

Metal center dependent coordination modes of a tricarbene ligand†

Ramananda Maity,^a Arnab Rit,^a Christian Schulte to Brinke,^a Constantin G. Daniliuc^b and F. Ekkehardt Hahn^{*a}

Cite this: *Chem. Commun.*, 2013, **49**, 1011

Received 12th October 2012,
Accepted 11th December 2012

DOI: 10.1039/c2cc37446c

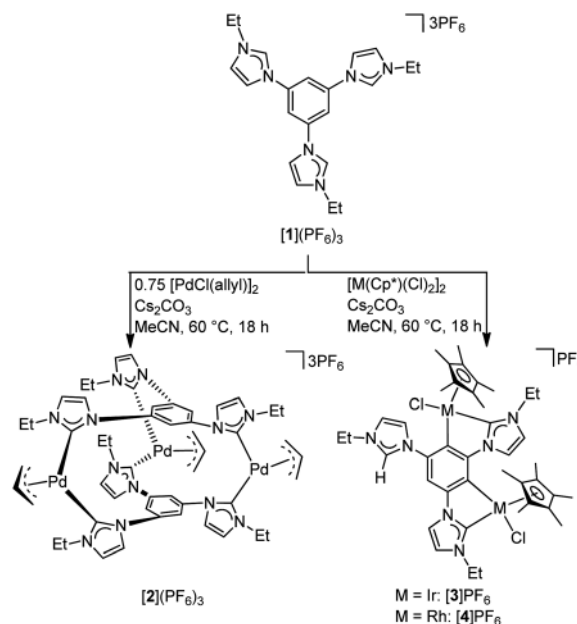
www.rsc.org/chemcomm

The reaction of the benzene derived trisimidazolium salt $[1](PF_6)_3$ with $[PdCl(allyl)]_2$ gave complex $[2](PF_6)_3$ featuring three $Pd(allyl)$ moieties sandwiched between two tricarbene ligands, whereas the reaction of $[1](PF_6)_3$ with $[M(Cp^*)(Cl)_2]_2$ ($M = Ir, Rh$) resulted in the formation of dinuclear M^{III} complexes $[3]PF_6$ ($M = Ir$) and $[4]PF_6$ ($M = Rh$) where each metal center is coordinated by an NHC donor and orthometallates the central phenyl ring. The remaining imidazolium group in $[4]PF_6$ can be metallated with $[Rh(Cp^*)(Cl)_2]_2$ to give the trinuclear triply orthometallated complex $[5]$.

N-Heterocyclic carbenes (NHCs)¹ have been extensively investigated over the last two decades due to their applications in various fields like as spectator ligands in catalytically active complexes,² in materials science,³ as biologically active compounds⁴ and very recently also in metallosupramolecular chemistry.⁵ Due to their strong σ -donor properties and the stability of their complexes, NHCs are considered an alternative to tertiary phosphines in organometallic chemistry.⁶

A number of synthetic transformations have been successfully catalyzed by complexes bearing monodentate NHCs.^{2,7} While such complexes show good catalytic activity, those bearing polydentate, chelating coordinated ligands like dicarbenes or NHC-pincer-type ligands normally exhibit a superior stability towards heat and moisture.⁸

Some poly-NHC ligands bearing a metal center at each NHC donor are known.^{3b,9} Tri- and tetracarbenes which form cylinder-like polynuclear structures with linearly coordinated metal centers like Ag^+ , Au^+ or Cu^+ are also known.^{5g,h} Here we report



Scheme 1 Preparation of complexes $[2](PF_6)_3$ – $[4]PF_6$.

on the reactivity of the trisimidazolium salt $[1](PF_6)_3$ (Scheme 1) which after deprotonation reacts to yield either a cylinder-like trinuclear palladium–NHC complex or dinuclear and trinuclear complexes with additional orthometallation of the central phenyl ring of the ligand ($M = Ir^{III}, Rh^{III}$).

While the tri-NHC ligand obtained from salt $[1](PF_6)_3$ has been shown to form cylinder-like three dimensional trinuclear assemblies with linearly coordinated metal ions,^{5g–i} we became interested in the coordination chemistry of deprotonated $[1](PF_6)_3$ with square-planar metal centers where two NHC donors are coordinated in a *cis*-fashion. The reaction of $[1](PF_6)_3$ with $[PdCl(allyl)]_2$ yields a cylinder-like trinuclear complex $[2](PF_6)_3$ (Scheme 1) demonstrating that such assemblies are also accessible with metal centers which are not coordinated in a linear fashion by two NHC ligands.

