Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. S. Ghadwal, J. Lamm, D. Rottschaefer, C. J. Schürmann and S. Demeshko, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT01778B.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C7DT01778B

Journal Name

COMMUNICATION

Facile Routes to Abnormal-NHC-Cobalt(II) Complexes†

Rajendra S. Ghadwal,*[a,b] Jan-Hendrik Lamm,[a,b] Dennis Rottschäfer,[a,b] Christian J. Schürmann,[c] and Serhiy Demeshko[c]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

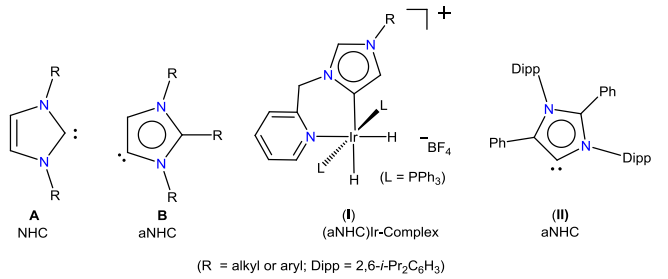
www.rsc.org/

Deprotonation of [IPr^{Ph}]I (1) with Co{N(SiMe$_3$)$_2$}$_2$ readily affords the abnormal N-heterocyclic carbene (aNHC) complex (aIPr^{Ph})$_2$CoI$_2$ (2) (aIPr^{Ph} = 1,3-bis(2,6-iPr$_2$C$_6$H$_3$)-2-phenyl-imidazol-4-ylidene). Treatment of 1 with NaHBEt$_3$ yields (aIPr^{Ph})BEt$_3$ (3) that serves as an aNHC-transfer agent and yields (aIPr^{Ph})Co{N(SiMe$_3$)$_2$}$_2$ (4) on reaction with Co{N(SiMe$_3$)$_2$}$_2$.

N-Heterocyclic carbenes (NHCs) (**A**, Chart 1) are very versatile neutral carbon-donor ligands in transition metal[1] as well as in main group chemistry.[2] They bind to metals at the C2 carbon atom and are known as normal NHCs.[3] The success of NHCs in catalysis and beyond has further prompted interest in new types of carbon-donor ligands.[4] In recent years, a different type of NHCs (**B**, Chart 1) that bind to metals at the imidazol-backbone (C4- or C5-) instead of the C2-carbon atom have emerged as very appealing ligands.[3] They are generally regarded as abnormal NHCs (aNHC) (**B**).[5] In 2001, Crabtree *et al.* described the first aNHC-metal complex (**I**), whereas Bertrand and co-workers reported the first metal free stable aNHC (**II**) in 2009.[6] Experimental and theoretical data[5] suggest that aNHCs (**B**) are stronger σ-donors than NHCs (**A**) and CAACs (cyclic alkyl amino carbenes), and hence offer exciting perspectives for their applications.[3c, 7] Nevertheless, the majority of aNHCs-complexes reported so far are serendipitous products.[3a, 3c] Therefore, the development of rational synthetic methods to aNHC-compounds is important and highly desired to facilitate their exploration.

Earth abundant base metal complexes are appealing candidates in sustainable catalysis as precious heavy metals surrogates.[8] The investigation of 3d-metal complexes with new sets of ligands is at the forefront of contemporary research. Despite the high potential of aNHCs, only a few structurally characterized aNHC-complexes featuring a base metal (Fe and Co in particular) are known.[9] This emphasizes the lack of their facile synthetic methods. We recently reported a catalytic method to C2-arylated imidazolium salts using an NHC, which are excellent synthons to aNHC-metal complexes.[7f, 7i, 10]

Chart 1. Normal- (**A**) and abnormal- (**B**) NHCs. The first aNHC-compound (I) and the first metal-free stable aNHC (**II**).



