Received: 30 May 2013,

Revised: 6 November 2013,

#### (wileyonlinelibrary.com) DOI: 10.1002/poc.3262

# Gas-phase studies of copper catalyzed aerobic cross coupling of thiol esters and arylboronic acids

Alexandra Tsybizova<sup>a</sup>, Detlef Schröder<sup>b</sup>, Jana Roithová<sup>a</sup>\*, Adam Henke<sup>c</sup> and Jiři Šrogl<sup>b</sup>

Electrospray ionization/mass spectrometry (ESI-MS) is used to monitor a Cu-catalyzed aerobic cross-coupling reaction between thiol esters and arylboronic acids. The ESI spectra show the formation of Cu-complexes with the starting thiol ester 1 and the coupling product. The formation of an ionic complex at m/z 305 is observed, most likely occurring upon the elimination of a mixed anhydride from [(1)CuOAc]<sup>+</sup>. An online monitoring of the reaction using ESI-MS was carried out allowing calculation of rate constants and thermodynamic parameters ( $\Delta H^{+}$ ,  $\Delta S^{+}$ , and  $\Delta G^{+}$ ) for the title reaction.

Keywords: boronic acids; catalysis; copper; cross coupling; electrospray ionization/mass spectrometry; kinetic studies; rate constants; thiol esters; thermodynamic parameters

### INTRODUCTION

Over the past few decades, an extensive development of metal catalyzed cross-coupling reactions has been carried out.<sup>[1–16]</sup> Cross-coupling reactions have been proved to be a powerful synthetic method in contemporary organic synthesis allowing the formation of different kinds of carbon–carbon or carbon–heteroatom bonds under the catalysis of different metal complexes or organometallic compounds.<sup>[17]</sup> Cross-coupling reactions have been successfully applied in laboratory preparations of a broad variety of organic compounds as well as in the large-scale syntheses.<sup>[18]</sup> However, despite the wide range of experiments carried out, the understanding of the processes occurring in the reaction mixture is still limited. It is highly desirable for our knowledge as well as for possible improvements of the existing procedures to understand the reaction mechanisms in detail. Several successful examples of such investigations have been reported.<sup>[19–30]</sup>

One of the possible experimental approaches for the investigation of reaction mechanisms is based on mass spectrometry (MS). Nowadays, the combination of electrospray ionization (ESI) and mass spectrometry is a highly preferable method for the analysis of different kinds of solutions, because the method is accurate, sensitive, and soft (i.e. the ionization process is believed to impose only a small energy to the species transferred to the gas phase, and therefore the gaseous ions often reflect the species contained in the sprayed solution). Moreover, ESI-MS appears to be the most convenient method for a successful investigation of organometallic compounds in the gas phase and, in numerous cases, was successfully applied for studying organometallic reaction mechanisms.<sup>[31–42]</sup>

Reactions involving boronic acids play an important role as these acids are stable, commercially available reagents with relatively low toxicity.<sup>[43,44]</sup> Their application is most popular in Suzuki couplings, where palladium complexes are applied as catalysts.<sup>[3]</sup> There are, however, also alternative reaction procedures, where expensive palladium complexes are replaced by copper catalysts. For example, Liebeskind *et al.* discovered copper catalyzed couplings of thiol esters and boronic acids under aerobic conditions (Scheme 1).<sup>[45,46]</sup> The reaction offers a convenient reaction pathway to directly yield nonsymmetrical ketones.

Here, we report a mass spectrometric study of the coppermediated coupling between thiol esters and boronic acids, including an "online" monitoring via ESI-MS. To this end, a specific reaction has been selected (Scheme 2).

### **EXPERIMENTAL SECTION**

The general procedure for the coupling of thiol esters with boronic acids was described elsewhere.<sup>[46]</sup> The reaction mixtures in the monitoring experiments were prepared by mixing the thiol ester **1** (0.0016 g, 4.64·10<sup>-6</sup> mol, 1.0 equiv) in a 10 mL vial equipped with a magnetic stirrer bar with a catalytic amount (5 mol %) of copper acetate and 4-tolylboronic acid (0.0014 g,  $10.6 \cdot 10^{-6}$  mol, 2.5 equiv). Then, 2 mL of dry dimethylformamide was added, and the mixture was stirred at a given temperature. After a given time from the beginning of the reaction, an aliquot (~20 µL) of the reaction solution was taken, dissolved in 2 mL of MeOH, and sprayed into the mass spectrometer. For the experiments in methanol only, all three components were mixed in a 1:1:1 ratio with the concentration of  $10^{-3}$  M. The catalyst and HPLC-grade solvents were purchased from Sigma-Aldrich.

