Supporting Information of

$Sc_3N@I_h$-C_{80} as a Novel Lewis Acid to Trap Abnormal N-Heterocyclic Carbene: Unprecedented Formation of a Singly Bonded [6,6,6]-adduct

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Experimental

General methods: High-performance liquid chromatography (HPLC) was conducted on an LC-9130 NEXT machine (Japan Analytical Industry Co., Ltd.) with toluene as mobile phase. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was measured on a BIFLEX III spectrometer (Bruker Daltonics Inc., Germany) using 1,1,4,4-tetraphenyl-1, 3-butadiene as matrix. UV-Vis-NIR spectra were obtained from a PE Lambda 750S spectrometer in toluene.

Synthesis of 2a: $Sc_3N@I_h$-C_{80} was synthesized with a direct-current arc discharge method and was isolated with HPLC. A mixture of $Sc_3N@I_h$-C_{80} (~5 mg, 4.5 μmol) and 1,3-bis(diisopropyl- phenyl)imidazol-2-ylene (87.5 mg, 0.22 mmol) dissolved in 10 mL *ortho*-dichlorobenzene (ODCB) was stirred at 90 °C in dark under argon atmosphere for 24 h. After removal of ODCB, the residual solid was dissolved in toluene and was subjected to HPLC separation.

Single crystal XRD measurement of 2a. A piece of crystal with dimensions of 0.04 × 0.02 × 0.02 mm was chosen for the single-crystal XRD measurement and provided all the structural information about **2a**. X-ray data were collected at 90 K on a Bruker Apex II machine equipped with a CCD detector (Bruker AXS Inc., Germany). The multi-scan method was used for absorption corrections. The structure was solved by using direct method and was refined with SHELXL-2014.[S1] CCDC-1406974 contains the supplementary crystallographic data for this paper which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Theoretical Calculations. DFT calculations were conducted with Gaussian 09 package[S2] using the B3LYP functional with the 6-31G basis set[S3] for C, H, N atoms and the ~dz basis set[S4] (with the ~dz effective core potential) for Sc atoms.

REFERENCES

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Table S1. Cartesian coordinates and energies of **2a** and **2b** optimized at the B3LYP/6-31G*/LANL2DZ(Sc) level.

2a

xyz file:

C	-1.2098	7.2807	4.1542
C	-1.3202	8.3907	3.264
C	-0.2156	8.9692	2.5716
C	1.0608	8.4144	2.8958
C	1.2484	7.3156	3.7878
C	0.0765	6.4808	4.3227
C	0.3137	6.4837	5.8118
C	-0.7245	6.5764	6.7917
C	-2.0605	6.9854	6.4914
C	-2.2634	7.35	5.1158
C	-3.0445	8.5658	4.7971
C	-2.4458	9.1749	3.6578
C	-2.4853	10.5894	3.4325
C	-1.415	11.1508	2.7053
C	-0.2771	10.3655	2.2914
C	0.8993	11.1849	2.3482
C	2.143	10.6461	2.7108
C	2.2443	9.2375	2.9453
C	3.1604	8.6418	3.8556
C	2.5453	7.42	4.3886
C	2.7673	7.0393	5.7679
C	1.589	6.5953	6.4346
C	1.3458	6.8045	7.8394
C	-0.0604	6.7992	8.0391
C	-0.6627	7.5892	9.0447
C	-1.9819	8.0647	8.7644
C	-2.6817	7.7648	7.5409
C	-3.4666	8.958	7.213
C	-3.6092	9.3808	5.8393
C	-3.6576	10.7994	5.5993
C	-3.1348	11.38	4.3996
C	-2.6622	12.6893	4.7147
C	-1.5257	13.2235	4.0553
C	-0.9235	12.4757	3.0186
C	0.5024	12.4893	2.7951
C	1.3646	13.2585	3.6102
C	2.672	12.7669	3.8941
C	3.0605	11.4539	3.4417
C	3.9531	10.8843	4.4271