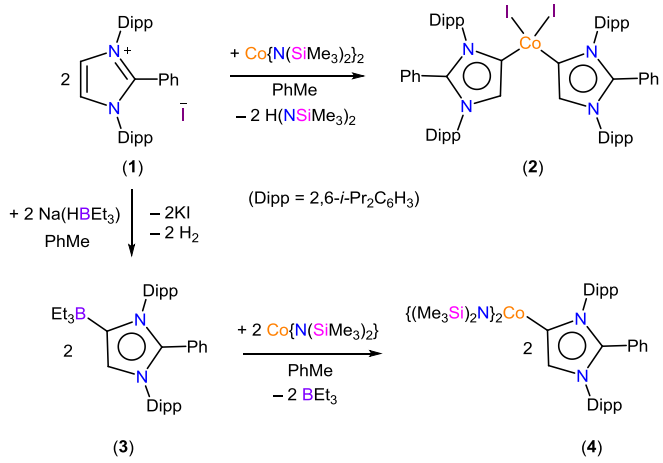
Herein, we report two synthetic strategies to aNHC-cobalt complexes (aIPr^{Ph})$_2$CoI$_2$ (**2**) and (aIPr^{Ph})Co{N(SiMe$_3$)$_2$}$_2$ (**3**) [1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene] by the utilization of the C2-arylated imidazolium salt (IPr^{Ph})I (**1**) [IPr^{Ph} = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazolium].

Reaction of **1** with Co{N(SiMe$_3$)$_2$}$_2$ in toluene leads to the formation of complex **2** as a turquoise crystalline solid in 79% yield (Scheme 1). NHC-coinage metal compounds are important carbene transfer agents.[1e, 11] Owing to the facile synthetic accessibility, stability and solubility in common organic solvents, NHC-main group compounds may be more appealing candidates for this purpose. In addition, the liberated main group species can be easily separated from the products. To the best of our knowledge, such approaches remained so far unexplored. A weak Lewis acid such as BEt$_3$ may be an interesting reagent due to its high volatility and commercial availability.[12] Reaction **1** with Na{HBEt$_3$} affords the desired compound (aIPr^{Ph})BEt$_3$ (**3**) in 75% yield. With **3** in hand, we decided to probe its suitability as carbene transfer agent. Indeed, **3** acts as an aNHC-transfer agent and affords (aIPr^{Ph})Co{N(SiMe$_3$)$_2$}$_2$ (**4**) on treatment with Co{N(SiMe$_3$)$_2$}$_2$.

[a] *Anorganische Molekülchemie und Katalyse, Am Lehrstuhl für Anorganische Chemie und Strukturchemie, Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, D-33615, Bielefeld, Germany. Email: rghadwal@uni-bielefeld.de*
[b] *Centrum für Molekulare Materialien, Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, 33615, Bielefeld, Germany.*
[c] *Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany.*
† aNHC (Abnormal N-heterocyclic carbene).
Electronic Supplementary Information (ESI) available: Synthesis, NMR spectra, and X-ray crystallographic details of **2**, **3**, and **4**. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7DT01778B

Scheme 1. Synthesis of compounds **2, 3**, and **4**.



Compounds **2–4** are soluble in common organics solvents and are stable under an inert gas atmosphere. Compound **2** and **4** are paramagnetic, each showing non-overlapping ^{1}H NMR signals, respectively in the δ – 3.35 to 26.51 and –26.10 to 44.83 ppm region. The C5-hydrogen atom of the imidazole-ring exhibits a broad ^{1}H NMR signal at δ 26.51 (for **2**) or 35.60 ppm (for **4**). The ^{1}H NMR spectrum of **4** shows resonances for the carbene and amide ligands. The ^{1}H NMR spectrum of **4** exhibits a signal at δ –19.08 ppm for the N(SiMe$_3$)$_2$ groups which is consistent with Layfield's cobalt amide derivative.[9b] ^{1}H and ^{13}C NMR spectra of **3** display expected resonances for carbene ligand and ethyl groups. The ^{11}B NMR spectrum of **3** shows a signal at δ – 14.36 ppm.