The reaction mixtures were studied using a Finnigan LCQ Classic iontrap mass spectrometer equipped with an ESI ion source. The operation conditions were the following (if not mentioned otherwise): spray voltage of 4,5 kV; capillary voltage of 0 kV, capillary temperature of  $150 \,^{\circ}$ C; tube lens offset of 0 kV, auxiliary gas flow rate of 50 arbitrary units, sheath gas flow rate of 30 arbitrary units. The samples were introduced at a flow rate of 0.7 mL/h. Mass spectra were recorded from *m/z* 50 to 1500. In order to support the assignments made, also experiments with a methyl-

 b D. Schröder, J. Šrogl Institute of Organic Chemistry and Biochemistry, Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic

c A. Henke

<sup>\*</sup> Correspondence to: J. Roithová, Department of Organic Chemistry, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic. E-mail: roithova@natur.cuni.cz

A. Tsybizova, J. Roithová
Department of Organic Chemistry, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic

Department of Chemistry, Columbia University in the City of New York, Broadway 3000, 10027 New York, USA.



Scheme 1. Aerobic coupling of thiol esters and boronic acids



**Scheme 2**. The reaction investigated in the electrospray ionization/mass spectrometry (ESI-MS) study

derivative of the corresponding thiol ester were carried out (see the supporting information, Figure S1), and the masses of the complexes were further determined on a SYNAPT G2 mass spectrometer (Waters, Manchester, UK) with a standard mass resolution of  $m/\Delta m \approx 20000$  (Table S1).<sup>[47]</sup>

The ion trap with the helium pressure on the order of  $\sim 10^{-3}$  mbar enables us to perform the variety of MS<sup>n</sup> experiments, including the determination of the appearance energies (AE) of the fragments of mass-selected ions. For an excitation period of 20 ms and a trapping parameter of  $q_z = 0.25$ , recently, an empirical calibration scheme was introduced that allows conversion of the experimental AEs of the fragmentations to an absolute energy scale.<sup>[48,49]</sup>

### **RESULTS AND DISCUSSION**

The strategy of our investigation consisted in studying the reaction in steps, starting from less to more complicated systems. Accordingly, we began with analyzing dilute solutions of the starting materials (corresponding thiol ester (1) and 4-tolylboronic acid (2)) in pure methanol. The positive ESI mass spectrum of the thiol ester (Fig. 1) shows strong signals of sodiated mono- and dimer complexes of the ester (m/z 370 and 717, respectively) and doubly charged calcium, magnesium and iron complexes (m/z 540.7, 532.6, 548.5 respectively). The collision-induced dissociation (CID) spectra of the peaks at m/z 717 and 540.7 have been measured and are shown in Figures S2 and S3.

The negative ESI-MS spectrum of the boronic acid shows the occurrence of the formation of boronic esters by condensation of 4-tolylboronic acid with methanol (Fig. 2).<sup>[50]</sup> The formation mechanisms of some of the observed ions are reported at the Scheme S1. In addition, we can also see a condensation of the boronic acid and the esters to form polyborates<sup>[50,51]</sup> (note that all of the masses are given for the most abundant isotope <sup>11</sup>B). We note in passing that we have also examined positive ESI-MS spectrum of the same solution, but only weak signals of impurities and their methanol complexes were detected.

