

# Cationic Tungsten-Oxo-Alkylidene-N-Heterocyclic Carbene Complexes: Highly Active Olefin Metathesis Catalysts

Roman Schowner,<sup>§</sup> Wolfgang Frey,<sup>‡</sup> and Michael R. Buchmeiser<sup>\*,§</sup>

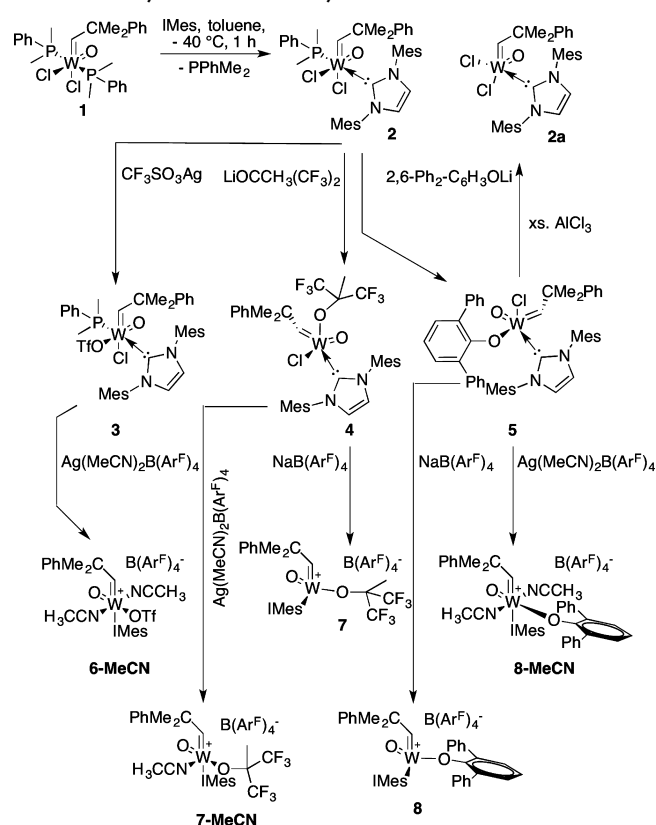
<sup>§</sup>Institute of Polymer Chemistry and <sup>‡</sup>Institute of Organic Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

**S** Supporting Information

**ABSTRACT:** The synthesis, structure, and olefin metathesis activity of the first neutral and cationic W-oxo-alkylidene-N-heterocyclic carbene (NHC) catalysts are reported. Neutral W-oxo-alkylidene-NHC catalysts can be prepared in up to 90% isolated yield. Depending on the ligands used, they possess either an octahedral ( $O_h$ ) or trigonal bipyramidal ligand sphere. They can be activated with excess  $AlCl_3$  to form cationic olefin metathesis-active W-complexes; however, these readily convert into neutral chloro-complexes. Well-defined, stable cationic species can be prepared by stoichiometric substitution of one chloro ligand in the parent, neutral W-oxo-alkylidene-NHC complexes with  $Ag(MeCN)_2B(Ar^F)_4$  or  $NaB(Ar^F)_4$ ;  $B(Ar^F)_4 = B(3,5-(CF_3)_2-C_6H_3)_4$ . They are highly active olefin metathesis catalysts, allowing for turnover numbers up to 10,000 in various olefin metathesis reactions including alkenes bearing nitrile, sec-amine, and thioether groups.