Solid-state molecular structures of **2** (Figure 1), **3** (Figure S11), and **4** (Figure 2) have been determined by single-crystal X-ray diffraction studies. Complex **2** features a distorted-tetrahedral geometry at the four-fold coordinated cobalt atom that binds to two aNHCs and two iodide ligands. The Co–I [2.6045(5) and 2.6254(6) Å] bond lengths are comparable with other NHC-cobalt complexes,[13] however the Co–C$_{(carbene)}$ [2.026(2) and 2.035(2) Å] bond lengths of **2** are remarkably shorter.[9b]

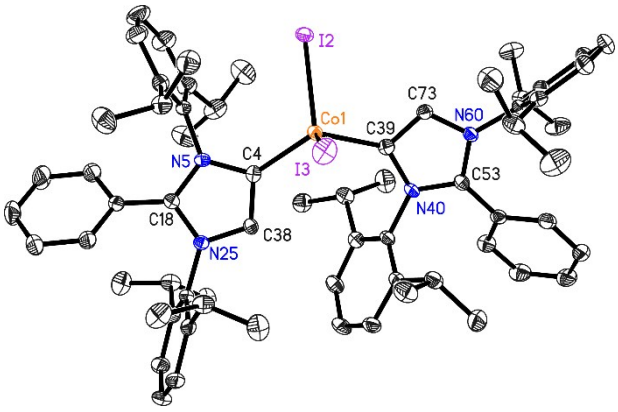


Figure 1. Molecular structure of cobalt complex (aIPr^{Ph})$_2$CoI$_2$ (**2**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co1–C4: 2.021(2); Co1–C39: 2.037(2); Co1–I2: 2.6067(5); Co1–I3: 2.6259(6); C4–C38: 1.369(3); N5–C4–C38: 102.0(2); C4–Co1–C39: 125.01(10); I2–Co1–I3: 111.722(14); C4–Co1–I2: 111.95(7); C4–Co1–I3: 103.70(7).

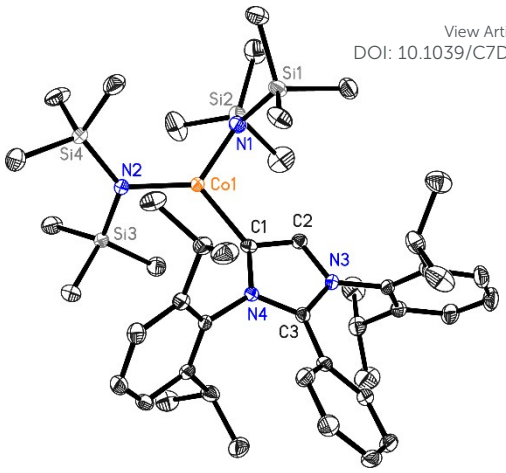


Figure 2. Molecular structure of cobalt complex (aIPr^{Ph})Co{N(SiMe$_3$)$_2$}$_2$ (**4**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co1–C1: 2.0748(16); Co1–N1: 1.9484(15); Co1–N2: 1.9342(14); C1–C2 1.366(2); N4–C1–C2: 102.38(13); C1–Co1–N1: 109.94(6); C1–Co1–N2: 127.70(6); N1–Co1–N2: 121.81(6).

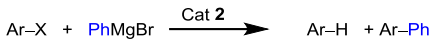
However, they are comparable with Layfield's aNHC-cobalt compound [2.059(2) Å].[9b] The angle C–Co–C [125.01(10)°] is the largest bond angle at the cobalt atom, whereas the C4–Co1–I3 bond angle is 103.72(7)°. The molecular structure of **4** (Figure 2) features a distorted trigonal-planar coordination geometry at the three-fold coordinated Co(II) center. The Co–C$_{(carbene)}$ bond length [2.0748(16) Å] is comparable with that of the reported aNHC-complex [2.059(2) Å],[9b] but shorter than those of the related (NHC)Co{N(SiMe$_3$)$_2$}$_2$ complexes.[14] The Co–N bond lengths of **4** are consistent with those of the reported Co(II) amide complexes.[9b, 14] Both species **2** and **4** feature the imidazol-ring C–C bond length of av. 1.37 Å and the C–C$_{(carbene)}$–N bond angle of av. 102.2°, clearly indicating the carbene nature of the cobalt-bound carbon atom.[5] Compound **2** exhibits a $\chi_M T$ value of 2.05 cm^{3}mol^{-1}K (corresponds to a magnetic moment of 4.05 μ_B) in the solid state at 200 K (Figure S9), which is consistent with other high-spin (S = 3/2) tetrahedral cobalt(II) complexes with some second-order orbital angular contribution to the moment (3.89 μ_B for spin-only d^7 configuration).

