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Putting Atoms and Molecules into Chemically Opened Fullerenes

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Abstract: We studied Ar, Kr, CO, and N_2 going into and out of a chemically opened fullerene, **1**. We measured the equilibrium constant, K_{eq}, for the formation of X@**1**. K_{eq} is particularly large for Ar, probably due to the large van der Waals attraction between the Ar atom and the fullerene cage. We measured rate constants and activation energies for the unimolecular reaction X@$\mathbf{1} \rightarrow$ X + **1** (X = Ar, CO, N_2). The reactions show an unusually small pre-exponential factor, probably due to the loose binding of X inside the cage.

Introduction

Putting an atom or molecule into a very small container can alter its physical and chemical characteristics. This has been done using zeolites,[1−3] carcerands,[4] and fullerenes.[5−11] For many years we have used a high-pressure, high-temperature method to put noble gases and small molecules inside fullerenes.[7−11] The problem with this method is that we get only 1% or less of the fullerene molecules to contain the atom. This is far below the equilibrium incorporation calculated from theory.[12−18] Indeed, if we take the result of one run and use it as the starting material for another run, we double the incorporation fraction,[19] showing that 1% is well below the equilibrium amount. A more recent approach involves molecular surgery, where a hole in the fullerene is opened by a series of chemical reactions. The first open-cage fullerene was prepared by Wudl et al.,[20] but the hole was not large enough to pass helium at any temperature that did not decompose the compound. Rubin et al. opened a larger hole that allowed both helium and hydrogen to pass through.[21,22] We used ^{3}He NMR to monitor the kinetics of ^{3}He escape and measured the activation energy. Komatsu et al. then opened another hole.[23,24] We studied the kinetics for the escape of ^{3}He and also measured the equilibrium constant, since helium went in and out sufficiently easily.[25] In the case of H_2, the Komatsu group was able to fill almost all the molecules with H_2 under high pressure. Then, in a series of reactions, they closed the hole to produce $H_2@C_{60}$.[26] Iwamatsu has produced C_{60} derivatives with 16- and 20-membered rings at the opening.[27−29] The larger of these was found to spontaneously incorporate water, even at room temperature and from solvents containing little water.[27,30] This compound can also be filled with CO[31] and NH_3.[32] Here, we examine putting Ar, Kr, CO, and N_2 inside. We measure the

