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Selective Complexation and Reactivity of Metallic Nitride and Oxometallic Fullerenes with Lewis Acids and Use as an Effective Purification Method

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Metallic nitride fullerenes (MNFs) and oxometallic fullerenes (OMFs) react quickly with an array of Lewis acids. Empty-cage fullerenes are largely unreactive under conditions used in this study. The reactivity order is $Sc_4O_2@I_h\text{-}C_{80}$ > $Sc_3N@C_{78}$ > $Sc_3N@C_{68}$ > $Sc_3N@D_{5h}\text{-}C_{80}$ > $Sc_3N@I_h\text{-}C_{80}$. Manipulations of Lewis acids, molar ratios, and kinetic differences within the family of OMF and MNF metallofullerenes are demonstrated in a selective precipitation scheme, which can be used either alone for purifying $Sc_3N@I_h\text{-}C_{80}$ or combined with a final high-performance liquid chromatography pass for $Sc_4O_2@I_h\text{-}C_{80}$, $Sc_3N@D_{5h}\text{-}C_{80}$, $Sc_3N@C_{68}$, or $Sc_3N@C_{78}$. The purification process is scalable. Analysis of the experimental rate constants versus electrochemical band gap explains the order of reactivity among the OMFs and MNFs.

Introduction

Metallic nitride fullerenes (MNFs, e.g., $Sc_3N@I_h\text{-}C_{80}$) consist of a trimetallic nitride cluster trapped within the carbon housing of fullerene cages.[1−5] In contrast, the newly discovered oxometallic fullerenes (OMFs) consist of encapsulated metal oxide clusters within fullerene cages.[6,7] For the OMFs, little is known with regard to their chemical reactivity. The dominant representatives of MNF and OMF compounds are $Sc_3N@I_h\text{-}C_{80}$ and $Sc_4O_2@I_h\text{-}C_{80}$, respectively. Of the former, $Sc_3N@D_{5h}\text{-}C_{80}$ is a structural isomer of minor abundance.[8,9]

The separation of C_{60} from other empty-cage fullerenes (e.g., C_{70}) using Lewis acids has been previously described[10] based on C_{60} being the more inert species. For our metallofullerene system, we hypothesize a dramatic increase in the reactivity for MNFs and OMFs based on their cages having formal charges of 6− versus the neutrality of empty-cage fullerenes.[11]

The major hurdle to MNF and OMF experimentation is the poor availability of isomerically pure samples. This paucity of materials is due to inefficient separation technologies, which historically include classical high-performance liquid chromatography (HPLC) methods. Recent reports of nonchromatographic methods for the isolation of MNFs are based on their resistance to reaction with solid supports such as cyclopentadiene immobilized on a Merrifield resin[12] or amino-capped silica.[13,14] A support free method of separating MNFs from empty-cage fullerenes has been achieved using molten 9-methylanthracene.[15] Another approach to separating MNFs is an electrochemical, oxidation-based differentiation between I_h and D_{5h} isomers of $Sc_3N@C_{80}$.[16] An alternative method to isolating non-MNF metallofullerenes (e.g., $Gd@C_{70}$, $Gd@C_{82}$) from empty-cage fullerenes exploits the differences in solubility and redox reactivity.[17]

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(1) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55–57.

(2) Stevenson, S.; Fowler, P. W.; Heine, T.; Duchamp, J. C.; Rice, G.; Glass, T.; Harich, K.; Hajdu, E.; Bible, R.; Dorn, H. C. *Nature* **2000**, *408*, 427–428.

(3) Olmstead, M. H.; de Bettencourt-Dias, A.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1223–1225.

(4) Dunsch, L.; Yang, S. F. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3067–3081.

(5) Dunsch, L.; Yang, S. *Small* **2007**, *3*, 1298–1320.

(6) Stevenson, S.; Mackey, M. A.; Stuart, M. A.; Phillips, J. P.; Easterling, M. L.; Chancellor, C. J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 11844–11845.

(7) Valencia, R.; Rodriguez-Fortea, A.; Stevenson, S.; Balch, A. L.; Poblet, J. M. *Inorg. Chem.* **2009**, *48*, 5957–5961.

(8) Duchamp, J. C.; Demortier, A.; Fletcher, K. R.; Dorn, D.; Iezzi, E. B.; Glass, T.; Dorn, H. C. *Chem. Phys. Lett.* **2003**, *375*, 655–659.

(9) Krause, M.; Dunsch, L. *ChemPhysChem* **2004**, *5*, 1445–1449.

(10) Olah, G. A.; Bucsi, I.; Ha, D. S.; Aniszfeld, R.; Lee, C. S.; Prakash, G. K. S. *Fullerene Sci. Technol.* **1997**, *5*, 389–405.

(11) Kobayashi, K.; Sano, Y.; Nagase, S. *J. Comput. Chem.* **2001**, *22*, 1353–1358.

(12) Ge, Z. X.; Duchamp, J. C.; Cai, T.; Gibson, H. W.; Dorn, H. C. *J. Am. Chem. Soc.* **2005**, *127*, 16292–16298.

(13) Stevenson, S.; Harich, K.; Yu, H.; Stephen, R. R.; Heaps, D.; Coumbe, C.; Phillips, J. P. *J. Am. Chem. Soc.* **2006**, *128*, 8829–8835.

(14) Stevenson, S.; Mackey, M. A.; Coumbe, C. E.; Phillips, J. P.; Elliott, B.; Echegoyen, L. *J. Am. Chem. Soc.* **2007**, *129*, 6072–6073.

