Abnormal N-Heterocyclic Carbenes

International Edition: DOI: 10.1002/anie.201507206
German Edition: DOI: 10.1002/ange.201507206

Synthesis of Complexes with Abnormal "Protic" N-Heterocyclic Carbenes

*Hanpeng Jin, Tristan Tsai Yuan Tan, and F. Ekkehardt Hahn**

Abstract: *Neutral 4-iodo-N-ethylimidazole **3** oxidatively adds to [Pt(PPh$_3$)$_4$] to give, in the presence of different tetraalkylammonium salts, complexes trans-[**4**], trans-[**5**], and trans-[**6**] containing an anionic C4-bound heterocycle with an unsubstituted ring-nitrogen atom. Complex trans-[**4**] reacts with the proton source NH$_4$I under protonation of the ring-nitrogen atom to produce complex trans-[**7**]I which bears an NH,NR-substituted aNHC ligand. The reaction of trans-[**4**] with CH$_3$I yields the complex trans-[**8**]I which has a classical aNHC ligand with two alkylated ring-nitrogen atoms.*

Research on metal complexes bearing N-heterocyclic carbene ligands (NHCs) **A** (Figure 1) has experienced an explosive development over the last two decades.[1] A vast number of differently substituted NHCs and their metal complexes have been described.[2] Due to the facile tunability of the excellent σ-donor properties of the NHC ligands and the rather high stability of their complexes, NHC complexes have found multiple applications in homogeneous catalysis[3] and other areas.[4]

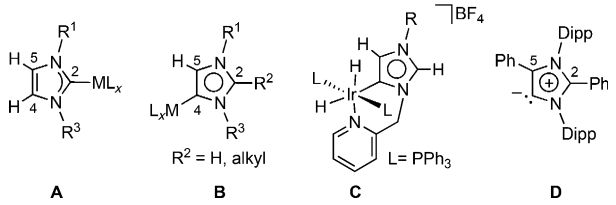
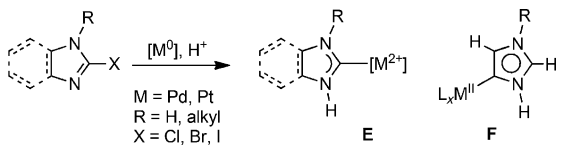


Figure 1. NHC and *a*NHC complexes.

Less common than complexes bearing normal NHCs are those bearing an abnormal NHC (*a*NHC, also called mesoionic carbenes, MICs)[5] ligand **B** (Figure 1) featuring a C4- or C5-metalated heterocycle. The first example of an *a*NHC complex, **C**, was described in 2001.[6] It has been demonstrated that *a*NHC ligands exhibit stronger σ-donor and weaker π-acceptor properties than their NHC congeners[2b,7] and even the stable free *a*NHC ligand **D** featuring protection groups at the C2 and C5 positions of the heterocycle has been isolated.[8] The superb σ-donor properties of *a*NHC ligands make their complexes an attractive synthetic target and some complexes bearing related potentially mesoionic remote NHCs (*r*NHCs) have also been described.[9]

The number of complexes bearing *a*NHC ligands is still limited and mainly two methods for their synthesis have emerged over the last years. The deprotonation method employs rather strong bases for the removal of the C4 or C5 proton from imidazolium salts to yield the *a*NHC in situ, which can then coordinate to a suitable metal center.[5,6] Given the high acidity of the C2 proton of imidazolium salts, deprotonation at this position constitutes a competing reaction to the C4/C5 deprotonation. The undesired deprotonation at the N-CH-N position is normally prevented by a protection group R^2 at the C2 position[5,8] (such as in **D**) or by the selection of the R^1 and R^3 substituents of the imidazolium salt.[10] In selected cases, the anion Y$^-$ present in the imidazolium salt also influences the ratio of C2 to C4/C5 deprotonation.[11] For the in situ generation of *a*NHC ligands, the base for the deprotonation can also be a ligand of the metal precursor to which the *a*NHC is subsequently supposed to coordinate.[12] An alternative method is the synthesis via oxidative addition of imidazolium salts. Low-valent Group 10 element (mostly Pd^0 and Pt^0) precursors have been used to activate the C4/C5–H bond of C2-protected imidazolium salts via an oxidative addition with formation of *a*NHC complexes.[13] If the imidazolium starting material bears both a donor substituent at one of the ring-nitrogen atoms and a C5–X bond (X = Br, I), protection of the C2 position is not necessary and exclusively oxidative addition of the C5–X bond to give the *a*NHC/N-donor chelate complex was observed.[14]