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(1) Hadjiivanov, K.; Knozinger, H.; Ivanova, E.; Dimitrov, L. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2531–2536.
(2) Bulanek, R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4208–4214.
(3) Gribov, E. N.; Cocina, D.; Spoto, G.; Bordiga, S.; Ricchiardi, G.; Zecchina, A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1186–1196.
(4) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: Cambridge, 1994.
(5) Weiske, T.; Böhme, D. K.; Hrusák, J.; Krätschmer, W.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 884–886.
(6) Weiske, T.; Hrusák, J.; Böhme, D. K.; Schwarz, H. *Chem. Phys. Lett.* **1991**, *186*, 459–462.
(7) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993**, *259*, 1428–1430.
(8) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Gross, M. L.; Giblin, D. E.; Poreda, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 2193–2194.
(9) Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693–1697.
(10) Shimshi, R.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **1997**, *119*, 1163–1164.
(11) Saunders, M.; Cross, R. J. *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer: Dordrecht, 2002; Vol. 3, pp 1−11.
(12) Pang, L.; Brisse, F. *J. Phys. Chem.* **1993**, *97*, 8562–8563.
(13) Cislowski, J. *Electronic Structure Calculations on Fullerenes and their Derivatives*; Oxford University Press: New York, 1995.
(14) Jiménez-Vázquez, H. A.; Cross, R. J. *J. Chem. Phys.* **1996**, *104*, 5589.
(15) Patchkovskii, S.; Thiel, W. *J. Chem. Phys.* **1997**, *106*, 1796.
(16) Son, M. S.; Sung, Y. K. *Chem. Phys. Lett.* **1995**, *245*, 113–118.
(17) Darzynkiewicz, R. B.; Scuseria, G. E. *J. Phys. Chem. A* **1997**, *101*, 7141–7144.
(18) Darzynkiewicz, R. B.; Scuseria, G. E. *J. Phys. Chem. A* **1998**, *102*, 3458–3458.
(19) Cross, R. J.; Khong, A.; Saunders, M. *J. Org. Chem.* **2003**, *68*, 8281–8283.
(20) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003–7004.
(21) Arce, M. J.; Viado, A. L.; An, Y. Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775–3776.
(22) Rubin, Y.; Jarrosson, T.; Wang, G. W.; Bartberger, M. D.; Houk, K. N.; Schick, G.; Saunders, M.; Cross, R. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1543–1546.
(23) Murata, Y.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2003**, *125*, 7152–7153.
(24) Murata, Y.; Murata, M.; Komatsu, K. *Chem. Eur. J.* **2003**, *9*, 1600–1609.
(25) Stanisky, C. M.; Cross, R. J.; Saunders, M.; Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2005**, *127*, 299–302.
(26) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238–240.
(27) Iwamatsu, S.; Uozaki, T.; Kobayashi, K.; Re, S.; Nagase, S.; Murata, S. *J. Am. Chem. Soc.* **2004**, *126*, 2668–2669.
(28) Iwamatsu, S.-i.; Kuwayama, T.; Kobayashi, K.; Nagase, S.; Murata, S. *Synthesis* **2004**, 2962–2964.
(29) Iwamatsu, S.-i.; Murata, S. *Synlett* **2005**, 2117–2129.
(30) Iwamatsu, S.-i.; Murata, S *Tetrahedron Lett.* **2004**, *45*, 6391–6394.
(31) Iwamatsu, S.; Stanisky, C. M.; Cross, R. J.; Saunders, M.; Mizorogi, N.; Nagase, S.; Murata, S. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 5337–5340.
(32) Whitener, K. E.; Frunzi, M.; Iwamatsu, S.; Murata, S.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **2008**, *130*, 13996–13999.

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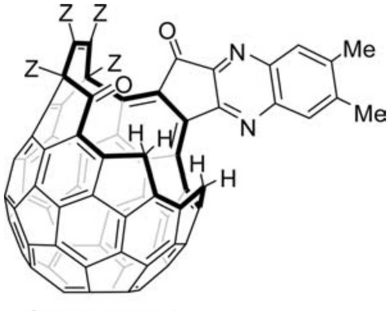


1 (Z=COOMe)

Figure 1. Iwamatsu's open-cage fullerene with a 20-membered ring, **1**.

Table 1. Conditions for the Incorporation Reaction

gas	solvent	*T* (°C)
Ar	TCE[a]	140
Kr	ODCB[b]	190
CO	TCE[a]	100
N_2	TCE[a]	140

[a] 1,1,2,2-Tetrachloroethane. [b] *o*-Dichlorobenzene.

