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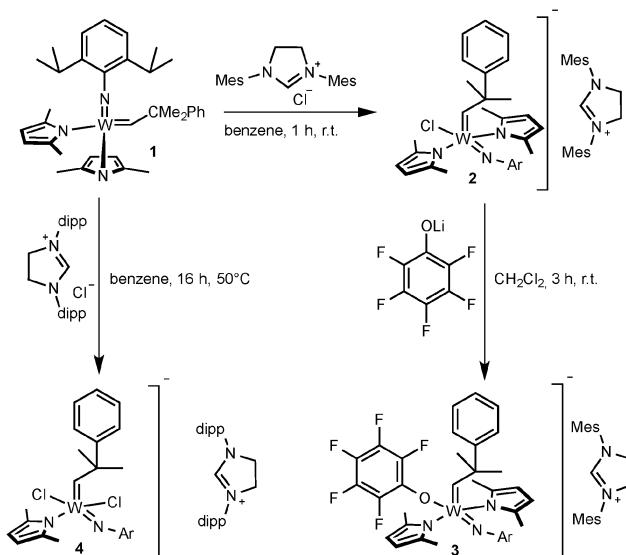
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The synthesis, single crystal X-ray structure and activity in olefin metathesis of novel anionic tungsten imido alkylidene complexes $[1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazolinium}]^+ [W(N-2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{-}(\text{CHCMe}_2\text{Ph})(2,5\text{-Me}_2\text{Pyr})_2\text{Cl}]^-$, $[1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazolinium}]^+ [W(N-2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2,5\text{-Me}_2\text{Pyr})_2(\text{OC}_6\text{F}_5)]^-$, and $[1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolinium}]^+ [W(N-2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{-}(\text{CHCMe}_2\text{Ph})(2,5\text{-Me}_2\text{Pyr})\text{Cl}_2]^-$ are reported. Additionally, the first example of a bis(N-heterocyclic olefinium) alkylidene tungstate, $W(N-2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2\text{-methylene-1,3,4,5-tetramethyl-imidazoline})_2(\text{OTf})_2$, is described, including preparation, crystal structure and catalytic activity.

Recently, our group reported on the synthesis of cationic tungsten oxo alkylidene N-heterocyclic carbene (NHC) and neutral as well as cationic molybdenum imido alkylidene NHC complexes.^{1–4} These complexes show high activity in olefin metathesis reactions. Importantly, their considerable reactivity is paired with substantial tolerance against functional groups, which previously presented a major complication for widespread application of tungsten- and molybdenum-derived metathesis catalysts.⁵ In view of these first promising results, we aimed for an extension of NHC-coordination to tungsten imido alkylidene based systems. Additionally, a newly emerging class of strongly electron-donating compounds, N-heterocyclic olefins (NHOs),⁶ presented itself as a potential alternative to NHCs and was likewise applied in tungsten imido complexes. The compounds resulting from these research efforts will be discussed in the following.



Scheme 1 Synthesis of complexes 2–4.

In search of novel W-imido alkylidene NHC complexes, the bispyrrolide precursor⁷ $[W(N-2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2,5\text{-Me}_2\text{NC}_4\text{H}_2)]$ (1) was reacted with 1,3-(2,4,6-trimethylphenyl)-imidazolin-2-ium chloride (Scheme 1). This procedure was expected to work *via in situ* deprotonation of the NHC precursor by pyrrolide, in analogy to similar findings of Schrock and co-workers, who introduced alkoxide ligands by reacting alcohols with pyrrolide-bearing complexes.⁸ This exchange of ligands was envisioned to serve as an elegant means to introduce an NHC ligand while keeping the electron count constant. Surprisingly, this reaction did not yield the desired W-imido alkylidene NHC complexes; instead, the corresponding anionic W-imido chloro alkylidene bispyrrolide was formed in high yield. While thwarting the attempts to introduce NHCs, this rather unexpected chloro-transfer offered access to anionic imido alkylidene complexes. Reports on such compounds are very rare and include only a limited number of examples,^{9–11} like Winter's $[W(\text{CHPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^{12}$

