

Room-Temperature C–C Bond Cleavage of an Arene by a Metallacarborane**

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The activation and cleavage of C–C bonds by transition-metal species is an area of intense current interest,^[1] and, although they are still relatively rare, a number of systems that afford the breaking of C–C single bonds are known.^[2–4] In contrast, the cleavage of aromatic C–C bonds is considered to be extraordinarily difficult. Six-carbon aromatic rings can be cleaved in the gas phase at high temperatures,^[5] whereas under less extreme conditions such rings are cleaved by enzymes, an important part of the global carbon cycle.^[6] However, there are very few reports of low-temperature cleavage reactions of aromatic rings in nonbiological systems. Of the examples that are known, (biomimetic) oxidative cleavage is the more common process but is generally regarded as difficult to control,^[7] whereas reductive cleavage is much more rare.^[8] However, both oxidative and reductive cleavage reactions typically involve significant initial chemical modification of the aromatic ring. Sattler and Parkin recently described the cleavage of a C–C bond in an aromatic heterocycle (a quinoxaline) at 90 °C.^[9] We report herein the unprecedented cleavage of an aromatic C–C bond in a simple arene at room temperature by a metallacarborane without other chemical modification to the arene.

Treatment of 1,1'-bis(*o*-carborane),^[10–11] 1-(1',2'-*closo*-C₂B₁₀H₁₁)-2-*closo*-C₂B₁₀H₁₁ (Figure 1), with an excess of Li in THF in the presence of naphthalene and subsequent reaction with [{Ru(*p*-cymene)Cl₂}]₂ (*p*-cymene = 1-*i*Pr-4-MeC₆H₄), affords the dark red metallacarborane 1-(1',2'-*closo*-C₂B₁₀H₁₁)-4-{C₁₀H₁₄Ru(*p*-cymene)}-4,1,6-*closo*-RuC₂B₁₀H₁₁ as the only isolable product (in ca. 20% yield)

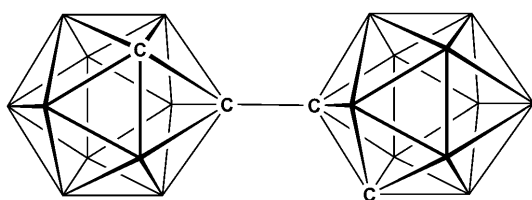


Figure 1. 1,1'-bis(*o*-carborane).

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[**] We thank the EPSRC for support (project EP/E02971X/1).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201001555>.

after workup (involves TLC methods). The product was characterized by mass spectroscopy, ¹H and ¹¹B{¹H} NMR spectroscopy, and ultimately by single-crystal X-ray diffraction.^[12]

In the ¹H spectrum there are, in addition to broad C_{cage}H resonances at approximately δ = 4.7 and 2.2 ppm, the normal resonances assigned to the CH₃C₆H₄CHMe₂ protons of a η⁶-*p*-cymene ligand in an asymmetric complex (four dd between δ = 6.5 and 5.5 ppm with ³J and ⁴J couplings of ca. 6 Hz and 1.5 Hz, respectively). However, the signals normally assigned to the CH₃C₆H₄CHMe₂, CH₃C₆H₄CHMe₂, and CH₃C₆H₄CHMe₂ protons all appear doubled. In addition there are two high-frequency doublet resonances (δ = 9.6, 9.4 ppm) and two additional resonances (δ = 4.5, 4.1 ppm) which appear as apparent triplets. Collectively these data suggest that there are two different C₁₀H₁₄ units in the product; one is a regular η⁶-*p*-cymene ligand but the other appears to have been subjected to a major structural change. The ¹¹B{¹H} spectrum is relatively uninformative with nine resonances between δ = 6 and –25 ppm, including a multiple signal at δ = –10.6 ppm that accounts for ten boron atoms. The mass spectrum confirms the molecular formula as C₂₅H₅₀B₂₀Ru₂ (envelope centered on *m/z* 757) which implies bis(carborane) plus two {RuC₁₀H₁₄} units, but, as is evident from the NMR spectra, the molecule is asymmetric and one of the *p*-cymene ligands has been substantially altered. A crystallographic study resulted in the molecular structure shown in Figure 2. Figure 3 shows an alternative view of the central part of the molecule.