Recently, complexes bearing protic NHC ligands **E** have been described (Scheme 1). Instead of possessing two alkylated or arylated nitrogen atoms, protic NHC ligands feature an NH,NR or NH,NH substitution pattern on the heterocycle. Complexes with protic NHCs can be obtained by the template-controlled cyclization of β-functionalized isocyanides[15] or more conveniently by the oxidative addition of 2-halogenoazoles to transition metals in a low oxidation state (Scheme 1).[16] The latter method also allows the convenient C8-metalation of biomolecules such as caffeine and adenine.[17] Complexes bearing the related protic *a*NHC ligand such as **F** (featuring a protonated ring-nitrogen atom and a C2



Scheme 1. Preparation of complexes with protic NHC ligands.

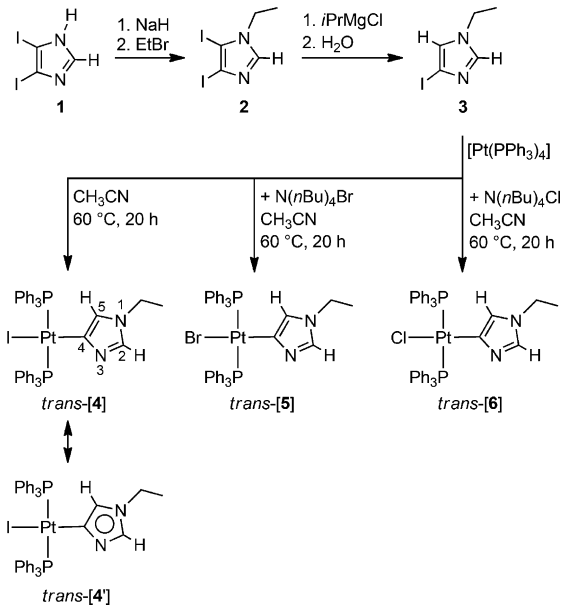
[*] H. Jin, T. T. Y. Tan, Prof. F. E. Hahn
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrassee 30, 48149 Münster (Germany)
E-mail: fehahn@uni-muenster.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507206.

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

proton) are not known yet. In our quest to prepare such complexes we studied the oxidative addition of 4-halogeno-*N*-alkylazoles to Pt^0 complexes. Here we describe this oxidative addition which in the presence of a proton source under mild conditions yields Pt^{II} complexes of type **F** bearing a protic *a*NHC ligand.

Compound 4-iodo-*N*-ethylimidazole **3** was obtained from 4,5-diiodoimidazole **1** by N-alkylation to give **2** followed by reductive removal of one iodo substituent using a published procedure for related compounds[18] (Scheme 2, see the



Scheme 2. Oxidative addition of 4-iodo-*N*-ethylimidazole to [Pt^0-(PPh_3)$_4$].

Supporting Information). Compound **3** reacts with [Pt-(PPh_3)$_4$] in acetonitrile at 60 °C over 20 h to afford complex *trans*-[**4**] in an excellent yield of 78% (Scheme 2). The oxidative addition proceeds under rather mild conditions without affecting the C2–H bond. In the presence of an excess of tetrabutylammonium bromide or tetrabutylammonium chloride, complexes *trans*-[**5**] and *trans*-[**6**] were obtained in 79% and 75% yield, respectively (see the Supporting Information). Complex *trans*-[**4**] and its derivatives can be considered to contain the heterocycle bonded to platinum(II) via a carbanionic C4 atom (*trans*-[**4**]) or, alternatively, as a complex bearing an anionic *a*NHC ligand (*trans*-[**4′**]) featuring an unsubstituted N3 ring-nitrogen atom.

