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ARTICLE TYPE

Synthesis of a sterically modulated pyridine–NHC palladium complex and its reactivity towards ethylene

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A new cationic pyridine-carbene palladium complex has been prepared that features a *C,N*-bidentate coordinating ligand with a shielded pyridine and a sterically less protected carbene moiety; evaluation of this complex in ethylene polymerization revealed competitive reductive elimination processes and provides guidelines for further catalyst design.

Over the last two decades substantial efforts have been devoted to develop late transition metal complexes as catalyst precursors for polymerization reactions.¹ Late transition metals are reckoned to offer significant advantages over early transition metals typically used in Ziegler-Natta-type catalysts,² including a high tolerance of functional groups, an inherently high robustness towards air and moisture, and a great potential to polymerize at low temperature.³ First proofs of concept have been demonstrated through seminal work by Brookhart and coworkers with the development of sterically shielded α -diimine complexes (type **A**, Fig. 1),⁴ and by Drent's palladium complexes comprising the *P,O*-bidentate ligand (**B**, Fig. 1).⁵ Prompted by the typically low incorporation of co-monomers,⁶ significant progress has been achieved over the last few years.⁷ Owing to the different electronic effects of the *P*- and *O*-donor sites in Drent's system, stabilization of different monomers in relative *trans* position is expected, thus providing a methodology for efficient co-polymerization of monomers with different functional entities.⁸

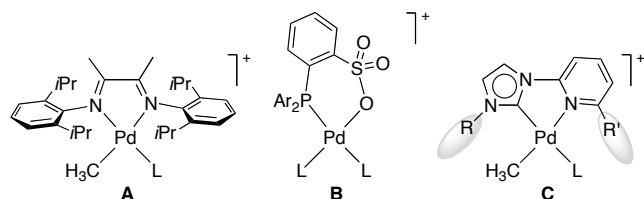


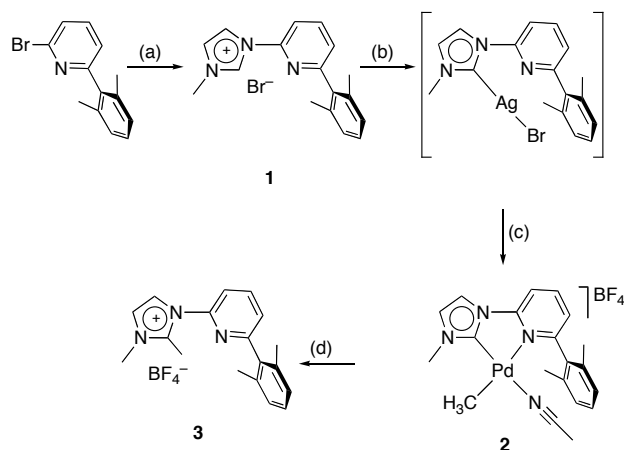
Fig. 1 Palladium-based polymerization catalysts based on Brookhart's α -diimine ligand (**A**), on Drent's *P,O*-ligand (**B**), and on sterically flexible NHC-imine ligands (**C**; for **C1** R = mesityl, R' = xylyl, L = MeCN).

In an attempt to combine the two strategies,⁹ we have recently developed an *C,N*-bidentate ligand that combines elements of the α -diimine system (N-coordinating pyridine as imine) and the strong donor properties of the phosphine in the *P,O*-system by using a NHC unit.¹⁰ Direct interlinking of the pyridine and the NHC provides a planar ligand in which the

steric shielding is independently adjustable on the NHC and on the pyridine side of the ligand (**C**, Fig. 1). Bulky substituents on both the pyridine and the NHC moiety (*cf* **C1**) resulted in catalysts that induce selective ethylene dimerization, which was attributed to a limited accessibility of the palladium center in the presence of the C_4 unit, thus promoting β -H elimination or β -H transfer to a coordinated ethylene monomer.¹⁰ In line with a steric trigger, complexes that lack a bulky substituent at the pyridine provided oligomeric mixtures (C_4 – C_{10} alkenes), but no polymers. Based on electronic and steric considerations, we concluded that bulky wingtip groups attached to the NHC unit hamper polymer chain growth. Due to the different *trans* influence of pyridine and the NHC ligand, the incoming olefin monomer preferably coordinates *trans* to the strongly donating NHC ligand, with the growing alkyl chain bound *trans* to the pyridine. Steric congestion at the NHC wingtip group is thus likely to destabilize a polymer chain and instead promotes β -hydrogen elimination. As a direct consequence of this rationale, steric shielding was considered to be more relevant at the pyridine, while a less-shielded NHC ligand should favor polymer growth. An obvious drawback of such a concept involving a small R group and a bulky R' substituent in **C** pertains to the mutual *cis* coordination of an alkyl unit and the sterically unprotected carbene, which has been shown to induce reductive elimination processes.¹¹ Here we report on the synthesis of a complex that fulfills these prerequisites and on its relative reactivity towards olefin insertion vs reductive elimination.

