Rhodium-Catalyzed Hydroarylation of Fullerene C$_{60}$ with Boronic Acids

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Abstract

This bachelor thesis covers the challenges and advantages of the rhodium-catalyzed hydroarylation of fullerene C\textsubscript{60} with boronic acids. Preparations of both mono- and diboronic acids were successfully accomplished, whereupon attempts to attach them to fullerenes via the Rh-catalyzed hydroarylation took place.

The coupling reaction performed with pure 4-tolylboronic acid succeeded and the crude product was purified through a silica plug and characterized by \textsuperscript{1}H NMR, HMBC and NOESY. The attempts to attach fullerenes to diboronic acid turned out to be more challenging than expected and in the end, the desired product was not obtained. However, the trials did bring about important observations that can be used for further improvement of the reaction.
Abbreviations

DCM     Dichloromethane
DMSO    Dimethyl sulfoxide
EtOH    Ethanol
HMBC    Heteronuclear Multiple Bond Correlation
MeOH    Methanol
MiW     Microwave
n-BuLi  n-Butyllithium
NOESY   Nuclear Overhauser Effect Spectroscopy
o-DCB   ortho-Dichlorobenzene
RT      Room temperature
Rb      Round bottom
THF     Tetrahydrofuran
TLC     Thin-layer chromatography
TMS     Tetramethylsilane
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1. Introduction

In November 1985, H. W. Kroto et al. published a paper discussing the structure of a recently discovered carbon allotrope.[1] This allotrope was thought to be built up by 60 sp²-hybridized carbon atoms arranged in a truncated icosahedron – a structure, which can also be found in soccer balls as well as the geodesic domes made famous by Richard Buckminster Fuller, see Figure 1. Due to the latter, the discoverers chose to call the young carbon allotrope “Buckminsterfullerene” and sometimes it is also referred to as the “Bucky ball”.

A truncated icosahedron has 60 vertices and 32 faces – 12 pentagons and 20 hexagons. In fullerene C₆₀, each vertex is occupied by an sp²-hybridized carbon atom and at an early stage, it was therefore suggested to be aromatic.[¹] Today it is known that this is not the case since the curvature of its spherical surface reduces the overlap of the p-orbitals.[²]

There exist fullerenes of other sizes than C₆₀ – like C₇₀, C₇₆ and C₈₄ – which have also been isolated. However, besides fullerene C₆₀, fullerene C₇₀ is the only one that forms in a relatively high amount. For fullerenes larger than C₇₀ there is a significant decrease of abundance with increasing mass. A possible explanation to why C₇₀ differs from this trend is that the binding energy between its atoms is higher than that found between the atoms of C₆₀. Nonetheless, fullerene C₆₀ is the one that is absolutely most abundant and that is probably due to it being more kinetically stable. In other words, after being formed C₇₀ is the most stable fullerene in terms of thermodynamic stability, but C₆₀ forms much faster.[³]
During the past thirty years, a considerable amount of the research on fullerene C\textsubscript{60} has been focused on its electronic properties. Exceptionally high conductivity upon potassium-doping, antiviral activity and good biocompatibility are just a few interesting characteristics, which together with a unique three-dimensional architecture, make the nanosized carbon ball a promising participant in a range of applications such as molecular electronics, lubricants and drug delivery models.\textsuperscript{[4–8]} Furthermore, the relatively low-lying triply degenerate, LUMO of the Bucky ball provides it with a high electron affinity and an ability to reversibly accept up to six electrons.\textsuperscript{[9]} Along with having a remarkably fast charge transfer, these qualities have made fullerenes attractive acceptors in the donor-acceptor systems studied for artificial photosynthesis as well as in the development of organic solar cells.\textsuperscript{[10,11]}

The nature of the bonds plays a crucial role regarding the reactivity of a molecule – a factor that in turn, has a huge impact on molecular functionalization. At the moment, theoretical, structural and experimental studies all support the model of fullerene C\textsubscript{60} having two different types of bonds depending on where in the molecule they are situated. Those located in the junctions of two hexagons exhibit similar behavior as isolated double bonds, while those found at the boundaries of hexagons and pentagons are more closely related to the sigma bonds formed between two sp\textsuperscript{2}-carbons.\textsuperscript{[12]}

One of many consequences arising from this bond nature is the fact that fullerenes tend to react in the same way as electron-deficient polyolefins.\textsuperscript{[13]} That is to say, they readily take part in various cycloadditions as well as in radical and nucleophilic addition reactions. Scheme 1 displays some of the methods for the functionalization of fullerene C\textsubscript{60}, of which the [3+2] cycloaddition of azomethine ylides to fullerene C\textsubscript{60} (the Prato reaction\textsuperscript{[14]}), is the most commonly used.

Fullerene functionalization pathways involving metal catalysts are in general less well-studied and there are still questions to be answered. Additionally, even though many articles have been written concerning the properties of fullerenes, there are still many blank pages to be filled in “the manual of fullerenes”, not least regarding their reactivity. By virtue of that, this bachelor thesis has been focused on the benefits and challenges of rhodium-catalyzed hydroarylation of fullerene C\textsubscript{60} using organoboron compounds or more specifically, boronic acids.
Scheme 1. Some of the more well-established $C_{60}$ functionalization methods: (a) [1+2] cycloaddition; (b) [2+2] cycloaddition; (c) Prato reaction; (d) Diels-Alder cycloaddition; (e) Bingel-Hirsch reaction; (f) Rh-catalyzed hydroarylation. Reproduced from Ref.[12] with permission of The Royal Society of Chemistry.

The reaction discussed in this report was inspired by the Rh-catalyzed conjugate addition of aryl- and alkenylboronic acids to enones – a reaction discovered in 1997 by Miyaura et al.[15] Since then, researchers all over the world have managed to increase the versatility of this reaction by showing that it works not only with boronic acids, but with organoboron compounds in general. As fullerenes react in a way similar to that of enones, Itami et al. suggested that this kind of conjugate addition might also be applicable on fullerenes and in a paper published in Chemistry – An Asian Journal, February 2011, they stated that the reaction
performed with fullerenes “proceeds with a high regioselectivity and in a mono-addition selective manner”.\textsuperscript{[16]}

This type of coupling reaction enhances the possibility of introducing many different organic groups to the fullerene by simply modifying organoboron compounds. It also opens up for the formation of a fully-conjugated system directly at the fullerene cage, as opposed to via the fulleropyrrolidene coupling. A general reaction scheme for the Rh-catalyzed hydroarylation of C\textsubscript{60} with organoboron compounds is presented in Scheme 2.