(15) Angeli, C. D.; Cai, T.; Duchamp, J. C.; Reid, J. E.; Singer, E. S.; Gibson, H. W.; Dorn, H. C. *Chem. Mater.* **2008**, *20*, 4993–4997.

(16) Elliott, B.; Yu, L.; Echegoyen, L. *J. Am. Chem. Soc.* **2005**, *127*, 10885–10888.

(17) Raebiger, J. W.; Bolskar, R. D. *J. Phys. Chem. C* **2008**, *112*, 6605–6612.

Herein we report the reactivity of OMF and MNF as new Lewis bases and their selective complexation with Lewis acids. Subsequent manipulation of kinetic differences between these species can be used in the development of a new separation scheme, which permits the isolation of individual OMF and MNF compounds.

Experimental Section

Synthesis and Characterization of Soot Extracts Containing OMFs and MNFs. Soots containing OMFs and MNFs were prepared using a cylindrical electric-arc reactor as previously described.[18] Cored rods were then packed with Cu (Cerac) or $Cu(NO_3)_2 \cdot 2.5\ H_2O$ (Aldrich) and vaporized using the CAPTEAR process[6,19] for enhanced yields of OMF and MNF compounds. The soot was extracted with CS_2 or *o*-xylene and filtered, and the solvent was removed under reduced pressure to furnish a dried extract, which was washed with diethyl ether or acetone. Soot extracts were weighed and characterized by HPLC to determine the type and amount of fullerene material present. HPLC peak areas were obtained using standard chromatographic integration software (Vernier, Logger Pro). HPLC separations were as follows: PYE column (4.6 mm × 250 mm), flow rates of 0.3 mL/min toluene or 0.5 mL/min xylene as the mobile phase, and UV detection at 360 nm.

A. Reaction of Metallofullerenes with Lewis Acids. For comparison of C_{60}, C_{70}, and $Sc_3N@I_h\text{-}C_{80}$ reactivities, 1.0 mg of each fullerene type was dissolved in 3 mL of carbon disulfide. To each solution was added 40 mg of $AlCl_3$. Time lapse photography was used to monitor and compare the loss of color (i.e., removal of fullerene from the solution via precipitation of the fullerene–Lewis acid complex). After 2 min of reaction time, the solution in the vial containing $Sc_3N@I_h\text{-}C_{80}$ was colorless.

B. Array of Lewis Acids. A total of 7.1 mg of $MgCl_2$, 10 mg of $AlCl_3$, 12 mg of $FeCl_3$, or 20 mg of $AlBr_3$ were added to four stirring solutions containing 15 mg each of fullerene extract dissolved in 150 mL of carbon disulfide. Equimolar amounts of Lewis acids were used to compare the speeds of the reactions, which were allowed to proceed for a minimum of 3 min. Reaction mixtures having slower kinetics were monitored for longer times.

C. Metallofullerene Selectivity and Kinetic Study. C.1. $Sc_3N@D_{5h}\text{-}C_{80}$ versus $Sc_3N@I_h\text{-}C_{80}$. A 1 g sample of extract (~1.2 mmol of fullerenes) was dissolved in 1 L of carbon disulfide. With stirring, 217 mg of $FeCl_3$ was added to the fullerene solution. Aliquots of the reaction mixture were taken and analyzed via HPLC, whose conditions were 0.3 mL/min toluene mobile phase, 360 nm UV detection, and 10 μL injection onto a 4.6 mm × 10 mm PYE column. Conversion from the peak area to molarity was performed via use of extinction coefficients and standardized samples of purified fullerenes as previously described.[20]

C.2. Reactivity of OMF versus MNF. To a 2 mg fullerene sample enriched in OMFs and MNFs was added 15 mL of CS_2. With stirring, 10 mg of $AlCl_3$ was added to generate a reaction mixture, from which aliquots were analyzed as described in section C.1 of the Experimental Section.

D. Scalability and Recovery of Metallofullerenes. Extract solutions containing ~1.3 g of fullerenes dissolved in 500 mL of carbon disulfide were prepared. To each of these three solutions were added separately, with stirring, 1.75 g of $AlBr_3$, 240 mg of $FeCl_3$, and 198 mg of $AlCl_3$. The reactions were allowed to proceed a minimum of 3 h. The reaction mixtures were filtered, and the precipitate contained primarily OMFs and MNFs complexed to the Lewis acid. Upon the addition of ice water, sodium bicarbonate, and carbon disulfide to the solid material remaining on the paper filter from a Buchner funnel, these fullerenes were released from the complex and readily dissolved in the CS_2 layer (i.e., bottom layer in a separatory funnel). After several washes with deionized water, this CS_2 fullerene solution was filtered by membrane filtration. The solvent was removed via rotary evaporation, and the solid material (i.e., recovered fullerenes) was ether-washed, dried, and weighed. The filtrate from the reaction mixture was also washed with water and sodium bicarbonate as described above. The masses of dried fullerenes obtained from the filtrate and precipitate were added and compared to the original extract mass for percent recovery calculations.

