Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for:

The boron-boron triple bond in NHC→B≡B←NHC

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Theoretical Methods

Geometry optimizations have been carried out using TurboMole 6.1 optimizer[1] and gradients at the BP86[2]/def2-TZVPP[3] level of theory. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory. For all calculations the resolution-of-identity method has been applied.[4] For the calculation of the force constants a rigid scan of the B-B bond with a step size of 0.001 A was performed. The force constant was then taken from a fitted polynomial of second order.

For the bonding analyses we calculated the molecules using the gradient corrected functional BP86[2] in conjunction with uncontracted Slater-type orbitals (STOs) as basis functions.[5] The latter basis sets for all elements have triple-ζ quality augmented by two sets of polarization functions (ADF-basis set TZ2P+). This level of theory is denoted BP86/TZ2P+. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[6] The BP86/TZ2P+ calculations were performed using with the program package ADF2013.01[7]

The interatomic interactions were investigated by means of an energy decomposition analysis (EDA, also termed extended transition state method - ETS) developed independently by Morokuma[8] and by Ziegler and Rauk.[9] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A–B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Eq. (1)].

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (1)$$

The term ΔE_{elstat} corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion ΔE_{Pauli} is the energy change associated with the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wavefunction $\Psi^0 = N\hat{A}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization (N = constant) of the product wavefunction. ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects. The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system.

The EDA-NOCV[10] method combines charge (NOCV) and energy (EDA) decomposition schemes to decompose the deformation density which is associated with the bond formation, Δρ, into different components of the chemical bond. The EDA-NOCV calculations provide pairwise energy contributions for each pair of interacting orbitals to the total bond energy. NOCV (Natural Orbital for Chemical Valence)[11] is defined as the eigenvector of the valence operator, $\hat{V}$, given by Equation (2):

$$\hat{V}\Psi_i = v_i\Psi_i \qquad (2)$$

In the EDA-NOCV scheme the orbital interaction term, ΔE_{orb}, is given by Equation (3):

$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{\frac{N}{2}} v_k \left[-F_{-k,-k}^{TS} + F_{k,k}^{TS} \right] \qquad (3)$$

In which $F_{-k,-k}^{TS}$ and $F_{k,k}^{TS}$ are diagonal transition state Kohn-Sham matrix elements corresponding to NOCVs with the eigenvalues $-v_k$ and v_k, respectively. The ΔE_k^{orb} term of a particular type of bond are assigned by visual inspection of the shape of the deformation density, $\Delta\rho_k$.

Table 1. Coordinates and energies of the calculated molecules.

$[(NHC)_2(B_2)]$
E(BP86/def2-TZVPP) = -659.580594 a.u.

N	3.194667	-0.250403	0.638309
C	2.175787	0.448447	0.000754
N	2.834001	1.492681	-0.638680
C	4.198111	1.426758	-0.403743
C	4.420951	0.349790	0.401068
B	0.719827	0.148506	0.001819
B	-0.719827	-0.148506	0.001819
C	-2.175787	-0.448447	0.000754
N	-3.194667	0.250403	0.638309
C	-4.420951	-0.349790	0.401068
C	-4.198111	-1.426758	-0.403743
N	-2.834001	-1.492681	-0.638680
C	-2.945585	1.409452	1.468438
C	-2.144947	-2.458763	-1.467547
C	2.144947	2.458763	-1.467547
C	2.945585	-1.409452	1.468438
H	5.342545	-0.034268	0.819387
H	4.891848	2.143816	-0.823555
H	-5.342545	0.034268	0.819387
H	-4.891848	-2.143816	-0.823555
H	-3.857944	2.013445	1.539262
H	-2.619736	1.116356	2.477945
H	-2.136600	1.997033	1.011100
H	-2.751473	-3.368041	-1.552521
H	-1.945846	-2.054233	-2.471433
H	-1.177037	-2.691166	-1.000603
H	1.945846	2.054233	-2.471433
H	1.177037	2.691166	-1.000603
H	2.751473	3.368041	-1.552521
H	2.136600	-1.997033	1.011100
H	3.857944	-2.013445	1.539262
H	2.619736	-1.116356	2.477945

$[(NHC)_2(Al_2)]$
E(BP86/def2-TZVPP) = -1094.803378 a.u.