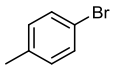
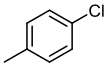
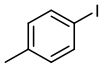
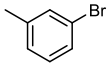
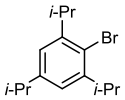
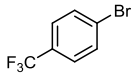
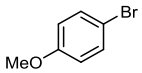
Preliminary catalytic activity of **2** has been investigated in Kumada cross coupling reactions using various aryl halides and phenylmagnesium bromide (Table 1). Biaryls (Ar–Ph) can be prepared up to 79% (entry 4) yield with aryl bromides, however, dehalohydrogenation that yields arenes Ar–H remains a competing reaction.[13] 4-Iodotoluene (entry 3) exclusively yields toluene whereas 4-chlorotoluene (entry 2) reacts rather sluggishly. Aryl bromide bearing sterically demanding substituents (entry 6) or an electron releasing group (entry 9) give arenes as major products (see ESI for further details).

In summary, rational synthesis protocols to aNHC-cobalt(II) complexes **2** and **4** are reported. Deprotonation of the imidazolium salt **1** with Co{N(SiMe$_3$)$_2$ affords **2** in 79%. The high yield accessibility and the presence easy leaving iodides make **2** a promising candidate for the synthesis of other, low-valent

in particular, cobalt complexes. The use of a main group compound **3** as an aNHC transfer agent is shown for the first time in the synthesis of **4**.

Table 1. Catalytic activity of **2** in Kumada coupling reactions.



Entry	Ar–X	Conversion, %[a] Ar–H / Ar–X / Ar–Ph
1		60.2 / – / 39.8
2		17.8 / 75.6 / 6.6
3		73.0 / 27.0 / –
4		20.7 / – / 79.3
5		35.9 / – / 64.1
6		100.0 / – / –
7		79.6 / – / 20.4
8		28.2 / 58.8 / 13.0
9		78.9 / – / 21.1

[a]after 20 h, determined by GC/MS.