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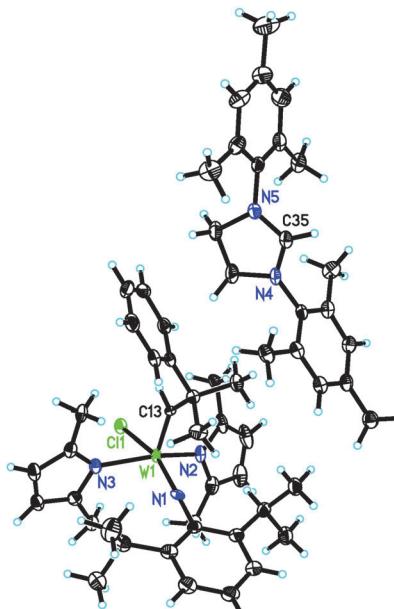


Fig. 1 Single crystal X-ray structure of **2**. Relevant bond lengths (pm) and angles (°): W(1)–N(1) 177.0(5), W(1)–C(13) 190.2(5), W(1)–N(2) 213.6(5), W(1)–N(3) 215.0(5), W(1)–Cl(1) 247.49(14), N(1)–W(1)–C(13) 100.2(2), N(1)–W(1)–N(2) 96.8(2), C(13)–W(1)–N(2) 101.8(2), N(1)–W(1)–N(3) 95.5(2), C(13)–W(1)–N(3) 101.1(2), N(2)–W(1)–N(3) 151.56(19), N(1)–W(1)–Cl(1) 156.81(16), C(13)–W(1)–Cl(1) 103.00(17), N(2)–W(1)–Cl(1) 79.08(14), N(3)–W(1)–Cl(1) 79.51(13); co-solvent omitted for clarity.

or $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\text{CHSiMe}_3)]_2[\text{Li}_2(\text{THF})_3]$ ¹³ as described by Legzdins. So far, all these complexes have been solely used as intermediates for the synthesis of non-ionic compounds and no activity in olefin metathesis reactions of these complexes was reported. To exploit the above-described reaction in a systematic manner, complexes **2–4** were prepared as outlined in Scheme 1. Starting from the literature-known precursor complex **1**,^{5,7} compound **2** was conveniently obtained in high yield by adding a suspension of 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride to a stirred solution of complex **1** in benzene. Analytically pure samples could be crystallized from CH_2Cl_2 by adding small amounts of pentane. Complex **2** crystallizes in the monoclinic space group $P2_1/c$, $a = 2168.65(19)$ pm, $b = 1887.37(16)$ pm, $c = 1610.05(13)$ pm, $\alpha = 90^\circ$, $\beta = 106.667(3)^\circ$, $\gamma = 90^\circ$, $Z = 4$. Relevant bond lengths and angles are summarized in Fig. 1.

In the solid state, complex **2** adopts a slightly distorted square pyramidal (SP) configuration with the alkylidene forming the apex. The tungsten alkylidene bond is 190.2(5) pm and the pyrrolides have almost the same distance to the metal centre (213.6(5) and 215.0(5) pm), respectively. Both, bond angles and bond lengths, indicate an η^1 -coordination of both pyrrolides. In the solid state, the alkylidene is observed in a *syn* configuration, which correlates with solution NMR data ($J_{\text{C}-\text{H}} = 121.63$ Hz (CD_2Cl_2)) at -20°C .

Nonetheless, broad signals observed in ^1H NMR for the alkylidene, pyrrolides and the 2-propyl groups of the imido ligand (Fig. S1 and S2, ESI[†]) suggest a dynamic structure in solution at room temperature.

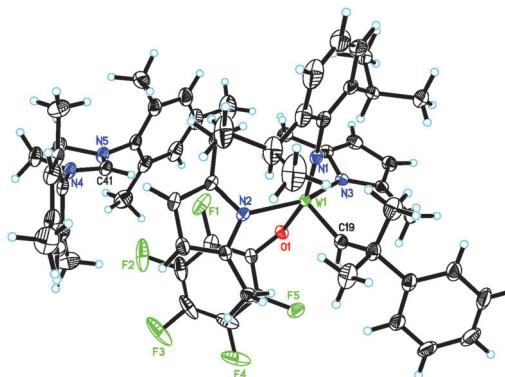


Fig. 2 Single crystal X-ray structure of **3**. Relevant bond lengths (pm) and angles (°): W(1)–N(1) 175.66(18), W(1)–C(19) 188.9(2), W(1)–O(1) 207.75(15), W(1)–N(3) 212.74(18), W(1)–N(2) 213.48(18), N(1)–W(1)–C(19) 98.47(10), N(1)–W(1)–O(1) 160.06(8), C(19)–W(1)–O(1) 101.37(9), N(1)–W(1)–N(3) 96.41(8), C(19)–W(1)–N(3) 102.18(8), O(1)–W(1)–N(3) 77.49(6), N(1)–W(1)–N(2) 95.36(8), C(19)–W(1)–N(2) 102.91(8), O(1)–W(1)–N(2) 82.21(6), N(3)–W(1)–N(2) 150.30(7); co-solvent omitted for clarity.

