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# Role of Copper Species in the Oxidative Dimerization of Arylboronic Acids: Synthesis of Symmetrical Biaryls

Ayhan S. Demir,* Ömer Reis, and Mustafa Emrullahoglu

*Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey*

*asdemir@metu.edu.tr*

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Certain Cu(I) and Cu(II) salts are able to mediate the dimerization of arylboronic acids in DMF. They provide the corresponding symmetrical biaryls in moderate to very good yields. It is possible to run the reaction catalytically under an oxygen atmosphere without a significant loss of yields.

## Introduction

There is a growing interest in the synthesis of valuable natural and unnatural biaryls. Catalytic cross-coupling reactions are the cornerstone of reactions developed for this purpose. Ullmann-type homocoupling is another possible approach; many useful and superior variants of this reaction have been developed for the synthesis of symmetrical biaryls.[1] For the symmetrical biaryls concerned, oxidative dimerization of organometallic species emerges as another method of choice. All of the approaches mentioned have been comprehensively reviewed recently.[2]

Arylboronic acids are organometallic species in the well-known Suzuki coupling,[3] and the homocoupling of arylboronic acids occurs in Suzuki coupling when the desired cross-coupling is slow.[3,4] Because of their greater stability and lower toxicity over organostannanes, it is not surprising that there have been many studies that have reported recently on the dimerization of arylboronic acids as a method of symmetrical biaryl synthesis.

Almost all of the methods rely on palladium catalysis and, as well, improvements made on the basis of the use of different ligands, bases, and solvents. Moreno-Mañas et al. reported on a study that aimed at understanding the mechanism of self-coupling in arylboronic acids. They proposed a mechanism based on Pd(0) as the active species derived from a variety of sources.[4] Later, it was shown by Jackson et al. that $Pd(OAc)_2$ in combination with a base provided synthetically useful yields of biaryls under an oxygen atmosphere.[5] It was also shown that $Cu(OAc)_2$ can be used as an oxidant in addition to or instead of air, but the effect is not uniform, providing much better yields for certain arylboronic acids and lower yields for others. In another study, $Pd(OAc)_2$ in a DMF solution was shown to provide the corresponding biaryls in a moderate yield, while the addition of phosphine ligands enhanced the reaction yields.[6] Interestingly, Koza et al. reported that $Pd(OAc)_2$ in DMF does not promote the self-coupling of phenylboronic acid, and $Pd(PPh_3)_4$ yields only trace amounts of biphenyl.[7] Moreover, contrary to the report by Jackson et al., $Pd(OAc)_2$ in ethanol furnished only trace amounts of the product, the only difference being the base. Their reaction conditions and reported yields are very similar to that of Jackson et al. except for $Cu(NO_3)_2$ being the oxidant instead of $Cu(OAc)_2$. Recently, the base-free homocoupling of arylboronic esters mediated by palladium-1,3-bis(diphenylphosphino)propane (DPPP) complex in DMSO under an oxygen atmosphere has been shown to provide high yields of biaryls.[8] Another improvement in the oxidative dimerization of arylboronic acids is the use of $Pd(OAc)_2$ in $H_2O$, with oxygen as the oxidant and NaOAc as the base.[9] Another variation that provides excellent yields for certain arylboronic acids utilizes *p*-toluenesulfonyl chloride as the additive and $PdCl_2$ as the metal, but *ortho*-substitution significantly lowers the yields.[10] Falck et al. reported that alkyl-, alkenyl-, and arylboronic acids undergo $Ag_2O/CrCl_2$-mediated homocoupling in good yields and are important in that all hybridization types on organoboronic acids are tolerated. This method is compatible with allylic acetates, which would cause problems with palladium-based methods. Labile organosilver and/or organo-chromium have been proposed as possible intermediates that subsequently dimerize.[11]

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* To whom correspondence should be addressed. Phone: + 90-312-2103242. Fax: +90-312-2101280.