The molecule consists of a 13-vertex docosahedral ruthenacarborane (cage A) with a 4,1,6-RuC₂B₁₀ architecture, the

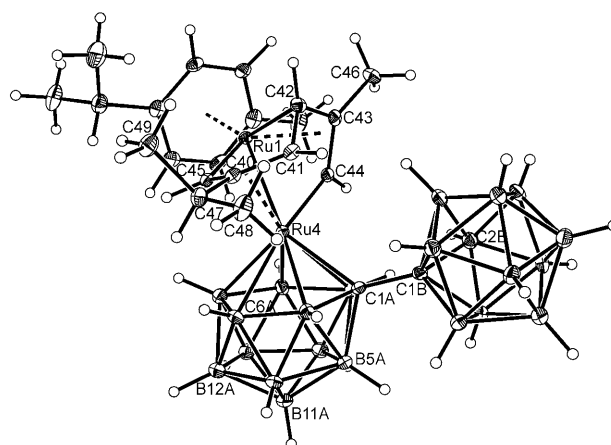


Figure 2. Perspective view of 1-(1',2'-*closo*-C₂B₁₀H₁₁)-4-{C₁₀H₁₄Ru(*p*-cymene)}-4,1,6-*closo*-RuC₂B₁₀H₁₁. Thermal ellipsoids drawn at 50% probability.

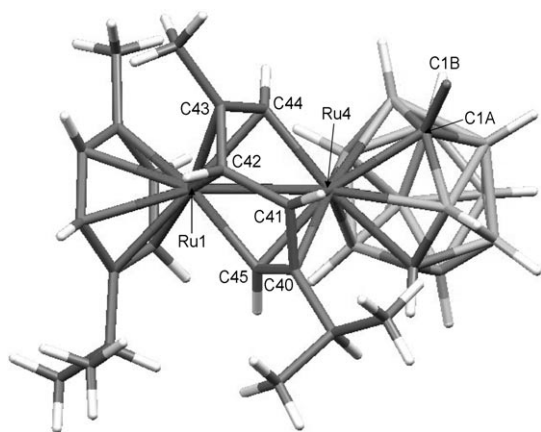


Figure 3. Alternative view of part of 1-(1',2'-closo-C₂B₁₀H₁₁)-4-{C₁₀H₁₄Ru(*p*-cymene)}-4,1,6-closo-RuC₂B₁₀H₁₁).

normal isomer obtained upon reduction and metallation of *o*-carborane.^[13] Carborane cage B has not been expanded and remains a 1,2-C₂B₁₀ icosahedron, connected to cage A at vertex C1A. A second Ru atom, Ru1, is bonded to Ru4 [Ru–Ru = 2.6984(4) Å] and to Ru1 is bound a conventional η⁶-*p*-cymene ligand. Ru4 and Ru1 are additionally linked by (what was) the second *p*-cymene ligand, which has undergone cleavage of the C44–C45 bond. The C41–C40–C45 unit is η³ bonded to Ru4 and the C42–C43–C44 unit is η³ bonded to Ru1, complemented by σ bonds between C42 and Ru1 and between C44 and Ru4.

Therefore, the molecule is an example of a “fly-over bridge” compound,^[14] in which the *p*-cymene ligand C40–C46 has been converted into a [μ-σ,η³:η³,σ-C₆]²⁻ ligand by reductive cleavage of the C44–C45 bond. Fly-over bridge compounds are well-established in organometallic chemistry, but all previously reported examples have been the result of condensation of three alkyne molecules onto a dimetal center. Upon heating, or treatment with Br₂^[15] or trimethylamine-*N*-oxide,^[16] fly-over bridge compounds can afford arenes by oxidative ring closure, lending support to the view that fly-over compounds represent intermediates in the metal-promoted cyclotrimerization of alkynes into arenes, at least by one possible pathway. However, as far as we are aware, the present species represents the first example of a fly-over bridge compound formed in the reverse direction, that is, from an arene.