Scheme 2. The Rh-catalyzed hydroarylation of fullerene C\textsubscript{60} with organoboron compounds.
2. Results and discussion

2.1. Literature study and choice of materials

This functionalization reaction requires three essential ingredients: a catalytically active rhodium complex, fullerenes and an organoboron compound. Moreover, these three reagents have to be able to come close enough for reaction to take place and thus, a suitable solvent system has to be found. All of these factors needed to be considered before any experimental work could be performed and therefore, an extensive literature study was conducted in order to gain some further understanding of previous research in the field.

Since it was the first time for this coupling reaction to be carried out within the group, it appeared convenient to start out by trying to perform an experiment in line with a previously reported reaction route. Therefore, the first reported Rh-catalyzed hydroarylation of \( \text{C}_{60} \) was consulted.\(^{[17]} \) This publication is included in a PhD thesis written by Nambo,\(^{[18]} \) which covers comparative studies of various Rh-complexes as well as sets of reaction conditions.

In almost all of the hydroarylation reactions conducted by Nambo, the solvent system used was a mixture of \( \text{H}_2\text{O} \) and ortho-dichlorobenzene (\( o\)-DCB). Initially, a ratio of 1:9 (\( \text{H}_2\text{O}:o\text{-DCB} \)) was employed but later on it was discovered that an increased amount of \( \text{H}_2\text{O} \) (1:4, \( \text{H}_2\text{O}:o\text{-DCB} \)) gave a higher yield\(^{[18]} \) and hence, a ratio of 1:3 was chosen for this project.

According to Nambo’s work, the three most promising catalysts in terms of highest yield were \([\text{Rh}\text{(cod)}_2]\text{BF}_4\), \([\text{Rh}\text{(cod)}_2]\text{SbF}_6\) and \([\text{Rh}\text{(cod)(MeCN)}_2]\text{BF}_4\) in ascending order (see Figure 2 for structures).\(^{[17]} \) Nevertheless, it is of equal importance for a catalyst to exhibit high selectivity, thus \([\text{Rh}\text{(cod)(MeCN)}_2]\text{BF}_4\), which had an insignificantly higher yield than the others but a lower selectivity, was disregarded.

![structure](image)

Figure 2. Molecular structure of: a) \([\text{Rh}\text{(cod)}_2]\text{BF}_4\); b) \([\text{Rh}\text{(cod)}_2]\text{SbF}_6\) and c) \([\text{Rh}\text{(cod)(MeCN)}_2]\text{BF}_4\)
Both $[\text{Rh(cod)}_2]\text{BF}_4$ and $[\text{Rh(cod)}_2]\text{SbF}_6$, whereof the former was already available in the lab, showed high selectivity (>95%) while their yields differed insignificantly at 61-64%.\textsuperscript{[17]} Keeping in mind that this reaction was not yet well-established, neither within nor outside of the group, for practical and precautionary reasons, $[\text{Rh(cod)}_2]\text{BF}_4$ was chosen for the first tryout before buying a new batch of catalyst.

Conditions like reaction time and temperature were also chosen in agreement with previously reported work\textsuperscript{[18]} and a general scheme for the coupling reactions carried out during this project can be seen in Scheme 3.

\[
\begin{align*}
\text{R-B(OH)}_2 & \quad \text{[Rh(cod)}_2]\text{BF}_4 \\
\text{H}_2\text{O/ο-DCB(1:3)} & \quad 60^\circ\text{C}, 6\text{h}
\end{align*}
\]

Scheme 3. General reaction scheme of the Rh-catalyzed hydroarylation of fullerene $\text{C}_{60}$ with boronic acids carried out in this particular project.

At an early stage, this project was limited to study the particular Rh-catalyzed hydroarylation of fullerene $\text{C}_{60}$ with organoboronic acids. This choice was partly based on the fact that boronic acids had shown to be more reactive than other organoboron compounds and for example, their corresponding pinacol esters require a much higher temperature for reaction to occur.\textsuperscript{[16]}

Boronic acids are not at all as exclusive as fullerenes or metal complexes and there are many commercially available derivatives. However, “many” does not equal “all” and if aiming towards making a complete study of how differently substituted boronic acids interact with fullerenes, there is a possibility of reaching a level where it becomes necessary to actually know how to synthesize them.

Moreover, a deeper understanding of the preparation of the reagents taking part in a reaction, most certainly brings about useful knowledge about the reaction itself. For example in this case, it could be interesting to know whether the purity of the boronic acid is critical or not. On basis of these arguments, attempts to synthesize the desired boronic acids were made instead of buying them directly from the manufacturer.
2.2. Project aim and target molecules

Due to it having a rather simple structure, including a tolyl group substituent providing easily located signals in the $^1$H NMR spectrum, the target molecule chosen for the reproduction was 1-(Methylphenyl)-1,9-dihydro[60]fullerene (1, Figure 3). If this reproduction ended up as intended, the aim was to continue the project by examining the same reaction with a diboronic acid (2, Figure 3) instead of a monoboronic one.

![Figure 3. Structures of the target molecules for this project: (1) 1-(Methylphenyl)-1,9-dihydro[fullerene]; (2) The product of the coupling reaction with the diboronic acid 4,4'-biphenyldiboronic acid and two fullerenes.]

As can be seen in Figure 3, performing coupling reactions between two equivalents of fullerene and one equivalent of diboronic acid could produce interesting precursors for building extended chains of fullerenes. Chains that in turn, could be highly valuable in the development of molecular electronics like molecular wires.[19]

To synthesize the target molecules depicted in Figure 3 via Rh-catalyzed hydroarylation, the corresponding boronic acids (4-tolylboronic acid and 4,4'-biphenyldiboronic acid) are needed. These can be prepared by several different methods and the procedures chosen for this project are described in Section 2.3.

2.3. Preparation of boronic acids

All the boronic acids that were used during this project are arylboronic acids, which according to literature are the most common. Their popularity is reflected in the vast number of methods that have been developed for making them, one of these being metal-halogen exchange with aryl halides.[20]
This is the method that was used in this project and in its first step an aryl halide is transformed into its corresponding arylmetal reagent. The transformation is done by the insertion of an electropositive metal like lithium or magnesium, the latter yielding a so-called Grignard reagent. In both cases, the generated arylmetal reagent will be strongly nucleophilic.\(^{[21]}\) By letting this nucleophilic intermediate react with a trialkylborate through electrophilic trapping, the boronic acid is formed upon aqueous work-up.