Importantly, further functionalization of **2** could be easily achieved. Reaction with one equivalent of lithium pentafluorophenoxide leads to the formation of **3** in high yield (Scheme 1), analytically pure samples of which were again crystallized from CH_2Cl_2 by adding small amounts of pentane. Complex **3** crystallizes in the monoclinic space group $P2_1/c$, $a = 1124.44(3)$ pm, $b = 2612.67(5)$ pm, $c = 2061.54(4)$ pm, $\alpha = 90^\circ$, $\beta = 94.9910(10)$, $\gamma = 90^\circ$, $Z = 4$. Relevant bond lengths and angles are summarized in Fig. 2. Similar to **2**, in the solid state complex **3** adopts a distorted square pyramidal configuration again with the alkylidene forming the apex. The tungsten alkylidene bond is 188.9(2) pm, which is comparable to the bond in **2**. Again, the pyrrolides have almost the same distance to the metal center (212.74(18) and 213.48(18) pm), and η^1 -bonding of the pyrrolide can be deducted from bond angles and bond lengths. In the solid state the alkylidene is observed in a *syn* configuration, which correlates with solution NMR data ($J_{\text{C}-\text{H}} = 123.0$ Hz (CD_2Cl_2)). The shorter bond lengths of the other ligands are believed to be a result of the more pronounced electron-withdrawing character of the pentafluorophenoxide compared to the chloro-ligand. Unlike **2**, compound **3** shows a sharp alkylidene and pyrrolide signal in proton NMR (S3), accompanied by a splitting of the 2-propyl groups at the imido ligand, which is indicative of the hindered rotation of the latter.

Notably, the reaction of the dipyrrolyl precursor $[\text{W}(\text{N}-2,6-\text{iPr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(2,5-\text{Me}_2\text{Pyr})_2]$ (**1**) with two equivalents of 1,3-(2,6-diisopropylphenyl)imidazolin-2-ium chloride leads to the formation of the anionic W-imido dichloro alkylidene pyrrolide complex **4**, underlining that this way to generate anionic alkylidenes is not limited to a “magic pair”, but might be achieved with a number of educts. Complex **4** crystallizes in the triclinic space group $P\bar{1}$, $a = 1055.91(3)$ pm, $b = 1362.70(5)$ pm, $c = 2123.26(7)$ pm, $\alpha = 86.879(2)^\circ$, $\beta = 81.476(2)^\circ$, $\gamma = 88.576(2)^\circ$, $Z = 2$. Relevant bond lengths and angles are summarized in Fig. 3.

As a solid, compound **4** adopts a distorted SP-configuration with the alkylidene forming the apex. The tungsten alkylidene

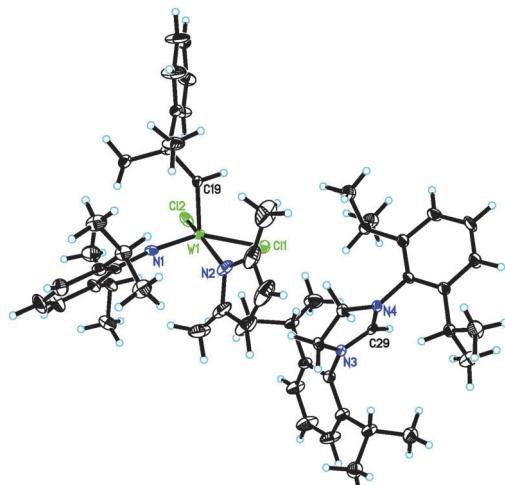
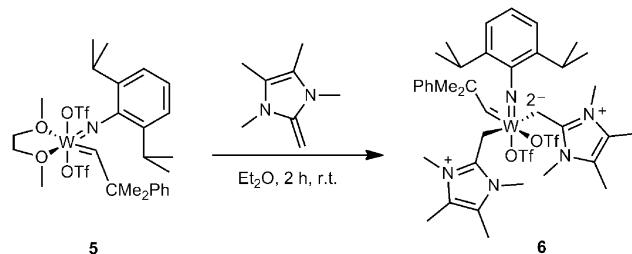