The 1H NMR spectrum of $[2](PF_6)_3$ (ESI[†]) exhibited the expected resonances for the tricarbene ligand with the original

^a Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, D-48149 Münster, Germany. E-mail: fehahn@uni-muenster.de; Fax: +49-251-8333108

^b Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, D-48149 Münster, Germany

† Electronic supplementary information (ESI) available: Preparation and spectroscopic properties of $[2](PF_6)_3$, $[3]PF_6$, $[4]PF_6$ and $[5]$ and details of the crystal structure determinations for $[2](PF_6)_3 \cdot Et_2O \cdot CH_3CN$, $[3]PF_6$ and $[5] \cdot 2MeCN$. CCDC 905534 ($[2](PF_6)_3 \cdot Et_2O \cdot CH_3CN$), 905535 ($[3]PF_6$) and 913772 ($[5] \cdot 2MeCN$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37446c

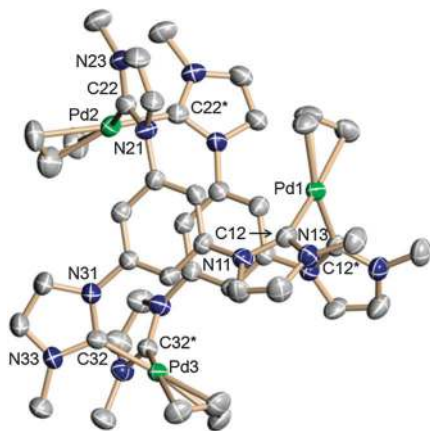


Fig. 1 Molecular structure of the trication $[2]^{3+}$ in $[2](PF_6)_3 \cdot CH_3CN \cdot Et_2O$ (hydrogen atoms have been omitted and only the first atom of the *N*-ethyl substituents is shown). The palladium atoms reside on a crystallographic mirror plane which bisects the cation. Selected bond distances (Å) and angles ($^\circ$): ranges Pd–C_{NHC} 2.057(7)–2.068(6), Pd–C_{allyl} 2.160(10)–2.198(7), N–C_{NHC} 1.355(8)–1.381(8); ranges C_{NHC}–Pd–C_{NHC} 91.2(4)–95.5(4), N–C_{NHC}–N 103.7(6)–104.4(5).

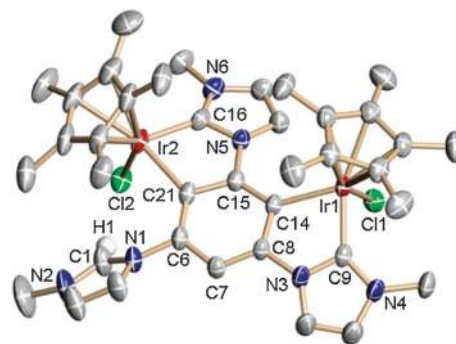


Fig. 2 Molecular structure of the cation $[3]^+$ in $[3]PF_6$ (hydrogen atoms except H1 have been omitted and only the first atom of each of the *N*-ethyl substituents is shown). Selected bond distances (Å) and angles ($^\circ$): Ir1–C1 2.4305(9), Ir1–C9 1.987(4), Ir1–C14 2.089(3), Ir2–C12 2.4395(9), Ir2–C16 1.989(4), Ir2–C21 2.091(3), N1–C1 1.319(5), N2–C1 1.334(5), range N–C_{NHC} 1.347(5)–1.364(4); C1–Ir1–C9 88.40(10), C1–Ir1–C14 96.04(9), C9–Ir1–C14 77.76(13), C12–Ir2–C16 89.16(10), C12–Ir2–C21 93.60(9), C16–Ir2–C21 76.72(14), N1–C1–N2 108.4(4), N3–C9–N4 105.1(3), N5–C16–N6 105.3(3).

imidazolium C2–H signal for $[1](PF_6)_3$ at $\delta = 9.15$ ppm^{5h} missing for $[2](PF_6)_3$. The ¹³C NMR spectrum showed the characteristic resonance for the C_{NHC} atoms at $\delta = 176.6$ ppm. The ESI mass spectrum of $[2](PF_6)_3$ showing peaks for the cationic complex ions $[[2](PF_6)_3 \cdot nPF_6]^{n+}$ ($n = 1-3$) as strongest signals supports the formation of the tripalladium complex as depicted in Scheme 1. The ¹³C NMR data indicate fluxionality of the cation caused by potentially different orientations of the palladium atoms relative to each other thereby eliminating the C₃-symmetry.