2.4.1. Synthesis of 4-tolylboronic acid from 4-iodotoluene

As mentioned above, both lithium and magnesium can be used to attribute the aryl with nucleophilic properties. Lithium is most often inserted using \(n\)-butyllithium (\(n\)-BuLi) while magnesium is introduced by the addition of magnesium turnings.

The reaction with \(n\)-BuLi is most often more vigorous than that with magnesium. Because of this, as well as earlier experience of working with the latter (magnesium forming Grignard reagents), the less violent approach was chosen for the first attempt of making a boronic acid.

Since the initiation of the Grignard reaction with aryl halides is known to be rather sluggish, microwave irradiation was used in the activation step.\(^{[22]}\) The chosen pathway can be followed in Scheme 4.

![Scheme 4](image)

Scheme 4. Reaction scheme for the synthesis of 4-tolylboronic acid (3c) from 4-iodotoluene (3a) through the formation of a Grignard intermediate (3b).

Due to the high reactivity of the Grignard reagent, it is important to keep this reaction under a dry and inert atmosphere. Furthermore, even though the reaction might not be as vigorous as the corresponding reaction with \(n\)-BuLi, it is still considered to be rather vivid and should therefore be carried out at low temperatures. With these precautionary measures taken into account, the synthesis was straightforward and went well up to the work-up and purification, which turned out to be more difficult than expected. The results of the different attempts to work-up and purify the crude product are presented in Table 1.
Table 1. Attempts to work-up and purify the crude 4-tolylboronic acid.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Work-up and purification</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Attempted precipitation from $n$-heptane</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Precipitated from and washed with $n$-heptane</td>
<td>Beige powder, cerise mother liquor</td>
</tr>
<tr>
<td>3</td>
<td>Attempted recrystallization from H$_2$O/EtOH</td>
<td>Pink sludge</td>
</tr>
<tr>
<td>4</td>
<td>Recrystallized from pure H$_2$O</td>
<td>White needle-like solid</td>
</tr>
<tr>
<td>5*</td>
<td>Precipitated from and washed with $n$-heptane</td>
<td>White solid</td>
</tr>
</tbody>
</table>

*: As reported in Ref.[23]

In line with literature,[23] $n$-heptane was added to the brown viscous liquid obtained after the removal of extraction solvent. No precipitation occurred and the solvent was removed under reduced pressure to regenerate the brown viscous extract. Once again, $n$-heptane was added and this time a brown precipitate could be observed. Upon cooling, this brown crude product turned into a coral-colored solid, which after several washes with hot $n$-heptane gave a beige powder along with a cerise and clear mother liquor indicating the presence of iodine.

In order to estimate the purity of the crude product, an $^1$H-NMR measurement was performed. The spectrum showed signals from both the expected product and its corresponding boroxine, which is the cyclotrimeric anhydride formed upon dehydration of the acid. Since the transition between the boroxine and the boronic acids is a reversible reaction, it was not considered to be an issue in terms of purity. Nonetheless, the reference stated that the pure product was a white solid (not beige) and thus, further purification had to take place.

By suggestions from literature,[20] a mixed solvent system of water and ethanol (EtOH) was used in the first attempt to purify the crude material by recrystallization. However, only an insignificant amount of solid was observed upon cooling and in the end, the recrystallization solvent that gave the best result was pure water. Recrystallizing the product from pure water yielded a white needle-like solid that appeared crystalline to the eye.

2.4.2. Synthesis of 4,4’-biphenyldiboronic acid from 4,4’-dibromobiphenyl

**Synthesis of 4,4’-biphenyldiboronic acid through the formation of a Grignard reagent**

Since the Grignard approach worked well for the preparation of 4-tolylboronic acid, the same procedure was chosen for the first attempt to synthesize 4,4’-biphenyldiboronic acid. The reaction conditions are to be seen in Scheme 5.
Difficulties were encountered in the extraction step since the phase boundary was not very distinct. However, eventually an extraction into diethyl ether was carried out and after removal of the solvent, *n*-hexane was added in order to precipitate the crude product. The obtained crude solid material was brown and several attempts to purify it by recrystallization were performed, see Table 2.

Table 2. Attempts to work-up and purify the crude 4,4′-biphenyldiboronic acid.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Work-up and purification</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Precipitated from and washed with <em>n</em>-hexane</td>
<td>Brown powder, cerise mother liquor</td>
</tr>
<tr>
<td>2</td>
<td>Attempted recrystallization from pure H₂O</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Attempted recrystallization from H₂O/EtOH</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Attempted recrystallization from toluene</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Washed with toluene</td>
<td>Pale yellow solid, pink supernatant</td>
</tr>
</tbody>
</table>

As reported in Table 2, none of the attempts to recrystallize the crude product succeeded. Toluene was used in one of these attempts,[24] but when adding it to the crude product, the solid material did not dissolve. Instead, the toluene seemed to solubilize contaminations like iodine, since it went from being colorless to being pink. Thus, several washes with toluene were performed and in the end a pale yellow solid was collected.

The ¹H NMR spectrum showed signals that were in agreement with those reported in the reference,[25] but once again visual inspection suggested that further purification was required, since the product was supposed to be white and not yellow.

Both the troubles with the recrystallizations as well as the long-winded extraction are thought to be consequences of the 4,4′-biphenyldiboronic acid being more ambiguous in terms of polarity compared to the 4-tolyldiboronic acid. Moreover, it seemed to be hard to get rid of the iodine that was added in the activation step. Due to these complications, another approach to synthesize the diboronic acid was considered.
Synthesis of 4,4’-biphenyldiboronic using \textit{n}-BuLi

According to literature\cite{23}, the method using \textit{n}-BuLi required neither iodine nor extraction since the product would precipitate directly upon quenching. As this responded to the demands at hand, an attempt to synthesize the diboronic acid using the \textit{n}-BuLi approach was performed (see Scheme 6 for conditions).

![Scheme 6. General reaction scheme for the synthesis of 4,4’-biphenyldiboronic acid (4c) from the aryl halide 4,4’-dibromobiphenyl (4a) using the organometallic reagent \textit{n}-BuLi.]

