Electronic Supplementary Information for Dalton Transactions



# Synthesis, Characterisation and Theoretical Studies of Amidinato-Indium(I) and Thallium(I) Complexes: Isomers of Neutral Group13 Metal(I) Carbene Analogues

**Cameron Jones,* Peter C. Junk, Jamie A. Platts, Daniel Rathmann and Andreas Stasch**

## SUPPLEMENTARY MATERIAL

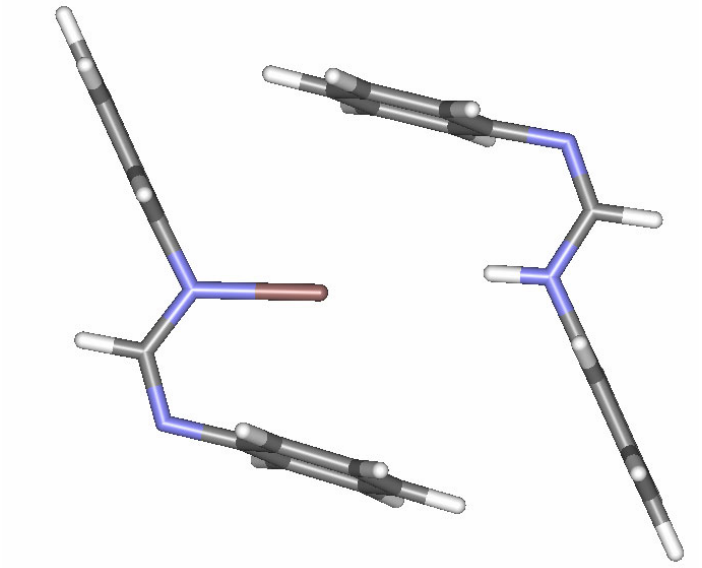

**Figure S1** Optimised geometry of [In{PhNC(H)NPh}].{PhNC(H)N(H)Ph}

## Computational Details

All DFT calculations were carried out using Gaussian03,[1] employing Adamo and Barone's mPW1PW91 functional[2] with a basis set consisting of 6-31+G(d) on C, N, and H[3] along with Stevens, Basch, and Krauss's basis set and ECP on In,[4] *i.e.* similar to that used in a recent study of indium diazadiene complexes carried out by Schoeller et al.[5] Population analysis employed Weinhold and co-workers' NBO scheme.[6] Calculated binding energy included the standard counterpoise correction for BSSE.[7]

1. Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara,

K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

2. C. Adamo, and V. Barone, *J. Chem. Phys.* 1998, **108**, 664.
3. (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (b) M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163; (c) T. Clark, J. Chandrasekhar and G. W. Spitznagel, *J. Comput.Chem.*,1983, **4**, 294.
4. (a) W. J. Stevens, H. Basch and M. Krauss, *J. Chem. Phys.*, 1984, **81**, 6026; (b) W. J. Stevens, M. Krauss, H. Basch and P. Jasien, *Can. J. Chem.*, 1992, **70**, 612; (c) T. Cundari and W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555.
5. W. W. Schoeller and S. Grogoleit, *Dalton Trans.*, 2002, 405.
6. A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
7. S. F. Boys, F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.

## Cartesian coordinates of optimised structures

compound **6a**: scf energy -800.663203

| | | | |
|---|---|---|---|
| In | -1.153169 | -0.545485 | 2.092009 |
| N | -0.217079 | 1.143135 | 0.671577 |
| C | 0.760058 | 0.360251 | 0.250483 |
| H | 1.575630 | 0.747255 | -0.373456 |
| N | 0.747393 | -0.891845 | 0.671023 |
| C | 1.689263 | -1.836013 | 0.273297 |
| C | 1.988039 | -2.893806 | 1.147117 |
| C | 2.909076 | -3.872925 | 0.794085 |
| C | 3.556826 | -3.823974 | -0.440100 |
| C | 3.256308 | -2.786926 | -1.321337 |
| C | 2.326978 | -1.809071 | -0.979492 |
| H | 1.493957 | -2.928425 | 2.113120 |
| H | 3.125109 | -4.677650 | 1.489716 |
| H | 4.276098 | -4.587642 | -0.714908 |
| H | 3.736946 | -2.745317 | -2.293839 |
| H | 2.075853 | -1.036522 | -1.698797 |
| C | -0.352027 | 2.469878 | 0.273696 |
| C | 0.069875 | 2.945595 | -0.980322 |
| C | -0.098939 | 4.283933 | -1.322496 |
| C | -0.709129 | 5.173782 | -0.440348 |
| C | -1.154500 | 4.704206 | 0.795105 |
| C | -0.979365 | 3.371517 | 1.148480 |
| H | 0.506894 | 2.261436 | -1.700215 |
| H | 0.235469 | 4.629008 | -2.295942 |
| H | -0.845147 | 6.213929 | -0.715403 |
| H | -1.638822 | 5.381464 | 1.491459 |
| H | -1.316831 | 3.011662 | 2.115488 |