In the next step, the mixture of thiol ester (1) with Cu(OAc)<sub>2</sub> ( $10^{-3}$  M) in methanol was analyzed. The spectrum shows formations of copper complexes with the starting ester at m/z 410, 469, and 757, which correspond to [(1)Cu]<sup>+</sup>, [(1)CuOAc]<sup>+</sup>, and [(1)<sub>2</sub>Cu]<sup>+</sup>, respectively (Fig. 3). We have probed the unimolecular reactivity of the [(1)CuOAc]<sup>+</sup> (m/z 469) complex in the CID experiment (Fig. 4). The activation of [(1)CuOAc]<sup>+</sup> leads to the elimination of Ph-CO-O-CO-CH<sub>3</sub>; hence, the mixed anhydride of benzoic

and acetic acids is formed. The energy resolved CID experiment allowed us to determine the appearance energy for the elimination of benzoylacetate from  $[(1)CuOAc]^+$ , which amounts to 121 kJ/mol (Fig. 4). The remaining ionic complex with m/z 305 (assigned as  $[(int)Cu]^+$ , where "int" stands for "intermediate") can be also observed in the source spectra (cf. Fig. 3). Note that all of the masses are given for the <sup>63</sup>Cu isotope.

The composition of the ions with *m/z* 305 was checked by a comparison of the experimental and simulated isotope patterns (Figure S4), and their structure was probed in the CID experiment (Figure S5). The most pronounced fragmentation corresponds to the elimination of the CO molecule. Accordingly, we expect that this intermediate has a cyclic structure, in which copper is bound to the sulfur atom and coordinated to the nitrogen atom of the amide function. This structure allows for the ring contraction associated with the CO loss (Scheme 3).

We have further investigated whether the ion with m/z 305 can be also formed from other detected complexes. As the intermediate complex contains copper(II), it is not likely that it could be formed in the fragmentations of copper(I) complexes. Accordingly, CID of [(1)Cu]<sup>+</sup> (m/z 410) does not yield this intermediate, but rather undergoes a rearrangement and eliminates



**Figure 1**. Positive electrospray ionization (ESI) mass spectrum of a diluted solution of the thiol ester (1) in MeOH



**Figure 2.** Negative electrospray ionization (ESI) mass spectrum of diluted solution of 4-tolylboronic acid in MeOH. Note that the peaks at m/z 221 and 299 do not have an isotope pattern associated with boron and therefore correspond to impurities and are not assigned



Figure 3. The electrospray ionization (ESI) mass spectrum of the mixture of thiol ester (1) and Cu(OAc)<sub>2</sub> in MeOH



**Figure 4**. The collision-induced dissociation (CID) spectrum and the breakdown curve of mass selected  $[(1)CuOAc]^+$ . Note that 'Bn' denotes the benzyl group



Scheme 3. Fragmentation of m/z 305 via collision-induced dissociation (CID)



**Figure 5**. The electrospray ionization (ESI) mass spectrum of the mixture of thiol ester (1), 4-tolylboronic acid and  $Cu(OAc)_2$  in MeOH. The spectrum is taken at room temperature and 1 h after mixing all reactants together. Note that this reaction mixture is in methanol only, and the results are thus different from the results in Table 1

benzoic acid (Figure S6). The complex with two molecules of 1,  $[(1)_2Cu]^+$  (*m/z* 757), upon collisional activation fragments to yield  $[(1)Cu]^+$  (Figure S7). Hence, the  $[(int)Cu]^+$  complex is formed from the initial reactant complex  $[(1)CuOAc]^+$ , and the reaction is not associated with a change of the oxidation state of copper, and the fragmentation most probably corresponds to the elimination of the mixed anhydride as suggested earlier. Copper(I) complexes are most likely formed during the electrospray process<sup>[52,53]</sup> and do not have a relevance for the reaction studied here.

Finally, the mixture of all three components of the reaction, thiol ester (1), boronic acid (2), and  $Cu(OAc)_2$ , was analyzed (Fig. 5). In addition to the formation of sodium and copper- complexes of the starting compound, we have observed also the formation of complexes with the coupling product (4) at m/z 356, 396, 455, 703, 729, and 743, which correspond to the formation

of the product complexes with sodium or copper ions (the CID spectra of the ions at m/z 396 and 455 are shown in Figures S8 and S9). Neither sodium nor copper complexes of the ketone product were observed in the spectrum. Although ketones usually form easily complexes with both metals, the absence of the ketone complexes here can be explained by the presence of much better multidentate "ligands" **1** and **4**.

