Electronic Supplementary Information

Cyclic (Amino)(Imino)Carbene Complexes by Borylene Transfer to Isocyanides

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Geneal Experimental Information

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. The complex $[(CO)_5Cr{=}B{=}N(SiMe_3)_2]$, mesityl-isocyanide and 2,6-diisopropyl-isocyanide were prepared according to published procedures.[1] NMR spectra were recorded on a Bruker Avance 400 or a Bruker Avance 500 FT-NMR spectrometer. Elemental analyses were obtained using a Elementar Vario MICRO cube instrument.

X-ray Crystallographic studies

The crystal data of **4–5** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the SHELX software package and expanded using Fourier techniques.[2] The SHELX was interfaced with SHELXLE GUI for most of refinement steps.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations. The 272 least-squares restraints reported for **5** as shown by _refine_ls_number_restraints key in CIF-file are attributed to DELU keyword in ShelXL input ('rigid bond' restraint for all bonds in the connectivity list; standard values of 0.01 for both parameters s1 and s2 were used).

Crystal data for **4**: $C_{31}H_{40}BCrN_3O_5Si_2$, $M_r = 653.65$, brown plate, 0.21×0.20×0.06 mm^3, monoclinic space group $P2_1$, $a = 9.0326(6)$ Å, $b = 22.2434(14)$ Å, $c = 9.4427(6)$ Å, $\beta = 114.527(3)°$, $V = 1725.99(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.258$ g·cm^{-3}, $\mu = 0.441$ mm^{-1}, $F(000) = 688$, $T = 100(2)$ K, $R_1 = 0.0334$, $wR^2 = 0.0710$, Flack –0.005(9), 9441 independent reflections [2θ≤61.02°] and 400 parameters.

Crystal data for **5**: $C_{37}H_{52}BCrN_3O_5Si_2$, $M_r = 737.81$, red palte, 0.40×0.34×0.08 mm^3, monoclinic space group Pc, $a = 20.1795(9)$ Å, $b = 11.1226(5)$ Å, $c = 18.0696(8)$ Å, $\beta = 103.233(2)°$, $V = 3948.0(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.241$ g·cm^{-3}, $\mu = 0.394$ mm^{-1}, $F(000) = 1568$, $T = 100(2)$ K, $R_1 = 0.0642$, $wR^2 = 0.1131$, Flack 0.007(13), 15470 independent reflections [2θ≤52.74°] and 895 parameters.

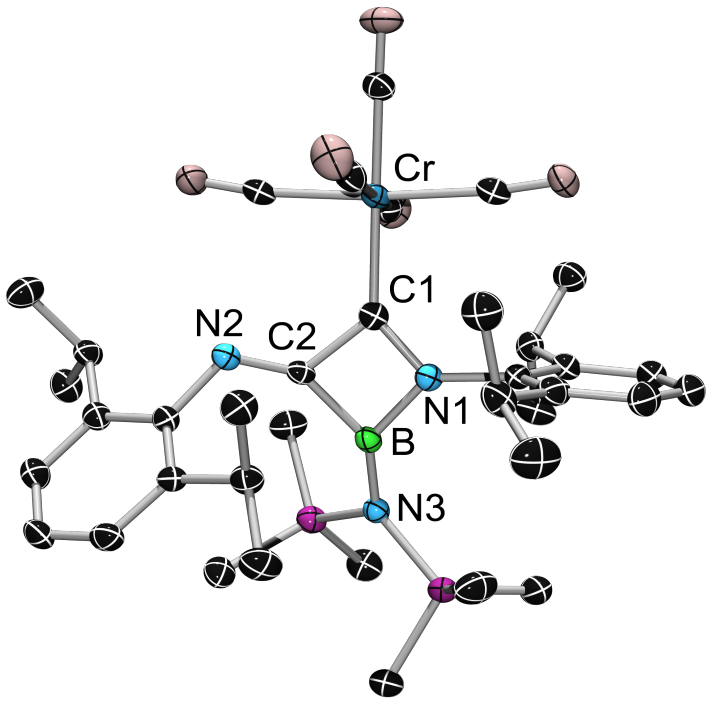

Figure 1. Molecular structure of **5**. Only one of the two independent molecules in the asymmetric unit is shown and the atom labels are not the same as appear in the CIF file. Thermal ellipsoids are plotted at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 900033 & 900034. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Computational Studies