An X-ray diffraction study on crystals of composition $[2](PF_6)_3 \cdot CH_3CN \cdot Et_2O$ confirmed the formation of the cylinder-like trinuclear palladium complex cation $[2]^{3+}$. Two *cis*-positions at each palladium atom occupied by two NHC donors from two different tricarbene ligands with unspectacular Pd–C distances¹⁰ and the remaining coordination sites at the Pd^{II} center are occupied by an η^3 -coordinated allyl ligand (Fig. 1, see ESI[†]).

The two central aryl rings of the tricarbene ligands are oriented in a coplanar fashion with a centroid to centroid separation of 3.712 Å indicating $\pi \cdots \pi$ interactions between these rings.¹¹ The complex cation $[2]^{3+}$ does not possess a cavity large enough for the encapsulation of multiatom substrates and consequently no encapsulation of solvent molecules or anions was observed. The three palladium atoms feature nonbonding Pd \cdots Pd distances in the range of 6.9156(10)–7.2267(9) Å.

Reaction of 1 equiv. of $[1](PF_6)_3$ with 1.5 equiv. of $[M(Cp^*)(Cl)_2]_2$ ($M = Ir, Rh$) in the presence of Cs₂CO₃ (to absorb the formed HCl) yielded the unexpected doubly cyclometallated complexes $[3]PF_6$ and $[4]PF_6$, featuring one unreacted imidazolium group at each ligand (Scheme 1). Variation of the reaction conditions or the amount of reagents did not lead to different reaction products *e.g.* no activation of the remaining imidazolium group or formation of a trinuclear species was observed.

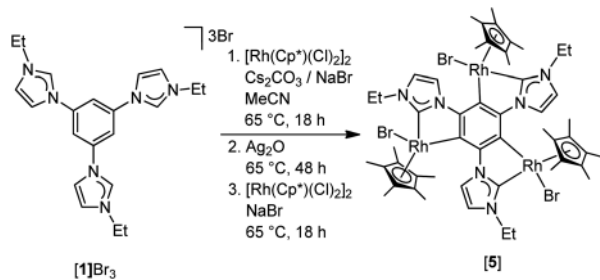
The ¹H NMR spectra show the characteristic resonances for the C2–H imidazolium protons at $\delta = 10.04$ ($[3]PF_6$) and 10.19 ($[4]PF_6$) ppm, respectively (ESI[†]). The ¹³C{¹H} NMR spectra revealed, as expected, two resonances for the carbene carbon atoms of each dinuclear complex ($[3]PF_6$: $\delta = 165.5$ and 163.6 ppm; $[4]PF_6$: $\delta = 182.7$ (d, ¹J_{C,Rh} = 53.7 Hz) and 180.7 (d, ¹J_{C,Rh} = 51.8 Hz) ppm).¹³ Potential isomers of $[3]^+$ and $[4]^+$ caused by differences in the orientation of the Cp* rings relative to the central phenylene ring were not detected either by NMR spectroscopy or X-ray crystallography.

The double orthometallation of the central phenylene group was confirmed by 2D correlation NMR spectroscopy. The observed Rh and C_{aryl} coupling as well as the upfield shift found for the non-orthometallated phenyl carbon atoms are clear indications of the double metallation of the aromatic ring and the presence of free imidazolium groups.

An X-ray diffraction analysis of crystals of $[3]PF_6$ confirmed the connectivity and coordination geometry of the cation $[3]^+$ (Fig. 2, see ESI[†]). The NHC moieties in $[3]^+$ feature typical parameters for coordinated *N*-heterocyclic carbenes. Two five membered iridacycles result from the orthometallation. The Ir–C_{NHC} bond lengths are shorter (1.987(4) and 1.989(4) Å)¹² than the Ir–C_{aryl} bond lengths (2.089(3) and 2.091(3) Å). The bite angles C_{NHC}–Ir–C_{aryl} found for the chelate units in $[3]^+$ (77.76(13) $^\circ$ and 76.72(14) $^\circ$) fall in the expected range.^{12c,d}

Currently it is not clear why the metallation of the tris-imidazolium cation $[1]^{3+}$ stops after formation of only two metallacycles in the dimetallated cations $[3]^+$ and $[4]^+$. We therefore studied alternative methods for the synthesis of a trimetallated derivative of $[1]^{3+}$. The more reactive salt $[1]Br_3$ reacts with $[Rh(Cp^*)(Cl)_2]_2$ to give initially the dimetallated complex $[4]Br$ which upon reaction with Ag₂O followed by addition of 0.5 equiv. $[Rh(Cp^*)(Cl)_2]_2$ yields the trinuclear triply orthometallated neutral complex $[5]$ in 53% yield (Scheme 2).