compound **6b**: scf energy -800.6479627

| | | | |
|---|---|---|---|
| In | -0.424565 | -0.521418 | 0.000000 |
| N | -1.465272 | -2.550824 | 0.000000 |
| N | -3.720383 | -1.827916 | 0.000000 |
| C | -2.802787 | -2.741374 | 0.000000 |
| C | 1.088056 | -5.919270 | 0.000000 |
| C | -0.635778 | -3.698289 | 0.000000 |
| C | -3.345030 | -0.495489 | 0.000000 |
| C | -2.768593 | 2.280108 | 0.000000 |
| H | -2.562063 | 3.344392 | 0.000000 |
| H | -3.152915 | -3.777553 | 0.000000 |
| H | 1.752845 | -6.776534 | 0.000000 |
| C | -0.194433 | -4.261931 | 1.205000 |
| C | -0.194433 | -4.261931 | -1.205000 |
| C | 0.658001 | -5.363742 | 1.203817 |
| C | 0.658001 | -5.363742 | -1.203817 |
| C | -3.177099 | 0.217062 | -1.208034 |
| C | -3.177099 | 0.217062 | 1.208034 |
| C | -2.903616 | 1.585752 | -1.202072 |
| C | -2.903616 | 1.585752 | 1.202072 |
| H | -0.534135 | -3.827646 | -2.140141 |
| H | -0.534135 | -3.827646 | 2.140141 |
| H | -3.311648 | -0.316079 | -2.143713 |
| H | -3.311648 | -0.316079 | 2.143713 |
| H | -2.802599 | 2.111528 | -2.146423 |
| H | -2.802599 | 2.111528 | 2.146423 |
| H | 0.986371 | -5.789459 | -2.146767 |
| H | 0.986371 | -5.789459 | 2.146767 |

[In{PhNC(H)NPh}].{PhNC(H)N(H)Ph}: scf energy -1412.640524

| | | | |
|---|---|---|---|
| In | -0.424653 | -0.548059 | 0.000000 |
| N | 1.715632 | 2.854613 | 0.000000 |
| N | 3.934500 | 1.992291 | 0.000000 |
| N | -1.430921 | -2.520918 | 0.000000 |
| N | -3.711215 | -1.835805 | 0.000000 |
| C | 3.078576 | 2.946870 | 0.000000 |
| C | -2.774854 | -2.730051 | 0.000000 |
| C | 0.862650 | 3.994175 | 0.000000 |
| C | -0.828259 | 6.226195 | 0.000000 |
| C | 3.499631 | 0.658587 | 0.000000 |
| C | 2.792023 | -2.076999 | 0.000000 |
| C | 1.079275 | -5.935546 | 0.000000 |
| C | -0.616558 | -3.684873 | 0.000000 |
| C | -3.354183 | -0.493873 | 0.000000 |
| C | -2.775004 | 2.287104 | 0.000000 |
| H | -1.483642 | 7.092431 | 0.000000 |
| H | 2.529803 | -3.130561 | 0.000000 |
| H | 1.291302 | 1.930658 | 0.000000 |
| H | -2.554100 | 3.349637 | 0.000000 |
| H | -3.103878 | -3.773799 | 0.000000 |
| H | 1.734698 | -6.801603 | 0.000000 |
| H | 3.449475 | 3.972782 | 0.000000 |
| C | 0.439385 | 4.555338 | 1.210203 |
| C | 0.439385 | 4.555338 | -1.210203 |
| C | -0.404118 | 5.668483 | -1.209341 |
| C | -0.404118 | 5.668483 | 1.209341 |
| C | 3.321268 | -0.037514 | -1.209529 |
| C | 3.321268 | -0.037514 | 1.209529 |
| C | 2.972243 | -1.389336 | -1.205346 |
| C | 2.972243 | -1.389336 | 1.205346 |