Compared to molybdenum or ruthenium alkylidenes, reports on tungsten-oxo-alkylidenes are scarce. They date back to the 1980's when Schrock et al.<sup>1–6</sup> described the first complexes of this kind. Mayer reported on the synthesis of  $W(O)Cl_2(PMe_2Ph)_2(CR_2)$  via reaction of  $W(Cl_2)(PMe_2Ph)_4$  with 2 equiv of an aldehyde or ketone.<sup>7,8</sup> A similar approach to W-oxo-alkylidenes starting from  $W_2(OCH_2-tBu)_6(pyridine)_2$  was used by Chisholm et al.<sup>9</sup> Boncella et al. described the complex  $W(O)Cl(CH-tBu)(Tp')$  ( $Tp'$  = hydrotris(3,5-dimethyl-1-pyrazolyl)borate).<sup>10</sup> Upon activation with  $AlCl_3$ , the precatalyst was active in the ring-opening metathesis polymerization (ROMP) of *cis*-cyclooctene and norborn-2-ene under ambient conditions. After a period in which only scattered reports on W-oxo-alkylidenes appeared,<sup>11–13</sup> the Schrock group<sup>13,14</sup> very recently created metathesis-active catalysts with the aid of pyrrolides and sterically demanding phenoxides, which display high *Z*-selectivity.<sup>15,16</sup> Furthermore, highly active silica-immobilized versions,<sup>17,18</sup> activation with boranes<sup>19</sup> and the use in stereospecific ROMP<sup>20,21</sup> have been reported. In view of the reactivity and, compared to other Mo-imido alkylidenes, high functional group tolerance of NHC-Mo-imidoalkylidene bistriflate complexes,<sup>22</sup> we were interested whether tungsten-oxo-alkylidene-NHC complexes as a novel class of metathesis catalysts could be prepared at all, and if yes, which reactivity in olefin metathesis they would display. Here we report our results.

Scheme 1. Synthesis of Catalysts 2–8

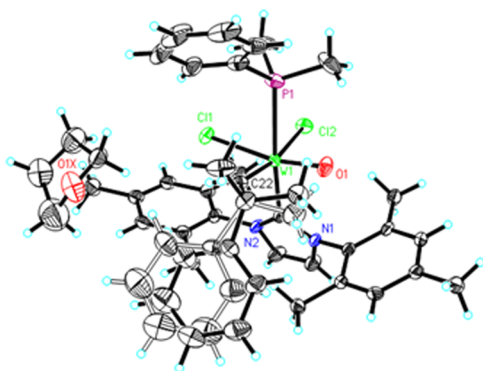


Catalysts 2–8 were prepared as outlined in Scheme 1. Notably, while W-NHC-complexes are known,<sup>23–28</sup> these are the first tungsten-oxo-alkylidene NHC complexes. The dichlorotungsten-oxo-alkylidene-NHC complex 2 was prepared from  $W(O)Cl_2(PMe_2Ph)_2(CHCMe_2Ph)$  (1)<sup>14</sup> via reaction with 1,3-dimesitylimidazol-2-ylidene (IMes). Attempts to remove the labile phosphine with  $CuCl$  resulted in decomposition.

Compound 2 (Figure 1) crystallizes in the triclinic space group,  $\bar{P}1$ ,  $a = 1126.91(6)$  pm,  $b = 1302.24(7)$  pm,  $c = 1656.58(9)$  pm,  $\alpha = 103.326(3)^\circ$ ,  $\beta = 96.653(3)^\circ$ ,  $\gamma = 102.402(3)^\circ$ ,  $Z = 2$ . Relevant bond lengths and angles are summarized in Figure 1.

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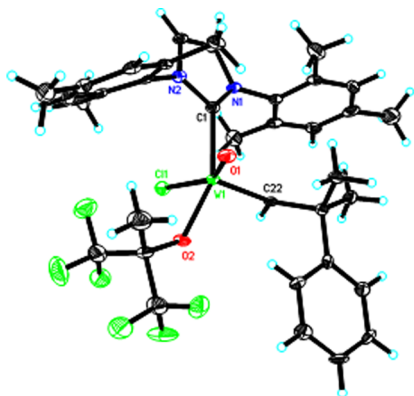
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**Figure 1.** Single crystal X-ray structure of **2**. Relevant bond lengths (pm) and angles (deg): W(1)–O(1) 170.4(3), W(1)–C(22) 194.9(4), W(1)–C(1) 224.6(4), W(1)–Cl(1) 249.43(10), W(1)–Cl(2) 253.87(10), W(1)–P(1) 255.74(11); O(1)–W(1)–C(22) 97.77(17), O(1)–W(1)–C(1) 95.52(14), C(22)–W(1)–C(1) 103.77(15), C(22)–W(1)–Cl(1) 86.52(12), C(1)–W(1)–Cl(1) 94.17(10), O(1)–W(1)–Cl(2) 92.31(12), C(1)–W(1)–Cl(2) 97(10), Cl(1)–W(1)–Cl(2) 82.66(4), O(1)–W(1)–P(1) 89.19(11), C(22)–W(1)–P(1) 95.09(12), Cl(1)–W(1)–P(1) 79.39(4); cosolvent omitted for clarity.