E. $Sc_4O_2@I_h\text{-}C_{80}$ and $Sc_3N@D_{5h}\text{-}C_{80}$ Enrichment and Isolation of Isomerically Pure $Sc_3N@I_h\text{-}C_{80}$. E.1. Enrichment of $Sc_4O_2@I_h\text{-}C_{80}$. A total of 982 mg of Sc fullerene extract was dissolved in 500 mL of carbon disulfide. With stirring, 340 mg of $AlCl_3$ was added to this solution. The reaction progress was monitored by loss of the HPLC peak area for $Sc_4O_2@I_h\text{-}C_{80}$. The reaction was stopped at 44 h. Upon filtration, the precipitate containing $Sc_4O_2@I_h\text{-}C_{80}$ OMF and contaminant MNFs was treated as described in section D of the Experimental Section. A second step using 45 mg of this OMF- and MNF-enriched fullerene material dissolved in 250 mL of carbon disulfide was used. With stirring, 135 mg of $AlCl_3$ was added. The reaction time was 4 h and 40 min, at which time the resulting precipitate was processed as described in section D of the Experimental Section to recover the enriched $Sc_4O_2@I_h\text{-}C_{80}$ fullerene sample.

E.2. Enrichment of $Sc_3N@D_{5h}\text{-}C_{80}$. An extract solution was prepared by dissolving ~1 g of fullerenes in 500 mL of CS_2. To this extract solution was added 340 mg of $AlCl_3$. The reaction proceeded for 44 h, at which time the collected precipitate was processed as described in section D of the Experimental Section.

E.3. Isolation of Isomerically Pure $Sc_3N@I_h\text{-}C_{80}$. This experiment used the filtrate obtained from step 1 (see $AlCl_3$ chemistry, Figure 6e). To the filtrate, with stirring, was added 150 mg of $FeCl_3$. After 70 min of reaction time, the I_h isomer of $Sc_3N@C_{80}$ had complexed with the Lewis acid and was precipitated from the solution. Upon filtration, the collected precipitate was processed as described in section D of the Experimental Section to obtain 27 mg of isomerically purified $Sc_3N@I_h\text{-}C_{80}$ (Figure 6f).

F. Isolation of Gram Quantities of $Sc_3N@I_h\text{-}C_{80}$. An extract solution of 1340 mg of fullerenes was dissolved in 500 mL of carbon disulfide. With stirring, 245 mg of $AlCl_3$ was added. After 21 h, the reaction mixture was filtered to remove OMF and MNF contaminants of $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@D_{5h}\text{-}C_{80}$. The filtrate, containing 1.072 g of fullerenes, of which $Sc_3N@I_h\text{-}C_{80}$ is the primary metallofullerene in addition to empty-cage fullerenes (e.g., C_{60}, C_{70}, C_{84}), was diluted to 1 L with CS_2. To this solution, with stirring, was added 217 mg of $FeCl_3$ to precipitate the I_h isomer of $Sc_3N@I_h\text{-}C_{80}$. After stirring for 55 min, the $Sc_3N@I_h\text{-}C_{80}$ complex was precipitated from the solution. The reaction mixture was filtered, and the precipitate was processed as described in section D of the Experimental Section. An isolated sample of 0.107 g of $Sc_3N@I_h\text{-}C_{80}$ was obtained.

Results and Discussion

A. Reaction of Metallofullerenes with Lewis Acids. For a comparison of the reactivity differences between empty-cage fullerenes and metallofullerenes having a $C_{80}{}^{6-}$ cage (e.g., OMFs, MNFs), an experiment was performed in which 1.0 mg each of C_{60} (1.4 μmol), C_{70} (1.2 μmol), and $Sc_3N@I_h\text{-}C_{80}$ (0.9 μmol) was dissolved in 3 mL of

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[18] Stevenson, S.; Mackey, M. A.; Thompson, M. C.; Coumbe, H. L.; Madasu, P. K.; Coumbe, C. E.; Phillips, J. P. *Chem. Commun.* **2007**, 4263–4265.

[19] Stevenson, S.; Thompson, M. C.; Coumbe, H. L.; Mackey, M. A.; Coumbe, C. E.; Phillips, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 16257–16262.

[20] McCluskey, D. M.; Smith, T. N.; Madasu, P. K.; Coumbe, C. E.; Mackey, M. A.; Fulmer, P. A.; Wynne, J. H.; Stevenson, S.; Phillips, J. P. *ACS Appl. Mater. Interfaces* **2009**, *1*, 882–887.

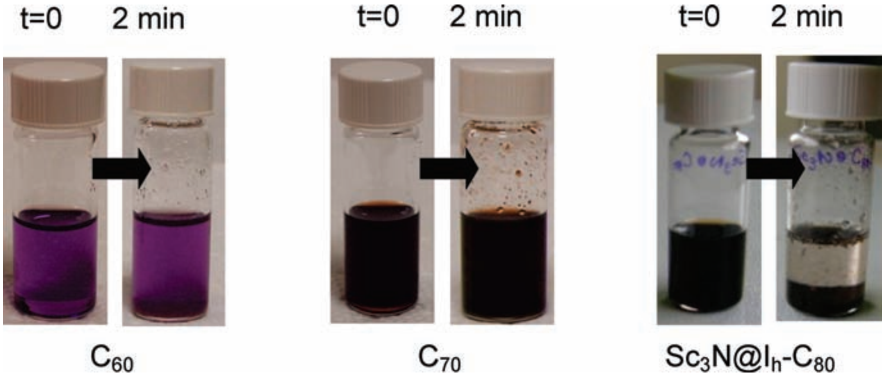

Figure 1. Selective complexation of MNF with a Lewis acid ($AlCl_3$).