The ligand precursor **1** comprised of an imidazolium salt and an *ortho*-xylyl-substituted pyridine was obtained by solvent-free coupling of 2-bromo-6-(2,6-dimethylphenyl)pyridine¹² with commercially available N-methylimidazole (Scheme 1). Palladium insertion was performed according to a transmetalation methodology.¹³ Hence, imidazolium **1** was converted to the corresponding silver carbene complex upon reaction with Ag_2CO_3 in refluxing CH_2Cl_2 , producing a dark green compound after filtration through Celite. Successful transpalladation was accomplished with $[Pd(Me)(NMe)(cod)]BF_4$, which was prepared in situ by treating $[PdCl(Me)(cod)]$ with one equiv. $AgBF_4$.[†] Complex **2** was obtained in rather low yield, probably due to the instability of the intermediate species. Formation of **2** was supported by the resonance at δ_H 0.88

ppm in the ^1H NMR spectrum, which was attributed to the Pd–Me group (CD_3CN solution). Notably, this group resonates at significantly lower field than in the corresponding complexes with a bulkier mesityl substituent at the NHC unit (δ_{H} 0.00 ppm). In line with a distinct interference of the NHC substituent and the palladium-bound methyl group, the resonance of the N–Me group shifted from δ_{H} 4.3 to 3.8 ppm upon palladation. These data point to a ligand arrangement comprising the methyl group *cis* to the carbene and *trans* to the pyridine unit, as expected from the relative *trans* influence of the ligands (Me > NCMe, and NHC > py). Chelation of the ligand is indicated by the 0.5–0.7 ppm upfield shift of the imidazolylidene resonances and the C3-bound pyridyl proton as a consequence of the rigidly coplanar arrangement of the two heterocycles in **2**. In the ^{13}C NMR spectrum, the palladium-bound methyl group appears at δ_{C} –7.8 ppm and the carbene at δ_{C} 166.8 ppm.



Scheme 1. Synthesis of complex **2**. *Reactions and conditions:* (a) *N*-methylimidazole, 160 °C; (b) Ag_2CO_3 , CH_2Cl_2 , reflux; (c) $[\text{Pd}(\text{Me})(\text{NCMe})(\text{cod})]\text{BF}_4$, $\text{CH}_2\text{Cl}_2/\text{MeCN}$; (d) CDCl_3 , several days.

Complex **2** is stable in CD_3CN solution for more than a day, but slowly decomposes upon standing in CDCl_3 . After 24 h, precipitated palladium black was noted and the NMR spectra revealed minor quantities of new species. Further accumulation of these species allowed this product to be unambiguously identified as imidazolium salt **3**. Obviously, **3** is the product of a reductive elimination process.^{11,14} In the ^1H NMR spectrum, the heterocyclic protons are shifted to lower field and resonate at frequencies that are close to those of the imidazolium precursor **1**, indicative for a non-planar arrangement of the two heterocycles due to demetallation. A diagnostic resonance at δ_{H} 2.7 ppm integrating for three protons suggests the imidazolium C2 position to be methylated (δ_{C} 11.1 ppm).¹⁵ The presence of a CH_3 group at the imidazolium unit was further supported by a strong correlation of the methyl protons and the ^{13}C NMR resonance at δ_{C} 145.1 ppm assigned to the imidazolium NCN nucleus. High-resolution MS afforded the correct mass for the $[\text{M}-\text{BF}_4]^+$ ion and thus further confirmed the reductive elimination and the formation of **3**.

An alternative strategy to synthesize complex **2** by transpalladation using $[\text{PdBr}(\text{Me})(\text{cod})]$ and subsequent halide abstraction on the complex met little success. The putative

neutral palladium complex $[\text{PdBr}(\text{Me})(\text{C},\text{N})]$, where *C,N* represents the bidentate carbene pyridine ligand, was obtained as a complex mixture of compounds, as observed previously with related xylyl-substituted pyridine systems.¹⁰ Subsequent silver(I)-mediated anion exchange in MeCN resulted in the rapid formation of a black precipitate, presumably palladium(0). Extraction of the residue with DMSO and filtration over Celite gave a clean fraction of the methylated imidazolium salt **3**. Apparently, the neutral complex is not stable, and may undergo reductive elimination, a process that may be promoted by the presence of Ag^+ ions.

Single crystals of **2** that were suitable for an X-ray diffraction analysis were obtained by slow Et_2O diffusion into a MeCN solution of **2**.[‡] The molecular structure (Fig. 2a) confirms the connectivity pattern deduced from NMR analysis in solution. The complex features the methyl group *trans* to the pyridine ligand. The bond lengths around palladium are within expectations and do not differ from the analogue **C1** containing a mesityl substituent instead of a methyl group at the NHC ligand.^{10,16} Significant distortion in the ligand arrangement was noted. For example, the bulky xylyl group is oriented out of the metal coordination plane by some 20.5° (Fig. 2b).¹⁷ The MeCN ligand is also bent out of this plane, yet pointing in the opposite direction. As a consequence, the coordination of MeCN is not linear, Pd–N4–C19 is 170.25(13°). Furthermore, the carbon atoms of this ligand are substantially displaced from the mean palladium coordination plane by 0.234 and 0.474 Å (C19 and C20, respectively). This bending is much more pronounced in **2** when compared to **C1**, where the C19 and C20 nuclei are only deviating by 0.124 and 0.244 Å, respectively, from the mean coordination plane.

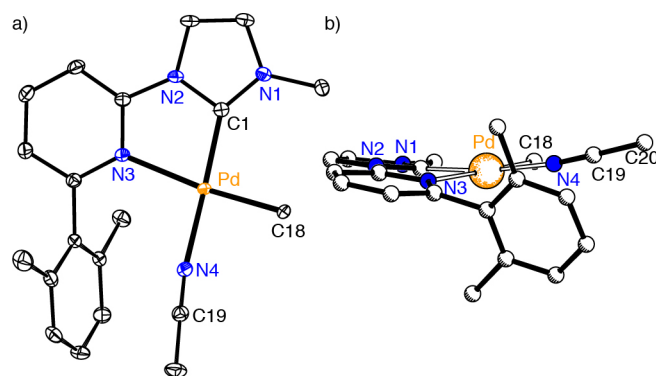


Fig. 2 a) ORTEP plot of complex **2** (50% probability, hydrogen atoms and BF_4^- anion omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd–C1 1.9722(15), Pd–C18 2.0400(14), Pd–N3 2.1904(12), Pd–N4 2.0553(13), C1–Pd–N3 79.12(5), C1–Pd–N4 173.07(6), N3–Pd–N4 100.47(5), Pd–N4–C19 170.25(13), N2–C1–Pd–N3 9.26(10); b) perspective view emphasizing the distortion around the MeCN ligand and the xylyl substituent.

The reactivity of complex **2** towards ethylene was investigated by *in situ* NMR spectroscopic experiments performed by saturating a 10 mM CD_2Cl_2 solution of the complex with ethylene at room temperature. The ^1H NMR spectrum recorded after 1 h showed the presence of complex **2** together with additional resonances that are indicative of the formation of propene, butenes, and a 2-*H*-imidazolium salt akin to **1** (Fig. S1). Of note, neither higher alkenes nor signals

pertaining to the imidazolium salt **3** have been detected. Time-resolved ^1H NMR spectroscopic monitoring of the reaction showed that the imidazolium salt and propene are produced in almost equimolar ratio, while formation of butenes is slow and clearly substoichiometric (Fig. 3).¹⁸ Propene is expected from ethylene insertion into the Pd–CH₃ bond and subsequent β -H elimination,¹⁹ thus generating a palladium hydride species that is supposed to be catalytically active (Scheme 2). The concomitant and stoichiometric formation of the imidazolium salt **1'** indicates, however, that reductive C_{NHC}–H elimination is substantially faster than olefin insertion into the Pd–H bond, required to initiate ethylene polymerization. It is interesting to note that reductive C_{NHC}–CH₃ elimination from the catalyst precursor has not been observed and is thus not a competitive process. Moreover, the absence of higher olefins suggests a high tendency of the palladium-bound alkyl chain to undergo β -hydrogen elimination, probably due to the lack of steric protection by shielding NHC substituents.²⁰

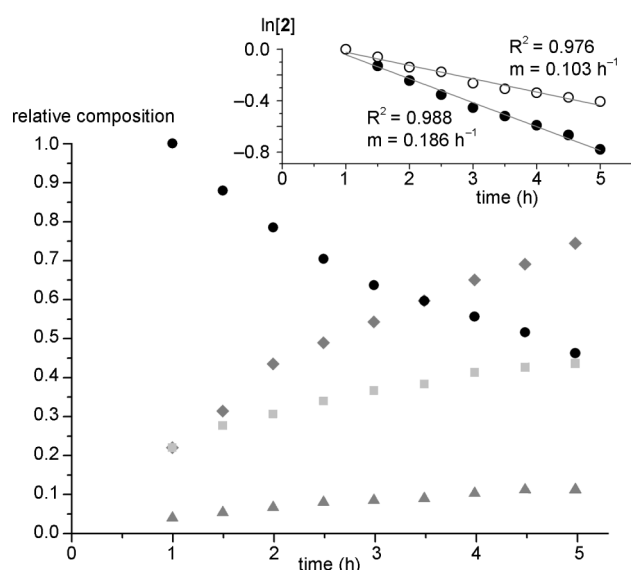


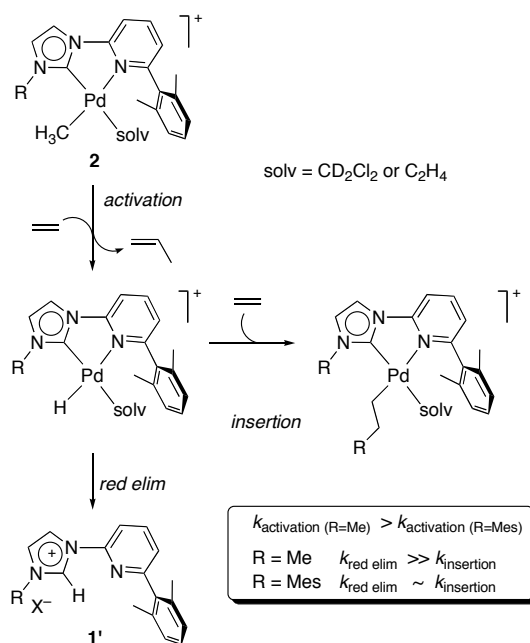
Fig. 3 Time-dependent consumption of **2** (●) and concomitant evolution of 2-butene (▲; mixture of isomers), propene (■), and imidazolium salt (**1'**) in an NMR-scale experiment using a 10 mM solution of complex **2** in CD_2Cl_2 saturated with ethylene; the inset shows a first order fit for the consumption of **2** (●) and for **1'** (○).

Comparison of these data with those obtained with a related complex containing a bulky mesityl wingtip group at the NHC site, **C1**,¹⁰ provides additional insights. For example after 2.5 h, the concentration of propene and imidazolium salt is 3 times higher than with the bulky system. In addition, the relative amount of 2-butene isomers generated by ethylene dimerization is some 12 times lower. Accordingly, the low steric shielding at the NHC unit induces a faster activation of the catalyst precursor and generates the catalytically competent palladium hydride species quicker than **C1**.¹⁰ The relative rate for the first-order consumption of **2** is $0.186(\pm 7) \text{ h}^{-1}$ (inset Fig. 3), while the same process is only about half as fast in the mesityl-containing analog **C1**, the relative rate is $0.103(\pm 6) \text{ h}^{-1}$. Due to the reduced shielding of the carbene, however, the palladium hydride species is much less stable and reductive elimination of the imidazolium salt is

substantially favored over ethylene insertion into the Pd–H bond.^{11,21} Hence, only small amounts of butenes are formed, and the predominant reaction pathway is demetallation.

A scale-up experiment in a 25 mL Büchi tinyclave steel reactor using ethylene (2.5 bar) and complex **2** in CH_2Br_2 as solvent afforded a similar mixture of products, containing propene and the imidazolium salt **1'** as major components, minor quantities of butenes (^1H NMR and GC-MS analysis), and a black residue, supposedly palladium(0).

In conclusion, a new pyridine-functionalized NHC palladium complex was synthesized that contains a bulky substituent on the pyridine ligand but not on the NHC unit. Catalytic tests towards ethylene polymerization revealed that low steric demand increases the initial reactivity of the complex towards ethylene, but reduces the catalytic activity due to a rapidly ensuing reductive elimination process involving the formation of an imidazolium salt. These studies lend further support to a limited utilizability of NHCs as spectator ligands in polymerization reactions.²² Large steric protection of the NHC increases the stability of the relevant



Scheme 2. Probable reactivity of complex **2** with ethylene.

Pd–H intermediate, but reduces the stability of larger alkyl groups during polymer growth and promotes β -H eliminations, thereby limiting the polymer length to dimers or oligomers at best. On the flipside, small steric protection reduces the stability of the carbene towards reductive elimination and induces a rapid depletion of the catalytically active species via reductive imidazolium salt formation before migratory insertion of ethylene units occurs. It may not be excluded, however, that optimization of the steric parameters at the NHC unit may allow the stability to be improved of both the catalytic resting state, *viz.* the palladium hydride, and the palladium-alkyl species during polymer growth.

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Experimental section

The imidazolium salt **1** (0.060 g, 0.17 mmol) was refluxed with Ag₂CO₃ (0.036 g, 0.13 mmol) in CH₂Cl₂ (5 ml) for 15 h and then filtered through a short pad of Celite, affording a solution of carbene silver complex.

Separately, AgBF₄ (0.039 g, 0.20 mmol) was added to a solution of [PdCl(Me)(cod)] (0.046 g, 0.17 mmol) in MeCN (2 ml). After stirring for 15 h, the mixture was filtered over Celite. The solution of carbene silver complex was added dropwise to this filtrate and the reaction mixture was stirred at room temperature for 4 h under exclusion of light. After filtration through Celite, all volatiles were removed under reduced pressure. The resulting brown oil was dissolved in CH₂Cl₂ (5 ml) and the solution was stirred over activated carbon for 30 min. and filtered again through Celite. The filtrate was concentrated in vacuo and the residue was recrystallized from MeCN/Et₂O to give an off-white solid (0.016 g, 18%).

Notes and references

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† Electronic Supplementary Information (ESI) available: NMR plot of catalytic reaction, experimental procedures and characterization, and crystallographic data in CIF format. See DOI: 10.1039/b000000x/

‡ Crystal data for **2**: C₂₀H₂₃BF₄N₄Pd, *M* = 512.63, monoclinic, space group P2₁/c (No. 14), *a* = 6.98977(7) Å, *b* = 20.8653(2) Å, *βc* = 14.1374(1) Å, *β* = 92.862(1)°, *U* = 2059.28(3) Å³, *T* = 100(2) K, *Z* = 4, 46383 total reflections, 5371 unique (*R*_{int} = 0.0307), *R*₁ = 0.0209, *wR*₂ = 0.0484, for *I* > 2σ(*I*), CCDC no. 872297.

- (a) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169. (b) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem. Int. Ed.*, 1999, **38**, 429.
- (a) P. Pino and A. Mühlebach, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 857. (b) A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587. (c) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1143. (d) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
- (a) L. S. Boffa and B. M. Novak, *Chem. Rev.*, 2000, **100**, 1479. (b) A. Sen and S. Borkar, *J. Organomet. Chem.*, 2007, **692**, 3291. (c) A. Nakamura, S. Ito and K. Nozaki, *Chem. Rev.*, 2009, **109**, 5215. (d) A. Berkefeld and S. Mecking, *Angew. Chem. Int. Ed.*, 2008, **47**, 2538. (e) J.-Y. Dong and Y. Hu, *Coord. Chem. Rev.*, 2006, **250**, 47.
- L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
- E. Drent, R. van Dijk, R. van Ginkel, B. van Oort and R. I. Pugh, *Chem. Commun.*, 2002, 744.

- (a) L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267. (b) S. Mecking, L. K. Johnson, L. Wang and M. Brookhart, *J. Am. Chem. Soc.*, 1998, **120**, 888.
- For selected examples, see: (a) C. S. Popeney, D. H. Camacho and Z. Guan, *J. Am. Chem. Soc.*, 2007, **129**, 10062. (b) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, **287**, 460. (c) F. Wu, S. R. Foley, C. T. Burns and R. F. Jordan, *J. Am. Chem. Soc.*, 2005, **127**, 1841.
- (a) S. Luo, J. Vela, G. R. Lief and R. F. Jordan, *J. Am. Chem. Soc.*, 2007, **129**, 8946. (b) D. Guironnet, P. Roesle, T. Rünzi, I. Göttker-Schnetmann and S. Mecking, *J. Am. Chem. Soc.*, 2009, **131**, 422.
- For a related approach, see: (a) J. Al Thagfi, S. Dastgir, A. J. Lough and G. G. Lavoie, *Organometallics*, 2010, **29**, 3133. (b) A. C. Badaj, S. Dastgir, A. J. Lough and G. G. Lavoie, *Dalton Trans.*, 2010, **39**, 3361. (c) X. Zhou and R. F. Jordan, *Organometallics*, 2011, **30**, 4632. (d) Y. Nagai, T. Kochi and K. Nozaki, *Organometallics*, 2009, **28**, 6131. (e) A. W. Waltman and R. H. Grubbs, *Organometallics*, 2004, **23**, 3105. (f) L. Benitez Junquera, M. C. Puerta and P. Valerga, *Organometallics*, 2012, **31**, 2175.
- V. Khlebnikov, A. Meduri, H. Mueller-Bunz, T. Montini, P. Fornasiero, E. Zangrando, B. Milani and M. Albrecht, *Organometallics*, 2012, **31**, 976.
- (a) D. S. McGuinness, N. Saendig, B. F. Yates and K. J. Cavell, *J. Am. Chem. Soc.*, 2001, **123**, 4029. (b) K. J. Cavell and D. S. McGuinness, *Coord. Chem. Rev.*, 2004, **248**, 671. (c) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247.
- N. M. Scott, T. Schareina, O. Tok and R. Kempe, *Eur. J. Inorg. Chem.*, 2004, 3297.
- H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972. (b) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663.
- (a) D. S. McGuinness, M. J. Green, K. J. Cavell, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1998, **565**, 165. (b) D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 4918. (c) A. T. Normand, S. K. Yen, H. V. Huynh, T. S. A. Hor and K. J. Cavell, *Organometallics*, 2008, **27**, 3153.
- (a) M. Heckenroth, E. Kluser, A. Neels and M. Albrecht, *Dalton Trans.*, 2008, 6242. (b) M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers and M. Albrecht, *Chem. Eur. J.*, 2009, **15**, 9375. (c) A. Krüger, L. J. L. Hüller, H. Müller-Bunz, O. Serada, A. Neels, S. A. Macgregor and M. Albrecht, *Dalton Trans.*, 2011, **40**, 9911.
- All bond lengths are very similar, the largest difference pertains to the Pd–N3 bond length, which is slightly shorter in **2** and which translates into a slightly larger ligand bite angle than in the mesityl analogue. Even though the metric differences are small, they appear to reflect intramolecular repulsion induced by the bulky mesityl and xyllyl groups.
- This distortion has been defined as the angle of the C(pyridyl)–C(xyllyl) bond with the least square plane of the palladium coordination sphere, *i.e.* Pd, C1, C18, N3, and N4. The mesityl analogue **C1** shows a similar distortion (18.8°).
- The quantity of 1-butene could not be reliably assessed by integration due to partial overlap of the diagnostic resonances with the signal of residual H₂O, though quantities were insignificant.
- F. C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746.
- For related reactivity, see (a) W. Keim, B. Hoffmann, R. Lodewick, M. Peukert, G. Schmitt, J. Fleischhauer and U. Meier, *J. Mol. Catal.*, 1979, **6**, 79. (b) Y. Chauvin, B. Gilbert and I. Guibard, *J. Chem. Soc., Chem. Commun.*, 1990, 1715. (c) G. M. DiRenzo, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 6225.
- For examples, see (a) N. D. Clement and K. J. Cavell, *Angew. Chem. Int. Ed.*, 2004, **43**, 3845. (b) A. T. Normand, K. J. Hawkes, N. D. Clement, K. J. Cavell and B. F. Yates, *Organometallics*, 2007, **26**, 5352.
- For examples, see: (a) D. McGuinness, *Dalton Trans.*, 2009, 6915. (b) A. A. Danopoulos, J. A. Wright, W. B. Motherwell and S. Ellwood, *Organometallics*, 2004, **23**, 4807. (c) B. E. Ketz, X. G. Ottenwaelde and R. M. Waymouth, *Chem. Commun.*, 2005, 5693. (d) A. El-Batta, A. W. Waltman and R. H. Grubbs, *J. Organomet. Chem.*, 2011, **696**, 2477.