Calculations based on the Kohn-Sham Density Functional Theory (DFT) were undertaken of the title compounds together with selected model systems with the aim of understanding the energetics, geometry, bonding situation and electronic structure. To facilitate the discussion of the different energy change of the molecular systems of interest, we consider the following energy decomposition for the representative A+B → C reaction: E = U(C)−[U(A) + U(B)] where U designate the total internal energy of each constituent, the geometrical and electronic preparation energy of each reactant (Eprep, geom/elec(A)+Eprep, geom/elec(B)) being implicitly considered. Figure 2 shows the overall energy profile of **A**, **B**, **C**, **D** and **E**. The calculated energy profile of **A** reacting with **B** to give **C** clearly shows that this reaction is exothermic for all substituents (R1 to R4), the most stable being when using R1 and the least when using R4. Interestingly, there is an evident correlation between the nature and the number of ring substituents with that of stability, that is, the more the rings are bulky the least stable the products are. As discussed below, product stability is dictated by both steric hindrance and π-interaction between the borirene and the aryl rings. Furthermore, reaction of **C** with a second **B** produce the same stability ordering with one interesting result, with R4 the product is endothermic, and molecule **D** will not be spontaneously formed, thus one is likely to trap molecule **C** when using R4 as side-chains.

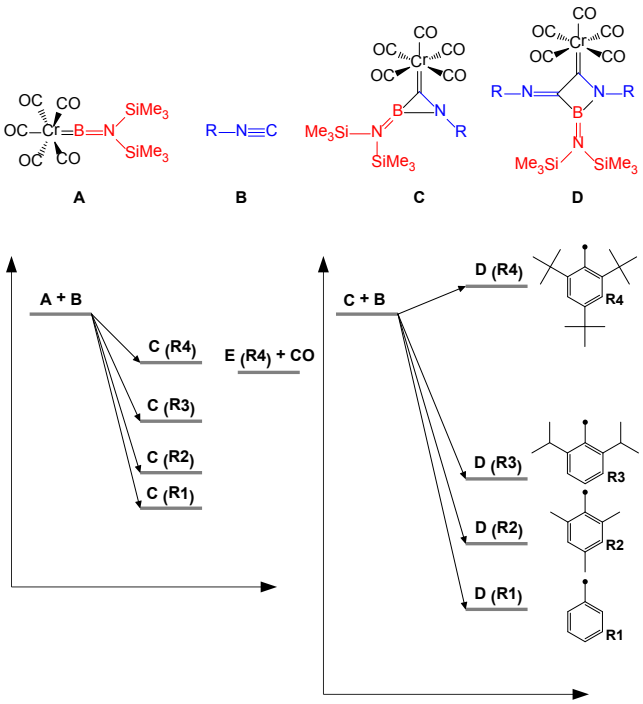

Figure 2. Reaction energy profile of **A**, **B**, **C**, **D** and **E**.

Figure 3 shows the structure of **C** with different R-groups. Steric hindrance is evident in these structures. With the simple phenyl as a side chain, as such, that is as an aromatic ring system, it would be more energetically favorable for the system to have the aryl coplanar with the borirene ring.

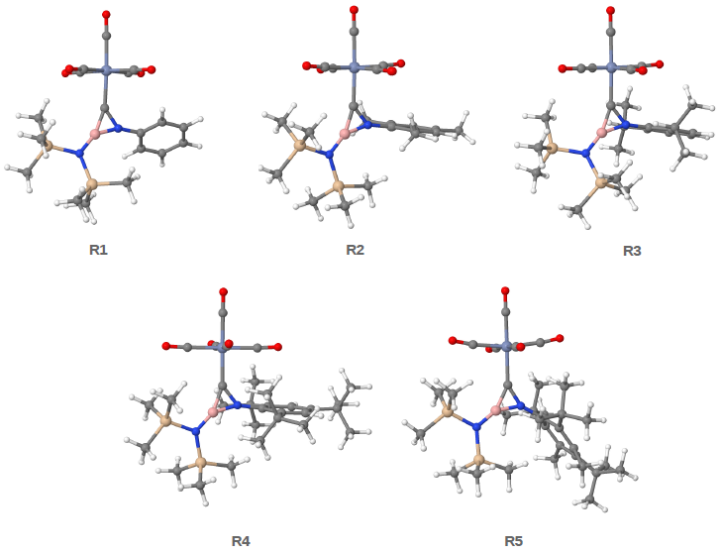

Figure 3. Optimzed structures of **C** with different R-groups.