Fig. 3 Single crystal X-ray structure of **4**. Relevant bond lengths (pm) and angles (°): W(1)–N(1) 173.9(2), W(1)–N(2) 210.4(2), W(1)–C(19) 188.6(2), W(1)–Cl(1) 244.58(6), W(1)–Cl(2) 244.18(6), N(1)–W(1)–C(19) 100.61(1), N(1)–W(1)–N(2) 93.24(9), C(19)–W(1)–N(2) 104.16(9), N(1)–W(1)–Cl(2) 98.3(2), C(19)–W(1)–Cl(2) 97.01(7), N(2)–W(1)–Cl(2) 155.30(6), N(1)–W(1)–Cl(1) 150.37(7), C(19)–W(1)–Cl(1) 109.02(7), N(2)–W(1)–Cl(1) 79.51(6), Cl(2)–W(1)–Cl(1) 81.68(2); co-solvent omitted for clarity.

bond is 188.6(2) pm, which is comparable to the corresponding one in complexes **2** and **3**. The pyrrolide has a shorter distance to the metal center (210.4(2) pm). η^1 -Bonding of the pyrrolide is again suggested by characteristic values of bond lengths and bond angles. As found for **2** and **3**, the alkylidene is observed in a *syn* configuration, which correlates with solution NMR data ($J_{C-H} = 122.06$ Hz (CD_2Cl_2)).

It should be noted that analogous reactions with 1,3-dimethylimidazolium iodide or [1,3-bis-(2,4,6-trimethylphenyl)-imidazolium] tetrafluoroborate did not result in the formation of the corresponding anionic complexes, most probably as a consequence of the decreased nucleophilicity of iodide and tetrafluoroborate, respectively. Use of iodide resulted in no reaction at all, while application of the tetrafluoroborate salt resulted in complete decomposition of the metal complex.

The anionic tungsten alkylidene complexes **2**, **3** and **4** were subjected to a set of simple olefin metathesis reactions to test for their activity and functional group tolerance in ring-closing metathesis (RCM), homometathesis (HM), self-metathesis (SM) and cross-metathesis (CM) reactions. Generally, the activity of group 6 metal alkylidenes in olefin metathesis reactions strongly depends on the polarization of the metal–alkylidene bond and the electrophilic character of the metal center.⁷ In this regard, no metathetical activity of anionic compounds **2**–**4** can be expected. Surprisingly, **2**–**4** show a low but significant propensity to catalyze olefin metathesis reactions (Table S1, ESI†): in the RCM of diallyldiphenylsilane and the HM of terminal alkenes such as 1-hexene and 1-octene turnover numbers (TONs) in the range of 50 to 410 could be achieved. Potential “activation” of complexes **2** and **4** by abstraction of chloride (using $AlCl_3$) has failed so far, but remains under investigation since this represents an attractive access to latent polymerization systems.^{14,15}



Scheme 2 Preparation of NHO alkylidene **6**.

In view of the above-described findings, attention was then shifted to NHOs. This class of very electron-rich and polarized olefins is currently receiving increasing interest.⁶ The charge separation characterizing the double bond in NHOs can be strong enough to allow for the formation of CO_2 -adducts;¹⁶ likewise, their considerable nucleophilicity and basicity were recently put to use in the first NHO-mediated organopolymerizations.^{17,18} A limited number of NHO–metal complexes are also known,^{19–23} and remarkably, it was found that NHOs can confer more electron density onto the metal centre than the traditionally strongly donating NHCs.²⁴ Furthermore, Rivard and co-workers have demonstrated that NHOs can be considered “soft” donors, with higher σ -donor propensity but less bonding strength than NHCs.²⁵ In summary, this recommends NHOs for deeper investigations in organometallic chemistry, particularly if considered what penetrating impact NHCs have had in this field. NHO alkylidenes have not been described before, and we were curious as to if it was possible to generate them by direct reaction with a precursor complex. Selecting 2-methylene-1,3,4,5-tetramethylimidazoline (Scheme 2) as a sterically non-hindered and synthetically well accessible, strongly polar NHO^{20,26} and $W(CHCMe_2Ph)(N-2,6-iPr_2C_6H_3)(OTf)_2(dme)$ ⁵ (**5**) as precursor alkylidene, it was found that direct reaction in diethyl ether using two equivalents of the NHO cleanly afforded complex **6**. This compound bears two NHO-derived ligands; reactions using only one equivalent of NHO resulted in 50 : 50 mixtures of educt **5** and compound **6**. Analytically pure samples were crystallized from CH_2Cl_2 by adding small amounts of pentane. Complex **6** crystallizes in the triclinic space group $P\bar{1}$, $a = 117.112(7)$ pm, $b = 203.641(13)$ pm, $c = 219.201(14)$ pm, $\alpha = 103.305(3)$ °, $\beta = 97.459(2)$ °, $\gamma = 100.855(3)$ °, $Z = 4$. Relevant data are summarized in Fig. 4.