C	3.9992	9.4833	4.6762
C	4.2719	9.0516	6.0096
C	3.6691	7.8478	6.5683
C	3.3521	8.1278	7.9475
C	2.2056	7.6102	8.6197
C	1.6108	8.3592	9.6821
C	0.1903	8.3484	9.8836
C	-0.212	9.651	10.3433
C	-1.4633	10.1974	9.977
C	-2.3547	9.3944	9.2168
C	-3.2552	9.9388	8.2497
C	-3.2664	11.3404	7.9805
C	-3.513	11.7457	6.6635
C	-2.8909	12.9259	6.0994
C	-1.997	13.6967	6.8906
C	-0.895	14.3621	6.2239
C	-0.6476	14.0511	4.8594
C	0.7498	14.0726	4.6377
C	1.3912	14.3813	5.8777
C	2.6584	13.7543	6.1781
C	3.3069	13.0024	5.1561
C	4.0883	11.8553	5.4931
C	4.2543	11.4225	6.8247
C	4.3501	10.0305	7.0775
C	3.8142	9.4618	8.2644
C	3.1789	10.2507	9.2736
C	2.0892	9.6798	9.999
C	0.9715	10.4538	10.4294
C	0.9026	11.8487	10.118
C	-0.3697	12.4172	9.8469
C	-1.5416	11.61	9.7828
C	-2.4205	12.158	8.7846
C	-1.794	13.3029	8.2204
C	-0.5254	13.4765	8.8798
C	0.5895	14.089	8.2223
C	0.3749	14.6083	6.8815
C	1.858	13.4993	8.5208
C	2.8907	13.3646	7.5171
C	3.6882	12.2281	7.8523
C	3.1601	11.6629	9.0447
C	2.0298	12.4385	9.4696
C	0.0277	5.0519	3.8226
C	0.0742	3.9056	4.5663
H	0.1271	3.8515	5.5133

C	-0.0584	3.3028	2.4489
H	-0.1181	2.7802	1.6576
C	0.0706	1.4346	4.0626
C	1.3182	0.8682	4.2897
C	1.3124	-0.4545	4.7275
H	2.1396	-0.8804	4.9198
C	0.1505	-1.1629	4.8923
H	0.1837	-2.0621	5.1945
C	-1.078	-0.5715	4.6176
H	-1.8771	-1.0753	4.7165
C	-1.1428	0.7567	4.1963
C	2.6221	1.6084	4.0406
H	2.3872	2.5005	3.656
C	3.4989	0.8848	3.0076
H	2.9856	0.7399	2.1852
H	3.7862	0.0207	3.3702
H	4.2866	1.4318	2.8079
C	3.402	1.8558	5.2843
H	4.1783	2.4166	5.0773
H	3.706	1.0009	5.6561
H	2.8342	2.3138	5.94
C	-2.4965	1.39	3.9216
H	-2.3421	2.3386	3.6468
C	-3.3814	1.3991	5.1597
H	-4.2648	1.754	4.9271
H	-2.9738	1.9637	5.8484
H	-3.4767	0.4841	5.5004
C	-3.1952	0.6738	2.7658
H	-4.0535	1.1083	2.5845
H	-3.3486	-0.2623	3.0076
H	-2.6312	0.7172	1.9654
C	-0.0851	5.4878	1.306
C	-1.3409	5.8989	0.8535
C	-1.3516	6.7129	-0.2747
H	-2.1783	7.0238	-0.6264
C	-0.1566	7.0755	-0.8902
H	-0.1822	7.6262	-1.6631
C	1.0692	6.6503	-0.3993
H	1.8696	6.9233	-0.8316
C	1.1335	5.8315	0.7162
C	-2.6243	5.4454	1.5184
H	-2.4169	5.235	2.4727
C	-3.1671	4.1542	0.8554
H	-3.3924	4.336	-0.0806