Once more, the reaction did not proceed as smoothly as stated in the papers and it turned out that extraction was unavoidable. In the end, a white solid was obtained by washing the yellow crude product with toluene and \textsuperscript{1}H NMR confirmed its purity. All the work-up and purification steps are summarized in Table 3 below.

Table 3. Work-up and purification steps for the synthesis of 4,4’-biphenyldiboronic acid using \textit{n}-BuLi.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Work-up and purification</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Attempted precipitation from HCl (aq., 2.0 M)</td>
<td>Yellow solution</td>
</tr>
<tr>
<td>2</td>
<td>Extracted into diethyl ether</td>
<td>Yellow organic phase</td>
</tr>
<tr>
<td>3</td>
<td>Solvent removal under reduced pressure</td>
<td>Thick, yellow sludge</td>
</tr>
<tr>
<td>4</td>
<td>Attempted recrystallization from H\textsubscript{2}O/EtOH</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Washed with toluene</td>
<td>White powder</td>
</tr>
</tbody>
</table>

2.4. Rh-catalyzed hydroarylation of fullerene C\textsubscript{60} with boronic acids

When the boronic acids had been prepared, it was time to investigate the functionalization reaction. As mentioned in the introduction, the first hydroarylation reaction carried out in this project was a reproduction of a relatively well-established coupling reaction that had previously been performed by Nambo \textit{et al.}\cite{17} and the general reaction conditions can be seen in Scheme 3.
It is important to conduct the functionalization reaction in an inert atmosphere[18] and this is most likely due to the fact that Rh-complexes are highly sensitive to atmospheric oxygen. By oxidizing either the ligands in the Rh-complex or the metal itself, presence of oxygen could inactivate the catalyst.

2.4.1. Rh-catalyzed hydroarylation of fullerene $C_{60}$ with monoboronic acids

Two attempts to functionalize fullerene $C_{60}$ with the synthesized 4-tolylboronic acids were conducted, one with the beige crude product and one with the white recrystallized product. The reaction scheme including the conditions is presented in Scheme 7.

The hydroarylation carried out with the beige crude product was collected as a dark violet solution after being left to stir at 60°C for 6 hours. Extraction into dichloromethane (DCM) was performed and thereafter, literature stated that the crude product would be obtained upon solvent removal.[17] However, it turned out that evaporating all the solvent was rather difficult and after several hours under reduced pressure, there was still solvent left. Most likely, the remaining solvent was o-DCB, which has a boiling point at 178-180°C.

![Scheme 7](image)

Scheme 7. Reaction scheme for the Rh-catalyzed hydroarylation of $C_{60}$ with 4-tolylboronic acid.

Addition of methanol (MeOH) gave a brown and fine precipitate, which was collected by the use of a centrifuge and removal of the resulting supernatant. Unfortunately, $^1$H NMR analysis did not show the presence of any product.

Performing the coupling reaction with the white and pure 4-tolylboronic acid resulted in a solution that was clear and auburn after being left on stirring for 6 hours (60°C) and all the solvent was easily evaporated under reduced pressure.

The dry crude product was obtained as a brown powder and the $^1$H NMR spectrum was in agreement with signals found in the reference.[17] Before any further characterization was conducted, attempts to purify the product were carried out.
In the reference article,[17] patented columns called “Bucky prep columns” were used for purification. The stationary phases of these columns contain groups like pyrenolpropyl and phenothiazienyl,[26] see Figure 4.

![Figure 4. The structures of: a) a pyrenolpropyl group and b) a phenothiazienyl group, attached to silica.](image)

Thin-layer chromatography (TLC) with solvents of different compositions was performed in order to find a suitable eluent for the separation of functionalized and unreacted fullerenes. No such eluent was found, however it was possible to separate the product from unreacted boronic acids by filtrating the crude material through a silica plug with toluene as eluent. Brown sludge left on the top of the plug after the filtration, indicated that metal residues had been removed as well.

The slightly purified product was characterized by conventional $^1$H NMR as well as by two 2D-NMR measurements – Heteronuclear Multiple Bond Correlation (HMBC) and Nuclear Overhauser Effect Spectroscopy (NOESY). A yield of 7% was calculated by NMR-quantification using dimethyl terephthalate as the reference.

Finally, an attempt to functionalize C$_{60}$ with commercial 4-hydroxyphenylboronic acid (purity controlled by $^1$H NMR) was performed. As in the case with the crude 4-tolylboronic acid, the reaction mixture was dark violet after 6 hours at 60°C and it was hard to get rid of all the solvent after the extraction step. The same procedure, with precipitation by the addition of MeOH followed by centrifugation, was used to obtain a brown crude product, but none of the desired signals were observed in the $^1$H NMR-spectrum.
2.4.2. Attempted Rh-catalyzed hydroarylation of fullerene C₆₀ with diboronic acids

After the successful functionalization of C₆₀ with 4-tolylboronic acid, the project continued by performing the same reaction but with diboronic acids. The general reaction scheme for all the reactions that were carried out is shown below.

![Scheme 8. General reaction scheme for the Rh-catalyzed hydroarylation of C₆₀ with 4,4'-biphenyldiboronic acid.](image)

Five experiments of different compositions in terms of solvent composition and purity level of diboronic acids, were carried out simultaneously by using a “Carousel 12 Plus Reaction Station™” from Radleys. However, none of them yielded any product. This was most likely due to the long and narrow test tubes of the carousel, which prevented efficient stirring and thus, resulted in poor mixing of the two immiscible solvents (H₂O and o-DCB).

Besides the fact that the reagents will not come close enough for reaction to occur if the solvents do not mix well, water has been suggested to take part in the mechanism[27] and if so, absence of water is obviously not to prefer.

In order to achieve better stirring, the next attempt was performed in a more compact reaction vessel (20 mL MiW vial) containing a smaller reaction volume (10 mL). However, this time a new batch of catalyst had to be used since the previous one was finished. To verify the activity of this new batch of catalyst, a replica of the succeeded coupling reaction (with pure 4-tolylboronic acid) was performed in parallel.