NHO alkylidene **6** adopts a slightly distorted octahedral configuration with one triflate and the imido ligand forming the apices. The tungsten alkylidene bond is 192.02(2) pm, which is comparable to the reported bistriflate NHC complexes.¹ The NHO ligands are in *trans*-position (153.42(9)°) to each other and sp^3 hybridized at the methylene moiety, which indicates full charge separation and formation of a covalent bond to the metal centre. In the solid state the alkylidene is *syn* to the imido ligand ($J_{C-H} = 114.06$ ppm). With 227.04(16) pm and 240.05(16) pm the triflate–metal bonds are very dissimilar and weak. This is compounded by ^{19}F NMR, which displays a signal at -78.4 ppm, suggesting a weakly bound triflate in solution that is close in chemical shift to free triflate (see Table S2 for a comparison of



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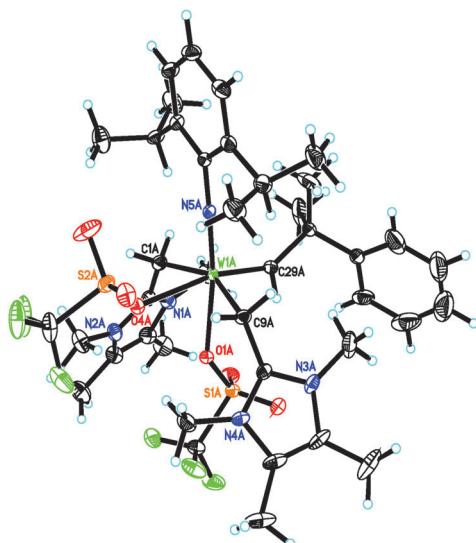


Fig. 4 Single crystal X-ray structure of **6**. Relevant bond lengths (pm) and angles ($^{\circ}$): W(1)–N(5) 175.0(2), W(1)–C(29) 192.0(2), W(1)–C(9) 226.6(2), W(1)–O(1) 227.04(16), W(1)–C(1) 227.4(2), W(1)–O(4) 240.05(16), N(5)–W(1)–C(29) 99.29(10), N(5)–W(1)–C(9) 96.47(9), C(29)–W(1)–C(9) 100.35(10), N(5)–W(1)–O(1) 170.81(7), C(29)–W(1)–O(1) 89.90(8), C(9)–W(1)–O(1) 81.84(8), N(5)–W(1)–C(1) 96.99(9), C(29)–W(1)–C(1) 99.95(10), C(9)–W(1)–C(1) 153.42(9), O(1)–W(1)–C(1) 81.22(7), N(5)–W(1)–O(4) 94.66(7), C(29)–W(1)–O(4) 166.02(8), C(9)–W(1)–O(4) 78.83(7), O(1)–W(1)–O(4) 76.14(6), C(1)–W(1)–O(4) 77.33(8); co-solvent omitted for clarity.

different alkylidene triflate complexes with regard to the chemical shift and bond length, ESI †).¹

Complex **6** was also subjected to a set of basic olefin metathesis reactions (Table S1, ESI †). The RCM of diallyldiphenylsilane and 1-hexene led to conversion with TONs in the range of 140 to 250, but the reactivity was generally low, most probably as a result of the steric (and electronic) saturation of complex **6**. Since NHOs are easily modulated, this situation is expected to improve soon and investigations are ongoing in our group.

