was disporportioned to diethyl ether and H_2O.

Scheme I

$$CH_3CH{=}O \rightleftharpoons CH_2{=}CHOH \underset{ROH}{\overset{ROD}{\rightleftharpoons}} CH_2{=}CHOD \rightleftharpoons$$

$$CH_2DCH{=}O$$

readily to ethylene and a metal–oxo species by analogy to the intermediates in the Tebbe–Grubbs reaction.[4] No ethylene could be detected in our reaction products.

Some insight into this mechanistic puzzle was provided by the discovery of a second hydrogen exchange process, which proceeds at comparable rates under the same reaction conditions. For example, optically active (*R*)-(–)-2-butanol was racemized at 200 °C in the presence of Zr or Ta alkoxides by this "α-exchange" process. Moreover, a mixture of ethanol and ethanol-*1,1-d₂* could be scrambled to the monodeuterated alcohol by using the same metal alkoxides (eq 4). It is noteworthy that *the OH and β-*

$$CH_3CH_2OH + CH_3CD_2OH \underset{}{\overset{M(OEt)_x}{\rightleftharpoons}} 2CH_3CHDOH \quad (4)$$
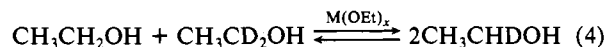
protons constitute one exchangeable pool and the α-protons constitute a separate, independently exchanging set of C–H's. There is no detectable crossover between these systems.

It seemed reasonable that such an α-exchange process might proceed through the intermediacy of the corresponding carbonyl compound (i.e. acetaldehyde, 2-butanone). This hypothesis was attractive because it also offers a possible mechanism for the β-exchange reaction. Thus, tautomerization of an intermediate carbonyl compound would result in the incorporation of deuterium of ROD into the β-position as illustrated for the case of ethanol-*d* in Scheme I. However, preliminary efforts to demonstrate the intermediacy of the aldehyde or ketone were inconclusive: (1) Vacuum transfer of ethanol-*d* from sodium borohydride prior to reaction did not diminish the rate of β-exchange. (2) Capillary column gas chromatographic analysis of the reaction products from ethanol-*d* or (*R*)-(–)-2-butanol showed no detectable amount of acetaldehyde or 2-butanone under conditions where 0.01 mol % of these materials could be observed. (3) Intentional spiking of the ethanol-*d* reaction with 0.1 mol % acetaldehyde results in only a modest (1.9×) increase in the rate of β-exchange. Therefore we desired a definitive test of whether the α- and β-exchange reactions involve a common intermediate.

To accomplish this we used *trans*-4-*tert*-butylcyclohexanol-*d* (3) as our starting alcohol. Treatment of 3 in ethanol-*d* with either tantalum or zirconium ethoxide as catalyst (220 °C, 14 h) gave respectively 9.2% and 5.5% conversion to the cis isomer. *O*-Silylation of the product mixture with *N,N*-dimethylaminotri-

methylsilane gave silyl ethers of the cis and trans alcohols, which were well separated by gas chromatography. For both catalysts the silylated cis alcohol was over-whelmingly tri- and tetradeuteriated (*m/e* = 231 and 232). In contrast, the authentic trimethylsilyl ether of unlabeled cis alcohol gave *m/e* = 228. Since the "deuteron pool" is continuously diluted by OH formed during the ongoing exchange, the reaction at very low conversions can reasonably be described as


3
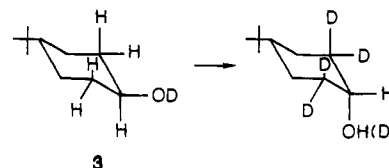
Thus, *that same alcohol which has undergone α-exchange has also undergone (multiple) β-exchange.* We take this as evidence for a common intermediate which we believe is the ketone, 4-*tert*-butylcyclohexanone.