Visual inspection of the reaction vessels after 6 hours at 60°C indicated that no reactions had occurred. Both white and black powder was observed upon removal of solvent, suggesting the presence of unreacted boronic acid as well as fullerene. The assumption was confirmed by ¹H NMR, which showed no trace of the expected product.
Nevertheless, it is still hard to say whether the outcome of this trial was actually due to the new catalyst being inactive or the fact that the heating plate turned itself off during night, since even the hydroarylation that succeeded (with pure 4-tolylboronic acid), did not give a particularly high yield. That is to say, the source of error might as well have been the human factor. To assure the activity of the catalyst, a better alternative would probably be to carry out a more well-established reaction, e.g. the Rh-catalyzed conjugate addition of organoboron compounds to enones,[15] and see whether it proceeds or not.

Until today, only one successful Rh-catalyzed hydroarylation of fullerene C\textsubscript{60} with a diboronic acid has been reported.[18] The diboronic acid used in that experiment has a quite strained structure and its full name is 9,9-dihexylfluorene-2,7-diboronic acid, see Figure 5.

![Figure 5. Structure of 9,9-dihexylfluorene-2,7-diboronic acid.](image)

Long aliphatic chains are often attached to a structure in order to improve its solubility. However, one might also think that the strained structure of this particular diboronic acid might as well promote the coupling reaction by preventing steric hindrance.

Dr. Nambo confirmed that the complicated structure of the diboronic acid had been designed to increase the solubility of the product.[28] He also clarified that a major challenge for this type of functionalized fullerenes, is how to solubilize them for further characterization.
3. Conclusions

During this project, two different boronic acids were synthesized: 4-tolylboronic acid and 4,4’-biphenyldiboronic acid. The former was prepared through the formation of a Grignard reagent while the latter had to be synthesized using n-BuLi in order to give a sufficiently pure product. In both cases, the pure solid material was white.

The two boronic acids were used to study the Rh-catalyzed hydroarylation of fullerene $C_{60}$. The first set of coupling reactions carried out between fullerene $C_{60}$ and 4-tolylboronic acids at different levels of purity, showed that the purity of the boronic acid taking part in the reaction is crucial since the less pure boronic acid did not yield any product.

On the other hand, the attempt to functionalize fullerene $C_{60}$ with 4-hydroxyphenylboronic acid purchased from Sigma-Aldrich, did not succeed either, leading to a discussion of what kind of impact a para-substituted electron donating group has on the coupling reaction.

After the successful hydroarylation of $C_{60}$ with the pure 4-tolylboronic acid, the next challenge was to understand how to purify the product. As previously mentioned, the difficulty to separate the functionalized and the unreacted fullerenes is attributed to their similar structures. In order to find a suitable eluent, TLC can be performed and also, reversed-phase chromatography should be considered.

Regarding the coupling reaction between fullerene $C_{60}$ and the diboronic acid, none of the attempts succeeded. Nevertheless, many interesting observations were made. First and foremost, the mixing of the two reaction solvents (water and $o$-DCB) seems to be very important. Not only because the fullerenes are probably found in the $o$-DCB phase while the boronic acids are most likely dissolved in the water phase. But also, due to the fact that water has been suggested to take part in the mechanism of the coupling reaction.[27]

This has been investigated by Nambo, who reported that no product was formed when carrying out this type of functionalization reaction in the absence of water, even though the reaction system was relatively well-established.[18] However, he also states that the glassware used for the coupling reaction should be pre-dried, which sounds contradictory, since the first step of the reaction includes the addition of water directly into the reaction vessel.

Another challenge of the hydroarylation with diboronic acids is the poor solubility of the products formed. Low solubility of the product clearly obstructs the characterization of the product, since a solid that cannot be dissolved will not be visible in for example NMR-measurements.
4. Future outlook

In today’s society, with all our electronic devices becoming smaller and smaller, there is a growing demand of components going in the same direction in terms of size. Related to this, is the very popular field of research called “molecular electronics” – the study of how to incorporate molecular building blocks into electronics.\(^{[19]}\)

Examples of electronic components that researchers are investigating at the moment are photoswitches and diodes, whereof a successful version of the latter was just reported in a paper\(^{[29]}\) published in Nature Nanotechnology.

The molecular wire is another example of a component that in the future could be part of molecular electronics.\(^{[19]}\) Such a wire can be thought of as a pearl necklace where each pearl is either electron donating or electron accepting, while the thread is conductive. A molecule that has been shown to possess such electron donating and accepting properties, is the fullerene. Therefore, it has become a very attractive candidate for the donor and acceptor moieties of molecular wires.

Looking at different ways of functionalizing fullerenes is essential in the search of new ways of connecting them into a wire and that is actually the origin of this project. If thinking about the molecular wire as a series of fullerenes interlinked by so called linkers, it is obvious that having a fully-conjugated linker would clearly be favorable. As mentioned in the introduction, this can be offered by the Rh-catalyzed hydroarylation and that is why this particular coupling reaction was studied in this project.

Within the time frame of the project, it was shown that this functionalization method works, at least for monoboronic acids. However, further improvement can still be done in terms of mastering different parameters of the reaction such as temperature, reaction time and solvent system.

The next challenge would be to master the Rh-catalyzed hydroarylation of fullerenes with diboronic acids and thereby, be able to produce so called dimers of fullerenes and a linker. In order for these to be applicable in molecular wires, their electrochemical behavior would have to be investigated and after that, one could continue by trying to make a trimer.

Later on, knowledge about the preparation of such a trimer could lead to the formation of an oligomer and in the distant future, the idea of a polymer of fullerenes interlinked by fully-conjugated linkers might come true.
5. Experimental

**Materials and methods**

Dry THF was freshly distilled from sodium under nitrogen atmosphere. All other reagents were purchased from Sigma-Aldrich and used as supplied without further purification. Pre-drying of glassware was performed in oven (160°C) for at least 10 hours. All the water used in the reactions was deionized.

MiW heating was conducted in a Biotage Initiator microwave using 2-5 mL Biotage MiW vials. Analytical TLC was performed on 0.25 mm pre-coated silica gel plates and visualized by UV-fluorescence. Column chromatography was conducted using Millipore 35-70 µm normal phase silica gel.

$^1$H NMR spectra were recorded using an Agilent 400 MR 400 MHz spectrometer. Relaxation delay was set to 4 seconds unless stated otherwise. HMBC and NOESY spectra were recorded on a Varian Unity 500 MHz spectrometer. $^1$H NMR spectra in CDCl$_3$ and CDCl$_3$:CS$_2$ (1:1) were referenced indirectly to TMS using residual solvent signals (chloroform-$d$ δ 7.26 ppm). $^1$H NMR spectra in DMSO were referenced indirectly to TMS using residual solvent signals (DMSO δ 2.50 ppm).