In conclusion, anionic tungsten imido alkylidene complexes have been reported and fully characterized, accessible *via* a very simple route using imidazolinium chlorides. Additionally, an alkylidene NHO complex could be synthesized, which represents the first of a class of potentially very promising catalysts for metathesis reactions.

References

- 1 M. R. Buchmeiser, S. Sen, J. Unold and W. Frey, *Angew. Chem., Int. Ed.*, 2014, **53**, 9384–9388.
- 2 R. Schowner, W. Frey and M. R. Buchmeiser, *J. Am. Chem. Soc.*, 2015, **137**, 6188–6191.
- 3 S. Sen, R. Schowner, D. A. Imbrich, W. Frey, M. Hunger and M. R. Buchmeiser, *Chem. – Eur. J.*, 2015, **21**, 13778–13787.
- 4 M. Pucino, V. Mougel, R. Schowner, A. Fedorov, M. R. Buchmeiser and C. Copéret, *Angew. Chem., Int. Ed.*, 2016, **55**, 4300–4302.
- 5 R. R. Schrock, R. T. DePue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. DiMare and M. Schofield, *Organometallics*, 1990, **9**, 2262–2275.
- 6 R. D. Crocker and T. V. Nguyen, *Chem. – Eur. J.*, 2016, **22**, 2208–2213.
- 7 R. R. Schrock and A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4592–4633.
- 8 R. R. Schrock, *Chem. Rev.*, 2009, **109**, 3211–3226.
- 9 M. T. Jan, S. Sarkar, S. Kuppuswamy, I. Ghiviriga, K. A. Abboud and A. S. Veige, *J. Organomet. Chem.*, 2011, **696**, 4079–4089.
- 10 M. Rudler-Chauvin and H. Rudler, *J. Organomet. Chem.*, 1981, **212**, 203–210.
- 11 S. Dovesi, E. Solari, R. Scopelliti and C. Floriani, *Angew. Chem., Int. Ed.*, 1999, **38**, 2388–2391.
- 12 J. E. Muir, A. Haynes and M. J. Winter, *Chem. Commun.*, 1996, 1765–1766.
- 13 P. Legzdins and S. F. Sayers, *Organometallics*, 1996, **15**, 3907–3909.
- 14 S. Monsaert, A. L. Vila, R. Drozdak, P. Van Der Voort and F. Verpoort, *Chem. Soc. Rev.*, 2009, **38**, 3360–3372.
- 15 S. Naumann and M. R. Buchmeiser, *Macromol. Rapid Commun.*, 2014, **35**, 682–701.
- 16 Y.-B. Wang, Y.-M. Wang, W.-Z. Zhang and X.-B. Lu, *J. Am. Chem. Soc.*, 2013, **135**, 11996–12003.
- 17 S. Naumann, A. W. Thomas and A. P. Dove, *ACS Macro Lett.*, 2016, **5**, 134–138.
- 18 S. Naumann, A. W. Thomas and A. P. Dove, *Angew. Chem., Int. Ed.*, 2015, **54**, 9550–9554.
- 19 N. Kuhn, H. Bohnen, D. Bläser and R. Boese, *Chem. Ber.*, 1994, **127**, 1405–1407.
- 20 H. Schumann, M. Glanz, J. Winterfeld, H. Hemling, N. Kuhn, H. Bohnen, D. Bläser and R. Boese, *J. Organomet. Chem.*, 1995, **493**, C14–C18.
- 21 S. M. Ibrahim Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2011, **47**, 6987–6989.
- 22 S. Kronig, P. G. Jones and M. Tamm, *Eur. J. Inorg. Chem.*, 2013, 2301–2314.
- 23 M. Iglesias, A. Iturmendi, P. J. Sanz Miguel, V. Polo, J. J. Perez-Torrente and L. A. Oro, *Chem. Commun.*, 2015, **51**, 12431–12434.
- 24 A. Fürstner, M. Alcarazo, R. Goddard and C. W. Lehmann, *Angew. Chem., Int. Ed.*, 2008, **47**, 3210–3214.
- 25 K. Powers, C. Hering-Junghans, R. McDonald, M. J. Ferguson and E. Rivard, *Polyhedron*, 2016, DOI: 10.1016/j.poly.2015.07.070.
- 26 N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser and R. Boese, *Chem. Commun.*, 1993, 1136–1137.