Several possible explanations can be offered for the source of the ketone under our reaction conditions. In one model, a reversible hydride elimination might be envisioned:

$$M{-}OCHRR' \rightleftharpoons M{-}H + RR'C{=}O$$
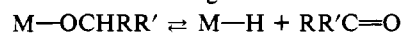
Such a model would require that an early-transition-metal hydride undergo readdition of the carbonyl compound[5] in preference to protonolysis despite the very vigorous conditions (180–220 °C, neat alcohol) of our experiments. Alternatively, one can propose that slow hydride elimination occurs, followed by a faster irreversible protonolysis:

$$M{-}H + ROH \rightarrow M{-}OR + H_2$$
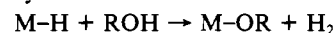
The amount of carbonyl compound accumulated by such a process, if it occurs, must necessarily be small since it cannot be detected in the final reaction product. However, *even a minute concentration of carbonyl compound would eventually allow all the alcohol in the system to pass through the carbonyl oxidation state since early transition metal alkoxides are excellent catalysts for the Meerwein–Ponndorf reaction.*[6] Because of this factor, even traces of carbonyl as a contaminant in the starting alcohol could suffice to promote this chemistry. The principal difficulty with such a model is the limited rate enhancement upon spiking authentic carbonyl compounds into the reaction.

Although additional mechanistic studies will be required to clarify these details, our results do offer an explanation for the initially puzzling aspects of this chemistry enumerated above. In addition, we can rule out cyclometallation reaction 3 despite the fact that eq 1 has been demonstrated for the corresponding reactions of early-transition-metal dialkylamides.[2,7,8] We report our results at this stage because of the interest generated by our earlier observations.[9]

Experimental Section

General Information. Ethanol-*d* (Aldrich), (*R*)-(–)-2-butanol (Ald-

(4) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270–3272.

(5) The addition of ketones to early-transition-metal hydrides is known to be facile. See, for example: Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 413–418.

(6) Seebach, D. In *Modern Synthetic Methods 1983*; Scheffold, R., Ed.; Otto Salle Verlag: Frankfurt am Main, FRG, 1983. Ishii, Y.; Nakano, T.; Inada, A.; Kishigami, Y.; Sakurai, K.; Ogawa, M. *J. Org. Chem.* **1986**, *51*, 240–242. See also: Mehrotra, R. C.; Verma, I. D. *J. Less-Common Met.* **1961**, *3*, 321–326.

(7) In further support of our earlier observations, a discrete η^2-imine complex of tantalum has now been prepared by a metalation route and was shown to undergo insertion of olefins into the Ta–C bond: Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651–2660. Mayer, J. M. Ph.D. Thesis, California Institute of Technology, 1982.

(8) However, for authentic examples of cyclometalation of alkoxide ligands, see: Chamberlain, L.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 1665–1666. Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *Ibid.* **1982**, *104*, 7338–7340. Green, M. L. H.; Parkin, G.; Moynihna, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540.

(9) Lewis, L. N.; Garbauskas, M. F. *Inorg. Chem.* **1985**, *24*, 363–366. Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Ibid.* **1984**, *23*, 2575–2578. Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Ibid.* **1984**, *23*, 1433–1436.

rich), and the early-transition-metal alkoxides (Alfa) were reagent grade materials used as received. The 90-MHz ^{1}H NMR spectra were obtained on a Varian EM390 spectrometer while 61.4-MHz ^{2}H NMR spectra were measured on a Bruker WP 400 instrument. GC–mass spectrometric studies were conducted by using a Varian Model 3700 GC interfaced with a Du Pont Model 491 mass spectrometer. Electron-impact studies were carried out at 70 eV ionizing voltage while chemical-ionization studies utilized isobutane as reagent.