**4-tolylboronic acid (3c)**

**General procedure**$^{[22,23]}$

Magnesium turnings (398.4 mg, 16.4 mmol), 4-iodotoluene (887.6 mg, 4.1 mmol) and iodine (21.8 mg, 85.9 µmol) were put into a pre-dried MiW vial equipped with a magnetic stirring bar. The MiW vial was placed under nitrogen atmosphere and dry THF (10 mL) was added using a syringe yielding a clear, brown solution. The reaction mixture was heated in a MiW at 120°C for 60 minutes. Upon cooling a clear pale yellow solution of 4-tolylmagnesium iodide as well as white precipitate and unreacted Mg turnings was obtained.

The previously obtained solution of 4-tolylmagnesium iodide was transferred to a pre-dried two-necked rb-flask, which was subjected to nitrogen. The rb-flask was then equipped with a stirring bar and dry THF (10 mL) was added. The rb-flask was cooled down to -44°C on a liquid nitrogen-acetonitrile bath.
Trimethyl borate (3.6 M in dry THF, 2.2 mL) bubbled with nitrogen, was added dropwise to the previously made Grignard reagent (4-tolylmagnesium iodide) on stirring (-44°C). The reaction mixture was left on stirring to reach room temperature (RT) over night.

The pale yellow and milky reaction mixture was quenched with HCl (aq., 2.0 M, 9.25 mL) by slow addition and the resulting solution was stirred for additionally 2 h. The mixture went from milky yellow to clear yellow and residual Mg turnings were dissolved.

Water (5 ml) was added to the reaction mixture, which was then extracted with diethyl ether (2x30 mL). The combined organic phases were washed with brine (30 mL) and dried over Na₂SO₄. The drying agent was filtered off through a plug of cotton and the solution was concentrated using a rotary evaporator until a brown and viscous liquid (like Hoisin sauce) was observed.

In order to precipitate the product, n-heptane (7 mL) was added. However, no precipitation occurred and therefore, all solvent was removed under reduced pressure until the brown and sticky gravy-like residue appeared again. A second addition of n-heptane (15 mL) yielded a pale brown precipitate.

The mixture was cooled on ice bath to enhance precipitation and a coral-colored fluffy precipitate with black residues at the bottom appeared. The precipitate was filtered off by suction filtration (Büchner set-up) yielding a beige powder along with a cerise mother liquor, which indicated the presence of iodine.

The solid was washed with warm n-heptane and a pale brown solid was obtained. After being left under high vacuum over the weekend, the solid underwent a significant color change (paler shade of brown), which confirmed the presence of I₂ even more.

Signals observed in the ¹H NMR spectrum (400MHz, CDCl₃), see Figure A1, were in agreement with the reference⁴ and showed a mixture of 4-tolylboronic acid and tri(4-tolyl) boroxine. δH (400MHz, CDCl₃) Boroxine: 8.13 (6H, d, J = 8.0 Hz), 7.32 (6H, d, J = 8.2 Hz). δH (400MHz, CDCl₃) Boronic acid: 7.63 (2H, d, J = 7.9 Hz), 7.23 (2H, d, J = 7.8 Hz), 4.45 (9H, s), 2.39 (4H, s).

**Purification**

Attempted recrystallization from water and EtOH did not yield sufficient amounts of recrystallized material to isolate, despite long-term cooling in refrigerator. The resulting solution was pale yellow and clear with only minor amounts of solid. The supernatant (mixture of H₂O and EtOH) was removed on a rotary evaporator and the pale yellow-brown
solid was dissolved in pure water on reflux. The dissolved yellow-brown crude product was hot-filtered and crystals were allowed to form on slow cooling.

A mixture of 4-tolylboronic acid and boroxine complex (0.137 g) was isolated as white needle-like crystals. The signals agreed with the reference[30] and the $^1$H NMR spectrum can be seen in Figure A2. δ$_\text{H}$ (400MHz, CDCl$_3$): 8.13 (6H, d, $J = 8.4$ Hz), 7.63 (4H, d, $J = 7.7$ Hz), 7.32 (6H, d, $J = 8.3$ Hz), 7.23 (4H, d, $J = 7.7$ Hz), 4.59 (3H, s), 2.45 (9H, s), 2.39 (4H, s).

4,4’-biphenyldiboronic acid (4c)

**General procedure using Grignard reagent**[22,23]

Mg turnings (388.9 mg, 16.0 mmol), 4,4’-dibromobiphenyl (1.306 g, 4.2 mmol) and iodine (33.1 mg, 130.4 µmol) were put into a pre-dried MiW vial equipped with a magnetic stir bar. The MiW vial was subjected to nitrogen atmosphere and dry THF (10 mL) was added using a syringe yielding a clear, brown solution. The reaction mixture was heated in a MiW at 120°C for 60 minutes. Upon cooling, a clear pale yellow solution of 4,4’-diphenylmagnesium bromide as well as white precipitate and unreacted Mg turnings could be observed.

The previously obtained Grignard reagent was transferred into a pre-dried two-necked rb-flask (250 mL), which had earlier been subjected to nitrogen. This rb-flask was equipped with a stirring bar, whereupon dry THF (10 mL) was added. The reaction flask was cooled down to -78°C on an acetone-dry ice cooling bath.

Trimethyl borate (3.7 M in dry THF, 2.2 mL) bubbled with was added to the Grignard reagent on stirring (-78°C). The reaction mixture was left on stirring to reach RT over night. The pale yellow and milky reaction mixture was quenched with HCl (aq., 2.0 M, 9.25 mL) by slow addition and the resulting solution was stirred for additionally 3 h. The mixture went from milky yellow to clear yellow and residual Mg turnings were dissolved.

Thereafter, the reaction mixture was extracted with diethyl ether (3x30 mL) and the combined organic phases were washed with brine (30 mL). The cloudy yellow organic phase was filtered through a cotton plug resulting in a clear yellow solution. Solvent removal on rotary evaporator yielded a viscous and brown liquid.

Addition of n-hexane (20 mL) to this brown liquid gave a cerise and clear liquid along with brown precipitate sticking to the walls. The rb-flask containing the cerise solution was put on ice bath to enhance precipitation but no significant change was observed. The brown
precipitate was filtered off using a Büchner set-up yielding brown solid and cerise mother liquor, indicating iodine.