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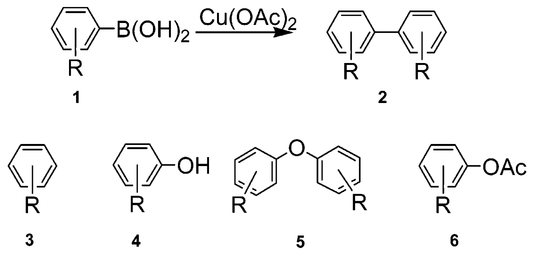
**SCHEME 1**



Recently, we have shown that arylboronic acids are a very good source of aryl radicals that can be generated by $Mn(OAc)_3$ and subsequently captured by aromatic solvents to obtain the corresponding biaryls.[12] Later we found that a similar oxidant, $Cu(OAc)_2$, is also able to mediate the same transformation. Since $Cu(OAc)_2$ is known to form C−O and C−N bonds from arylboronic acids and aryl-copper intermediates have been proposed for these transformations,[13] homolysis prone aryl-copper and aryl-manganese intermediates might play a role in the formation of aryl radicals in benzene.

Recently, many reports by Liebeskind[14] and Buchwald[15] have shown that excellent results can be obtained with catalysts based on copper instead of or in addition to palladium. Therefore, the feasibility of using copper in a variety of reactions deserves attention; one such reaction is the oxidative dimerization of arylboronic acids. In addition, copper species are generally the first choice when a co-oxidant is required to restore the catalytically active species, but their use can be disastrous. Herein we report our investigation on the use and role of $Cu(OAc)_2$ and related copper species in the oxidative dimerization of arylboronic acids.

## Results and Discussion

Initially we investigated the reaction of 4-bromophenylboronic acid **1b** and 2 equiv of $Cu(OAc)_2$ in a variety of solvents for the conversion depicted in Scheme 1. Typical side products of this reaction were expected to be the corresponding arene **3**, phenol **4**, symmetrical diaryl ether **5,** and acetoxylation product **6** on the basis of previous reports.[13a,16] Among the solvents tried (MeOH, MeCN, cyclohexane, dichloromethane), THF and DMF were found to be suitable for the desired conversion. Other solvents resulted in poor conversions or the formation of side products. For example, a reaction in dichloromethane under ordinary conditions resulted in the formation of symmetrical diaryl ether **5**, whereas acetoxylation product **6** was observed under anhydrous conditions in the presence of molecular sieves (GC−MS). DMF was the solvent of choice; only desired product **2b** was found in the crude product ($^1$H NMR) although no precautions were taken to avoid the presence of water during the handling of chemicals or to remove it from the reaction mixture with molecular sieves.[17]

After a series of reactions we found that 0.5 equiv of $Cu(OAc)_2$ respect to 1 equiv of arylboronic acid is enough for the desired conversion. Under this condition, **1b** was found to be providing the corresponding symmetrical biaryl **2b** in 95% yield. The progress of the reaction is relatively slow at room temperature. Reaction time decreased dramatically at elevated temperatures (100 °C) without significantly affecting the yield (93%). According to these results several arylboronic acids reacted with $Cu(OAc)_2$ in DMF at 100 °C, and results are summarized in Table 1.

A closer inspection of the results revealed that the reaction is sensitive to the position of substituents. Substituents on the *ortho*-position lower the yields. Whereas 2-naphthaleneboronic acid provided the corresponding dimer in a 71% yield, sterically congested 1-naphthaleneboronic acid provided 49% binaphthyl together with 35% naphthalene. 2,6-Disubstituted arylboronic acids (entries 22 and 23) only provided the corresponding arene. This behavior was attributed either to the instability of the formed aryl-copper intermediate or the sterically slowed transmetalation of the second aryl moiety onto the metal center as a result of substitution on the *ortho*-position, eventually resulting in decomposition.

It is also possible to carry out this homocoupling reaction in the presence of catalytic $Cu(OAc)_2$. We carried out the reaction with 0.1 equiv of $Cu(OAc)_2$ in respect to 1 equiv of **1b** under an oxygen atmosphere at 100 °C. $^1$H NMR analysis of the crude product showed phenol and diaryl ether type side products in the crude mixture opposed to the stoichiometric reaction, possibly related to the sensitivity of catalytic reaction to the presence of water. Molecular sieves were added to reaction mixture to suppress the formation of these side products, and **2b** was obtained in an 86% isolated yield. Additional examples showed that slightly lower but still acceptable yields of symmetrical biaryls can be obtained with catalytic amounts of copper (entries 2, 4, 10, 12, 14, 16). An oxygen atmosphere was necessary, and the use of an inert atmosphere resulted in low conversions.

Another interesting aspect of the reaction is the source of copper. $CuCl_2$ was found to be ineffective, and heating resulted in slow protodeboronation. Addition of sodium acetate did not promote the reaction. $Cu(NO_3)_2$ provided **2b** from **1b** albeit in a lower yield than with $Cu(OAc)_2$. The conversion rates were so low with $Cu(OTf)_2$ that only trace amounts of the product was observed after 24 h at room temperature. Addition of sodium acetate to a DMF

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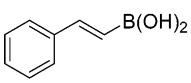
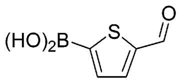
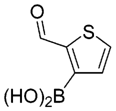
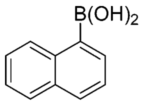
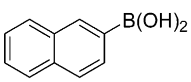
[17] It has been shown that the presence of water results in formation of side product **5**; molecular sieves trap the water released by arylboronic acids via anhydride formation. For an example, see ref 13a.

**TABLE 1. Yields of Symmetrical Biaryls**

| entry | Arylboronic acid R | biaryls, yield(%)[a] |
|---|---|---|
| 1 | **1a,** H | **2a**, 78 |
| 2[b] | **1a** | **2a**, 72 |
| 3 | **1b,** 4-Br | **2b**, 93 |
| 4[b] | **1b** | **2b**, 86 |
| 5 | **1c,** 2-Br | **2c**, 30 |
| 6 | **1d,** 3-Br | **2d**, 77 |
| 7 | **1e,** 2-OMe | **2e**, 44 |
| 8 | **1f,** 3-OMe | **2f**, 81 |
| 9 | **1g,** 4-OMe | **2g**, 90 |
| 10[b] | **1g** | **2g**, 81 |
| 11 | **1h,** 4-$OCF_3$ | **2h**, 93 |
| 12[b] | **1h** | **2h**, 82 |
| 13 | **1i,** 4-F | **2i**, 50 |
| 14[b] | **1i** | **2i**, 45 |
| 15 | **1j,** 3,5-F | **2j**, 95 |
| 16[b] | **1j** | **2j**, 90 |
| 17 | **1k,** 2-Me | **2k**, 70 |
| 18 | **1l,** 2-$CF_3$ | **2l**, 45 |
| 19 | **1m,** 2-CHO | **2m**, 36 |
| 20 | **1n,** 3-CHO | **2n**, 52 |
| 21 | **1o,** 4-CHO | **2o**, 77 |
| 22 | **1p,** 2,6-$(OMe)_2$ | - |
| 23 | **1r,** 2,6-$(Me)_2$ | - |
| 24 | **1s**<br> | **2s**, 30 |
| 25 | **1t**<br> | **2t**, 41 |
| 26 | **1u**<br> | **2u**, 35 |
| 27 | **1v**<br> | **2v**, 49 |
| 28 | **1y**<br> | **2y**, 71 |

[a] Isolated yields. All compounds are known except for **2h** and **2u**, and all analytical data are in agreement with the previously reported data. Compounds **2h** and **2u** gave satisfactory analytical data (Experimental Section). When the yields were low, corresponding arenes were isolated together with biaryls summing up to >90% of the starting material. In the case of volatile arenes, product content was detected with GC−MS. Although all of the reactions were carried out on a 1 mmol scale, reaction with 5 mmol of **1b** worked equally well. [b] Run with catalytic $Cu(OAc)_2$.

