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Metallacarboranes

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

David Ellis, David McKay, Stuart A. Macgregor, Georgina M. Rosair, and Alan J. Welch**

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*-$C_2B_{10}H_{11}$)-2-*closo*-$C_2B_{10}H_{11}$ (Figure 1), with an excess of Li in THF in the presence of naphthalene and subsequent reaction with $[\{Ru(p\text{-cymene})Cl_2\}_2]$ (*p*-cymene = 1-*i*Pr,4-MeC_6H_4), affords the dark red metallacarborane 1-(1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-$\{C_{10}H_{14}Ru(p\text{-cymene})\}$-4,1,6-*closo*-$RuC_2B_{10}H_{11}$ as the only isolable product (in ca. 20% yield) after workup (involves TLC methods). The product was characterized by mass spectroscopy, ^1H and $^{11}B\{^1H\}$ NMR spectroscopy, and ultimately by single-crystal X-ray diffraction.[12]

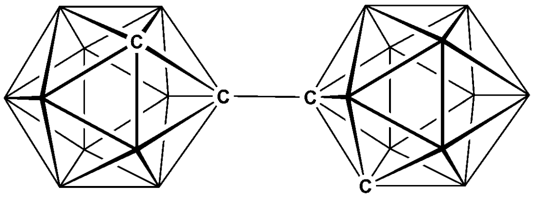

Figure 1. 1,1′-bis(*o*-carborane).

In the ^1H spectrum there are, in addition to broad $C_{cage}H$ resonances at approximately $\delta = 4.7$ and 2.2 ppm, the normal resonances assigned to the $CH_3C_6H_4CHMe_2$ protons of a η^6-*p*-cymene ligand in an asymmetric complex (four dd between $\delta = 6.5$ 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 $CH_3C_6H_4CHMe_2$, $CH_3C_6H_4CHMe_2$, and $CH_3C_6H_4CHMe_2$ protons all appear doubled. In addition there are two high-frequency doublet resonances ($\delta = 9.6$, 9.4 ppm) and two additional resonances ($\delta = 4.5$, 4.1 ppm) which appear as apparent triplets. Collectively these data suggest that there are two different $C_{10}H_{14}$ units in the product; one is a regular η^6-*p*-cymene ligand but the other appears to have been subjected to a major structural change. The $^{11}B\{^1H\}$ spectrum is relatively uninformative with nine resonances between $\delta = 6$ and -25 ppm, including a multiple signal at $\delta = -10.6$ ppm that accounts for ten boron atoms. The mass spectrum confirms the molecular formula as $C_{25}H_{50}B_{20}Ru_2$ (envelope centered on *m*/*z* 757) which implies bis(carborane) plus two $\{RuC_{10}H_{14}\}$ 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-RuC_2B_{10} architecture, the

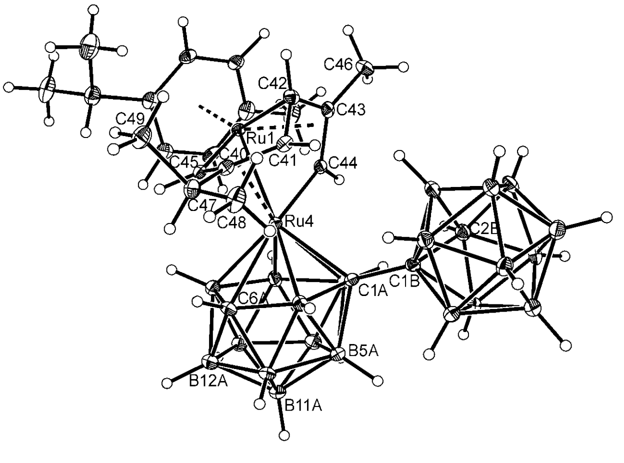

Figure 2. Perspective view of 1-(1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-$\{C_{10}H_{14}Ru(p\text{-cymene})\}$-4,1,6-*closo*-$RuC_2B_{10}H_{11}$. Thermal ellipsoids drawn at 50% probability.