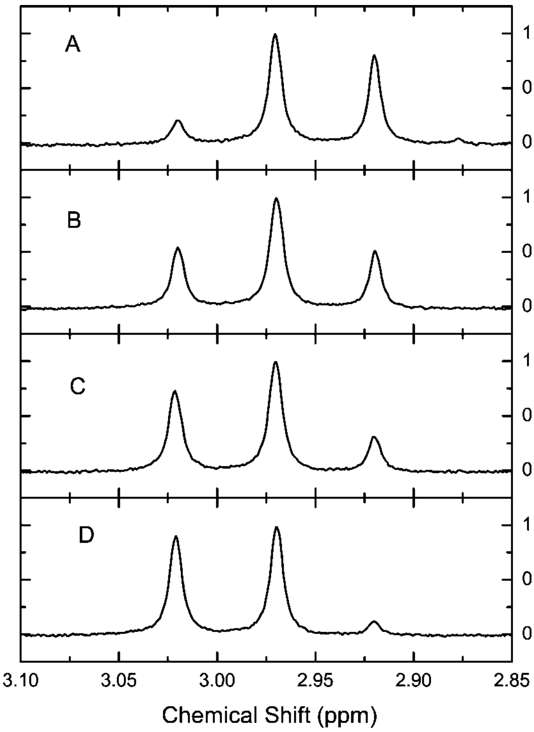


Figure 2. Proton NMR of Ar@**1**, showing the two protons in the throat after heating at 90 °C for varying times, allowing the Ar to escape: A, initial; B, 1.4 h; C, 2.8 h; D, 5.5 h.

kinetics for the escape reaction to obtain the barrier for going through the opening. We also measure the equilibrium constants for the incorporation. Since the inside of the molecule closely resembles the interior of C_{60}, the equilibrium constant should be close to the equilibrium constant for the incorporation into unmodified C_{60}. There have been several calculations predicting the equilibrium constants for C_{60}, but no measurements.[12−18] Ab initio calculations are very difficult in that they require a very accurate potential energy for interaction of the molecule with the C_{60} cage. One of the main contributors to this potential is the van der Waals attraction. Including this requires the use of electron correlation and a very large basis set.[15]

Iwamatsu's open-cage fullerene with a 20-membered ring, **1**, is shown in Figure 1. There are two sets of methylene protons on the rim of the orifice that give four doublets in the ^{1}H NMR spectrum. Two of these protons are sufficiently close to an included atom or molecule that the doublets are shifted upfield when the fullerene is filled.[31] Thus, we can use ordinary ^{1}H NMR to measure the fraction of **1** that contains a guest. We can easily measure the equilibrium constant and follow the kinetics for the escape of the guest.

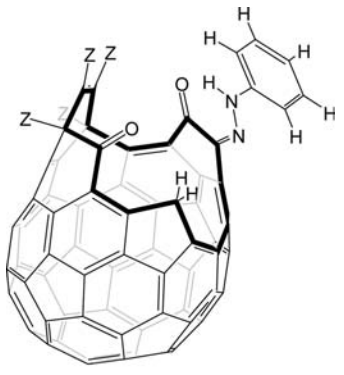
Experimental Section

Compound **1** was prepared as in the literature.[27,28] The incorporation reaction was carried out by dissolving several milligrams of **1** in a suitable solvent (see Table 1) and putting it into a high-pressure vessel. The vessel was then pressurized with the gas and held at a suitable temperature for a few hours. It was then cooled and depressurized. The choice of solvent and temperature, of course, depended on the gas. Table 1 gives the conditions. Two different high-pressure vessels were used. Some experiments employed a homemade device made of thick stainless-steel pipe, capable of withstanding 15 atm; others used an autoclave which could be connected directly to a gas cylinder without a regulator. For Ar, CO, and N_2, we used the full cylinder pressure (typically 80−100 atm or more). For Kr, this would be too expensive. Since Kr is condensable, we cooled the vessel with liquid nitrogen and condensed a known volume of Kr into it. Warming it up to the running temperature gave a pressure of 180 atm. In each case, we let the system stay at the high pressure for 18 h or more and then cooled it and released the pressure. Each of the products of the incorporation reaction was characterized by electrospray ionization (ESI) mass spectrometry. The mass spectrum had a series of peaks starting at $m/e = 1172$ and going to higher mass, due to empty **1** containing varying numbers of ^{13}C's. A second series of peaks appeared at the mass corresponding to X@**1**. Ionization of X@**1** can cause the loss of X, particularly if the barrier for escape is small. Therefore, the fraction of **1** containing X is an upper limit. ESI was chosen, since it puts less energy into the ion than most other methods. Several spectra are shown in the Supporting Information.