Even though we tried to detect some copper complexes containing the original boronic acid, we have never succeeded. Probably, such intermediates are highly reactive and rapidly yield the product complexes. We also cannot reproducibly detect ions, which would be a result of transmetalation; that is, the exchange of acetate in the ions

with m/z 469 by the tol-4-yl group (m/z 501). Nevertheless, the complex with m/z 305 (identified earlier as a result of the elimination of the mixed anhydride from the reactant complex [(1) CuOAc]<sup>+</sup>) can in fact also represent an intermediate after the elimination of the ketone product from the reactant, where the acetate group was previously exchanged by phenylborate (alternatively – acetate could be exchanged by transmetallation by phenyl). Hence, the ions with m/z 305 can thus also represent

the ions, which undergo a subsequent reaction with phenylborate to yield the second product (cf. Scheme 1). As the observed elimination of benzoylacetate from [(1)CuOAc]<sup>+</sup> is not detected during the reaction in bulk, it means that the concurrent steps in the reaction cycle leading to the ketone formation are most probably energetically more feasible. The determined appearance energy for the elimination of benzoylacetate from [(1)CuOAc]<sup>+</sup> (121 kJ/mol) thus represents an upper limit for the energy barriers in the whole catalytic cycle.

We note in passing that during our experiments, we have never observed complexes of copper containing oxygen atoms. In this respect, it has been suggested that the reaction may proceed via copper clusters with the [Cu<sub>2</sub>  $(\mu$ - $\eta^2$ : $\eta^2$ -O<sub>2</sub>]<sup>2+</sup> or [Cu<sub>2</sub>( $\mu$ -O<sub>2</sub>]<sup>2+</sup> core.<sup>[46,54]</sup> We have neither observed binuclear doubly charged copper complexes nor complexes

containing oxygen atoms under the conditions of the present experiments. We, therefore, believe that this mechanism is not operative if  $Cu(OAc)_2$  is used as a catalyst, and reaction is performed in methanol.

In addition to the results discussed earlier, we have carried out a series of experiments with thiol (5), in order to simulate the formation of the intermediate complex at m/z 305 and figure out, whether similar reaction conditions would lead to the formation of the coupling product (4), as it is shown in Scheme 4.

Although the ESI-MS spectrum shows that the product (4) is formed (Fig. 6), we have observed also oxidation of the thiol **5** 



Scheme 4. Reaction of thiol (5) with tolylboronic acid investigated here



**Figure 6**. The electrospray ionization (ESI) mass spectrum of the mixture of thiol (5), 4-tolylboronic acid and  $Cu(OAc)_2$  in MeOH, and a putative structure of the complex at m/z 304

leading to (**5**-H<sub>2</sub>). We did not observe any formation of the ion at m/z 305. Instead, we can see the complex between the oxidized thiol and copper(I), that is, [(**5** $-H<sub>2</sub>)Cu]^+$  at m/z 304. (The CID spectrum of the ion at m/z 304 is shown at the Figure S10)

## AN "ONLINE" MONITORING OF THE COUPLING REACTION

In order to study the reaction deeper, we have decided to carry out its monitoring using ESI-MS. A solution of thiol ester **1** with 2.5 equiv of 4-tolylboronic acid and 5 mol % of copper(II) acetate in *N*,*N*-dimethylformamide was stirred at 50 °C (details can be

found in the Experimental Section). Aliquots of the reaction mixture were taken after given times, dissolved in methanol, and the corresponding ESI-MS spectra were recorded (Figures S11 and S12). Table 1 shows some of the most abundant ions observed in this experiment. It can be seen that, already after 15 min from the start of the reaction, a small amount of the product complex was detected. Because of the dominance of the sodium complexes in this experiment, the detection of the copper complexes was very limited.

As previously mentioned, we did not observe any ions containing a boron atom during the monitoring of the reaction. Most probably, the boron-containing intermediates are low abundant and cannot be detected because of the preference of highly abundant sodium complexes, or they are formed strictly in a neutral form, and hence, escape the MS detection.

The same monitoring was repeated under different temperatures, and several kinetic curves were obtained (see the Supporting Information, Figures S13 and Table S2).