References

1. (a) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676; (b) P. de Fremont, N. Marion and S. P. Nolan, *Coord. Chem. Rev.*, 2009, **253**, 862-892; (c) F. Glorius, ed., *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer-Verlag, Berlin Heidelberg, 2007; (d) W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, **41**, 1290-1309; (e) S. P. Nolan, *Acc. Chem. Res.*, 2011, **44**, 91-100; (f) G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151-5169; (g) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122-3172; (h) L. Mercs and M. Albrecht, *Chem. Soc. Rev.*, 2010, **39**, 1903-1912; (i) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561-3598.
2. (a) Y. Wang and G. H. Robinson, *Inorg. Chem.*, 2014, **53**, 11815-11832; (b) Y. Wang and G. H. Robinson, *Dalton Trans.*, 2012, **41**, 337-345; (c) Y. Wang and G. H. Robinson, *Inorg. Chem.*, 2011, **50**, 12326-12337; (d) D. Martin, M. Melaimi, M. Soleilhavoup and G. Bertrand, *Organometallics*, 2011, **30**, 5304-5313; (e) R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444-456.
3. (a) R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755-766; (b) P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596-609; (c) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445-3478; (d) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485-496.
4. R. S. Ghadwal, *Dalton Trans.*, 2016, **45**, 16081-16095.
5. (a) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723-6753; (b) T. Droge and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 6940-6952.
6. E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Science*, 2009, **326**, 556-559.
7. (a) G. Vijaykumar and S. K. Mandal, *Dalton Trans.*, 2016, **45**, 7421-7426; (b) M. Bhunia, P. K. Hota, G. Vijaykumar, D. Adhikari and S. K. Mandal, *Organometallics*, 2016, **35**, 2930-2937; (c) S. C. Sau, S. R. Roy, T. K. Sen, D. Mullangi and S. K. Mandal, *Adv. Synth. Catal.*, 2013, **355**, 2982-2991; (d) Y. D. Bidal, M. Lesieur, M. Melaimi, F. Nahra, D. B. Cordes, K. S. Athukorala Arachchige, A. M. Z. Slawin, G. Bertrand and C. S. J. Cazin, *Adv. Synth. Catal.*, 2015, **357**, 3155-3161; (e) P. Eisenberger, B. P. Bestvater, E. C. Keske and C. M. Crudden, *Angew. Chem., Int. Ed.*, 2015, **54**, 2467-2471; (f) D. Rottschäfer, C. J. Schürmann, J.-H. Lamm, A. N. Paesch, B. Neumann and R. S. Ghadwal, *Organometallics*, 2016, **35**, 3421-3429; (g) S. C. Sau, R. Bhattacharjee, P. K. Vardhanapu, G. Vijaykumar, A. Datta and S. K. Mandal, *Angew. Chem. Int. Ed.*, 2016, **55**, 15147-15151; (h) A. P. Singh, R. S. Ghadwal, H. W. Roesky, J. J. Holstein, B. Dittrich, J.-P. Demers, V. Chevelkov and A. Lange, *Chem. Commun.*, 2012, **48**, 7574-7576; (i) R. S. Ghadwal, D. Rottschafer and C. J. Schurmann, *Z. Anorg. Allg. Chem.*, 2016, **642**, 1236-1240; (j) J. I. Bates, P. Kennepohl and D. P. Gates, *Angew. Chem. Int. Ed.*, 2009, **48**, 9844-9847.
8. (a) B. Su, Z.-C. Cao and Z.-J. Shi, *Acc. Chem. Res.*, 2015, **48**, 886-896; (b) P. J. Chirik, *Acc. Chem. Res.*, 2015, **48**, 1687-1695; (c) G. Cahiez, A. Moyeux and J. Cossy, *Adv. Synth. Catal.*, 2015, **357**, 1983-1989; (d) D. Bezier, J. B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, **355**, 19-33; (e) M. J. Ingleson and R. A. Layfield, *Chem. Commun.*, 2012, **48**, 3579-3589.
9. (a) V. Lavallo, A. El-Batta, G. Bertrand and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2011, **50**, 268-271; (b) B. M. Day, K. Pal, T. Pugh, J. Tuck and R. A. Layfield, *Inorg. Chem.*, 2014, **53**, 10578-10584; (c) B. M. Day, T. Pugh, D. Hendriks, C. F. Guerra, D. J. Evans, F. M. Bickelhaupt and R. A. Layfield, *J. Am. Chem. Soc.*, 2013, **135**, 13338-13341; (d) F. Hering, J. H. J. Berthel, K. Lubitz, U. S. D. Paul, H. Schneider, M. Härterich and U. Radius, *Organometallics*, 2016, **35**, 2806-2821.
10. R. S. Ghadwal, S. O. Reichmann and R. Herbst-Irmer, *Chem. Eur. J.*, 2015, **21**, 4247-4251.
11. (a) O. Santoro, F. Lazreg, D. B. Cordes, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2016, **45**, 4970-4973; (b) H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972-975; (c) S. T. Liddle, I. S. Edworthy and P. L. Arnold, *Chem. Soc. Rev.*, 2007, **36**, 1732; (d) I. J. B. Lin and C. S. Vasam, *Coord. Chem. Rev.*, 2007, **251**, 642-670.
12. Y. Wang, M. Y. Abraham, R. J. Gilliard, Jr., P. Wei, J. C. Smith and G. H. Robinson, *Organometallics*, 2012, **31**, 791-793.
13. K. Matsubara, T. Sueyasu, M. Esaki, A. Kumamoto, S. Nagao, H. Yamamoto, Y. Koga, S. Kawata and T. Matsumoto, *Eur. J. Inorg. Chem.*, 2012, **2012**, 3079-3086.
14. A. Massard, P. Braunstein, A. A. Danopoulos, S. Choua and P. Rabu, *Organometallics*, 2015, **34**, 2429-2438.

View Article Online
DOI: 10.1039/C7DT01778B

TOC:

Deprotonation of **1** with Co{N(SiMe$_3$)$_2$}$_2$ affords aNHC-Co(II) complex **2**, whereas carbene transfer from **3** to Co{N(SiMe$_3$)$_2$}$_2$ enables access to complex **4**.