First attempt
Quantities used: Mg turnings (388.9 mg, 16.0 mmol), 4,4’-dibromobiphenyl (1.306 g, 4.2 mmol) and iodine (33.1 mg, 130.4 µmol). Unfortunately, the extraction for this trial was so troublesome that no crude was obtained even after three attempts to work it up. No purification was performed due to insignificant quantities of crude material.

Second attempt
Quantities used: Mg turnings (392.1 mg, 16.1 mmol), 4,4’-dibromobiphenyl (1.267 g, 4.1 mmol) and iodine (68.1 mg, 268.3 µmol). Crude solid obtained: 212.6 mg. Presence of 4,4’-biphenyldiboronic acid was confirmed by $^1$H NMR.$^{[25]}$

\[
\delta_H (400MHz, DMSO): 8.07 \text{ (4H, s)}, 7.88 \text{ (4H, d, } J = 8.1 \text{ Hz)}, 7.66 \text{ (4H, d, } J = 10.1 \text{ Hz)}.
\]

Recrystallization from pure water was attempted but since the crude product did not dissolve, the solvent was removed under reduced pressure. Another recrystallization was attempted but from a mixed solvent system of water and EtOH, however that did not work either and in the end, the crude was purified by several cycles of toluene washes and centrifugation, yielding a pale yellow powder.

The signals observed in the $^1$H NMR (400 MHz, DMSO) spectrum, see Figure A3, confirmed the presence of 4,4’-dibromobiphenyl according to the reference.$^{[25]}$

\[
\delta_H (400MHz, DMSO): 8.08 \text{ (4H, s)}, 7.88 \text{ (4H, d, } J = 8.8 \text{ Hz)}, 7.66 \text{ (4H, d, } J = 7.88 \text{ Hz)}.
\]

However, visual inspection indicated that the product was not pure since it was supposed to be white and not yellow and thus another approach to synthesize 4,4’-biphenyldiboronic acid was considered.

General procedure using $n$-BuLi$^{[23]}$
4,4’-dibromobiphenyl (1.881 g, 6.0 mmol) was dissolved in dry THF (60 mL) in a 500 mL pre-dried two-necked rb-flask under nitrogen equipped with a magnetic stirring bar. Dropwise addition of n-BuLi (1.6 M in hexane, 18 mL) via septum resulted in a clear yellow solution.

After 4 h of stirring, 4.5 mL of trimethyl borate (3.7 M in dry THF) was added slowly at -78°C. The reaction mixture went from being pale yellow and cloudy to pale yellow and clear, whereupon it was left to reach RT over night.

The reaction was quenched by the addition of HCl (aq., 2.0 M, 150 mL). When about 10 mL had been added, a white precipitate was observed and after additionally 10 mL of acid,
the solution was cloudy. The reaction mixture remained cloudy when all HCl had been added. Extraction with ether (2x30 mL) resulted in a clear and yellow organic phase. The solvent was removed on rotary evaporator revealing a pale yellow solid.

**Purification**

An attempt to recrystallize the crude from a mixed solvent system (water and EtOH) was performed. However, it did not succeed and thus, the crude was dissolved in toluene and distributed into small test tubes. These test tubes were centrifuged (5 minutes at 4500 rpm) to obtain a pale yellow solid in a slightly pink supernatant. The latter was removed using a Pasteur pipette and the white solid was washed additionally two times by the addition of toluene followed by centrifugation and removal of supernatant. The resulting white solid was dissolved in pentane and transferred to a rb-flask which was put on a rotary evaporator.

A white powdery solid was observed and the $^1$H NMR (400 MHz, DMSO) spectrum, see Figure A4, confirmed a sufficiently pure product according to reference.$^{[25]}$ $\delta_{\text{H}}$ (400MHz, DMSO): 8.08 (4H, s), 7.88 (4H, d, $J = 8.0$ Hz), 7.66 (4H, d, $J = 8.0$ Hz).

**Rh-catalyzed hydroarylation of fullerene C$_{60}$ with monoboronic acids**

**General procedure$^{[17]}$**

Fullerene C$_{60}$, crude 4-tolylboronic acid and [Rh(cod)$_2$]BF$_4$ catalyst were placed in a rb-flask equipped with a stir bar. A reflux condenser was attached to the rb-flask and the system was repeatedly evacuated and subjected to nitrogen atmosphere.

A two-phased mixture of H$_2$O (10 mL) and o-DCB (30 mL) was degassed by bubbling nitrogen through the solution under ultrasonication for at least 20 minutes. The resulting white emulsion (20 mL) was added to the reaction flask via septum yielding a violet solution, which was left on stirring at 60°C over night.

The reaction mixture (dark violet and clear) was allowed to reach RT and thereafter, it was extracted into DCM (30 mL). Then, the remaining water phase was further extracted with DCM (2x30 mL) before the organic phases were combined and the solvent was removed on reduced pressure. Completely removing the o-DCB was difficult (probably due to its high boiling point) and the obtained mixture was a viscous, dark brown liquid.

The previously obtained liquid was distributed into test tubes and to each of them, equal amounts of MeOH were added. The addition of MeOH resulted in precipitation of a brown
solid and the test tubes were centrifuged (5 minutes at 4500 rpm) to obtain a brown solid in a clear pale brown supernatant. The latter was removed using a Pasteur pipette and the solid was washed twice using the just mentioned procedure (addition of MeOH followed by centrifugation). The resulting brown solid was dissolved in toluene and transferred to a rb-flask. Removing the solvent on rotary evaporator resulted in a dark brown solid.

**Hydroarylation with crude 4-tolylboronic acid**

Quantities used: Fullerene C$_{60}$ (86.5 mg, 120.0 µmol), crude 4-tolylboronic acid (23.2 mg, 170.6 µmol) and [Rh(cod)$_2$]BF$_4$ (4.6 mg, 11.3 µmol). The resulting crude solid material was analyzed by $^1$H NMR (400 MHz, CDCl$_3$:CS$_2$, 1:1), however no signals corresponding to the expected product could be observed.

**Hydroarylation with recrystallized 4-tolylboronic acid**

Quantities used: Fullerene C$_{60}$ (86.9 mg, 120.6 µmol), 4-tolylboronic acid (21.2 mg, 155.9 µmol) and [Rh(cod)$_2$]BF$_4$ (4.6 mg, 11.3 µmol). For the extraction with DCM, water (5mL) had to be added in order to visualize the phase boundary. The color of the reaction mixture was significantly more reddish-brown, compared to the dark violet solution observed in the previous attempts. No precipitation with MeOH and centrifugation was needed since the o-DCB was successfully removed by subsequent co-evaporation with toluene (reduced pressure). Crude solid material obtained: 23.9 mg.