In the solid state, **2** adopts an octahedral ( $O_h$ ) configuration with the phosphine and the NHC forming the apexes. The W-alkylidene bond is 194.9(4 pm) and thus comparable to those in other W-oxo-alkylidenes;<sup>14</sup> the W-NHC bond is 224.6(4) pm. Finally, the W-oxo bond length is 170.4(3) pm). As in solution, the alkylidene is *syn* to the oxo-ligand ( $J_{C-H} = 125.3$  Hz) and is disordered.

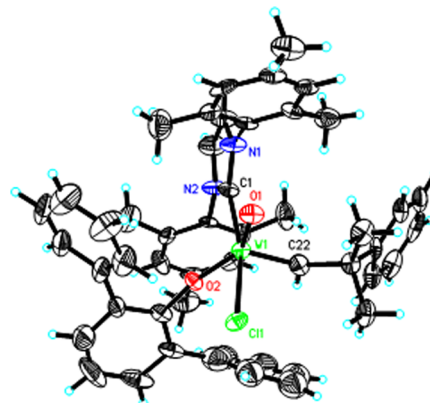
Reaction of **2** with 1 equiv of silver triflate, Li-hexafluoro-*t*-butoxide or Li-2,6-diphenylphenolate resulted in the formation of complexes **3–5** in 81, 82, and 90% isolated yield, respectively. Compound **4** (Figure 2) crystallizes in the orthorhombic space group,  $Pbca$ ,  $a = 1833.11(8)$  pm,  $b = 1573.59(7)$  pm,  $c = 2338.15(10)$  pm,  $\alpha = \beta = \gamma = 90^\circ$ ,  $Z = 8$ . Relevant bond lengths and angles are summarized in Figure 2. In the solid state, **4** adopts a strongly distorted trigonal bipyramidal (TBP) configuration. The W-alkylidene bond



**Figure 2.** Single crystal X-ray structure of **4**. Relevant bond lengths (pm) and angles (deg): W(1)–O(1) 170.4(3), W(1)–C(22) 188.5(4), W(1)–O(2) 201.0(3), W(1)–C(1) 224.6(4), W(1)–Cl(1) 241.45(11); O(1)–W(1)–C(22) 102.15(18), O(1)–W(1)–O(2) 97.60(13), C(22)–W(1)–O(2) 101.21(15), O(1)–W(1)–C(1) 89.30(15), C(22)–W(1)–C(1) 101.41(17), C(22)–W(1)–Cl(1) 105.70(14), O(2)–W(1)–Cl(1) 83.19(9), C(1)–W(1)–Cl(1) 79.20(12).

(188.5(4) pm) is shorter than in **2**, while the W-NHC bond, which is 224.6(4) pm, is exactly the same. The W-oxo bond length (170.4(3) pm) is also identical with the one in **2**. As in **2**, the alkylidene is *syn* to the oxo-ligand ( $J_{C-H} = 121.3$  Hz).

Compound **5** (Figure 3) crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 1175.04(12)$  pm,  $b = 2199.9(2)$  pm,  $c =$



**Figure 3.** Single crystal X-ray structure of **5**. Relevant bond lengths (pm) and angles (deg): W(1)–O(1) 170.2(5), W(1)–C(22) 188.4(9), W(1)–O(2) 194.3(5), W(1)–C(1) 223.1(8), W(1)–Cl(1) 246.05(18); O(1)–W(1)–C(22) 105.6(3), O(1)–W(1)–O(2) 143.9(2), C(22)–W(1)–O(2) 110.4(3), O(1)–W(1)–C(1) 90.1(2), C(22)–W(1)–C(1) 97.1(3), O(2)–W(1)–C(1) 87.9(2), O(1)–W(1)–Cl(1) 90.56(15), C(22)–W(1)–Cl(1) 94.7(2), O(2)–W(1)–Cl(1) 84.14(14).