N	3.956664	-0.888851	0.000000
C	2.823333	-0.095336	0.000000
N	3.329263	1.189983	0.000000
C	4.713461	1.182249	0.000000
C	5.108057	-0.122637	0.000000
Al	0.921521	-0.814802	0.000000
C	2.506492	2.384359	0.000000
C	3.914327	-2.339386	0.000000
Al	-0.921565	0.814665	0.000000
C	-2.823304	0.095271	0.000000
N	-3.329163	-1.189989	0.000000

C	-4.713381	-1.182357	0.000000
C	-5.108142	0.122749	0.000000
N	-3.956624	0.888788	0.000000
C	-2.506511	-2.384394	0.000000
C	-3.914374	2.339412	0.000000
H	-6.097882	0.561609	0.000000
H	-5.297436	-2.093785	0.000000
H	6.097814	-0.561598	0.000000
H	5.297444	2.093853	0.000000
H	4.937951	-2.729622	0.000000
H	3.384528	-2.706125	0.891565
H	3.384528	-2.706125	-0.891565
H	3.156970	3.265975	0.000000
H	1.852451	2.393801	-0.885077
H	1.852451	2.393801	0.885077
H	-1.852453	-2.393788	-0.885038
H	-1.852453	-2.393788	0.885038
H	-3.156966	-3.265885	0.000000
H	-3.384469	2.706152	-0.891659
H	-4.938065	2.729648	0.000000
H	-3.384469	2.706152	0.891659

[$(NHC)_2(Ga_2)$]
E(BP86/def2-TZVPP) = -4460.173667 a.u.

N	3.916804	-0.994757	0.000000
C	2.813933	-0.165716	0.000000
N	3.355229	1.101595	0.000000
C	4.740240	1.051674	0.000000
C	5.093648	-0.264911	0.000000
Ga	0.859228	-0.825181	0.000000
C	2.562105	2.316077	0.000000
C	3.820331	-2.442686	0.000000
Ga	-0.859162	0.824385	0.000000
C	-2.813912	0.165603	0.000000
N	-3.355374	-1.101737	0.000000
C	-4.740316	-1.051571	0.000000
C	-5.093687	0.265146	0.000000
N	-3.916771	0.994948	0.000000
C	-2.562297	-2.316138	0.000000
C	-3.820081	2.442740	0.000000
H	-6.069404	0.734781	0.000000
H	-5.352829	-1.944164	0.000000
H	6.069420	-0.734492	0.000000
H	5.352636	1.944354	0.000000
H	4.827955	-2.872020	0.000000
H	3.277328	-2.788153	0.891853
H	3.277328	-2.788153	-0.891853
H	3.233200	3.181868	0.000000
H	1.909464	2.340756	-0.885577
H	1.909464	2.340756	0.885577
H	-1.909668	-2.340855	-0.885597

H	-1.909668	-2.340855	0.885597
H	-3.233572	-3.181760	0.000000
H	-3.276931	2.788141	-0.891969
H	-4.827711	2.872184	0.000000
H	-3.276931	2.788141	0.891969

$[(NHC)_2(In_2)]$
E(BP86/def2-TZVPP) = -990.455381 a.u.

N	-4.378587	-0.168772	0.000000
C	-3.117468	0.382197	0.000000
N	-3.354163	1.735878	0.000000
C	-4.713632	2.010697	0.000000
C	-5.360423	0.810740	0.000000
In	-1.121146	-0.815720	0.000000
C	-2.298963	2.733263	0.000000
C	-4.617535	-1.600863	0.000000
In	1.121150	0.815714	0.000000
C	3.117478	-0.382194	0.000000
N	3.354161	-1.735860	0.000000
C	4.713641	-2.010695	0.000000
C	5.360425	-0.810745	0.000000
N	4.378573	0.168761	0.000000
C	2.298960	-2.733266	0.000000
C	4.617531	1.600876	0.000000
H	6.418041	-0.578043	0.000000
H	5.102864	-3.020843	0.000000
H	-6.418049	0.578040	0.000000
H	-5.102865	3.020848	0.000000
H	-5.696142	-1.790149	0.000000
H	-4.170792	-2.061366	-0.893170
H	-4.170792	-2.061366	0.893170
H	-2.746645	3.732633	0.000000
H	-1.661535	2.609111	0.888366
H	-1.661535	2.609111	-0.888366
H	1.661535	-2.609112	0.888363
H	1.661535	-2.609112	-0.888363
H	2.746644	-3.732632	0.000000
H	4.170798	2.061361	0.893159
H	5.696134	1.790148	0.000000
H	4.170798	2.061361	-0.893159

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