H	-3.9697	3.8555	1.3316
H	-2.4834	3.4531	0.8975
C	-3.7155	6.515	1.5019
H	-4.0578	6.6197	0.5898
H	-3.3423	7.3679	1.8115
H	-4.4465	6.2457	2.0954
C	2.4479	5.2724	1.2364
H	2.3276	5.0421	2.2016
C	3.5758	6.2836	1.1283
H	3.7863	6.4395	0.1832
H	4.3701	5.9364	1.5862
H	3.3	7.1266	1.5459
C	2.8219	3.9877	0.4836
H	2.9629	4.1949	-0.4652
H	2.0959	3.336	0.5715
H	3.6451	3.6155	0.8627
N	0.3343	10.3777	6.2642
N	0.0312	2.8373	3.6871
N	-0.05	4.6343	2.5039
Sc	1.8618	9.1281	5.8483
Sc	-1.2147	9.0861	6.2126
Sc	0.3428	12.358	6.6163

E= -4402.81785765 a.u.

2b

xyz file:

C	-0.99167	1.67628	-1.48097
C	-0.02352	1.87101	-2.53143
C	0.41098	0.80207	-3.37509
C	-0.16921	-0.48244	-3.13507
C	-1.14175	-0.7051	-2.09216
C	-1.49103	0.36563	-1.20925
C	-2.18036	0.06707	0.10744
C	-1.56291	1.00094	1.18265
C	-1.00872	2.28232	0.91636
C	-0.81257	2.71097	-0.47896
C	0.36853	3.51024	-0.89255
C	0.83244	2.96059	-2.16252
C	2.21334	2.95152	-2.59003
C	2.62706	1.9122	-3.47933
C	1.7291	0.85431	-3.88385
C	2.49308	-0.35969	-4.05691
C	1.94121	-1.64328	-3.75658
C	0.55626	-1.70126	-3.34591
C	0.00133	-2.73403	-2.47847

C	-1.10329	-2.1072	-1.70644
C	-1.28046	-2.37934	-0.26814
C	-1.6538	-1.30832	0.58727
C	-1.24131	-1.19283	1.95868
C	-1.17388	0.19683	2.31535
C	-0.17191	0.6582	3.23072
C	0.36788	1.96575	3.00462
C	-0.02314	2.75937	1.8591
C	1.12815	3.55627	1.45754
C	1.3783	3.90377	0.07503
C	2.75316	3.91518	-0.34651
C	3.16427	3.48869	-1.67499
C	4.48024	2.92089	-1.57657
C	4.8598	1.81527	-2.39762
C	3.94816	1.34606	-3.38564
C	3.86573	-0.05519	-3.74191
C	4.69147	-1.03421	-3.12054
C	4.16873	-2.34677	-2.9127
C	2.80164	-2.65074	-3.23208
C	2.3103	-3.6098	-2.25621
C	0.93459	-3.64809	-1.84148
C	0.68551	-3.98256	-0.45505
C	-0.38293	-3.35378	0.3092
C	0.06301	-3.24163	1.68224
C	-0.33041	-2.145	2.51755
C	0.58306	-1.70065	3.51146
C	0.66359	-0.30396	3.86439
C	2.03831	-0.00413	4.18216
C	2.60251	1.26912	3.87294
C	1.73557	2.26797	3.31787
C	2.21249	3.23327	2.36092
C	3.57297	3.23199	1.92294
C	3.82919	3.60788	0.56514
C	4.89436	2.99854	-0.19277
C	5.71687	1.98852	0.39512
C	6.2312	0.93446	-0.45421
C	5.73555	0.83536	-1.8088
C	5.65439	-0.5552	-2.16227
C	6.09902	-1.34048	-1.03223
C	5.44731	-2.60706	-0.77203
C	4.53478	-3.11936	-1.74586
C	3.38856	-3.89383	-1.3392
C	3.13846	-4.18458	0.04003
C	1.77428	-4.24612	0.46257