Proton NMR spectra were taken at 400 MHz in $CDCl_3$. The full NMR spectra were identical to the spectrum for empty **1**, except for the lines due to the two methylene protons in the throat. Each of these is split due to the coupling to the neighboring hydrogen. The doublet for one of the methylene protons at the throat is seen at ∼3 ppm. When an atom or molecule is inside **1**, these lines shift upfield. Figure 2 shows this region of the spectrum for various concentrations of Ar inside **1**. The shift is such that the left-hand peak for the doublet from Ar@**1** almost exactly coincides with the right-hand peak of empty **1**. Thus, in the figure there are only three peaks. The area under the left-hand peak is proportional to the concentration of **1**; the area under the right-hand peak is proportional to the concentration of Ar@**1**; and the area of the center peak is proportional to the sum of the two concentrations. The Supporting Information shows a larger view of this region of the NMR spectrum.

The kinetics for the escape reactions were studied by dissolving the samples in $CDCl_3$ and sealing them in NMR tubes under vacuum. After taking the initial NMR spectra, the samples were heated in an oil bath, and subsequent spectra were acquired. This process was repeated until all the gas escaped.

The opening in **1** is so large that Ne goes in and out rapidly at room temperatures. We were able to study the kinetics for Ne escape from Iwamatsu's open-cage fullerene with a 16-membered ring, **2**, shown in Figure 3. A few milligrams of **2** was wrapped in aluminum foil and placed into a high-pressure autoclave. The autoclave was filled with 500 atm of Ne and then heated to 180 °C. The pressure rose to 825 atm. After 9 h the autoclave was cooled and the sample



2 (Z=COOMe)

Figure 3. Iwamatsu's open-cage fullerene with a 16-membered ring, **2**.

removed. ESI mass spectrometry showed that 42% of **2** contained Ne. The Supporting Information shows the mass spectrum and the NMR spectrum. The kinetics for escape were followed by dissolving the sample in *o*-dichlorobenzene and heating portions of it to 120 °C and higher. Aliquots were analyzed by ESI mass spectrometry.

Equilibrium constants were measured by holding the sample in the autoclave at high pressure for a time much longer than the half life. The largest source of error was the accuracy of the pressure gauge.

Results and Discussion

Kinetics. The rate of escape of Ar from Ar@**1** was measured at 60, 70, 80, and 90 °C. The half-lives ranged from 1.73 h at 90 °C to 30.1 h at 60 °C. Figure 4 shows the Arrhenius plot. The least-squares fit gives

$$\ln k_{\mathrm{Ar}} = (23.0 \pm 0.95) - (11600 \pm 331)K/T \qquad (1)$$

with $R^2 = 0.9984$. This corresponds to an activation energy of 96.7 ± 3 kJ/mol (23.1 ± 0.7 kcal/mol). The pre-exponential factor is $\log_{10}A = 10.0 \pm 0.41$.

Similar data were taken for N_2 and CO. Data for N_2 were taken at 60, 70, 80, and 90 °C, giving half-lives of 0.299 h at 90 °C and 3.80 h at 60 °C. The Arrhenius fit gave

$$\ln k_{\mathrm{N2}} = (19.7 \pm 2.37) - (9860 \pm 825)K/T \qquad (2)$$

with $R^2 = 0.9862$. The activation energy and pre-exponential factor are given in Table 2. Data for CO were taken at 40, 50, 60, and 70 °C, giving half-lives of 0.39 h at 70 °C and 8.0 h at 40 °C. The Arrhenius fit gave

$$\ln k_{\mathrm{CO}} = (23.9 \pm 0.42) - (10800 \pm 138)K/T \qquad (3)$$

with $R^2 = 0.9997$.

We were unable to study the kinetics for Kr@**1**. No suitable high-boiling solvent was available. We also suspected that the reaction would require temperatures so high that the compound would decompose.

Kinetic data for Ne escape from **2** were followed by ESI mass spectroscopy, and the measurements were somewhat less accurate than for the other systems. The Arrhenius fit gave

$$\ln k_{\mathrm{Ne}} = 22.36 - 12700K/T \qquad (4)$$

with $R^2 = 0.9737$.