The ¹³C{¹H} NMR spectrum of $[5]$ (ESI[†]) reveals only one resonance for the carbene carbon atoms of the C₃-symmetric trinuclear complex. The triple orthometallation of the central



Scheme 2 Preparation of complex [5].

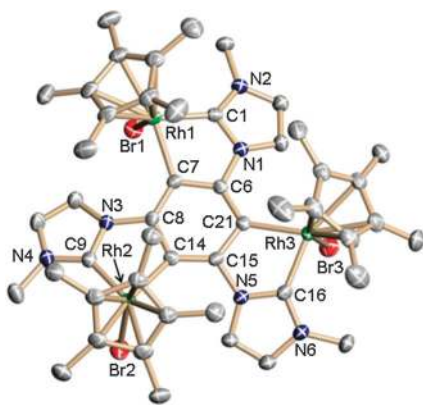


Fig. 3 Molecular structure of [5] in [5]·2CH₃CN (hydrogen atoms have been omitted and only the first atom of each of the *N*-ethyl substituents is shown). Selected bond distances (Å) and angles (°): ranges Rh–C_{NHC} 1.975(2)–1.983(2), Rh–C_{aryl} 2.078(2)–2.085(2); C_{NHC}–Rh–C_{aryl} 77.46(8)–77.54(8), N–C_{NHC}–N 105.4(2)–105.6(2).

phenylene group was confirmed by 2D correlation NMR spectroscopy.

An X-ray diffraction study on single crystals of [5] confirmed the formation of the triply orthometallated complex featuring three five-membered rhodacycles fused to the central phenylene ring. In complex [5] all bromine atoms are oriented in the same direction relative to the central phenylene ring and away from the cyclopentadienyl rings. Complex [5] can only form after all three NHC donors rotate in a position almost coplanar to the central phenylene ring to allow for the orthometallation. The small residual torsion angles (average C_{NHC}–N–C_{aryl}–C_{aryl} 9.11°), however, are sufficient to cause an offset of the Rh₃ plane from the central phenylene ring by about 0.415 Å. The Rh–C_{NHC} bond lengths fall in the expected range^{13c} of 1.975(2)–1.983(2) Å and are slightly shorter than the Rh–C_{aryl} bond lengths (2.078(2)–2.085(2) Å) (Fig. 3).

In conclusion, we have described the formation of different types of polynuclear complexes [2](PF₆)₃, [3]PF₆[4]PF₆ and [5] obtained from the trisimidazolium salts [1](X)₃ (X = PF₆, Br). The metal precursors employed determined the outcome of the reaction leading to different new homopolynuclear structures. We could demonstrate that a modification of the reaction conditions allowed the stepwise preparation of the doubly or triply orthometallated complexes. This discovery allows the planned preparation of heterobimetallic complexes and corresponding studies are underway.

The authors thank the Deutsche Forschungsgemeinschaft (SFB 858) for financial support. AR and RM thank the NRW Graduate School of Chemistry, Münster, for predoctoral grants.