β-Exchange Studies. Typical Run. A Carius tube of ca. 5-mL volume was charged with ethanol-*d* (2.45 g, 50 mmol), and the transition-metal ethoxide catalyst (1.0 mg-atom metal). The tube was frozen in liquid nitrogen and evacuated on a vacuum line. After three freeze–pump–thaw cycles the tube was sealed with a torch. Sets of four tubes were placed in a stainless-steel autoclave, which was half-filled with hexane to equalize the pressure during heating. The autoclave was maintained at the indicated temperature (usually 200 °C) for 14 h. Cooled tubes were opened in a nitrogen-filled glovebox. Total H–D exchange was determined by integrating the OH resonance vs. the methylene resonance in the 90-MHz ^{1}H NMR spectrum. (Neat material was required to avoid overlap of these resonances which occurred on dilution.) The 61.4-MHz ^{2}H NMR spectrum was then examined; the integration of the resonances at δ 0.98, 0.96, and 0.94 gave the relative amount of mono-, di-, and trideuteriated ethanol, respectively.

α-Exchange Studies. The reaction was carried out as above except that the ethanol-*d* was replaced with a 1:1 mixture of ethanol and ethanol-*1,1-d$_2$*. The resultant ethanol was then analyzed by electron-impact GC–MS, correcting for the isotopic distribution of the starting mixture of alcohols. In a typical run (220 °C, 40 h, 0.25 M tantalum ethoxide catalyst) the conversion to monodeuteriated alcohol was 4%. Alternatively, heating a 1:1 (volume) mixture of ethanol-*1,1-d$_2$* and 0.3 M metal octoxide in 1-octanol for 80 h at 220 °C followed by fractional distillation gave the following levels of ^{1}H incorporation into the methylene group by NMR: 33% (Ta); 11% (Zr). In appropriate control reactions, the methylene ^{1}H NMR resonance was 2%, consistent with the isotopic purity (98%) of the starting alcohol.

Racemization of 2-Butanol. In a typical run, heating of a 1:1 (volume) mixture of (*R*)-(−)-2-butanol and 0.3 M zirconium octoxide in 1-octanol at 220 °C followed by fractional distillation afforded 2-butanol with [α]$_D^{25}$-6.3 ± 0.2° (20 h) and −3.0 ± 0.1° (40 h). A control containing no catalyst after 20 h at 220 °C gave −12.4 ± 0.2°, essentially identical with that of the starting alcohol (−12.5 ± 0.2°).

Preparation of Labeled 4-*tert*-Butylcyclohexanols. Commercial *tert*-butylcyclohexanol as received was a 70:30 mixture of trans and cis material. Flash chromatography of a 5.0-g sample in 30% ethyl acetate and 70% hexane following the general procedure of Still[10] afforded from cuts 11–13 the cis isomer (1.15 g) and from cuts 15–20 the trans isomer (2.85 g). The purified alcohols were *O*-deuteriated by repeated treatment with excess ethanol-*d* followed by distillation of the ethanol in vacuo.

Exchange Studies with 4-*tert*-Butylcyclohexanol-*d*. Tubes were charged as above with *trans*-4-*tert*-butylcyclohexanol-*d* (0.75 g), ethanol-*d* (0.75 g), and metal alkoxide catalyst (0.15 g). The mixture was heated for 14 h at 220 °C. The cooled solutions were added to water (50 mL), extracted with ether (50 mL), and dried (MgSO$_4$). Removal of the solvent afforded a white solid, which was *O*-silylated by stirring a sample (0.1 g) overnight with excess (0.5 g) (dimethylamino)trimethylsilane in toluene (2 mL). The products were analyzed by GC–MS. The extent of isomerization was 9.2% (Ta catalyst) and 5.5% (Zr catalyst). In each case molecular ion for the cis silyl ethanol was observed at *m/e* 231 and 232 (roughly 1:1). In contrast, an authentic sample of silylated starting material showed only *m/e* 228. The large M − 15 peaks at *m/e* 213 (authentic unlabeled alcohol) and at *m/e* 216 and 217 (reaction products) further corroborated this result.

(10) Still, W. C. *J. Org. Chem.* **1978,** *43,* 2923–2925.