Table 2 lists all the activation energies and pre-exponential factors for this and for previous work on escape from other open-cage fullerenes.

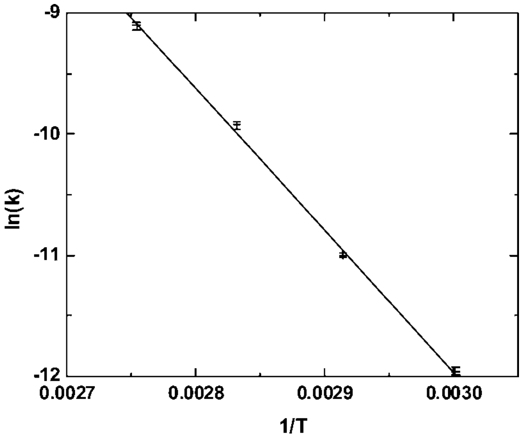


Figure 4. Arrhenius plot of the escape of Ar from **1**.

Table 2. Activation Energies and Pre-Exponential Factors for Escape from Open-Cage Fullerenes

system[a]	activation energy kJ/mol	activation energy kcal/mol	$\log_{10}$ A	ref
^{3}He@R14	103 ± 3.3	24.6 ± 0.8	9.6	22
^{3}He@K13	95.8 ± 2.9	22.9 ± 0.7	11.2 ± 0.5	25
H_2@K13	144 ± 2.9	34.3 ± 0.7	11.8 ± 0.3	23
H_2@I16	99.2	23.7	10.8	33
Ne@I16	106 ± 6.7	25.3 ± 1.6	9.70 ± 1.6	
Ar@I20	96.7 ± 2.9	23.1 ± 0.7	10.0 ± 0.41	
N_2@I20	82.1 ± 6.7	19.6 ± 1.6	8.6 ± 1.0	
CO@I20	90.0 ± 1.3	21.5 ± 0.3	10.4 ± 0.2	

[a] Open-cage fullerenes: R14 (Rubin's 14-membered ring), K13 (Komatsu's 13-membered ring), I16 (Iwamatsu's 16-membered ring, **2**), I20 (Iwamatsu's 20-membered ring, **1**).

Two trends are obvious. As the included atom or molecule gets larger, the activation energy increases, and, as the hole gets larger, it decreases. The number of atoms surrounding the hole, while important, is not decisive. The shape and three-dimensional structure are also important. Note that ^{3}He has a lower barrier for escape from K13 than from R14, although the hole in R14 is nominally larger. It is interesting that CO, which is isoelectronic with N_2, has a larger activation energy, although only just beyond the experimental uncertainty. Also, H_2 has a larger barrier in getting out of K13 than ^{3}He. One might imagine that H_2 could squeeze through along the long axis with a smaller barrier. The most unusual features of the data are the small pre-exponential factors. Generally, for a unimolecular reaction $A = 10^{12}$ to 10^{13} s^{-1}. Eyring's transition state theory gives,

$$k = \frac{k_B T}{h} \frac{q^\dagger}{q_r} \exp(-\Delta E^\dagger / k_B T) \qquad (5)$$

where k_B is Boltzman's constant, $q^\dagger$ is the partition function for the transition state, excluding the reaction coordinate, and q_r is the partition function for the reactants. At 300 K, $k_B T/h = 6 \times 10^{12}$ s^{-1}. In most reactions the vibration frequencies decrease slightly in going from reactants to the transition state. Since the vibrational partition function is usually close to one, the ratio of partition functions in eq 5 is usually close to one. In the present case, the reactant is only loosely held inside the cage. A molecule can rotate freely inside, and the force constant as it moves away from the center is very small. Calculations for He@C_{60} show that the potential is quite flat at the center and nearly quartic rather than quadratic.[14,15] This means that q_r can be much larger than one. In the transition state, however,

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(33) Iwamatsu, S.-i.; Murata, S.; Andoh, Y.; Minoura, M.; Kobayashi, K.; Mizorogi, N.; Nagase, S. *J. Org. Chem.* **2005**, *70*, 4820–4825.