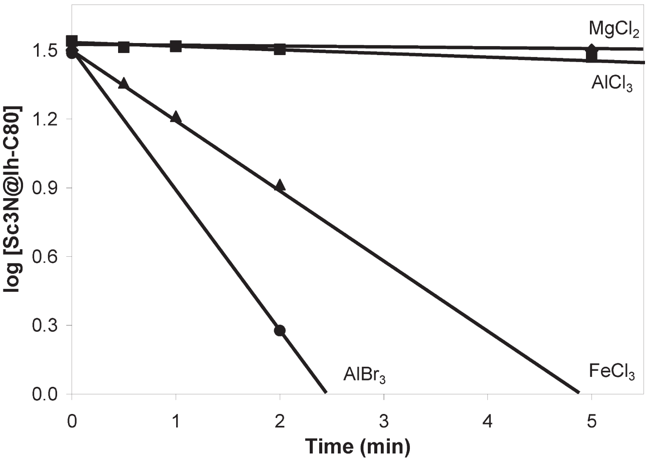

Figure 2. Effect of a Lewis acid on the $Sc_3N@I_h$-C_{80} complexation rate.

carbon disulfide with a large molar excess of $AlCl_3$ (40 mg, 300 μmol). Results from Figure 1 demonstrate the removal of $Sc_3N@I_h$-C_{80} within 2 min. In contrast, empty-cage fullerenes C_{60} and C_{70} were more resistant to complexation and precipitation.

B. Array of Lewis Acids. Given this difference in reactivity, we expanded the palette of Lewis acids. Weaker Lewis acids such as $MgCl_2$ were nonresponsive under our experimental conditions, with the stronger Lewis acids of $AlCl_3$, $FeCl_3$, and $AlBr_3$ being much more reactive to MNFs. For these experiments, equimolar ratios of Lewis acids were used for direct comparison. Assuming pseudo-first-order kinetics, graphs obtained from the log of fullerene concentration versus time (Figure 2) resulted in linear plots, from which k_{obs} rate data were readily obtained. These rate constants for reactions of $Sc_3N@I_h$-C_{80} with Lewis acids were 0.605 min^{-1} ($AlBr_3$), 0.302 min^{-1} ($FeCl_3$), 0.0124 min^{-1} ($AlCl_3$), and ~0 min^{-1} ($MgCl_2$). The data indicate that $AlBr_3$ and $FeCl_3$ react much more quickly with MNFs than does $AlCl_3$.

C. Metallofullerene Selectivity and Kinetic Study. C.1. $Sc_3N@D_{5h}$-C_{80} versus $Sc_3N@I_h$-C_{80}. It is well-known that the I_h isomer of $Sc_3N@C_{80}$ is less reactive than $Sc_3N@D_{5h}$-C_{80} for other types of reactions (i.e., non-Lewis acid reactions) such as cycloadditions.[21-26] To determine whether a similar trend occurs with Lewis acids, an experiment was performed with a stronger Lewis acid such as $FeCl_3$ to ensure sufficient reaction with both isomers. Aliquots at arbitrary times were collected to monitor the loss of the peak area for both $Sc_3N@C_{80}$ isomers from solution. Using first-order kinetics of uptake (Figure 3a), the ratio of k_{obs} ($Sc_3N@D_{5h}$-C_{80}) to k_{obs} ($Sc_3N@I_h$-C_{80}) was 1.6. Our finding of $Sc_3N@D_{5h}$-C_{80} being more reactive than $Sc_3N@I_h$-C_{80} to Lewis acids is consistent with literature reports of $Sc_3N@D_{5h}$-C_{80} being more reactive than $Sc_3N@I_h$-C_{80}.[21-26] The data in Figure 3b clearly show that isomeric purity can be achieved at only 55 min of reaction time. This more rapid removal (55 min) is compared with the 13 h of reaction time for $Sc_3N@D_{5h}$-C_{80} removal with the SAFA process, which uses aminosilica to selectively bind reactive fullerene and metallofullerene species.[13,14]

C.2. Reactivity of OMF versus MNF. For reactivity comparisons among other MNF and OMF metallofullerenes, we selected $AlCl_3$ based on its slower reaction kinetics. Of particular interest was probing of the reactivity of the OMF $Sc_4O_2@I_h$-C_{80} species relative to MNF compounds such as $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, $Sc_3N@D_{5h}$-C_{80}, and $Sc_3N@I_h$-C_{80}. For these experiments, 2 mg of a fullerene sample enriched in these compounds was dissolved in 15 mL of CS_2. With stirring, 10 mg of $AlCl_3$ was added to generate a reaction mixture from which aliquots were taken at arbitrary times to monitor fullerenes remaining in the solution (i.e., fullerenes not bound and precipitated by the Lewis acid). The amounts of C_{60} and C_{70} remaining in the solution are relatively constant. The logarithm of the fullerene concentration was plotted as a function of time, and first-order kinetics were observed. The results comparing the reactivities of OMFs and MNFs are summarized in Table 1. The significance of these results is the notion that one could manipulate these reactivity differences and develop a new method for purifying these metallofullerenes.

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(21) Cai, T.; Ge, Z. X.; Iezzi, E. B.; Glass, T. E.; Harich, K.; Gibson, H. W.; Dorn, H. C. *Chem. Commun.* **2005**, 3594–3596.

(22) Cai, T.; Slebodnick, C.; Xu, L.; Harich, K.; Glass, T. E.; Chancellor, C.; Fettinger, J. C.; Olmstead, M. M.; Balch, A. L.; Gibson, H. W.; Dorn, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 6486–6492.