Complexes *trans*-[**4**]—*trans*-[**6**] were fully characterized by NMR spectroscopy. While the complexes are stable towards air and moisture, they are only poorly soluble in nonpolar solvents. Thus, a mixture of CD_3OD and CD_2Cl_2 (10:1, v/v) was used for the NMR measurements. The ^{1}H NMR spectrum of *trans*-[**4**] (see the Supporting Information) features the resonances for the H2 and H5 protons as singlets at $\delta = 6.71$ ppm and $\delta = 5.51$ ppm, respectively. The resonance for the H2 proton disappeared after 12 h which is indicative of enhanced acidity and an H/D exchange at the C2 position after C4 metalation. The ^{1}H NMR spectra of *trans*-[**5**] and *trans*-[**6**] feature very similar resonances for the H2 and H5 protons. The $^{13}C\{^1H\}$ NMR spectrum in addition to the heteronuclear multiple-bond correlation spectrum (HMBC, recorded due to signal overlap in the $^{13}C\{^1H\}$ spectra) show the signal of the C4 carbon atom of complex *trans*-[**4**] at $\delta =$ 130.9 ppm. The equivalent resonances for *trans*-[**5**] ($\delta =$ 126.2 ppm) and *trans*-[**6**] ($\delta = 124.0$ ppm) were found at similar chemical shifts. Compared to the starting material **3** (δ(C4) = 81.3 ppm in $CDCl_3$) the signals for the C4 carbon atom in complexes *trans*-[**4**]—*trans*-[**6**] experience a significant downfield shift upon metalation with Pt^{II}. The degree of the downfield shift for the C4 resonances corresponds to the donor effect of the halogens in the order I > Br > Cl.[7b,19] Only one singlet was detected in the $^{31}P\{^1H\}$ NMR spectra of *trans*-[**4**]—*trans*-[**6**] (*trans*-[**4**] $\delta = 20.0$ ppm, $^1J_{Pt,P} = 2930$ Hz; *trans*-[**5**] $\delta = 22.1$ ppm, $^1J_{Pt,P} = 2942$ Hz; *trans*-[**6**] $\delta =$ 23.1 ppm, $^1J_{Pt,P} = 2987$ Hz) and the chemical shift of this resonance also depends on the halogeno ligand present.[19] These singlet resonances indicate the coupling of two chemically equivalent phosphorus atoms to the platinum atom and this implies a *trans* arrangement of the phosphorus donors in square–planar complexes. While no platinum complexes of type *trans*-[**4**] have been described yet, the C4 $^{13}C\{^1H\}$ resonances observed for *trans*-[**4**]—*trans*-[**6**] compare well with the C(*a*NHC) resonances observed for platinum complexes with conventional (both ring-nitrogen atoms alkylated) *a*NHC ligands (δ(*a*NHC) = 124.4 and 126.3 ppm;[13] δ(*a*NHC) = 119.0–126.0 ppm[12]). Formation of complexes *trans*-[**4**]—*trans*-[**6**] was also confirmed by mass spectrometry. The HR-ESI mass spectra (positive ions) show for all three complexes the peak with highest intensity for the complex cations $[\mathbf{4}+H]^+$, $[\mathbf{5}+H]^+$, and $[\mathbf{6}+H]^+$, each with the correct isotope distribution (see the Supporting Information).

