Supplementary Material (ESI) for Chemical Communications

Synthesis and Characterization of the First Trimetallic Nitride Template Endohedral Metallofulleropyrrolidines

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Experimental Details

♦Synthesis and Isolation

1. $Sc_3N@C_{80}$ pyrrolidine derivative **2a** (natural abundance carbon):

To a solution of 5.0 mg (4.5 μmol) of $Sc_3N@C_{80}$ in 50 mL of *o*-dichlorobenzene, 1.2 mg (14 μmol) of N-methylglycine and 1.6 mg (53 μmol) of paraformaldehyde were added. The mixture was heated at 110°C in oil bath for 10 h. The solvent was removed *in vacuo* and the crude solid was purified by silica gel column chromatography (eluent: *o*-dichlorobenzene). The collected solid was dissolved in CS_2 and injected into an HPLC for final purification. HPLC condition: PYE [2-1-(pyrenyl)ethyl silica] column (10 × 250 mm), mobile phase (CS_2), flow rate: 0.5mL/min, λ = 390nm. This led to the isolation of 2 mg (40%) of pure **2a** as a black solid.

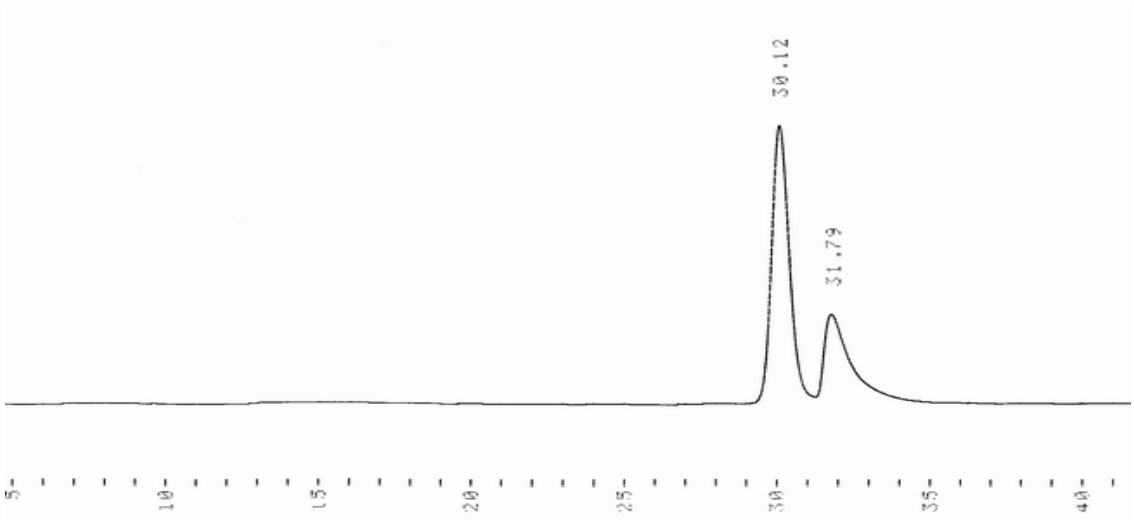
2. $Sc_3N@C_{80}$ pyrrolidine derivative **2a** (99% ^{13}C labeled)

To a solution of 2.0 mg (1.8 μmol) of $Sc_3N@C_{80}$ in 30 mL of *o*-dichlorobenzene, 0.7 mg (9 μmol) of N-methylglycine and 3 μl (0.03 mmol) of formaldehyde (99% ^{13}C, ~20% W/W in H_2O) (Cambridge Isotope Laboratory, Inc.) were added. The product was purified as indicated above. This led to the isolation of 0.6 mg (30%) of pure **2a** as a black solid.

3. $Er_3N@C_{80}$ pyrrolidine derivative **2b** (99% ^{13}C labeled)