(23) Cardona, C. M.; Kitaygorodskiy, A.; Ortiz, A.; Herranz, M. A.; Echegoyen, L. *J. Org. Chem.* **2005**, *70*, 5092–5097.

(24) Cardona, C. M.; Elliott, B.; Echegoyen, L. *J. Am. Chem. Soc.* **2006**, *128*, 6480–6485.

(25) Cardona, C. M.; Kitaygorodskiy, A.; Echegoyen, L. *J. Am. Chem. Soc.* **2005**, *127*, 10448–10453.

(26) Pinzon, J. R.; Plonska-Brzezinska, M. E.; Cardona, C. M.; Athans, A. J.; Gayathri, S. S.; Guldi, D. M.; Herranz, M. A.; Martin, N.; Torres, T.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4173–4176.

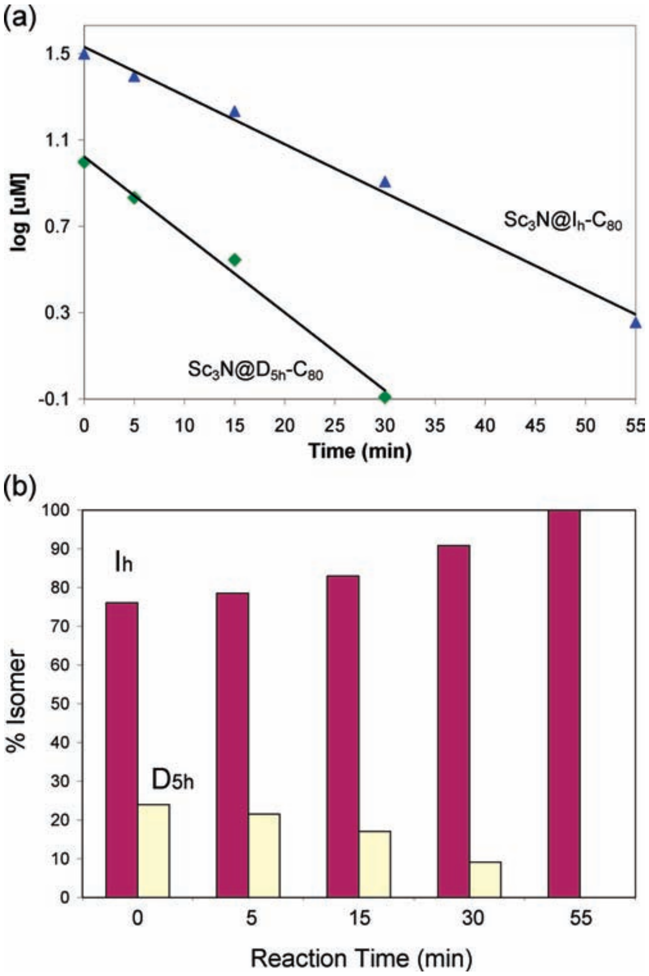

Figure 3. (a) Semilog plot comparing losses of D_{5h} and I_h $Sc_3N@C_{80}$ from the solution and (b) increases in the isomeric purity for $Sc_3N@I_h$-C_{80} with reaction time.

Table 1. Kinetic Data for Lewis Acid Reactions with OMFs and MNFs

	k_{obs} (min^{-1})	$t_{1/2}$ (min)	R^2	relative rate (I_h)
$Sc_4O_2@I_h$-C_{80}	0.035 ± 0.004	20	0.989	3.5
$Sc_3N@C_{78}$	0.029 ± 0.003	24	0.971	2.9
$Sc_3N@C_{68}$	0.019 ± 0.002	36	0.967	1.9
$Sc_3N@D_{5h}$-C_{80}	0.016 ± 0.002	43	0.952	1.6
$Sc_3N@I_h$-C_{80}	0.010 ± 0.001	69	0.993	1.0

The variation in rate constants among these metallofullerenes may be related to the electrochemical (EC) band gap. When our experimental kinetic data (i.e., k_{obs}) from Table 1 are plotted versus published EC data for C_{70},[27,28] $Sc_3N@I_h$-C_{80},[9,16,29] $Sc_3N@D_{5h}$-C_{80},[29] $Sc_3N@C_{68}$,[30] and $Sc_3N@C_{78}$,[31] a correlation can be made as shown in Figure 4. On the basis of this proportionality between the rate constant and band gap, a predicted EC band gap of ~1 V for $Sc_4O_2@I_h$-C_{80} can be made.

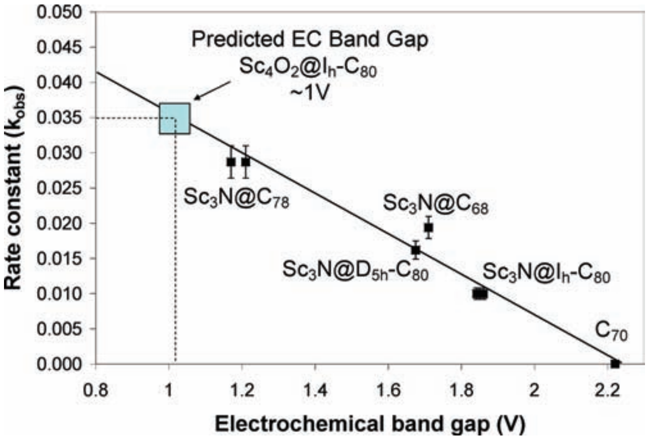

Figure 4. Correlation of the rate constants from metallofullerene reactions with Lewis acids versus the EC band gap.