The composition and coordination geometry of *trans*-[**4**] was unequivocally established by an X-ray diffraction study. Crystals of composition *trans*-[**4**]·2 CH_3OH were obtained by the slow diffusion of pentane into a saturated methanol solution of *trans*-[**4**] at ambient temperature. The structure analysis (Figure 2)[20] confirms the *trans* arrangement of the

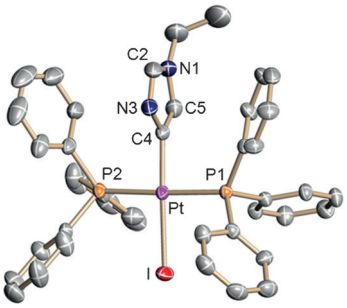


Figure 2. Molecular structure of *trans*-[**4**] in *trans*-[**4**]·2 CH_3OH. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt-I 2.6858(3), Pt-P1 2.3055(9), Pt-P2 2.3048(9), Pt-C4 2.005(4), N1-C2 1.338(7), N1-C5 1.375(6), N3-C2 1.330(6), N3-C4 1.395(5), C4-C5 1.383(6); I-Pt-P1 92.23(2), I-Pt-P2 89.82(2), I-Pt-C4 174.81(11), P1-Pt-P2 177.63(4), P1-Pt-C4 87.41(10), P2-Pt-C4 90.44(10), C2-N1-C5 106.4(4), C2-N3-C4 105.5(4), N1-C2-N3 112.9(4), N3-C4-C5 107.8(4), N1-C5-C4 107.5(4).

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

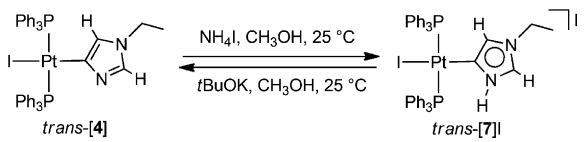
two triphenylphosphine donors. The coordination geometry around the platinum atom is slightly distorted square–planar with bond angles of P1-Pt-P2 177.63(4)° and I-Pt-C4 174.81-(11)°. The plane of the *a*NHC ligand is oriented almost perpendicular to the platinum coordination plane. The Pt–C4 bond length of 2.005(4) Å falls in the range observed previously for conventional platinum *a*NHC complexes.[12]

Both the classical NHC bearing (type **A**)[21] and the protic NHC bearing (type **E**)[16c,d] analogues of *trans*-[**4**] have been described. A comparison of the Pt-C2/4 bond lengths in these complexes reveals that the *N*,*N*-dimethylimidazolylidene complex (type **A**) features a Pt–C2 bond length of 1.995(5) Å, which is identical within experimental error to the Pt–C4 bond length observed for *trans*-[**4**]. For the complex bearing the protic NH,NH-NHC ligand (type **E**) a shorter Pt–C2 bond length of 1.978(5) Å was found which might be due to sterics as the protic NH,NH-NHC ligand lacks sterically demanding N,N′ substituents. No indications for the enhanced σ-donor capability of the aNHC ligand in *trans*-[**4**] can be derived from this comparison of the Pt–C bond lengths. The Pt–I bond length in *trans*-[**4**] (2.6858 (3) Å), however, is significantly longer (≈0.04 Å) than the equivalent distance in the NMe,NMe-NHC complex (type **A**, 2.6449(5) Å)[21] and the complex bearing the protic NH,NH-NHC ligand (type **E**, 2.6472(5) Å).[16c] This may, however, be due to the negative charge of the heterocycle in *trans*-[**4**].

An inspection of the bond lengths within the heterocycle reveals only small variations thereby giving some additional weight to resonance structure *trans*-[**4′**] (Scheme 2). A localization of the negative charge of the heterocycle at atom C4 should have resulted in a shortening of the N3–C4 separation based on electrostatic interactions but contrary to this, the N3–C4 bond length of 1.395(5) Å is the longest within the heterocycle.

Complex *trans*-[**4**] contains an anionic heterocycle with an unsubstituted ring-nitrogen atom. The metalation enhances the basicity of this nitrogen atom over that of the starting material **3**. Consequently, *trans*-[**4**] reacts with the weak acid NH_4I at 0 °C under protonation of the N3 ring-nitrogen atom to give complex *trans*-[**7**]I in 90 % yield. With both ring-nitrogen atoms bearing substituents, the heterocycle can now be considered an *a*NHC although it is the first example of a protic *a*NHC. The protonation reaction is reversible[22] and the reaction of *trans*-[**7**]I with *t*BuOK results in N3-deprotonation and reformation of complex *trans*-[**4**] in 89 % yield. (Scheme 3, see the Supporting Information). Similar behavior has been observed for the deprotonation of protic NHC ligands in complexes of type **E**.