From these kinetic curves, rate constants of the reaction can be obtained using Eqn (1):

$$\frac{dI}{dt} = k(T)[1]^m [2]^n \tag{1}$$

The relationship between ln (l) (where I represents the sum of the abundances of  $[(1)Na]^+$ ,  $[(1)(4)Na]^+$ , and  $[(1)_2Na]^+$  divided by

	m/z					
	356	370	396	689	703	717
Time, h	[( <b>4</b> )Na] <sup>+</sup>	[( <b>1</b> )Na] <sup>+</sup>	[( <b>4</b> )Cu] <sup>+</sup>	[( <b>4</b> ) <sub>2</sub> Na] <sup>+</sup>	[( <b>1</b> )( <b>4</b> )Na] <sup>+</sup>	$[(1)_2 Na]^+$
0.25	0.3	19.6	0	0.6	10.5	69
0.5	0.6	14.3	0.4	1.4	13.1	70.2
1	0.7	10.3	0.3	2.6	21.4	64.7
2	0.9	7.9	0.4	7.8	31.3	51.7
3.25	1.7	7.7	1.1	11.3	38.2	40
5.33	2	5	0	21.2	43.9	27.9
6.67	3.3	5.7	0	26.6	42.3	22.1
8.2	3.7	5.6	0	32.2	42	16.5
23	4.7	0.7	0	71.9	20.8	1.9
ESI, electrospra	ay ionization; DMF,	dimethylformamide	2.			

**Table 1.** Relative intensities of the major complexes observed in the ESI mass spectra sampled from the reaction mixture in DMF (50 °C) diluted by methanol



**Figure 7**. (a) Logarithmic plot of the abundance of the reactant complexes in dependence on the reaction time at different temperatures; (b) Arrhenius (1) and Eyring (2) plots for thiol ester 1 coupling with 4-tolylboronic acid. The resulting values were determined from two independent measurement (I represents the sum of the abundances of  $[(1)Na]^+$ ,  $[(1)(4)Na]^+$ , and  $[(1)_2Na]^+$  divided by the sum of the abundances of all complexes in Table 1)

The temperature dependency of the rate constants can be further used for derivation of the activation energy ( $E_a$ ) according to the Arrhenius Eqn (2) or activation Gibbs energy according to the Eyring Eqn (3).

$$\ln(k) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln(A)$$
 (2)

$$\ln \frac{k}{T} = \frac{-\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{n} \qquad (3)$$
$$+ \frac{\Delta S^{\ddagger}}{R}, \Delta G^{\ddagger}(T)$$
$$= \Delta H^{\ddagger} - \frac{T \cdot \Delta S^{\ddagger}}{1000}$$

where k is the rate constant, A is the frequency factor, R is the universal gas constant, T is the absolute temperature,  $E_a$  is the activation energy,  $k_B$  is the Boltzmann's constant, and h is the Planck's constant.



Scheme 5. Proposed illustration of the processes occurring in liquid and gas phase

the sum of the abundances of all complexes in Table 1) and the reaction time is linear (Fig. 7, note that experiments at 60 and 80  $^{\circ}$ C showed a linear dependence only during the first few hours), which suggests that the reaction proceeds (under the given conditions) under pseudo-first order kinetics. The data demonstrate that with the increasing temperature, the rate of the reaction increases. The evaluation of the results according to the Arrhenius equation leads to a value of  $E_a = 81 \pm 5 \text{ kJ mol}^{-1}$ . The alternative Eyring equation gives the activation enthalpy of  $76 \pm 5 \text{ kJ mol}^{-1}$  and the activation entropy of  $-100 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ , which leads to a value of  $103 \pm 5 \text{ kJ mol}^{-1}$  for the activation Gibbs energy at 298 K.

### CONCLUSION

Using the mass spectrometric approach, we have followed the kinetics of the title reaction. We were able to determine the concentration changes of reactants and the products. The observation of reaction intermediates was not entirely successful probably due to a high reactivity of either the copper-boronate complexes or complexes, which can be formed by a transmetallation step (Scheme 5). Both of the two possible reaction pathways lead to the reaction intermediate [(**int**)Cu]<sup>+</sup>. We observe this intermediate, however, probably as a result of a fragmentation of the reactant complex [(1)CuOAc]<sup>+</sup>. We have determined the activation barrier for this fragmentation as 121 kJ/mol. As this reaction channel is not observed in the reaction in bulk, this energy value represents an upper limit for the real activation energy of the reaction.