Table 3. Equilibrium Constants

system[a]	K_{eq} atm^{-1}	T (°C)	ref
$^3He@K13$	3.4×10^{-4}	60	25
$H_2@K13$	0.006	200	23
Ne@I16	9×10^{-4}	180	
Ar@I20	0.20	130	
Kr@I20	0.06	190	
$N_2@I20$	0.12	100	
CO@I20	0.06	100	

[a] Open-cage fullerenes: R14 (Rubin's 14-membered ring), K13 (Komatsu's 13-membered ring), I16 (Iwamatsu's 16-membered ring, **2**), I20 (Iwamatsu's 20-membered ring, **1**).

the atom or molecule is severely constrained. Thus, the pre-exponential factor is smaller than in most unimolecular reactions.

Equilibrium Constants. Measurement of the equilibrium constant for the incorporation is simple. We just expose **1** to the gas of interest at a known pressure for a long time. We then cool the sample to freeze the equilibrium and take the NMR. From the relative areas of the methylene peaks, we can determine the incorporation fraction and then the equilibrium constant,

$$K_{eq} = \frac{[X@\mathbf{1}]}{[1]p_{gas}} \tag{6}$$

Of course, we have to wait until equilibrium is established. Except for Kr, we have the kinetic data that tells us how long to wait. In the case of Kr, we did several runs at 190 °C and measured the amount of incorporation. Waiting 20 h gave a constant level. Accuracy is limited by the pressure gauge used. The measured equilibrium constants are tabulated in Table 3.

Ideally, the equilibrium constants should have been measured at the same temperature. However, at 190 °C, which is needed to get Kr into **1**, there is appreciable decomposition, and this is why we could not study the kinetics for the escape reaction. Since the interior of **1** is fairly similar to the interior of C_{60}, these equilibrium constants should be similar to those for C_{60}. Calculations on C_{60} have shown that helium basically rattles around, vibrating with a large amplitude.[15] The potential is quite flat at the center of the cage, rising rapidly at the edge. It is anharmonic, although not a hard wall. Calculations are difficult, because an important part of the interaction is due to the van der Waals attraction; thus, the calculation requires electron correlation and the use of a large basis set. The energy of $He@C_{60}$ is very slightly less than the energy of He + C_{60}. As the noble gas atom gets larger, there is less room, and the equilibrium constant should get smaller. However, the van der Waals attraction becomes stronger, and the incorporation reaction becomes more exothermic. This increases K_{eq}. It would appear that Ar is fairly strongly bound, and that Kr, while bound, is large enough that the potential is less attractive. Even Xe fits inside the cage, as we have made $Xe@C_{60}$,[8,34,35] but we could not get Xe to fit through the opening in **1**. In principal, we could measure K_{eq} over a range in temperatures to get ΔH for the reaction. In practice, the uncertainties in K_{eq} are too large, and the available range in temperature is too small. If the sample is cooled too much, we cannot reach equilibrium in a reasonable amount of time. If it is heated, **1** will decompose.

In summary, we have measured the rates of escape of atoms and small molecules from an open-cage fullerene. These studies present model systems for particles of various sizes moving through constrictions with low barriers. We have also obtained the equilibrium constants for the incorporation of the atoms and molecules. These should be similar to the equilibrium constants for C_{60}. Bear in mind that no formal chemical bonds exist between the guests and the fullerenes. Thus, our results reveal the importance of the van der Waals contributions to these interactions.

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Supporting Information Available: Several ESI mass spectra and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) Syamala, M. S.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **2002**, *124*, 6216–6219.

(35) Frunzi, M.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **2007**, *129*, 13343–13346.