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Reactions of HCl(g), DCl(g), and HBr(g) with the Adduct Pyrazine–Phosphorus(V) Chloride

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In previous communications we have reported the synthesis, molecular structure, and solution properties of the acid–base adduct formed from pyrazine (pz), C$_4$H$_4$N$_2$, and phosphorus(V) chloride, PCl$_5$.[1,2] In the solid state the molecule, pz·PCl$_5$, belongs to point group C_{2v} with octahedral geometry around phosphorus. The plane of the pyrazine ring bisects the Cl-P-Cl 90° angle, and the P-N bond is unusually long, 2.021 Å. In solution of nitromethane, the adduct is in equilibrium with PCl$_5$ and pz.

$$N\bigcirc N\text{-PCl}_5 \rightleftharpoons N\bigcirc N + \text{PCl}_5 \qquad (1)$$
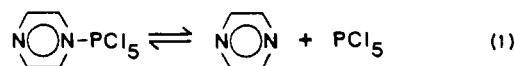
This rapid exchange is responsible for a singlet in the ^{1}H NMR spectrum, even at −100 °C.

Because a second nitrogen base site on the adduct is available for further reaction, we have investigated the possibility of coordinating a second mole of acid to the adduct. Lever, Lewis, and Nyholm have reported the addition of 2 mol of BCl$_3$ to pz, yielding a stable compound,[3] but we find no evidence of a reaction of pz with a second mole of PCl$_5$. This could be due to a combination of reduced acidity and/or more severe steric requirements of PCl$_5$ compared to BCl$_3$. In this communication we report reactions between pz·PCl$_5$ and the acids HCl(g), DCl(g), and HBr(g). Reactions were performed in a *dispersive* medium, rather than in solution, to avoid the influence of the equilibrium of eq 1.

Experimental Section

Materials. Experiments were performed on a standard vacuum line,[4] employing a mercury diffusion pump and a CO$_2$-calibrated, U-trap system for gas measurements and trap-to-trap fractionation.

Pz·PCl$_5$ was synthesized as has been described elsewhere.[1,2] Purification was achieved by vacuum sublimation at 60–64 °C. The pyridine (py) adduct py·PCl$_5$ was synthesized and purified in a manner analogous to that for pz·PCl$_5$. Anal. Calcd for C$_5$H$_5$NPCl$_5$: Cl, 61.69; P, 10.78. Found: Cl, 60.63; P, 10.72.

Hydrogen chloride gas (Matheson) was used after several fractionations through a −96 °C U-trap. The purity was checked by infrared spectroscopy utilizing a 10-cm gas cell fitted with NaCl windows.

Two sources of hydrogen bromide were used: (i) from the bromination of toluene in the vacuum system, and (ii) from Airco. Purification and identification were achieved in the same manner as for HCl.

Deuterium chloride was prepared from freshly sublimed PCl$_5$ and 99.96 atom % D$_2$O (Aldrich).[5]

Carbon tetrachloride and methylene chloride were each stirred for several days over P$_4$O$_{10}$, distilled, and stored in an inert-atmosphere glovebox.

(1) Ishley, J. N.; Knachel, H. C. *Inorg. Chem.* **1975,** *14,* 2558.
(2) Meyer, B. N.; Ishley, J. N.; Fratini, A. V.; Knachel, H. C. *Inorg. Chem.* **1980,** *19,* 2324.
(3) Lever, A. P. B.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1963,** 3156.
(4) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.
(5) Great difficulty was encountered in obtaining a clean infrared spectrum of DCl, free of HCl. It was determined that the major source of HCl was due to H–D exchange from moisture in the KBr or NaCl windows of the IR cell. Once DCl was introduced into the IR cell, the relative intensity of the HCl band at 2880 cm^{-1} increased with time as the DCl band at 2080 cm^{-1} decreased. The use of new o-ring seals and heating of the salt plates to 400 °C, under vacuum, reduced significantly the amount of H–D exchange, yielding minimum HCl production in the IR cell. In addition, the vacuum line and the IR cell were both exposed to D$_2$O vapors for several hours after the heat treatments. Thereafter, additional flaming of the vacuum system followed by pumping was used to insure minimal availability of adsorbed H$_2$O in the system.