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[*] Dr. D. Ellis, D. McKay, Prof. S. A. Macgregor, Dr. G. M. Rosair, Prof. A. J. Welch
Department of Chemistry, Heriot-Watt University
Edinburgh EH14 4AS (UK)
Fax: (+44) 131-451-3217
E-mail: s.a.macgregor@hw.ac.uk
a.j.welch@hw.ac.uk

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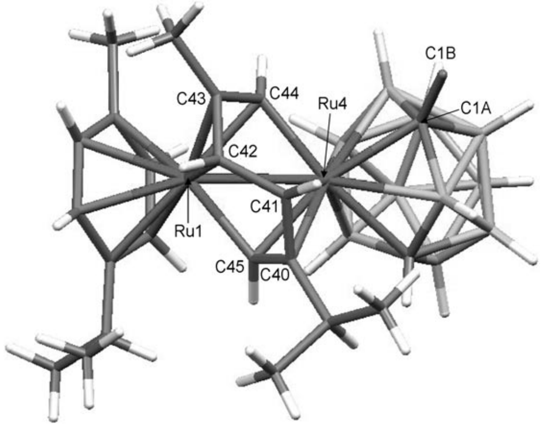

Figure 3. Alternative view of part of 1-(1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-{$C_{10}H_{14}$Ru-(*p*-cymene)}-4,1,6-*closo*-$RuC_2B_{10}H_{11}$).

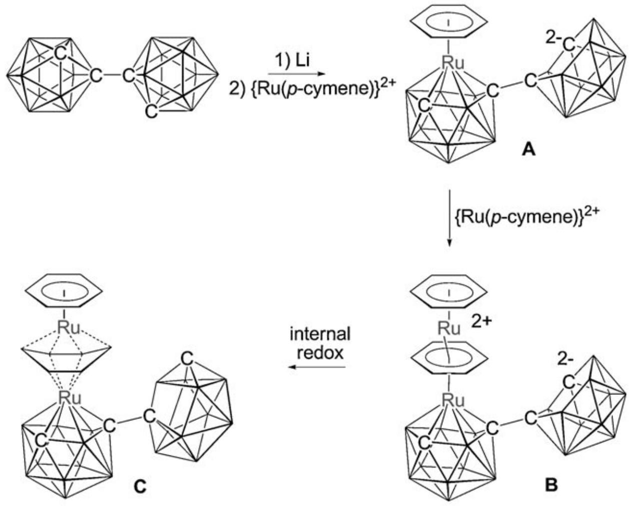

Figure 4. Proposed mechanism for the formation of intermediate **C** (the alkyl groups of the *p*-cumene ligand were disregarded in the calculation).

normal isomer obtained upon reduction and metallation of *o*-carborane.[13] Carborane cage B has not been expanded and remains a 1,2-C_2B_{10} 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 η^6-*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 η^3 bonded to Ru4 and the C42-C43-C44 unit is η^3 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 $[\mu\text{-}\sigma,\eta^3{:}\eta^3,\sigma\text{-}C_6]^{2-}$ 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 Br_2[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 $\{Ru(C_6H_6)\}^{2+}$ fragment to give intermediate **A**. The second $\{Ru(C_6H_6)\}^{2+}$ 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 the pendant nido cage in **B** into the central C_6H_6 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*-C_2B_{10} cage,[19] and 2) the boat-like structure of the sandwiched $\{C_6H_6\}$ moiety, consistent with its reduction and the disruption of its aromaticity (Figure 5).