The resulting crude solid material was analyzed by $^1$H NMR (400 MHz, CDCl$_3$:CS$_2$, 1:1), see Figure A5, confirming formation of the desired product as well as presence of unreacted boronic acid.$^{[17]}$ The crude mixture was further purified by filtration through a silica plug using toluene as eluent and the resulting $^1$H NMR spectrum is presented in Figure A6. δ$_H$ (400MHz, CDCl$_3$:CS$_2$, 1:1): 8.34 (2H, m), 7.59 (2H, m), 6.75 (1H, s), 2.60 (3H, s).

Also HMBC and NOESY measurements confirmed the presence of the desired product and their spectra are to be seen in Figure A7 and Figure A8, respectively. The yield was determined to 7% by $^1$H NMR quantification using dimethyl terephthalate as standard.

**Hydroarylation with 4-hydroxyphenylboronic acid**

Quantities used: Fullerene C$_{60}$ (38.3 mg, 53.1 µmol), 4-hydroxyphenylboronic acid (19.8 mg, 143.6 µmol), [Rh(cod)$_2$]BF$_4$ (6.3 mg, 15.5 µmol). Upon extraction with DCM water (5mL) had to be added in order to see the phase boundary clearly. The resulting crude solid material
was analyzed by $^1$H NMR (400 MHz, CDCl$_3$:CS$_2$, 1:1), however no signals corresponding to the expected product could be observed.

**Hydroarylation with recrystallized 4-tolylboronic acid and new Rh-catalyst**

Quantities used: Fullerene C$_{60}$ (72.5 mg, 100.6 µmol), 4-tolylboronic acid (14.0 mg, 103.0 µmol) and [Rh(cod)$_2$]BF$_4$ (4.4 mg, 10.8 µmol). This reaction was carried out in a smaller volume (10 mL, H$_2$O/o-DCB, 1:3) and the reflux set-up was exchanged to a concealed MiW vial. The color of the reaction mixture was still violet after being stirred over night. Some error seemed to have occurred during night concerning the heating plate and none of the expected signals were observed in the $^1$H NMR spectrum.

**Rh-catalyzed hydroarylation of fullerene C$_{60}$ with a diboronic acid**

**General procedure**

Fullerene C$_{60}$, crude 4,4’-biphenyldiboronic acid and [Rh(cod)$_2$]BF$_4$ catalyst were placed in a rb-flask equipped with a stir bar. A reflux condenser was attached to the rb-flask and the system was repeatedly evacuated and subjected to nitrogen atmosphere.

A two-phased mixture of H$_2$O (10 mL) and o-DCB (30 mL) was degassed by bubbling nitrogen gas through the solution under ultrasonication for at least 20 minutes. The resulting white emulsion (20 mL) was added to the reaction flask via septum yielding a violet solution, which was left on stirring over night at 60°C.

The reaction mixture was allowed to reach RT before it was extracted into DCM (30 ml). This was followed by further extraction of the water phase (with DCM, 2x30 mL), whereupon the organic phases were combined and the solvent removed on a rotary evaporator.

**Hydroarylation with 4,4’-biphenyldiboronic acid in Radley test tubes**

Quantities used: Fullerene C$_{60}$ (238.4 mg, 330.8 µmol), 4,4’-biphenyldiboronic acid (40.0 mg, 165.4 µmol) and [Rh(cod)$_2$]BF$_4$ (11.9 mg, 29.3 µmol). Problems regarding the stirring occurred during this trial and the reaction mixture was separated in two immiscible phases. Still, extraction was performed and removal of the solvents on rotary evaporator revealed a mix of black and white solid precipitate, which is suspected to be unreacted starting material. The crude was analyzed by $^1$H NMR (400 MHz, CDCl$_3$:CS$_2$, 1:1) but no signals corresponding to the expected product could be observed.
Hydroarylation with 4,4’-biphenyldiboronic acid with new batch of Rh-catalyst

Quantities used: Fullerene C\textsubscript{60} (228.9 mg, 317.6 \textmu mol), 4,4’-biphenyldiboronic acid (9.7 mg, 40.1 \textmu mol) and [Rh(cod)\textsubscript{2}]BF\textsubscript{4} (3.6 mg, 8.9 \textmu mol). In order to solve the stirring problem, this reaction was carried out in a smaller volume and in addition, the reflux set-up was exchanged to a concealed 20 mL MiW vial. However, a mixture of black and white precipitate was observed after evaporation of extraction solvents and \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}:CS\textsubscript{2}, 1:1) measurements did not show any expected signals.
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References


[28] M. Nambo, Personal Communication


Appendix
Spectral data for 4-tolylboronic acid (3c)

Figure A1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) for the crude 4-tolylboronic acid.

Figure A2. $^1$H NMR spectrum (400 MHz, CDCl$_3$) for the pure 4-tolylboronic acid.
Spectral data for 4,4'-biphenyldiboronic acid made via Grignard reagent (4c)

Figure A3. $^1$H NMR data (400 MHz, DMSO) for 4,4'-biphenyldiboronic acid after being washed with toluene.

Spectral data for 4,4'-biphenyldiboronic acid made via n-BuLi (4c)

Figure A4. $^1$H NMR data (DMSO) for 4,4'-biphenyldiboronic acid after being washed with toluene.
Spectral data for 1-(4-Methylphenyl)-1,9-dihydro[60]fullerene (I)

Figure A5. $^1$H NMR data (400 MHz, CDCl$_3$:CS$_2$, 1:1) for crude 1-(4-Methylphenyl)-1,9-dihydro[60]fullerene.

Figure A6. $^1$H NMR data (400 MHz, CDCl$_3$:CS$_2$, 1:1) for 1-(4-Methylphenyl)-1,9-dihydro[60]fullerene after being filtered through a silica plug.
Figure A7. HMBC data (500 MHz, CDCl$_3$: CS$_2$, 1:1) for 1-(4-Methylphenyl)-1,9-dihydro[60]fullerene.

Figure A8. NOESY data (500 MHz, CDCl$_3$: CS$_2$, 1:1) for 1-(4-Methylphenyl)-1,9-dihydro[60]fullerene.