The mechanism by which this compound is formed is clearly of great interest and we have investigated this using density functional theory (DFT) calculations (with the *p*-cymene ligand replaced by benzene for computational expedience).^[17] The components of the molecule can be assembled as depicted in Figure 4. Initial four-electron reduction of 1,1'-bis(*o*-carborane)^[18] gives a bis(nido) species, one face of which is capped by a {Ru(C₆H₆)}²⁺ fragment to give intermediate **A**. The second {Ru(C₆H₆)}²⁺ unit is then added, resulting in the formally zwitterionic triple-decker intermediate **B**. Calculations on plausible model structures of **B**, however, led instead to an alternative form, **C**. The geometry of **C** suggests that an internal redox process had occurred, whereby two electrons have been transferred from

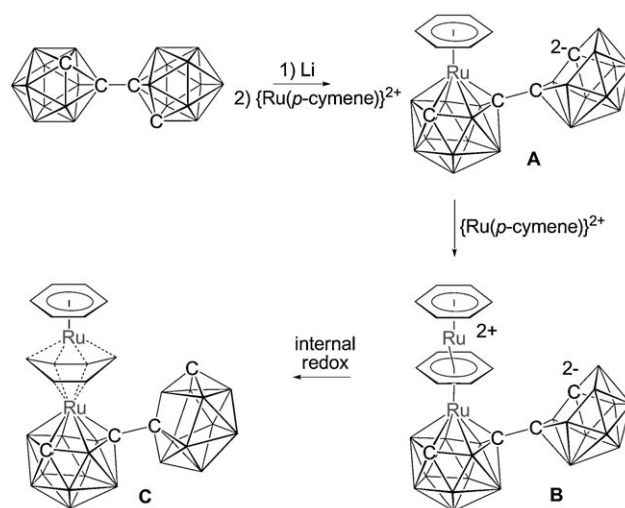


Figure 4. Proposed mechanism for the formation of intermediate **C** (the alkyl groups of the *p*-cymene ligand were disregarded in the calculation).

the pendant nido cage in **B** into the central C₆H₆ ligand. Evidence for this transfer is 1) the geometry of the pendant cage B exhibits a basket-shaped structure, which is the initial (kinetic) consequence of two-electron oxidation of a *nido*-C₂B₁₀ cage,^[19] and 2) the boat-like structure of the sandwiched {C₆H₆} moiety, consistent with its reduction and the disruption of its aromaticity (Figure 5).

The central {C₆H₆} moiety in **C** interacts with both Ru centers, although in different ways (see Figure 5 for a view of the DFT optimized structure of **C** and Figure 6 which shows the central {RuC₆H₆Ru} core). With Ru1 an η⁴-binding mode is computed involving the C41–C40–C45–C44 unit, whereas with Ru4 an η²:η² interaction is seen with the C42–C43 and C40–C45 bonds. As a result most of the ring C–C bonds lengthen substantially and lie in the range 1.47–1.52 Å (only C42–C43 is relatively unaffected at 1.41 Å). Elongation of C44–C45 then allowed the location of a C–C bond-cleavage transition state, TS(**C**–**D**) (*E* = +21.3 kcal mol^{−1}), in which lengthening of the C44–C45 distance to 2.77 Å is accompanied by rotation about the C41–C42 bond [the C40–C41–C42–C43 torsion is 46.6° in **C**; compared to 89.8° in TS(**C**–**D**)]. Characterization of this transition state led to intermediate **D** (*E* = −4.0 kcal mol^{−1}) in which both the {μ-σ,η³:η³,σ-C₆} binding mode and a Ru–Ru bond (Ru1–Ru4 = 2.76 Å) have been established. Electron counting suggests the Ru–Ru interaction is best formulated as a dative bond in which Ru1 donates two electrons to Ru4.

The second step in the formation of the product involves isomerization of the C₂B₁₀ group of cage B from a basket to an icosahedral geometry. This isomerization occurs in an analogous fashion to that described previously^[19] via TS(**D**–**E**) with a barrier of only 10.7 kcal mol^{−1}. During this process the {RuC₆H₆Ru} core is largely a spectator and the only significant change is a slight lengthening of the Ru1–Ru4 distance to 2.85 Å. TS(**D**–**E**) leads to the very stable product species **E** (*E* = −42.0 kcal mol^{−1}). **E** is a simple isomer of the crystallographically determined structure in which the fly-