Although the copper complexes were little abundant, we have profited from the large abundance of the sodium complexes with the reagent and the product, which allowed us to follow the kinetics of the reaction using ESI-MS. Obtained rate constants enabled us to determine the activation energy for the reaction according to the Arrhenius equation as  $81 \pm 5 \text{ kJ mol}^{-1}$ . Similarly, we were also able to estimate the activation Gibbs energy at 298 K as  $103 \pm 5 \text{ kJ mol}^{-1}$  in that the activation enthalpy represents  $76 \pm 5 \text{ kJ mol}^{-1}$  and the activation entropy  $-100 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ .

### Acknowledgements

This work was supported by the Academy of Sciences of the Czech Republic (RVO 61388963), the European Research Council (AdG HORIZOMS), and the Grant Agency of the Czech Republic (207/11/0338 a 207/12/0846).

### REFERENCES

- X.-F. Wu, P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* 2010, 49, 9047–9050.
- [2] E. Negishi, Angew. Chem. Int. Ed. 2011, 50, 6738-6764.
- [3] A. Suzuki, Angew. Chem. Int. Ed. **2011**, 50, 6722–6737.
- [4] K. C. Nicolaou, P. G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 2005, 44, 4442–4489.
- [5] B. E. Kahn, R. D. Rieke, Chem. Rev. 1988, 88, 733-745.
- [6] C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, Angew. Chem. Int. Ed. 2012, 51, 5062–5085.
- [7] H. Doucet, J.-C. Hierso, Angew. Chem. Int. Ed. 2007, 46, 834–781.
- [8] E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, Angew. Chem. Int. Ed.
- **2007**, *46*, 2768–2813. [9] R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417–1792.
- [10] A. F. Littke, G. C. Fu, Angew. Chem. Int. Ed. **2002**, 41, 4176–4211.
- [10] A. F. Littke, G. C. Fu, Angew. Chem. Int. Ed. **2002**, 41, 4170-
- [11] G. Cahiez, A. Moyeux, *Chem. Rev.* **2010**, *110*, 1435–1462.
- [12] A. C. Frisch, M. Beller, Angew. Chem. Int. Ed. **2005**, 44, 674–688.
- [13] S. Chemler, D. Trauner, S. Danishefsky, Angew. Chem. Int. Ed. 2001, 40, 4544–4568.
- [14] G. Evano, N. Blanchard, M. Toumi, Chem. Rev. 2008, 108, 3054–3131.
- [15] B. M. Rosen, K. W. Quasdorf, D. a Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg, V. Percec, *Chem. Rev.* **2011**, *111*, 1346–1416.
- [16] I. P. Beletskaya, A. V. Cheprakov, Organometallics 2012, 31, 7753–7808.
- [17] I. J. S. Fairlamb, Annu. Rep. Prog. Chem., Sect. B 2003, 99, 104–137.
- [18] A. de Meijere, F. Diederich, Eds., Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2004.
- [19] A. E. King, L. M. Huffman, A. Casitas, M. Costas, X. Ribas, S. S. Stahl, J. Am. Chem. Soc. 2010, 132, 12068–12073.