solution of $Cu(OTf)_2$ prior to the addition of arylboronic acid provided a result similar to that of $Cu(OAc)_2$. Moreover, the addition of the sodium salt of *N*-benzoylphenylglycine instead of sodium acetate furnished **2b** in 51% yield in an unoptimized reaction at 100 °C, whereas sodium trifluoroacetate was ineffective. It could be envisioned that acetate ion in the solution activates the arylboronic acid as boronate that has a propensity to transmetalate onto the active metal. However, our results seem to indicate that acetate ligand bound to copper activates the arylboronic acid. Similar behavior was reported by Liebeskind: copper(I) thiophene-2-carboxylate (CuTC) activates arylboronic acids toward transmetalation onto palladium under base-free conditions.[14d,e] However, the picture could be much more complicated keeping in mind that truly active species in the reaction medium is not known. So we investigated the reactivity of various Cu(I) salts. Cu(I) salts (CuOAc, CuOTf.1/2PhH, $CuBr{\cdot}Me_2S$, CuCl, CuI, CuTC) and $Cu(OAc)_2$ were made to react under the same set of conditions. Because conditions were not optimized for each Cu(I) compound, yields are not an indication of the potential of that particular Cu(I) salt, but they are well useful for comparison with Cu(II) sources. Contrary to Cu(II) salts, all of the examined Cu(I) salts afforded the corresponding dimer as shown in Table 2. CuI afforded vast amount of the corresponding iodoarene in addition to dimer (GC−MS). CuOAc provided the highest conversion, and the yield is just comparable to that of $Cu(OAc)_2$. Another similarity between CuOAc and $Cu(OAc)_2$ was observed for **2v** not only in terms of yield of dimer but also that of a protodeboronation product. CuTC gave mainly protodeboronation together with small amounts of dimer under the same conditions.[18]

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(18) It was previously shown that 2-naphthaleneboronic **1y** gave complete protodeboronation with CuTC in THF.[14d]

**TABLE 2. Comparison of Cu(I) Salts with $Cu(OAc)_2$[a]**

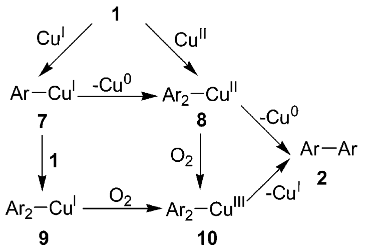
| entry | copper salt | arylboronic acid | yield (%) |
|---|---|---|---|
| 1 | $Cu(OAc)_2$ | **2b** | 77 |
| 2 | CuOAc | **2b** | 72 |
| 3 | CuOTf·1/2PhH | **2b** | 44 |
| 4[b] | $Cu(O_2CCF_3)$ | **2b** | 31 |
| 5 | CuTC | **2b** | 48 |
| 6 | $CuBr.Me_2S$ | **2b** | 34 |
| 7 | CuCl | **2b** | 65 |
| 8[c] | CuOAc | **2v** | 51 |
| 9[d] | CuTC | **2v** | 16 |

[a] All reactions were carried out under the same set of conditions: 0.5 mmolof **2a** and 0.25 mmol of Cu(I) or Cu(II) in 1 mL of DMF at room temperature for 24 h. Isolated yields; no side products were observed. [b] Sodium trifluoroacetate was mixed with CuOTf·1/2PhH in DMF prior to the reaction. [c] 48 h for complete conversion; 36% naphthalene was isolated. [d] 74% naphthalene was isolated

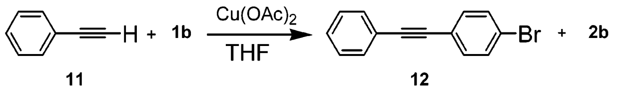
Although the mechanism of dimerization of arylboronic acids by copper salts is not obvious at this stage, we want to emphasize the following points: (1) investigation with Cu(I) salts showed that although $Cu(OTf)_2$, $Cu(O_2CCF_3)_2$, and $CuCl_2$ were not suitable for this transformation, corresponding Cu(I) salts were useful. Moreover, CuOAc and $Cu(OAc)_2$ gave very similar results in terms of product yield and distribution (Table 1, entry 27; Table 2, entry 8). These seem to be pointing out the necessity of the formation of corresponding Cu(I) salts that are either chiefly active species or act together with Cu(II) salts.[19] This could be understandable if one considers that highly electronegative ligands (triflate and trifluoroacetate) may retard the reduction of the presumably inactive Cu(II) salts to the corresponding Cu(I) salts (which were shown to be active), even though chloride does not perfectly fit into this picture. A deeper understanding of these possibilities requires the detection of oxidation states of copper species present in reaction mixture and prior knowledge of the redox behavior of various copper species under the specified reaction conditions, for which studies are currently underway. (2) In most cases, we observed the precipitation of metallic copper. Moreover, we also observed the complete or partial disappearance of the precipitated copper. Separate control reactions were carried out with metallic copper and sodium acetate both under oxygen and nitrogen atmosphere, even though these conditions are not a perfect imitation of the real process. Reaction under inert gas showed no sign of change, and only starting material was obtained. However, the formation of green color was observed under oxygen, providing a low yield of biaryl together with side products. Moreover homocoupling reaction under inert atmosphere gave inferior yields either with CuOAc or $Cu(OAc)_2$.