| | | | |
|---|---|---|---|
| C | -0.186935 | -4.258092 | 1.207484 |
| C | -0.186935 | -4.258092 | -1.207484 |
| C | 0.652976 | -5.373976 | 1.207001 |
| C | 0.652976 | -5.373976 | -1.207001 |
| C | -3.192453 | 0.219378 | -1.210072 |
| C | -3.192453 | 0.219378 | 1.210072 |
| C | -2.916298 | 1.590575 | -1.203969 |
| C | -2.916298 | 1.590575 | 1.203969 |
| H | -0.520715 | -3.817914 | -2.143412 |
| H | -0.520715 | -3.817914 | 2.143412 |
| H | -3.330457 | -0.313415 | -2.146716 |
| H | -3.330457 | -0.313415 | 2.146716 |
| H | 3.481142 | 0.489315 | -2.145974 |
| H | 3.481142 | 0.489315 | 2.145974 |
| H | 0.774614 | 4.111694 | -2.143293 |
| H | 0.774614 | 4.111694 | 2.143293 |
| H | -0.728175 | 6.101194 | -2.151503 |
| H | -0.728175 | 6.101194 | 2.151503 |
| H | -2.812677 | 2.116750 | -2.149178 |
| H | -2.812677 | 2.116750 | 2.149178 |
| H | 2.849292 | -1.913474 | -2.149589 |
| H | 2.849292 | -1.913474 | 2.149589 |
| H | 0.974856 | -5.806012 | -2.150715 |
| H | 0.974856 | -5.806012 | 2.150715 |

NBO details for the In atom in compound **6b**

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | In | 1 | S | Cor( 4S) | 1.99968 | -4.60052 |
| 2 | In | 1 | S | Val( 5S) | 1.92206 | -0.31562 |
| 3 | In | 1 | S | Ryd( 6S) | 0.00175 | 1.36623 |
| 4 | In | 1 | S | Ryd( 7S) | 0.00001 | 96.03324 |
| 5 | In | 1 | px | Cor( 4p) | 1.99987 | -3.04162 |
| 6 | In | 1 | px | Val( 5p) | 0.09272 | 0.01517 |
| 7 | In | 1 | px | Ryd( 6p) | 0.00076 | 0.54730 |
| 8 | In | 1 | px | Ryd( 7p) | 0.00005 | 3.47247 |
| 9 | In | 1 | py | Cor( 4p) | 1.99958 | -3.03326 |
| 10 | In | 1 | py | Val( 5p) | 0.14354 | 0.08715 |
| 11 | In | 1 | py | Ryd( 6p) | 0.00098 | 0.70394 |
| 12 | In | 1 | py | Ryd( 7p) | 0.00006 | 3.44815 |
| 13 | In | 1 | pz | Cor( 4p) | 1.99993 | -3.04347 |
| 14 | In | 1 | pz | Val( 5p) | 0.06481 | -0.02998 |
| 15 | In | 1 | pz | Ryd( 6p) | 0.00032 | 0.41738 |
| 16 | In | 1 | pz | Ryd( 7p) | 0.00001 | 3.44876 |
| 17 | In | 1 | dxy | Cor( 4d) | 1.99829 | -0.75919 |
| 18 | In | 1 | dxy | Ryd( 5d) | 0.00021 | 1.02920 |
| 19 | In | 1 | dxy | Ryd( 6d) | 0.00002 | 2.98693 |
| 20 | In | 1 | dxz | Cor( 4d) | 1.99953 | -0.76535 |
| 21 | In | 1 | dxz | Ryd( 5d) | 0.00049 | 0.79689 |
| 22 | In | 1 | dxz | Ryd( 6d) | 0.00002 | 2.87448 |
| 23 | In | 1 | dyz | Cor( 4d) | 1.99944 | -0.76082 |
| 24 | In | 1 | dyz | Ryd( 5d) | 0.00044 | 0.77187 |
| 25 | In | 1 | dyz | Ryd( 6d) | 0.00001 | 2.85103 |
| 26 | In | 1 | dx2y2 | Cor( 4d) | 1.99782 | -0.75797 |
| 27 | In | 1 | dx2y2 | Ryd( 5d) | 0.00029 | 1.11766 |
| 28 | In | 1 | dx2y2 | Ryd( 6d) | 0.00003 | 3.06794 |
| 29 | In | 1 | dz2 | Cor( 4d) | 1.99878 | -0.76370 |
| 30 | In | 1 | dz2 | Ryd( 5d) | 0.00024 | 0.96060 |
| 31 | In | 1 | dz2 | Ryd( 6d) | 0.00002 | 2.94141 |

| Atom | No | Charge | Core | Valence | Rydberg | Total |
|---|---|---|---|---|---|---|
| In | 1 | 0.77826 | 45.99291 | 2.22313 | 0.00570 | 48.22174 |

| Atom | No | Natural Electron Configuration |
|---|---|---|
| In | 1 | [core] 5S(1.92) 5p(0.30) |