D. Scalability and Recovery of Metallofullerenes. Several key issues include the scalability and ability to release the fullerene from the precipitated Lewis acid complex. To address these concerns, several gram-scale reactions were performed using three different types of Lewis acids. Solutions of ~1300 mg of Sc−fullerene extract in 500 mL of CS_2 were prepared for reaction with 1.75 g of $AlBr_3$, 240 mg of $FeCl_3$, or 198 mg of $AlCl_3$. After 3 h of reaction time, the reaction mixture was filtered to yield a precipitate, to which was added ice water, sodium bicarbonate, and CS_2. Under these conditions, OMFs and MNFs were released from the Lewis acid−fullerene complexes and dissolved in CS_2. As a representative example, HPLC chromatograms from the $FeCl_3$ experiments are shown in Figure 5. The HPLC results indicate selective precipitation and removal of OMFs and MNFs from the unreacted empty-cage fullerenes remaining in the solution (Figure 5b). The OMFs and MNFs are readily recovered from the precipitate (Figure 5c) using the procedure in section D of the Experimental Section. Fullerene recoveries were 83−86%, regardless of which Lewis acid was utilized. Results from these scale-up and recovery experiments are provided in Table 2.

E. $Sc_4O_2@I_h$-C_{80} and $Sc_3N@D_{5h}$-C_{80} Enrichment and Isolation of $Sc_3N@I_h$-C_{80}. E.1. Enrichment of $Sc_4O_2@I_h$-C_{80}. Moving to other species beyond the more chemically inert $Sc_3N@I_h$-C_{80}, it would be advantageous to develop and optimize this new method of selective Lewis acid precipitation toward the more reactive MNFs and OMFs. The advantage of determining the reactivity order of OMFs and MNFs is the ability to subsequently manipulate the kinetics such that the more reactive species can be precipitated, at which time the reaction can be stopped, thereby leaving the majority of the more chemically inert species still in solution (Figure 6a). To demonstrate this concept, 982 mg of fullerene extract obtained from the vaporization of Sc_2O_3-packed graphite rods was dissolved in 500 mL of CS_2. With stirring, 340 mg of $AlCl_3$ was added. The reaction progress (i.e., fullerene loss from the solution) was monitored at arbitrary times. Mass spectral data (Supporting Information) indicates that $Sc_4O_2@I_h$-C_{80} is the first of the OMF and MNF species to be precipitated from the solution (t = 20 h). This result is consistent with the reactivity

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(27) Yang, Y. F.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801–7804.

(28) Xie, Q.; Arias, F.; Echegoyen, L. *J. Am. Chem. Soc.* **1993**, *115*, 9818–9819.

(29) Cai, T.; Xu, L. S.; Anderson, M. R.; Ge, Z. X.; Zuo, T. M.; Wang, X. L.; Olmstead, M. M.; Balch, A. L.; Gibson, H. W.; Dorn, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 8581–8589.

(30) Yang, S. F.; Rapta, P.; Dunsch, L. *Chem. Commun.* **2007**, 189–191.

(31) Zhang, L.; Chen, N.; Fan, L. Z.; Wang, C. R.; Yang, S. H. *J. Electroanal. Chem.* **2007**, *608*, 15–21.

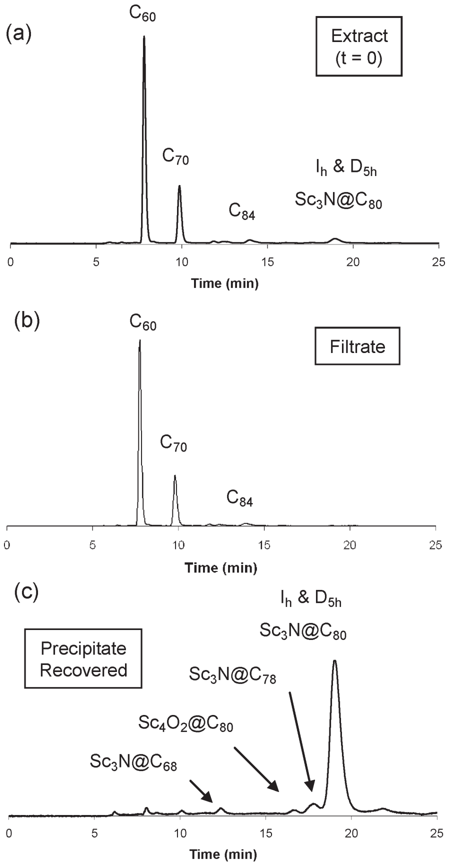


Figure 5. HPLC chromatograms of (a) the starting fullerene extract, (b) the resulting filtrate after 3 h of reaction time with $FeCl_3$, and (c) fullerenes recovered from the precipitate. HPLC conditions are 0.5 mL/min xylenes, 360 nm, a 4.6 × 250 mm PYE column, and 50 μL injection.