C	1.38023	-3.8035	1.77569
C	2.33551	-3.29066	2.71508
C	1.90671	-2.26449	3.60895
C	2.80373	-1.21816	4.03355
C	4.1482	-1.1764	3.55865
C	4.7375	0.10747	3.33496
C	3.97832	1.31876	3.49484
C	4.45407	2.28896	2.53593
C	5.50199	1.67166	1.77065
C	5.68159	0.31528	2.26099
C	6.14553	-0.75076	1.42076
C	6.48999	-0.42071	0.04075
C	5.54312	-2.02915	1.6649
C	5.2302	-2.96086	0.59411
C	4.10009	-3.74862	1.00259
C	3.70727	-3.3053	2.32049
C	4.59883	-2.25543	2.73492
C	-3.58084	0.02977	0.08112
C	-4.3492	-1.09653	0.22019
H	-4.04973	-2.11173	0.38459
C	-5.74996	0.59341	-0.0879
H	-6.64703	1.16772	-0.20562
C	-6.82345	-1.64464	0.20736
C	-7.2659	-2.28489	-0.96875
C	-8.34262	-3.1736	-0.84329
H	-8.71119	-3.68603	-1.72043
C	-8.9401	-3.41173	0.39219
H	-9.76781	-4.10406	0.46484
C	-8.47284	-2.76842	1.53595
H	-8.94053	-2.96993	2.48888
C	-7.40037	-1.86815	1.47477
C	-6.60895	-2.07058	-2.33226
H	-5.86099	-1.28118	-2.23499
C	-7.62591	-1.60377	-3.39707
H	-8.14983	-0.69985	-3.0817
H	-8.37436	-2.37142	-3.60087
H	-7.11157	-1.38874	-4.33526
C	-5.86363	-3.3434	-2.79733
H	-5.35997	-3.15873	-3.74751
H	-6.55535	-4.17607	-2.9389
H	-5.10915	-3.65262	-2.07278
C	-6.88451	-1.20762	2.7532
H	-6.14566	-0.45246	2.47803
C	-6.16456	-2.23637	3.65708

H	-5.75877	-1.7423	4.5414
H	-5.33817	-2.72025	3.13468
H	-6.85246	-3.01523	3.99201
C	-8.00722	-0.48231	3.5269
H	-7.58786	0.04245	4.38689
H	-8.75464	-1.18327	3.90256
H	-8.51867	0.2491	2.89883
C	-4.23207	2.51969	-0.3084
C	-4.16176	3.34607	0.83281
C	-3.93148	4.71049	0.61482
H	-3.85374	5.37669	1.46103
C	-3.79697	5.2214	-0.6737
H	-3.60907	6.27689	-0.81603
C	-3.90714	4.38344	-1.77989
H	-3.81016	4.79802	-2.77221
C	-4.13272	3.00918	-1.62769
C	-4.39895	2.8195	2.24956
H	-4.20183	1.74515	2.25146
C	-5.87704	3.03653	2.66075
H	-6.11472	4.10185	2.68747
H	-6.05749	2.62552	3.65591
H	-6.57351	2.56073	1.9667
C	-3.46198	3.44292	3.30366
H	-3.67817	4.50102	3.46306
H	-2.41699	3.34592	3.01744
H	-3.59788	2.93589	4.26034
C	-4.32926	2.11892	-2.85676
H	-4.13654	1.0844	-2.56194
C	-3.35833	2.44213	-4.01057
H	-3.5708	3.41483	-4.45811
H	-3.46019	1.69288	-4.79751
H	-2.32423	2.43939	-3.67347
C	-5.79192	2.20879	-3.35982
H	-6.0234	3.22621	-3.68121
H	-6.51359	1.93581	-2.58715
H	-5.94138	1.54308	-4.21199
N	2.25227	-0.11014	-0.2284
N	-5.69006	-0.73383	0.11364
N	-4.49586	1.09206	-0.11572
Sc	0.86341	-1.47396	-0.75967
Sc	1.05462	1.50335	-0.0211
Sc	4.20213	-0.28536	0.02442

E= -4402.81707388 a.u.