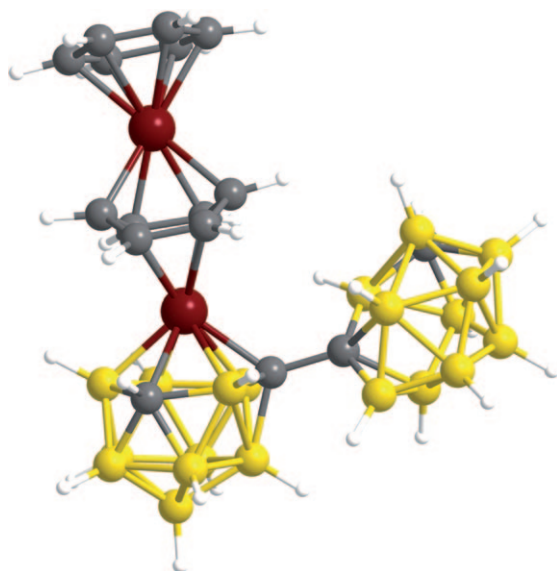


Figure 5. Computed structure of intermediate **C**. C gray, B yellow, Ru red, H white.

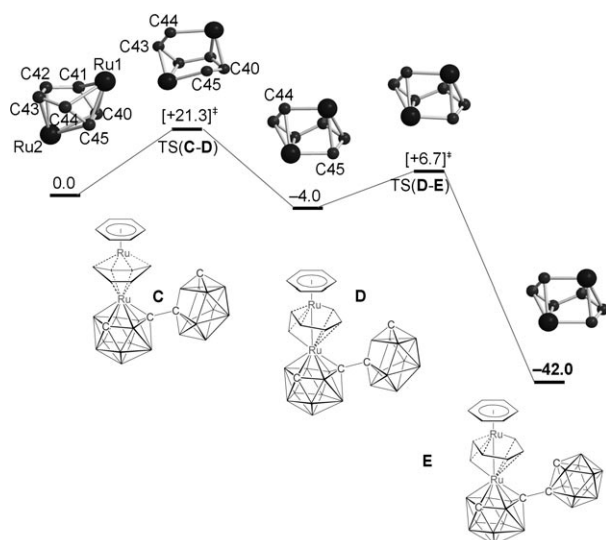


Figure 6. Computed reaction profile (kcal mol^{-1}) for C–C bond cleavage in intermediate **C** to form a fly-over bridge compound. Geometry changes within the central $\{\text{Ru}_2\text{C}_6\text{H}_6\}$ core are shown at the top of the figure.

over bridging ligand adopts an alternative conformation (the computed energy of the actual structure is $-56.1 \text{ kcal mol}^{-1}$), but nevertheless this computational study identifies the key features of the probable mechanism of cleavage of the C44–C45 bond and reveals that the energy barriers for this mechanism are modest.

In conclusion, we have discovered a unique system in which an aromatic C–C bond in a simple arene is reductively cleaved at room temperature with no other chemical modification, and we have used DFT calculations to elucidate an accessible reaction pathway by which this could occur. Central to the cleavage is an internal redox step in which the pendant reduced carborane is oxidized and transfers two

electrons to the central arene of a triple decker intermediate. We are currently exploring the scope and implications of this reaction.

Received: March 15, 2010

Published online: June 10, 2010

Keywords: boron · metallaboranes · redox chemistry · ruthenium · X-ray diffraction

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- [12] Crystallography: a crystal was mounted in inert oil on a glass fiber and cooled to 100(2) K on a Bruker X8 APEX2 diffractometer equipped with $\text{MoK}\alpha$ X-radiation. Intensity data were corrected for absorption semi-empirically and structures solved by direct and difference-Fourier methods. Cage C atoms C6A and C2B were unambiguously identified on the basis of refined (as B) U_{eq} values and interatomic distances. Refinement^[20] was by full-matrix least-squares analysis on F^2 . Crystal data for **1**: $\text{C}_{24}\text{H}_{50}\text{B}_{20}\text{Ru}_2 \cdot 2 \text{CH}_2\text{Cl}_2$, $M = 926.83$, orthorhombic, $P2_12_12_1$, $a = 9.9886(10)$, $b = 19.6115(19)$, $c = 21.631(2) \text{ \AA}$, $V = 4237.3(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.453 \text{ Mg m}^{-3}$, $\mu = 0.987 \text{ mm}^{-1}$, $F(000) = 1864$, 12759 out of 90211 independent reflections collected to $\theta_{\text{max}} = 30.60^\circ$ ($R_{\text{int}} = 0.0574$), $R_1 = 0.0308$, $wR_2 = 0.0631$ for data with $I > 2\sigma(I)$, $S = 1.119$, Flack parameter 0.00(13), largest peak 0.62 and deepest hole $-0.77 \text{ e \AA}^{-3}$. CCDC 769687 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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