Table 2. Summary of Data from Fullerene Recovery Experiments

Lewis acid	mg of fullerenes (filtrate)	mg of fullerenes (from precipitate)	fullerene recovery (%)
$AlBr_3$	883	205	83
$FeCl_3$	1040	76	86
$AlCl_3$	973	56	83

comparisons described above (e.g., $Sc_4O_2@I_h$-C_{80} > $Sc_3N@C_{78}$ > $Sc_3N@C_{68}$ > $Sc_3N@D_{5h}$-C_{80} > $Sc_3N@$-I_h-C_{80}). Reaction beyond 20−44 h results in the further precipitation of $Sc_3N@C_{78}$, $Sc_3N@C_{68}$, $Sc_3N@D_{5h}$-C_{80}, and a small quantity of $Sc_3N@I_h$-C_{80}, as shown in Figure 6b. A second step with Lewis acid chemistry to enrich this sample in $Sc_4O_2@I_h$-C_{80} also utilizes $AlCl_3$. Shown in Figure 6c,d are the HPLC chromatogram and MALDI mass spectrum for the fullerene-recovered precipitate obtained after 4 h and 40 min for the reaction mixture of a 45 mg sample from Figure 6b, 250 mL of CS_2, and 135 mg of $AlCl_3$. On the basis of the MALDI data (Figure 6d), $Sc_4O_2@I_h$-C_{80} is the dominant species.

E.2. Enrichment of D_{5h} Isomer of $Sc_3N@C_{80}$. Reaction conditions for isolating enriched samples of $Sc_3N@D_{5h}$-C_{80} involve stirring a fullerene solution of ~1 g fullerene extract in 500 mL CS_2 with 340 mg $AlCl_3$ for 44 h. The data in Figure 6b clearly indicate isolation of an enriched fraction of $Sc_3N@D_{5h}$-C_{80} (50 mg sample). Note that the dominant peak in the HPLC chromatogram (Figure 6b) is the D_{5h} isomer of $Sc_3N@C_{80}$. With the overwhelming majority of fundamental science focusing on the I_h isomer, a benefit of this Lewis acid approach is the ability to obtain samples in which the dominant species is $Sc_3N@D_{5h}$-C_{80}. If desired, a final HPLC pass of this sample would yield a purified sample of $Sc_3N@D_{5h}$-C_{80}, and HPLC details for isolating $Sc_3N@D_{5h}$-C_{80} have been published elsewhere.[8,9]

E.3. Isolation of Isomerically Pure $Sc_3N@I_h$-C_{80}. For the isolation of isomerically pure $Sc_3N@I_h$-C_{80}, the filtrate obtained after $AlCl_3$ chemistry (step 1, Figure 6a) can be mixed with 150 mg of $FeCl_3$, as shown in Figure 6e. With other MNFs previously precipitated as described in section E.1 of the Results and Discussion section, this filtrate contains empty-cage fullerenes along with $Sc_3N@I_h$-C_{80} as the predominant metallofullerene. Hence, precipitation of this MNF via reaction with $FeCl_3$ (70 min) and subsequent workup result in isomerically purified $Sc_3N@I_h$-C_{80} as confirmed by HPLC (Figure 6f). To determine the purity of $Sc_3N@I_h$-C_{80} relative to other fullerenes, a MALDI mass spectrum (Figure 6g) indicates a sample of >99% metallofullerene purity.

F. Isolation of Gram Quantities of $Sc_3N@I_h$-C_{80}. With $Sc_4O_2@I_h$-C_{80} OMF being a “bookend” compound with the highest reactivity, one can manipulate the kinetics in favor of the other “bookend” species, the more inert $Sc_3N@I_h$-C_{80}. Isolation of the I_h isomer of $Sc_3N@C_{80}$ is accomplished by monitoring the loss of peak areas for the other MNF and OMF species (i.e., selective precipitation of $Sc_4O_2@I_h$-C_{80}, $Sc_3N@C_{78}$, $Sc_3N@C_{68}$, and $Sc_3N@D_{5h}$-C_{80}) and stopping the reaction when these contaminant peaks disappear from the HPLC plot. Optimal chromatographic conditions include use of a PYE (pyrenylethyl) stationary phase with slow flow rates such that the elution of D_{5h} and I_h isomers of $Sc_3N@C_{80}$ is at least 60 min. Because $Sc_3N@D_{5h}$-C_{80} is adjacent to $Sc_3N@I_h$-C_{80} in the reactivity trend for Lewis acids, monitoring the loss of the peak area for the D_{5h} isomer is critical for knowledge of when to cease the reaction. Upon the loss of the HPLC peak area for the D_{5h} isomer, the filtrate contains only unreacted empty-cage fullerenes (e.g., C_{60}, C_{70}, C_{76}, C_{78}, C_{84}) and predominantly $Sc_3N@I_h$-C_{80}. The $Sc_3N@I_h$-C_{80} can then be rapidly precipitated via the reaction with a stronger Lewis acid (e.g., $AlBr_3$, $FeCl_3$). An overview of the sequential separation of metallofullerenes is provided in Scheme 1.

To demonstrate this concept in Scheme 1 and to isolate large quantities of $Sc_3N@I_h$-C_{80}, an extract solution of 1340 mg of fullerenes was dissolved in 500 mL of carbon disulfide. With stirring, 245 mg of $AlCl_3$ was added. After 21 h, the reaction mixture was filtered to remove OMF and MNF contaminants of $Sc_4O_2@I_h$-C_{80}, $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@D_{5h}$-C_{80}. The filtrate (1.072 g of fullerenes), of which $Sc_3N@I_h$-C_{80} is the primary metallofullerene, was diluted to 1 L with CS_2. To this stirring solution was added 217 mg of $FeCl_3$ to precipitate $Sc_3N@I_h$-C_{80}. After 55 min of reaction, $Sc_3N@I_h$-C_{80} was precipitated from the solution. The precipitate containing $Sc_3N@I_h$-C_{80} complexed to $FeCl_3$ was processed as described in section D of the Experimental Section. Upon solvent removal and drying, 0.107 g of purified $Sc_3N@I_h$-C_{80} was obtained. The resulting HPLC trace and MALDI mass spectrum for this isolated sample are of purity equivalent to those shown in Figure 6f,g.