Complex *trans*-[**7**]I is stable towards air and moisture in the solid state. It is soluble in CH_2Cl_2 and DMSO. The ^{1}H NMR spectrum of *trans*-[**7**]I features the resonance for the strongly deshielded N3-H proton at $\delta = 12.34$ ppm (in



Scheme 3. Reversible protonation of the heterocycle in *trans*-[**4**].

[D_6]DMSO). In addition, the H2 and H5 protons are detected at $\delta = 7.95$ ppm and $\delta = 6.27$ ppm, respectively, more than 1 ppm downfield relative to the analogous signals of *trans*-[**4**]. The ^{13}C{^{1}H} NMR spectrum (in [D_6]DMSO) features the resonance for the C4 carbon atom as a triplet at $\delta = 126.3$ ppm ($^2J_{C,P} = 10.6$ Hz). In spite of the protonation, this resonance is shifted slightly upfield compared to the C4 resonance for *trans*-[**4**] ($\delta = 130.9$ ppm). Only one singlet was observed in the ^{31}P{^{1}H} NMR spectrum ($\delta = 17.2$ ppm, $^1J_{Pt,P} = 2658$ Hz) confirming the *trans* arrangement of the two PPh_3 ligands.

An X-ray diffraction analysis with crystals of the composition *trans*-[**7**]I, obtained by slow diffusion of diethyl ether into a concentrated solution of *trans*-[**7**]I in dichloromethane at ambient temperature, confirms the conclusions drawn from the NMR spectra. Most of the metric parameters found in *trans*-[**7**]I (Figure 3)[20] fall in the range observed for the neutral complex *trans*-[**4**]. For example, the protonation does

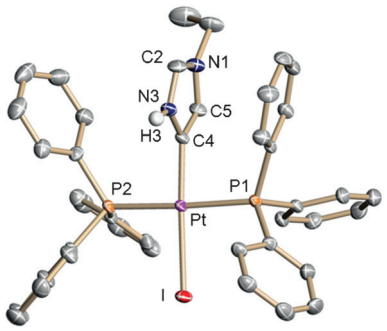


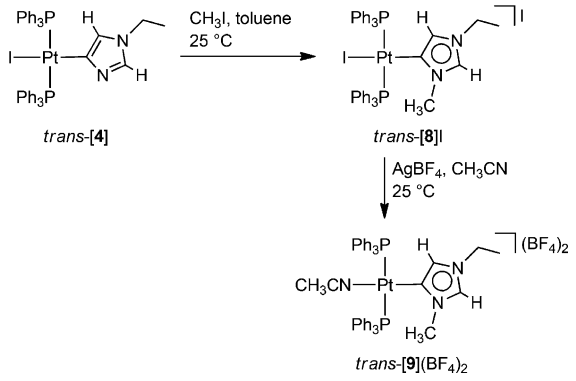
Figure 3. Molecular structure of *trans*-[**7**]$^+$ in *trans*-[**7**]I (hydrogen atoms except for H3 have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt-I 2.6647(3), Pt-P1 2.3157(12), Pt-P2 2.3067(12), Pt-C4 2.000(4), N1-C2 1.327(7), N1-C5 1.384(6), N3-C2 1.335(6), N3-C4 1.379(6), C4-C5 1.366(6); I-Pt-P1 91.20(3), I-Pt-P2 91.82(3), I-Pt-C4 176.91(14), P1-Pt-P2 175.49(4), P1-Pt-C4 87.07(14), P2-Pt-C4 89.75(14), C2-N1-C5 108.4(4), C2-N3-C4 110.6(4), N1-C2-N3 107.9(4), N3-C4-C5 104.8(4), N1-C5-C4 108.2(4).

not significantly change the Pt–C4 bond lengths (2.005(4) Å for *trans*-[**4**]; 2.000(5) Å for *trans*-[**7**]I). An exception is the Pt–I separation in *trans*-[**7**]I (2.6647(3) Å) which is about 0.2 Å shorter than in *trans*-[**4**]. This may be attributed to the overall positive charge of *trans*-[**7**]$^+$ compared to the overall neutral charge found in *trans*-[**4**].