Closer inspection shows however, that upon geometry optimization, starting from a completely perpendicular configuration, the phenyl ring rotates towards the parallel configuration but only to a certain extent due to becoming very close to the Cr bound CO groups.

As substituents get bulkier, rotation around the N-C bond becomes more hindered and the aryls are forced to adapt a geometry more perpendicular to the borirene, thus making the systems more energetic. The strategically designed R5 side-chain (Figure 4) confirms the inter-group repulsion further, indeed, the ring construct in this case with so much electron inflow loses its π-electron delocalization character and the carbon centers tend to adopt sp^3 structure.

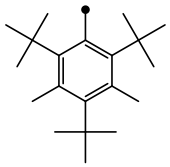

Figure 4. The R5 side-chain.

The consequence of which is to have methyls point towards the Cr bound CO groups not only on the ring side but also on the trimethylsilyl side – the Cr-C-O segment is now bent showing the extreme tension (see Figure 3). In the **A** + **B** reaction, that rather a trans substitution product forms the major reaction product, in the case of R4, is rationalized by the slightly relative lower energy of the trans product $[(OC)_4Cr{=}B{=}N(SiMe_3)_2(CNMes^*)]$ **E** (see Figure 2) compared to product **C**. Figure 5 shows the optimized structure of **E**, closer examination suggests that steric hindrance can further be exploited to achieve higher yield of **C**.

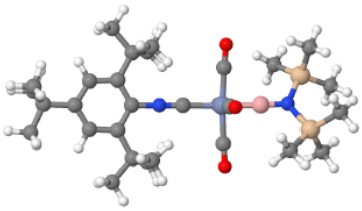

Figure 5. Structure of **E**.

The interaction energy of **C** with R1 and R4 was further quantified using the so called fragment approach as implemented in the Amsterdam Density Functional (ADF) programme. In this scheme, we looked at the interaction energy Eint between the fragments (R1 or R4) and $(CO)_5$Cr-CNB-N$(SiMe_3)_2$ (see Figure 6). The interaction energy Eint is divided into three components: Eint = Eelstat + EPauli + Eorb. The first term, Eelstat, corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the fragments (the overall density being the superposition of the fragment densities). The second term, EPauli, expresses the energy change that arises upon going from the simple superposition of the fragment densities to the wavefunction that obeys the Pauli principle through antisymmetrization and normalization of the product of the fragment wavefunctions. In the last term, Eorb, the energy that originates from the contributions from stabilizing orbital interactions (electron pair bonding, charge transfer, polarization) is given. For **C**(R1), the interaction energy between the aryl and the [borirene] amounts to 354 kcal/mol, whereas for **C**(R4) this value equals to 381 kcal/mol. The stabilization energy due to electronic effect is 27 kcal/mol more stable when using the bulky ring, and yet the overall energy difference still amounts to 12 kcal/mol in favour of the non-subtituted aryl, that's it, steric hindrance clearly dictates the overall outcome of the reaction.

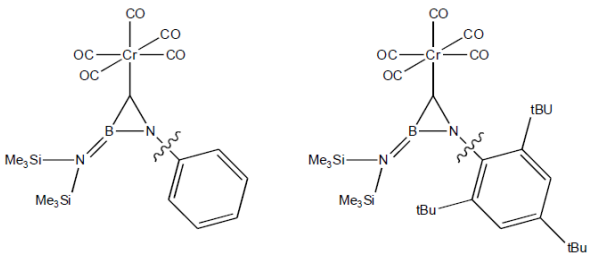

Figure 6. Fragmentation scheme of **C**(R1) and **C**(R4).

Computational details

Geometry optimizations were conducted at the B3LYP/6-311G*[4–9] level using Gaussian03,[10] the Amsterdam Density Functional (ADF) programme[11, 12] was used for bonding energy decomposition analysis (EDA)[11, 13] based on the methods of Morokuma[14] and Ziegler and Rauk[15] at the B3LYP/TZP[16–20] level. Spin-restricted calculations were performed by constraining the projection of the total electronic spin along a reference axis to zero. Frequency calculations were conducted to determine if each stationary point corresponds to a minimum. The Jmol[21] programme was used for vizualisation purposes.

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