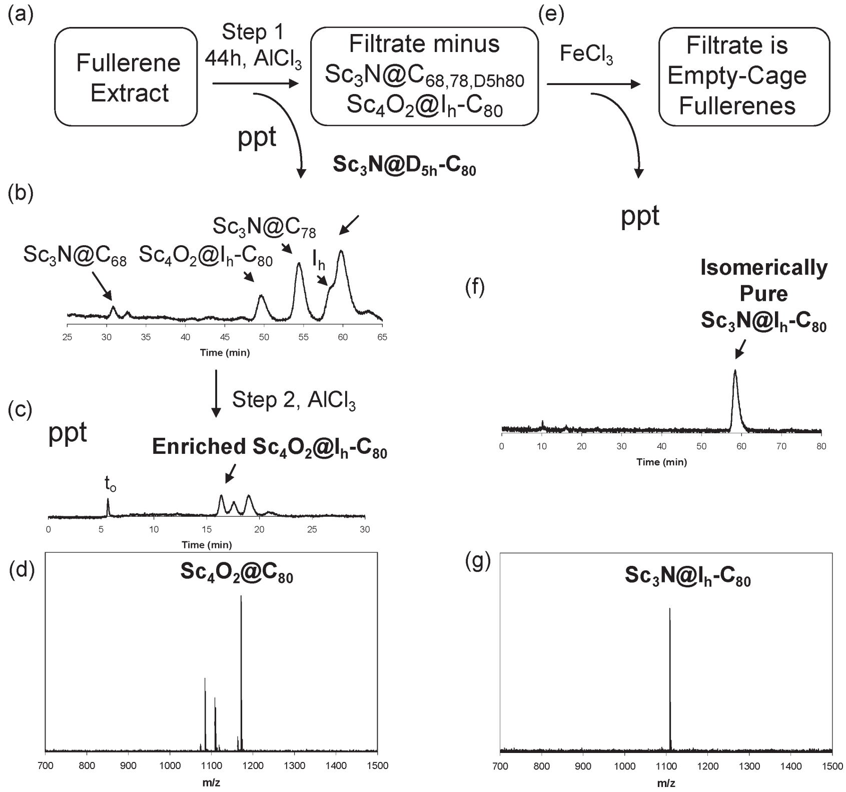
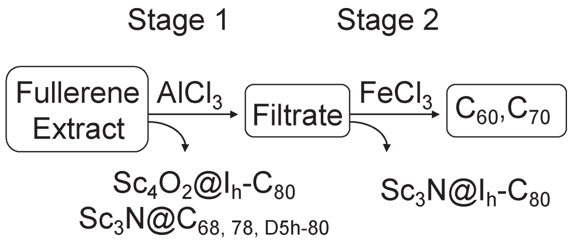


Figure 6. (a−d) Scheme, HPLC, and MALDI data demonstrating the isolation of enriched samples of $Sc_4O_2@I_h$-C_{80}, $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@D_{5h}$-C_{80} using complexation with $AlCl_3$ and subsequent decomplexation via the addition of water. (e−g) Isolation scheme, HPLC chromatogram, and MALDI mass spectrum of isomerically purified $Sc_3N@I_h$-C_{80} using the complexation/decomplexation approach. HPLC flow rates are (b,f) 0.3 mL/min toluene and (c) 0.5 mL/min xylenes with 360 nm detection, a 4.6 × 250 mm PYE column, and injection volumes of 50 μL.

Scheme 1. Removal of Non-$Sc_3N@I_h$-C_{80} Metallofullerenes with $AlCl_3$ (Stage 1) and the Subsequent Isolation of Isomerically Purified $Sc_3N@I_h$-C_{80} with $FeCl_3$ (Stage 2)



Conclusions

OMF and MNF endohedral metallofullerenes react quickly with Lewis acids. The empty-cage fullerenes are largely unreactive under the molar ratios used in this study. The reactivity order is $Sc_4O_2@I_h$-C_{80} > $Sc_3N@C_{78}$ > $Sc_3N@C_{68}$ > $Sc_3N@D_{5h}$-C_{80} > $Sc_3N@I_h$-C_{80}. Graphical analysis of the experimental rate constants versus the EC band gap explains the order of reactivity among the OMFs and MNFs. Manipulation of the Lewis acids and kinetic differences results in a selective precipitation scheme, which can be used alone for $Sc_3N@I_h$-C_{80} or combined with a final HPLC pass for $Sc_4O_2@I_h$-C_{80}, $Sc_3N@D_{5h}$-C_{80}, $Sc_3N@C_{68}$, and $Sc_3N@C_{78}$. The purification process is scalable. Efforts to expand this approach to other homometallic nitride fullerenes (e.g., $Gd_3N@C_{80}$) and mixed-metal nitride fullerenes (e.g., $LaSc_2N@C_{80}$) are underway.

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Supporting Information Available: MALDI data at various reaction times. This material is available free of charge via the Internet at http://pubs.acs.org.