The central $\{C_6H_6\}$ 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 $\{RuC_6H_6Ru\}$ core). With Ru1 an η^4-binding mode is computed involving the C41-C40-C45-C44 unit, whereas with Ru4 an $\eta^2{:}\eta^2$ 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**) ($E = +21.3\ \text{kcal mol}^{-1}$), 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** ($E = -4.0\ \text{kcal mol}^{-1}$) in which both the $\{\mu\text{-}\sigma,\eta^3{:}\eta^3,\sigma\text{-}C_6\}$ 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 C_2B_{10} 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 $10.7\ \text{kcal mol}^{-1}$. During this process the $\{RuC_6H_6Ru\}$ 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** ($E = -42.0\ \text{kcal mol}^{-1}$). **E** is a simple isomer of the crystallographically determined structure in which the fly-

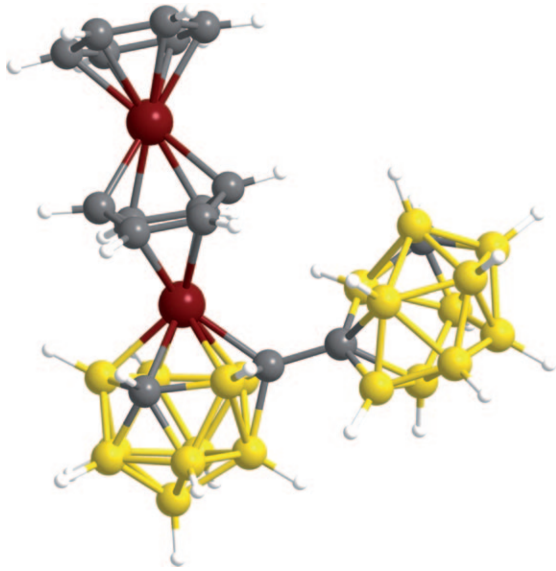

Figure 5. Computed structure of intermediate **C**. C gray, B yellow, Ru red, H white.

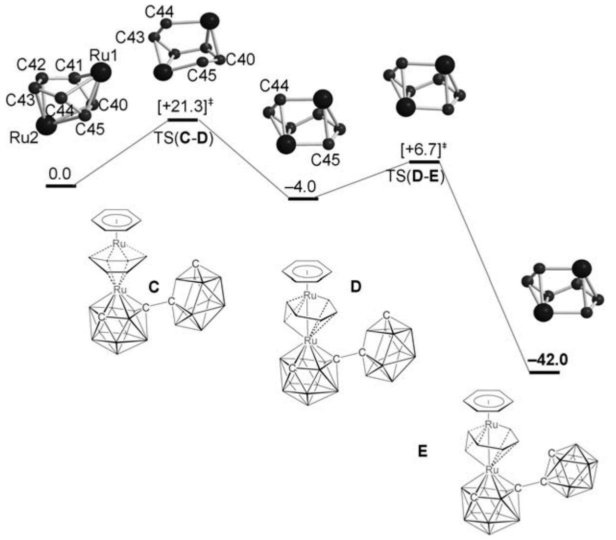

Figure 6. Computed reaction profile (kcal mol^{-1}) for C–C bond cleavage in intermediate **C** to form a fly-over bridge compound. Geometry changes within the central {RuC$_6$H$_6$Ru} core are shown at the top of the figure.

over bridging ligand adopts an alternative conformation (the computed energy of the actual structure is -56.1 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.

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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 Mo$_{K\alpha}$ *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**: $C_{24}H_{50}B_{20}Ru_2{\cdot}2\,CH_2Cl_2$, $M = 926.83$, orthorhombic, $P2_12_12_1$, $a = 9.9886(10)$, $b = 19.6115(19)$, $c = 21.631(2)$ Å, $V = 4237.3(7)$ Å^3, $Z = 4$, $\rho_{cald} = 1.453$ Mg m^{-3}, $\mu = 0.987$ mm^{-1}, $F(000) = 1864$. 12759 out of 90211 independent reflections collected to $\theta_{max} = 30.60°$ ($R_{int} = 0.0574$), $R_1 = 0.0308$, $wR_2 = 0.0631$ for data with $I > 2\sigma(I)$, $S = 1.119$, Flack parameter 0.00(13), largest peak 0.62 and deepest hole -0.77 e Å^{-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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