Possible simplistic mechanisms for both Cu(I) and Cu(II) compounds are depicted in Scheme 2. Formation of metallic copper suggests the intermediacy of diarylcopper(II) **8**, which reductively eliminates to afford **2**; **8** could be generated by $Cu(OAc)_2$ via double transmetalation of **1**. Alternatively, arylcopper(I) intermediates **7** formed by CuOAc can disproportionate to form **8** according to a mechanism proposed by van Koten.[20] A similar mechanism was also proposed by Piers for the oxidative dimerization of organostannes by stoichiometric CuCl.[21] If the route through **8** is operational in catalytic reaction with either Cu(I) or Cu(II) as the active species, regeneration of active copper salt from Cu(0) with oxygen is necessary, which was shown to be feasible (see above). However, a critical role of oxygen might also be an indication of a Cu(III) oxidation state that is advocated by some researchers while others criticized it being energetically unfavorable.[22] This invokes a possible Cu(I)/Cu(III) catalytic cycle. Although it is difficult to figure out the exact timing of the transmetalation, one possible route is as follows: a second aryl moiety transmetalates onto **7** to form diarylcopper(I) **9**, which is oxidized by oxygen to diarylcopper(III) **10**, subsequently releasing Cu(I) upon reductive elimination. Considering that there is no information currently available on the active species, it is hard to justify a more lengthy discussion based on speculation

**SCHEME 2. Possible Mechanisms of Homocoupling of Arylboronic Acids**



**SCHEME 3**



Although investigation of both stoichiometric and catalytic formation of arylcopper intermediates from arylboronic acids is still in progress in order to develop new synthetic applications, preliminary results have revealed the following potentially important results: First, homocoupling reaction does not interfere with the Suzuki-type cross-coupling reactions under the specified conditions; 4-iodoanisole stayed intact during the homocoupling reaction of **1b** in the presence of $Cu(OAc)_2$ as Cu(II) source and CuOAc (or CuTC) as Cu(I) source both at room temperature and 100 °C. Second, it is possible to cross-couple phenylacetylene **11** and **1b**. Addition of **1b** and $Cu(OAc)_2$ to a solution of **11** and NaH in dry THF (MS 4A°) at room temperature afforded a mixture of **12** and **2b** (GC−MS) in an unoptimized reaction as shown in Scheme 3.

In conclusion, we showed that certain copper species are able to mediate the homocoupling of arylboronic acids in DMF with moderate to very good yields. This method allows the use of a cheap Cu(I) or Cu(II) species for this popular transformation and offers very good results for certain substrates. Reaction is sensitive to steric crowding around the reacting center, and disubstitution completely hinders the dimerization. Additionally, a variety of

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(19) Oxidation of DMF by Cu(II) was reported: Dhar, S. K.; Abdelaziz, J.; Cozzi, P.; Jasien, P.; Mason, C.; Zalenas, R. *J. Chem. Soc., Chem. Commun.* **1984**, 8.