Journal of Physical Organic Chemistry

- [20] A. E. King, T. C. Brunold, S. S. Stahl, J. Am. Chem. Soc. 2009, 131, 5044–5045.
- [21] A. E. King, B. L. Ryland, T. C. Brunold, S. S. Stahl, Organometallics 2012, 31, 7948–7957.
- [22] S. I. Gorelsky, D. Lapointe, K. Fagnou, J. Org. Chem. 2012, 77, 658–668.
- [23] G. B. Smith, G. C. Dezeny, D. L. Hughes, A. O. King, T. R. Verhoeven, J. Org. Chem. **1994**, 59, 8151–8156.
- [24] P. Espinet, A. M. Echavarren, Angew. Chem. Int. Ed. 2004, 43, 4704–4734.
- [25] Z. Li, Y.-Y. Jiang, Y. Fu, Chem. Eur. J. 2012, 18, 4345–4357.
- [26] S. E. Denmark, R. F. Sweis, J. Am. Chem. Soc. 2004, 126, 4876–4882.
- [27] X. He, S. Zhang, Y. Guo, H. Wang, G. Lin, Organometallics 2012, 31, 2945–2948.
- [28] J. Zhang, C. M. Medley, J. a. Krause, H. Guan, Organometallics 2010, 29, 6393–6401.
- [29] D. Evrard, D. Lucas, Y. Mugnier, P. Meunier, J.-C. Hierso, Organometallics 2008, 27, 2643–2653.
- [30] M. Kalek, J. Stawinski, Organometallics 2007, 26, 5840-5847.
- [31] L. Santos, *Reactive Intermediates*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2009**.
- [32] D. Agrawal, D. Schröder, C. M. Frech, Organometallics 2011, 30, 3579–3587.
- [33] J. Srogl, J. Hývl, A. Révész, D. Schröder, Chem. Commun. 2009, 3463–3465.
- [34] N. Taccardi, R. Paolillo, V. Gallo, P. Mastrorilli, C. F. Nobile, M. Räisänen, T. Repo, *Eur. J. Inorg. Chem.* **2007**, 2007, 4645–4652.
- [35] K. L. Vikse, M. a Henderson, A. G. Oliver, J. S. McIndoe, Chem. Commun. 2010, 46, 7412–7414.
- [36] P. S. D. Robinson, G. N. Khairallah, G. da Silva, H. Lioe, R. a. J. O'Hair, Angew. Chem. 2012, 124, 3878–3883.
- [37] L. O. Sraj, G. N. Khairallah, G. da Silva, R. A. J. O'Hair, Organometallics 2012, 31, 1801–1807.
- [38] V. P. Ananikov, J. V. Ivanova, L. L. Khemchyan, I. P. Beletskaya, *Eur. J. Org. Chem.* **2012**, *2012*, 3830–3840.
- [39] B. Chiavarino, R. Cipollini, M. E. Crestoni, S. Fornarini, F. Lanucara, A. Lapi, J. Am. Chem. Soc. 2008, 130, 3208–3217.
- [40] R. S. Sanchez, F. a Zhuravlev, J. Am. Chem. Soc. 2007, 129, 5824–5825.
- [41] J. Roithová, D. Schröder, Chem. Eur. J. 2008, 14, 2180–2188.
- [42] J. Roithová, Š. Janková, L. Jašíková, J. Váňa, S. Hybelbauerová, Angew. Chem. Int. Ed. 2012, 51, 8378–8382.
- [43] A. Henke, J. Srogl, Chem. Commun. **2011**, 47, 4282–4284.
- [44] H. Prokopcová, C. O. Kappe, Angew. Chem. Int. Ed. 2008, 47, 3674–3676.
- [45] L. S. Liebeskind, J. Srogl, Org. Lett. 2002, 4, 979–981.
- [46] J. M. Villalobos, J. Srogl, L. S. Liebeskind, J. Am. Chem. Soc. 2007, 129, 15734–15735.
- [47] A. B. Kanu, P. Dwivedi, M. Tam, L. Matz, H. H. Hill, J. Mass Spectrom. 2008, 43, 1–22.
- [48] A. Révész, P. Milko, J. Zabka, D. Schröder, J. Roithová, J. Mass Spectrom. 2010, 45, 1246–1252.
- [49] E.-L. Zins, C. Pepe, D. Schröder, J. Mass Spectrom. 2010, 45, 740-749.
- [50] D. G. Hall, Boronic Acids, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2005.
- [51] A. L. Korich, P. M. Iovine, Dalton Trans. 2010, 39, 1423-31.
- [52] A. Tintaru, L. Charles, P. Milko, J. Roithová, D. Schröder, Journal of Physical Organic Chemistry 2009, 22, 229–233.
- [53] P. Milko, J. Roithová, N. Tsierkezos, D. Schröder, J. Am. Chem. Soc. 2008, 130, 7186–7187.
- [54] A. Varela-Álvarez, L. S. Liebeskind, D. G. Musaev, Organometallics 2012, 31, 7958–7968.

### SUPPORTING INFORMATION

Additional supporting information may be found in the online version at the publisher's website.