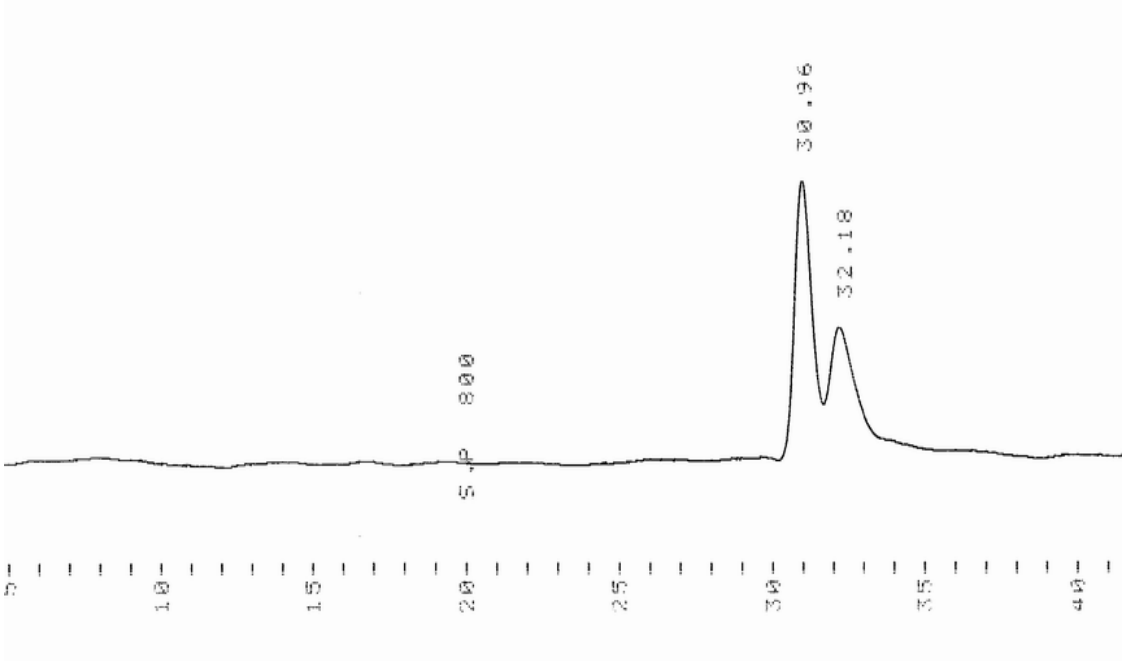
To a solution of 2.2 mg (1.5 μmol) of $Er_3N@C_{80}$ in 30 mL of *o*-dichlorobenzene, 0.6 mg (7 μmol) of N-methylglycine and 2~3 μl (0.02 mmol) of formaldehyde (99% ^{13}C, ~20% W/W in H_2O) (Cambridge Isotope Laboratory, Inc.) were added. The product was purified as indicated above. This led to the isolation of 0.7 mg (30%) of pure **2b** as a black solid.

♦ HPLC trace of monoadduct **2a** and unreacted $Sc_3N@C_{80}$ (**1a**).



Retention times: 30.12 min ($Sc_3N@C_{80}$); 31.79 min (**2a**)

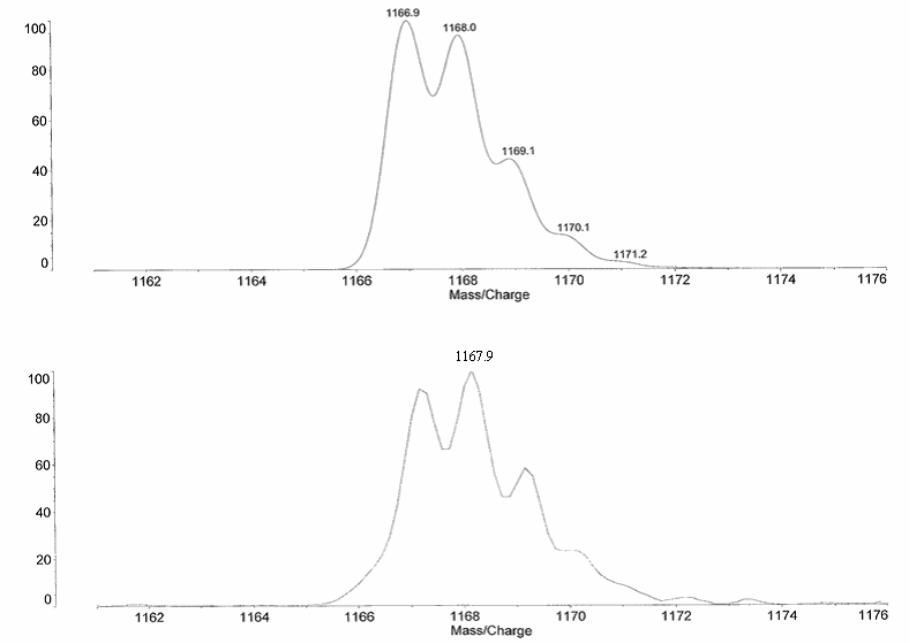
♦ HPLC trace of monoadduct **2b** and unreacted $Er_3N@C_{80}$ (**1b**).



Retention times: 30.96 min ($Er_3N@C_{80}$); 32.18 min (**2b**)

♦Comparison of computer simulated mass spectra with experimental mass spectra
(Assuming $A_3N_2C_{83}H_8$ is equivalent to $A_3N_2C_{83}H_7$ with one carbon which is 100% ^{13}C labeled)

1. Computer simulated mass spectrum of the molecule with formula of $Sc_3N_2C_{83}H_8$ (top)
Experimental mass spectrum of **2a** (99% ^{13}C labeled) (bottom)



2. Computer simulated mass spectrum of the molecule with formula of $Er_3N_2C_{83}H_8$ (top)
Experimental mass spectrum of **2b** (99% ^{13}C labeled) (bottom)