1667.6(2) pm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 103.918(3)^\circ$ ,  $Z = 4$ . Relevant bond lengths and angles are summarized in Figure 3. In the solid state, **5** also adopts a distorted TBP configuration with the chloro and NHC ligand forming the apexes. Unlike in **4**, where the hexafluoro-*t*-butoxide is the ligand with the most pronounced *trans*-orientation to the NHC ( $154.35^\circ$ ), in **5** it is the chloro-ligand that is *trans* to the NHC ( $167.4^\circ$ ). Such a profound difference must be expected to influence the reactivity of the catalyst, some implications of which are discussed below. The W-alkylidene bond (188.4(9) pm), the W-NHC bond (223.1(8) pm) as well as the W-oxo bond length (170.2(5) pm) are very comparable to the ones in **4**. As in **2** and **4**, the alkylidene is *syn* to the oxo-ligand ( $J_{C-H} = 123.3$  Hz). Generally, the tungsten-oxo-alkylidene NHC complexes **3–5** are all based on two different anionic ligands, i.e., Cl/OTf, Cl/OCCH<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>, and Cl/terphenoxide. Unlike in Ru-alkylidenes but like in other W-oxo-alkylidene complexes,<sup>15,16</sup> no ligand scrambling is observed.<sup>29,30</sup>

$O_h$ -coordinated **3** and TBP-coordinated **4** and **5** are completely inactive in ring-closing metathesis (RCM), enyne metathesis, self-metathesis (SM), cross-metathesis (CM), and homometathesis (HM; for the set of substrates used, see the Supporting Information (SI)). Also, activation by B-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>19,21</sup> does not lead to any olefin metathesis-active species. Clearly, Lewis-acid activation of these complexes through the oxo-ligand is insufficient since the complexes remain  $O_h$  or TBP, i.e., six- or five-coordinated.

However, upon *in situ* activation with 10 equiv of AlCl<sub>3</sub>, which is expected to result in tetrahedral cationic species via removal of one chloro-ligand, catalysts **3–5** become highly active catalysts in a series of olefin metathesis reactions of hydrocarbons but also thioethers, allowing for turnover numbers (TONs) up to 9800, e.g., in the HM of 1-hexene

(Table S1). Notably, these reactions proceed at room temperature. In these reactions, particularly **5**/AlCl<sub>3</sub> shows high activity, which is attributed to the most pronounced *trans*-position of the chloro-ligand with respect to the NHC, at least in the solid state, resulting in a comparably long W–Cl bond (W(1)–Cl(1) 246.05(18), *vide supra*). However, the cationic species formed from **5** is not stable and interconverts into the corresponding tungsten dichloro-complex **2a** within <1 h (Scheme 1). Its structure was confirmed by single crystal X-ray analysis (Figure S28). Similar rearrangement of, e.g., W(O)(AlCl<sub>3</sub>)(OCH<sub>2</sub>-*t*Bu)<sub>2</sub>(CH<sub>2</sub>R)<sub>2</sub> into WX<sub>2</sub>(=CHR)(OCH<sub>2</sub>-*t*Bu)<sub>2</sub> has been observed by the Osborn group.<sup>31</sup>

Accordingly, catalyst **4** quickly reacts with excess AlCl<sub>3</sub> as confirmed by <sup>19</sup>F NMR (Figure S1), where complete removal of the labile hexafluoro-*t*-butoxide group is observed within 3 h. This seems surprising at first, especially since chloro-ligands are present. However, it is the alkoxide and not the chloride in **4** that is fairly *trans* to the NHC and experiences a pronounced *trans* effect (W(1)–O(2) = 201.0(3) pm vs 194.3(5) pm in **5**). Consequently, the hexafluoro-*t*-butoxide group is already labile as such, resulting in its partial dissociation from the metal and formation of a cationic complex ([WOCI(NHC)(CHR)(acetonitrile)<sub>x</sub><sup>+</sup> OR<sup>−</sup>]) in a strongly coordinating solvent such as acetonitrile but not in C<sub>6</sub>D<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub>, even in the absence of AlCl<sub>3</sub> (Figure S1). Also, abstraction of chloride could be kinetically driven, abstraction of alkoxide thermodynamically driven. In line with the formation of the corresponding dichloro-complexes in the presence of AlCl<sub>3</sub> (and in contrast to the stable cationic catalysts **6–8**, *vide infra*), AlCl<sub>3</sub>-activated complexes **4–6** showed virtually no activity in olefin metathesis reactions involving the functional olefins listed in Table 1 and in the SI.