The protonation of the imidazole scaffold in *trans*-[**4**] to give the protic *a*NHC ligand in *trans*-[**7**]I causes some geometrical changes within the heterocycle. The differences in the N–C bond lengths become smaller in accord with the formation of a delocalized 6π electron aromatic system. The C2-N3-C4 angle of the heterocycle in the nonprotonated complex *trans*-[**4**] (105.5(4)°) expands significantly upon protonation and measures 110.6(4)° in *trans*-[**7**]I.

Complex *trans*-**4** also reacts with methyl iodide at room temperature in toluene to give the platinum(II) complex *trans*-[**8**]I with a conventional *a*NHC ligand in 89 % yield. Complex *trans*-[**8**]I reacts further with $AgBF_4$ in acetonitrile to give compound *trans*-[**9**]$(BF_4)_2$ in 90 % yield (Scheme 4).

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 4. N-Alkylation *of trans*-[**4**] and ligand exchange in *trans*-[**7**]I.

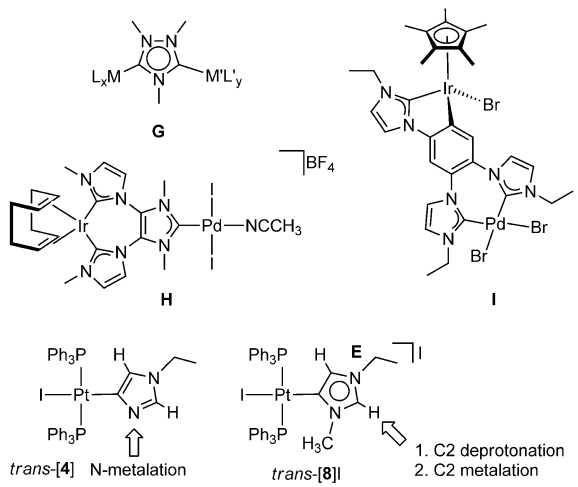


Figure 4. Heterobimetallic NHC complexes and metalation sites at *a*NHC complexes.

Compounds *trans*-[**8**]I and *trans*-[**9**]$(BF_4)_2$ are stable towards air and moisture in the solid state. They are soluble in CH_2Cl_2 or DMSO. $^{13}C\{^1H\}$ NMR spectra show the resonance for the C4 carbon atom at $\delta = 134.4$ ppm (in CD_2Cl_2) for complex *trans*-[**8**]I and at $\delta = 119.6$ ppm (in CD_2Cl_2) for complex *trans*-[**9**]$(BF_4)_2$, respectively. The $^{31}P\{^1H\}$ NMR spectra of the complexes feature resonances at $\delta = 16.5$ ($^1J_{Pt,P} = 2577$ Hz) for (*trans*-[**8**]I and 16.7 ($^1J_{Pt,P} = 2478$ Hz) for *trans*-[**9**]$(BF_4)_2$ confirming the *trans* arrangement of the two chemically equivalent PPh_3 ligands (see the Supporting Information).

We have developed a new straightforward synthetic method for the preparation of platinum(II) complexes bearing different types of *a*NHC ligands. The oxidative addition of neutral 4-iodo-*N*-ethylimidazole to $[Pt(PPh_3)_4]$ yields the complex *trans*-[**4**] which can be regarded as a complex bearing an *a*NHC ligand with an unsubstituted N3 ring-nitrogen atom. Complex *trans*-[**4**] can be reversibly protonated at the N3 ring-nitrogen atom to yield complexes *trans*-[**7**]I bearing a unique protic *a*NHC ligand. The N-methylation of the heterocycle in *trans*-[**4**] to give complex *trans*-[**8**]I with a conventional *a*NHC ligand is also possible. We assume that it will be possible to extend the scope of the oxidative addition to other low-valent transition metals.