Notes and references

- (a) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810–8849; (b) P. de Frémont, N. Marion and S. P. Nolan, *Coord. Chem. Rev.*, 2009, **253**, 862–892; (c) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172.
- (a) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309; (b) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676.
- (a) A. G. Tennyson, J. W. Kamplain and C. W. Bielawski, *Chem. Commun.*, 2009, 2124–2126; (b) L. Mercs, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Dalton Trans.*, 2009, 7168–7178.
- K. M. Hindi, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. J. Youngs, *Chem. Rev.*, 2009, **109**, 3859–3884.
- (a) X. Hu, I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 12237–12245; (b) F. E. Hahn, C. Radloff, T. Pape and A. Hepp, *Chem.–Eur. J.*, 2008, **14**, 10900–10904; (c) F. E. Hahn, C. Radloff, T. Pape and A. Hepp, *Organometallics*, 2008, **27**, 6408–6410; (d) C. Radloff, F. E. Hahn, T. Pape and R. Fröhlich, *Dalton Trans.*, 2009, 9392–9394; (e) C. Radloff, J. J. Weigand and F. E. Hahn, *Dalton Trans.*, 2009, 9392–9394; (f) Y. Han, L. J. Lee and H. V. Huynh, *Chem.–Eur. J.*, 2010, **16**, 771–773; (g) A. Rit, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2010, **132**, 4572–4573; (h) A. Rit, T. Pape, A. Hepp and F. E. Hahn, *Organometallics*, 2011, **30**, 334–347; (i) A. Rit, T. Pape and F. E. Hahn, *Organometallics*, 2011, **30**, 6393–6401; (j) F. M. Conrady, R. Fröhlich, C. Schulte to Brinke, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2011, **133**, 11496–11499; (k) M. Schmidtendorf, T. Pape and F. E. Hahn, *Angew. Chem., Int. Ed.*, 2012, **51**, 2195–2198.
- (a) R. H. Crabtree, *J. Organomet. Chem.*, 2005, **690**, 5451–5457; (b) S. Díez-González and S. P. Nolan, *Coord. Chem. Rev.*, 2007, **251**, 874–883.
- (a) T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18–29; (b) S. J. Connon and S. Blechert, *Angew. Chem., Int. Ed.*, 2003, **42**, 1900–1923; (c) A. Fürstner, *Angew. Chem., Int. Ed.*, 2000, **39**, 3012–3043.
- (a) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239–2246; (b) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677–3707; (c) D. Pugh and A. A. Danopoulos, *Coord. Chem. Rev.*, 2007, **251**, 610–641.
- (a) M. Poyatos, P. Uriz, J. A. Mata, C. Claver, E. Fernandez and E. Peris, *Organometallics*, 2003, **22**, 440–444; (b) A. Prades, E. Peris and M. Alcarazo, *Organometallics*, 2012, **31**, 4623–4626; (c) S. Gonell, M. Poyatos, J. A. Mata and E. Peris, *Organometallics*, 2012, **31**, 5606–5614.
- (a) W. A. Herrmann, C.-P. Reisinger and M. Spiegler, *J. Organomet. Chem.*, 1998, **557**, 93–96; (b) F. E. Hahn and M. Foth, *J. Organomet. Chem.*, 1999, **585**, 241–245; (c) M. Heckenroth, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Inorg. Chim. Acta*, 2006, **359**, 1929–1938; (d) S. Ahrens, A. Zeller, M. Taige and T. Strassner, *Organometallics*, 2006, **25**, 5409–5415; (e) M. Nonnenmacher, D. Kunz, F. Rominger and T. Oeser, *J. Organomet. Chem.*, 2007, **692**, 2554–2563; (f) C. Radloff, H.-Y. Gong, C. Schulte to Brinke, T. Pape, V. M. Lynch, J. L. Sessler and F. E. Hahn, *Chem.–Eur. J.*, 2010, **16**, 13077–13081; (g) X.-Q. Xiao, A.-Q. Jia, Y.-J. Lin and G.-X. Jin, *Organometallics*, 2010, **29**, 4842–4848.
- C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885–3896.
- (a) F. Hanasaka, Y. Tanabe, K.-i. Fujita and R. Yamaguchi, *Organometallics*, 2006, **25**, 826–831; (b) Y. Tanabe, F. Hanasaka, K.-i. Fujita and R. Yamaguchi, *Organometallics*, 2007, **26**, 4618–4626; (c) R. Corberán, M. Sanaú and E. Peris, *J. Am. Chem. Soc.*, 2006, **128**, 3974–3979; (d) R. Corberán, M. Sanaú and E. Peris, *Organometallics*, 2006, **25**, 4002–4008; (e) M. Vogt, V. Pons and D. M. Heinekey, *Organometallics*, 2005, **24**, 1832–1836; (f) F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola and L. A. Oro, *Organometallics*, 2005, **24**, 2203–2209.
- (a) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo and S. P. Nolan, *J. Am. Chem. Soc.*, 2005, **127**, 3516–3526; (b) M. Poyatos, M. Sanaú and E. Peris, *Inorg. Chem.*, 2003, **42**, 2572–2576; (c) R. J. Rubio, G. T. S. Andavan, E. B. Bauer, T. K. Hollis, J. Cho, F. S. Tham and B. Donnadieu, *J. Organomet. Chem.*, 2005, **690**, 5353–5364.