In view of the instability of the cationic species formed *in situ*, it was impossible to correlate catalytic activity with structure. We therefore prepared the stable cationic complexes **6-MeCN**, **7-MeCN**, and **8-MeCN**. Compound **6-MeCN** can be synthesized via the reaction of **3** with 2 equiv of Ag(MeCN)<sub>2</sub>B(Ar<sup>F</sup>)<sub>4</sub>. The second equiv of the silver salt is required to quantitatively remove the phosphane from tungsten; consequently, the use of 1 equiv resulted in a mixture of **6** and starting material. Compounds **7-MeCN** and **8-MeCN** were prepared from **4** and **5** in an analogous manner using 1 equiv of Ag(MeCN)<sub>2</sub>B(Ar<sup>F</sup>)<sub>4</sub>. Notably, these compounds can also be prepared *in situ*. In such an approach, spectroscopic data are consistent with the proposed cationic species, too, and indicate quantitative formation of the desired compounds. According to NMR, the *in situ* generated cationic catalysts **6–8** contain one or two acetonitrile molecules (Scheme 1). These coordinated solvent molecules are probably only weakly bound. Alternatively, solvent-free **7** and **8** can be prepared using NaB(Ar<sup>F</sup>)<sub>4</sub>. In this case the reaction proceeds somewhat slower. Generally, catalysts **7–8** are, similar to the W-oxo-MAP-catalysts,<sup>14–16,20,21</sup> chiral at tungsten; however, in view of the synthetic route, they must be expected to exist in their racemic forms. In contrast to complexes **3–5** they do not require any activating cocatalyst but are active in olefin metathesis as such. Table 1 summarizes the results obtained in various RCM, HM, CM, and SM reactions with *in situ* generated catalysts. Clearly, the cationic W-oxo-alkylidene-NHC complexes **6-MeCN**, **7-MeCN**, and **8-MeCN** represent highly active and, at least to some extent, functional group tolerant catalysts. Thus, silanes, esters, ethers, sulfonamides, nitriles, and, notably, thioethers and *sec*-amines are tolerated. Both in terms of functional group tolerance and

**Table 1.** TONs Obtained in Olefin Metathesis Reactions with the Cationic Catalysts **6–8**<sup>a</sup>

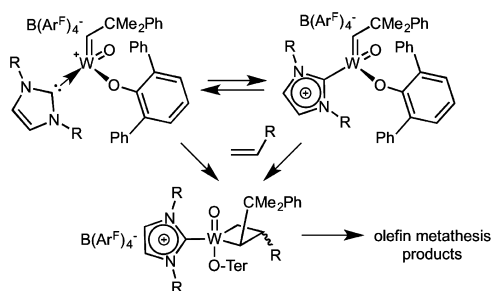
substrate/reaction type	6-MeCN	7-MeCN	8-MeCN
RCM			
diallyldiphenylsilane	4800 <sup>b</sup>	3400 <sup>d</sup>	7600 <sup>d</sup>
<i>N,N</i> -diallyl- <i>p</i> -toluolsulfonamide	1700 <sup>b</sup>	1350	1700 <sup>a</sup>
octa-1,7-diene	970 <sup>b</sup>	710	1500 <sup>a</sup>
diallylmalodinitrile	130 <sup>b</sup>	660	1400 <sup>d</sup>
diallyl ether	0	0	5700 <sup>d</sup>
diallyl thioether	4800 <sup>b</sup>	0	4900 <sup>d</sup>
4,4-dicyano-octa-1,7-diene	470 <sup>b</sup>	430	2600 <sup>d</sup>
diethyl diallyl malonate	1600 <sup>b</sup>	660	3200 <sup>d</sup>
HM, Values in Brackets = E-content			
allylbenzene	200 (55) <sup>b</sup>	480 (60)	635 (85) <sup>d</sup>
1-hexene	2000 (60) <sup>b</sup>	1640 (65)	5400 (85) <sup>d</sup>
1-octene	3300 (60) <sup>b</sup>	1320 (65)	6100 (85) <sup>d</sup>
allyl phenyl sulfide	0	0	300 (>95) <sup>c</sup>
trimethylallylsilane	4100 (55) <sup>b</sup>	1710 (55)	1500 (60)
CM with Allyltrimethylsilane, Values in Brackets = E-content <sup>e</sup>			
hex-5-ene-1-yl acetate	480 (55)	450 (60)	500 (80)
4-octene	500 (50)	490 (65)	500 (80)
<i>N</i> -phenyl-(1-phenyl-but-3-ene-1-yl)amine	200 (60)	0	0
SM, Values in Brackets = E-content			
methyl oleate	1500 (60)	0 <sup>b</sup>	10,000 (70) <sup>c</sup>

<sup>a</sup>Catalyst:substrate = 1:2000, 70 °C. <sup>b</sup>Catalyst:substrate = 1:5000, 70 °C. <sup>c</sup>Catalyst:substrate = 1:5000, 25 °C. <sup>d</sup>Catalyst:substrate = 1:10,000, 25 °C. <sup>e</sup>Catalyst:substrate = 1:20,000, 70 °C. <sup>f</sup>Reactions were run at T = 25 °C in 1,2-dichloroethane for 4 h using a ratio of substrate:catalyst of 2000:1 unless stated otherwise.

TONs, the novel cationic W-oxo-alkylidene-NHC complexes are clearly superior to the few existing cationic Mo-alkylidenes.<sup>32,33</sup> Though they cannot rival our recently reported Mo-imido alkylidene bistriflate-NHC complexes<sup>22</sup> in terms of functional group tolerance, they exceed them by far in olefin metathesis activity. Particularly **8** is a highly active olefin metathesis catalysts of both simple and functional olefins. As can be deduced from Table 1, a TON of 10,000 is reached in the self-metathesis of methyl oleate. In all other RCM, HM, and CM reactions, TONs up to 7600 were achieved.

Common to all cationic catalysts **6–8** discussed here is the presence of a non-innocent imidazolium-based NHC-ligand, which is potentially able to stabilize the positive charge via rearomatization (Scheme 2). Conceptually, one can consider these cationic catalysts as highly delocalized cationic systems, which can easily adopt to the electronic situation of many

**Scheme 2.** Stabilization of the Cationic Metal Center by the NHC Ligand and Tungstacyclobutane Formed via a *trans* Approach of the Olefin to the NHC



different alkenes, which explains the high activity, e.g., of **8** vs both electron-rich and electron-poor alkenes. According to calculations on other metal alkylidenes,<sup>34–36</sup> the substrate (olefin) should then approach the catalyst *trans* to the strongest  $\sigma$ -donor, i.e., the NHC. With a second bulky anionic ligand, high *Z*-selectivity should be achieved. Clearly, neither the triflate, the hexafluoro-*t*-butoxide, nor the 2,6-Ph<sub>2</sub>-phenoxide applied here provide sufficient steric constraints to induce such *Z*-selectivity for which probably larger ligands, e.g., the 2',2'',4',4'',6',6''-hexakis(2-propyl)-2,2'-terphenyl-1-oxo-(HIPTO) ligand,<sup>37,38</sup> maybe in combination with small NHCs, are required. Consequently, with complexes **6–8** predominantly *E*-olefins were formed (55–85%, Table 1). *Z*-selectivity is subject of ongoing research.

In summary, the first neutral and cationic tungsten-oxo-alkylidene NHC-complexes have been reported. They represent a novel class of olefin metathesis catalysts with high catalytic activity and pronounced functional group tolerance. Current studies involve variations in the NHC as well as in the anionic ligands and their influence on olefin metathesis activity, *Z*-selectivity, and functional group tolerance. Furthermore, the proposed structure of the tungstacyclobutane needs to be confirmed. Finally, cationic complexes are excellent candidates for application in supported, biphasic conditions, and further investigations in this respect seem certainly worthwhile.<sup>30,39</sup> These results will be reported in due course.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental details and characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03788.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*michael.buchmeiser@ipoc.uni-stuttgart.de

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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