Apart from their novelty, complexes *trans*-[**4**] and *trans*-[**8**]I are potentially useful starting materials for the preparation of novel heterobimetallic complexes with an imidazole scaffold. NHCs have been used as spectator ligands in catalytically active transition metal complexes.[3a,b] Recent interest has focused on heterobimetallic complexes derived from poly-NHC scaffolds which have already found applications in cooperative catalysis.[3c] Most heterobimetallic NHC complexes have been prepared by the stepwise metalation of suitable ligand precursors leading to complexes of types **G**[23] or **H**[24] (Figure 4), but even the single-step, site-selective metalation of a tricarbene ligand leading to complex **I** has been reported[25] in addition to other heterobimetallic complexes featuring NHC donors.[26] While complexes **G–I** feature a rather large separation of the metal centers, the N3-metalation of *trans*-[**4**] (instead of N3-protonation or N3-alkylation) would generate a heterobimetallic complex with a short Pt–M separation. Alternatively, heterobimetallc complexes would result from the deprotonation and metalation of the C2 position of *trans*-[**8**]I (Figure 4) and we are currently investigating the preparation of heterobimetallic complexes starting from *trans*-[**4**].

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 858 and IRTG 2027) for financial support.

Keywords: alkylation · N-heterocyclic carbenes · oxidative addition · platinum · protonation

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13811–13815
Angew. Chem. **2015**, *127*, 14016–14020

[1] a) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485–496; b) M. C. Jahnke, F. E. Hahn, *Top. Organomet. Chem.* **2010**, *30*, 95–129; c) P. G. Edwards, F. E. Hahn, *Dalton Trans.* **2011**, *40*, 10278–10288; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; *Angew. Chem.* **2008**, *120*, 3166–3216.

[2] a) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952; *Angew. Chem.* **2010**, *122*, 7094–7107; b) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; *Angew. Chem.* **2010**, *122*, 8992–9032; c) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; d) M. C. Jahnke, F. E. Hahn, *Chem. Lett.* **2015**, *44*, 226–237.

[3] a) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; b) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677–3707; c) J. A. Mata, F. E. Hahn, E. Peris, *Chem. Sci.* **2014**, *5*, 1723–1732.

[4] a) L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903–1912; b) W. Liu, R. Gust, *Chem. Soc. Rev.* **2013**, *42*, 755–773; c) K. M. Hindi, M. J. Panzner, C. A. Tessier, C. L. Cannon, W. J. Youngs, *Chem. Rev.* **2009**, *109*, 3859–3884; d) F. E. Hahn, *ChemCatChem* **2013**, *5*, 419–430; e) A. Grossmann, D. Enders, *Angew. Chem. Int. Ed.* **2012**, *51*, 314–325; *Angew. Chem.* **2012**, *124*, 320–332; f) M. Schmidtendorf, T. Pape, F. E. Hahn, *Angew. Chem. Int. Ed.* **2012**, *51*, 2195–2198; *Angew. Chem.* **2012**, *124*, 2238–2241;