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(22) Lindley, J. *Tetrahedron* **1984**, *40*, 1433 and references therein.

acetate ligands can be bound on the metal surface for a specific reason, such as salts of amino acids as exemplified above. Moreover, it is possible to run the reaction catalytically under an oxygen atmosphere without a significant loss of yields. A variety of Cu(I) compounds have activity and can be potentially useful in other reactions based on copper and arylboronic acids; excellent examples have already been reported.[14,15] Development of new synthetic applications through the generation of arylcopper intermediates in this context are under investigation.[23]

## Experimental Section

**General Methods.** All arylboronic acids **1a**−**y** and copper salts (CuTC was prepared as reported previously)[14b] were commercially available and used as obtained. Compounds **2a**,**b**,**f**,**g**,**i**,**k**,**s**,[24a] **2c**,[24b] **2d**,[24c] **2e**,**j**,[24d] **2l**,**n**),[24e] **2m**,[24f] **2o**,[24g] **2t**,[24h] and **2v**,**y**[7] are known. Although no special precautions were taken during weighing and handling of chemicals, DMF was distilled under vacuum and stored over 4A° molecular sieves. Because most Cu(I) salts are relatively air-sensitive, they were stored under a blanket of argon and handled quickly.

**Typical Procedure for Symmetrical Biaryls by Stoichiometric Cu(OAc)$_2$.** To a mixture of Cu(OAc)$_2$ (45 mg, 0.25 mmol) in 1 mL DMF was added 4-bromophenylboronic acid (100 mg, 0.5 mmol), and the resulting mixture was stirred at 100 °C for 1 h. After completion of the reaction (formation of the products was monitored by TLC and GC−MS), the mixture was filtered through a pad of silica using hexane or petroleum ether as eluent. Concentration under reduced pressure furnished 4,4′-dibromobiphenyl (**2b**) (73 mg, 93%) confirmed by NMR and GC−MS.

**Typical Procedure for Symmetrical Biaryls by Catalytic Cu(OAc)$_2$.** A flask was charged with powdered 4A° molecular sieves and heated under vacuum for 2−3 h. After the flask cooled to room temperature under argon, Cu(OAc)$_2$ (9 mg, 0.05 mmol) and 1 mL DMF were added followed by 4-bromophenylboronic acid (100 mg, 0.5 mmol). The resulting mixture was stirred at 100 °C under an oxygen atmosphere for 3 h. After that period, the mixture was worked up as for the stoichiometric reaction to obtain 4,4′-dibromobiphenyl **2b** (67 mg, 86%).

**4,4′-Bis(trifluoromethoxy)biphenyl (2h).** Yield 93%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (4H, d, $J = 8.4$ Hz), 7.46 (4H, d, $J = 8.4$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 120.8 (q, $J = 256$ Hz), 121.6, 128.7, 138.9, 149.3. Anal. Calcd for C$_{14}$H$_8$F$_6$O$_2$: C, 52.19; H, 2.50. Found: C, 52.31; H, 2.76.

**3,3′-Diformyl-2,2′-bithienyl (2u).** Yield 35%, bright yellow solid; mp 131−131.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (2H, d, $J = 4.8$ Hz), 7.75 (2H, $J = 4.8$ Hz), 9.74 (2H, s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 127.4, 132.3, 141.2, 141.9, 183.0. Anal. Calcd for C$_{10}$H$_6$O$_2$S$_2$: C, 54.03; H, 2.72. Found: C, 54.15; H, 2.91.

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[23] It is worth mentioning that Mn(OAc)$_3$ mediates the homocoupling of arylboronic acids albeit in lower yields; this is thought to be an indication of formation of arylmanganese intermediates in a manner similar that of to arylcopper compounds.

[24] (a) These compounds are commercially available. (b) Dougherty, T. K.; Lau, K. S. Y.; Hedberg, F. L. *J. Org. Chem*. **1983**, *48*, 5273. (c) Tarpley, A. R.; Goldstein, J. H. *J. Phys. Chem*. **1971**, *75*, 421. (d) Courtois, V.; Barhdadi, R.; Troupel, M.; Périchon, J. *Tetrahedron* **1997**, *53*, 11569. (e) Lourak, M.; Vanderesse, R.; Fort, Y.; Caubére, P. *J. Org. Chem*. **1989**, *54*, 4840. (f) Ligtenbarg, A. G. J.; van den Beuken, E. K.; Meetsma, A.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *J. Chem. Soc., Dalton Trans.* **1998**, 263. (g) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227. (h) Mitsumori, T.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 2467.