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

g) Y.-F. Han, G.-X. Jin, F. E. Hahn, *J. Am. Chem. Soc.* **2013**, *135*, 9263 – 9266.
[5] a) M. Viciano, M. Feliz, R. Corberán, J. A. Mata, E. Clot, E. Peris, *Organometallics* **2007**, *26*, 5304 – 5314; b) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596 – 609; M. Albrecht, *Chem. Commun.* **2008**, 3601 – 3610.
[6] S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *Chem. Commun.* **2001**, 2274 – 2275.
[7] a) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461 – 2468; b) H. V. Huynh, Y. Han, R. Jothibasu, J. A. Yang, *Organometallics* **2009**, *28*, 5395 – 5404.
[8] E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556 – 559.
[9] a) Y. Han, H. V. Huynh, *Dalton Trans.* **2011**, *40*, 2141 – 2147; b) H. V. Huynh, H. L. Ong, J. C. Bernhammer, G. Frison, *Eur. J. Inorg. Chem.* **2013**, 4654 – 4661.
[10] H. Lebel, M. K. Janes, A. B. Charette, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5046 – 5047.
[11] M. Baya, B. Eguillor, M. A. Esteruelas, M. Oliván, E. Oñate, *Organometallics* **2007**, *26*, 6556 – 6563.
[12] V. Khlebnikov, M. Heckenroth, H. Müller-Bunz, M. Albrecht, *Dalton Trans.* **2013**, *42*, 4197 – 4207.
[13] D. Bacciu, K. J. Cavell, I. A. Fallis, L.-l. Ooi, *Angew. Chem. Int. Ed.* **2005**, *44*, 5282 – 5284; *Angew. Chem.* **2005**, *117*, 5416 – 5418.
[14] E. Kluser, A. Neels, M. Albrecht, *Chem. Commun.* **2006**, 4495 – 4497.
[15] a) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704 – 712; b) A. Flores-Figueroa, T. Pape, K.-O. Feldmann, F. E. Hahn, *Chem. Commun.* **2010**, *46*, 324 – 326.
[16] a) T. Kösterke, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2011**, *133*, 2112 – 2115; b) T. Kösterke, J. Kösters, E. Würthwein, C. Mück-Lichtenfeld, C. Schulte to Brinke, F. Lahoz, F. E. Hahn, *Chem. Eur. J.* **2012**, *18*, 14594 – 14598; c) R. Das, C. G. Daniliuc, F. E. Hahn, *Angew. Chem. Int. Ed.* **2014**, *53*, 1163 – 1166; *Angew. Chem.* **2014**, *126*, 1183 – 1187; d) R. Das, A. Hepp, C. G. Daniliuc, F. E. Hahn, *Organometallics* **2014**, *33*, 6975 – 6987.
[17] D. Brackemeyer, A. Hervé, C. Schulte to Brinke, M. C. Jahnke, F. E. Hahn, *J. Am. Chem. Soc.* **2014**, *136*, 7841 – 7844.
[18] X. Yang, P. Knochel, *Chem. Commun.* **2006**, 2170 – 2172.
[19] H. V. Huynh, S. Guo, W. Wu, *Organometallics* **2013**, *32*, 4591 – 4600.
[20] CCDC 1415499 (*trans*-[**4**]·2 MeOH) and CCDC 1415500 (*trans*-[**7**]I contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
[21] D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton, A. H. White, *J. Am. Chem. Soc.* **2001**, *123*, 8317 – 8328.
[22] B. Crociani, F. Dibianca, A. Giovenco, *J. Organomet. Chem.* **1985**, *291*, 259 – 272.
[23] a) A. Zanardi, R. Corberán, J. A. Mata, E. Peris, *Organometallics* **2008**, *27*, 3570 – 3576; b) A. Zanardi, J. A. Mata, E. Peris, *J. Am. Chem. Soc.* **2009**, *131*, 14531 – 14537; c) S. Sabater, J. A. Mata, E. Peris, *Organometallics* **2012**, *31*, 6450 – 6456; d) S. Sabater, J. A. Mata, E. Peris, *Nat. Commun.* **2013**, *4*, 2553.
[24] S. Gonell, M. Poyatos, J. A. Mata, E. Peris, *Organometallics* **2012**, *31*, 5606 – 5614.
[25] R. Maity, H. Koppetz, A. Hepp, F. E. Hahn, *J. Am. Chem. Soc.* **2013**, *135*, 4966 – 4969.
[26] a) D. Mendoza-Espinosa, B. Donnadieu, G. Bertrand, *Chem. Asian J.* **2011**, *6*, 1099 – 1103; b) M. T. Zamora, M. J. Ferguson, M. Cowie, *Organometallics* **2012**, *31*, 5384 – 5395; c) M. T. Zamora, M. J. Ferguson, R. McDonald, M. Cowie, *Organometallics* **2012**, *31*, 5463 – 5477; d) C. Schulte to Brinke, F. E. Hahn, *Eur. J. Inorg. Chem.* **2015**, 3227 – 3231.

Received: August 3, 2015
Published online: September 25, 2015

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim