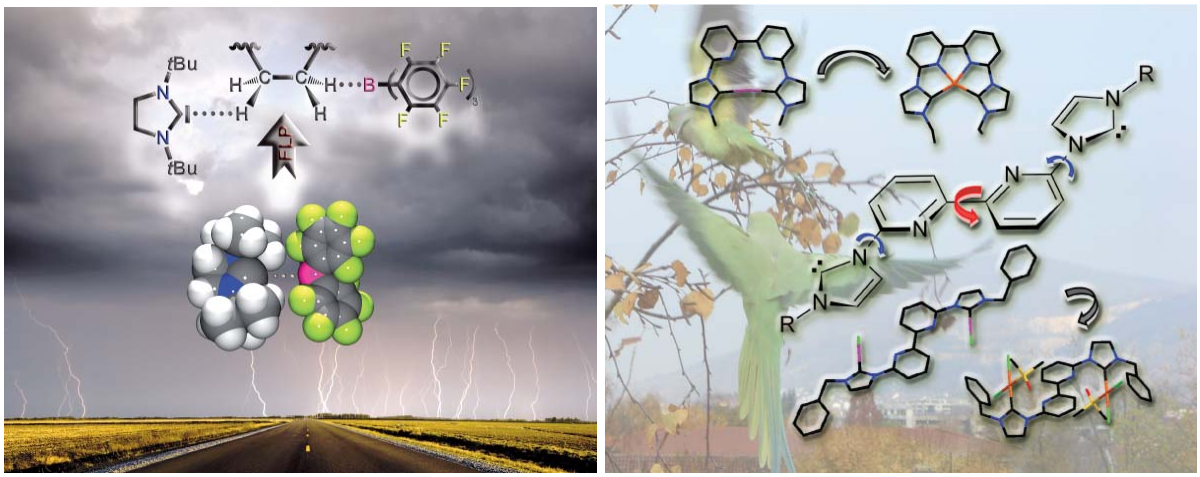
This paper is published as part of a *Dalton Transactions* themed issue on:

N-Heterocyclic Carbenes

Guest Editor Ekkehardt Hahn

Westfälische Wilhelms-Universität, Münster, Germany

Published in issue 35, 2009 of *Dalton Transactions*



Images reproduced with permission of Matthias Tamm (left) and Doris Kunz (right)

Articles published in this issue include:

PERSPECTIVES:

HOT PAPERS:

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research
www.rsc.org/dalton

Stable crystalline annulated diaminocarbenes: coordination with rhodium(I), iridium(I) and catalytic hydroformylation studies†

Sarim Dastgir,*‡[a] Karl S. Coleman,[b] Andrew R. Cowley[a] and Malcolm L. H. Green*[a]

Received 30th March 2009, Accepted 26th June 2009
First published as an Advance Article on the web 23rd July 2009
DOI: 10.1039/b905729c

Stable annulated diaminocarbene ligands 7,9-bis(2,4,6-trimethylphenyl)-6b,9a-dihydroace naphtha[1,2-d]imidazolin-2-ylidene and 7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydroacenaphtho-[1,2-d]imidazolin-2-ylidene; designated as (BIAN-SIMes, **5a**,) and (BIAN-SIPr, **5b**), respectively, have been prepared. The base dependent decomposition of imidazolinium salts *via* ring opening at the backbone was also observed. The corresponding rhodium(I) and iridum(I) complexes (η^4-1,5-COD)-M(BIAN-SIMes)Cl and (η^4-1,5-COD)M(BIAN-SIPr)Cl; M= Rh (**6a**, **6b**) and Ir (**7a**, **7b**) have been synthesised by the reaction of free carbene with $[M(\eta^4\text{-}1,5\text{-COD})(\mu\text{-Cl})]_2$; where M= Rh, Ir. The cationic Ir(I) complexes $[(\eta^4\text{-}1,5\text{-COD})Ir(BIAN\text{-}SIMes)Py]BF_4$ **8a** and $[(\eta^4\text{-}1,5\text{-COD})Ir(BIAN\text{-}SIPr)Py]PF_6$ **8b** have also been synthesised. Compounds **4b**, **5a**, **6a**, **6b**, **7b** and **8b** have been structurally characterised. The catalytic activities for the rhodium(I) complexes **6a** and **6b** were evaluated for the hydroformylation of 1-octene.

Introduction

The pioneering work on the coordination chemistry of *N*-heterocyclic carbenes (NHCs) was independently reported by Wanzlick *et al.*[1] in 1968 and Öfele *et al.*[2] in 1970 but it was almost two decades later when the first stable imidazole-2-ylidene (NHC) was successfully isolated by Arduengo *et al.* in 1991.[3] Since this significant breakthrough, the chemistry of NHCs have put this valuable class of potent ligands at the forefront of current research. In general, NHCs have been considered as strong Lewis bases and weak π-acceptors, consequently making their complexes more stable towards degradative cleavage.[4,5] However, it is worth mentioning that the extent of π-back bonding abilities in NHCs have been revised extensively in recent literatures.[4–8] Unlike phosphines for which the wide spectrum of compounds with tuneable sterics and electronics are known,[9] the tunability in NHCs is more restricted due to their confined architectures. Although a broad range of architectures containing annulated NHCs have been synthesised, these modifications are limited to the unsaturated carbenes, presumably due to the more ubiquitous dimerisation for saturated carbenes to produce enetetramines.[10–14] Studies on the annulated backbone substituted NHCs[11–15] have demonstrated that the σ-donating ability of NHCs varies substantially with a change in the substituent (π-donor/acceptor) attached to the imidazole ring.[16]

We have continued our interest in the organometallic chemistry of *N*-heterocyclic carbenes,[17–21] and now we report the synthesis of the first two members of a bulky acenaphthylene-annulated backbone substituted imidazolin-2-yilidene ligand D (Fig. 1). Such ligand modification on monodentate imidazolin-2-yilidene systems could alter the coordination behaviour of these ligands by their greater steric bulk away from the coordination site, which may provide the opportunity for small molecule activation and catalyst fine tuning since a slight change in the steric properties can play a very significant role. During the course of our investigation some annulated *N*-heterocyclic carbene ligands were reported,[12–14,22,23] but their attempted synthesis to deprotonate the imidazolinium salts failed to generate the *N*-heterocyclic carbene cleanly.[22,23]

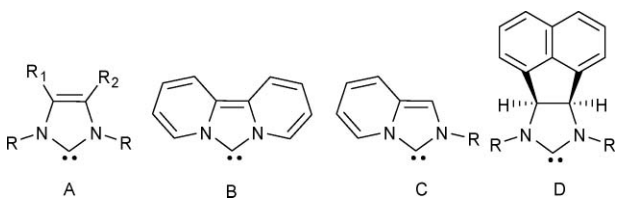


Fig. 1 Examples of *N*-heterocyclic carbene compounds.

Results and discussion

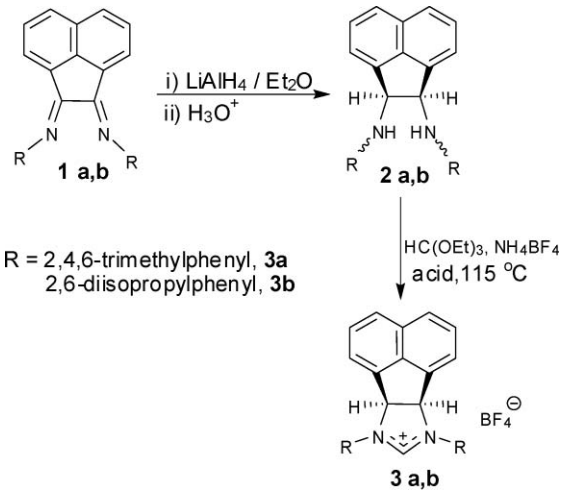
Synthesis and characterization of the imidazolinium salts [(BIAN-SIMes)(H)]BF_4 (3a) and [(BIAN-SIPr)(H)]BF_4 (3b)

The imidazolium salts **3a** and **3b** were synthesised in good yields (60–75%) from Ar-BIAN;[24,25] where Ar = 2,4,6-trimethylphenyl **3a** and 2,6-diisopropylphenyl **3b**, by reduction with $LiAlH_4$ followed by cyclisation with triethylorthoformate in the presence of NH_4BF_4 and an acid catalyst. (Scheme 1) The detailed synthetic

[a]*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: malcolm.green@chem.ox.ac.uk, sarim.dastgir@lmh.oxon.org; Fax: +44 (0)1865 272690; Tel: +44 (0)1865 272600*
[b]*Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*

† Electronic supplementary information (ESI) available: Experimental details. CCDC reference numbers 719732 (**4b**), 719731 (**5a**), 719730 (**6b**) 719729 (**6a**), 719728 (**7b**), 719727 (**8b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b905729c

‡ Present address: Department of Chemistry, York University, 4700 Keele Street, Toronto, ON, Canada M3J 2Z3. Tel: +1 416 736 2100 Ext. 77720; Fax: +1 416 736 5936

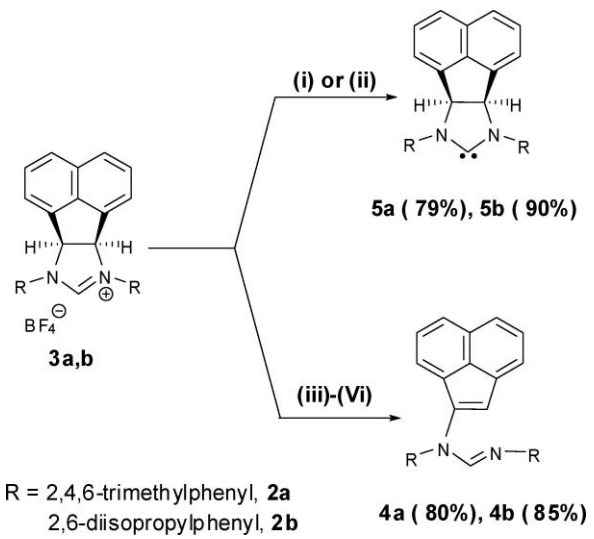


Scheme 1 Synthesis of imidazolinium salts.

protocol of their synthesis, crystal structures and corresponding palladium(II) complexes is published elsewhere.[26]

Synthesis and characterization of diaminocarbenes BIAN-SIMes (5a) and BIAN-SIPr (5b)

The solvent, as well as the base, play a vital role in the clean deprotonation of imidazolium salts. The choice of an appropriate solvent and the corresponding base for the synthesis of NHCs may be restricted due to the insolubility of the imidazolium salts and/or the decomposition of NHCs once it has been generated.[27] It is also noteworthy that a slight change to the imidazolium architecture has a dramatic effect on the deprotonation behaviour. (Scheme 2) Our initial attempts to generate the free carbenes BIAN-SIMes, **5a** and BIAN-SIPr, **5b** under standard conditions with $KN(SiMe_3)_2$, KO^{t}Bu and potassium pentalate in THF at −78 °C failed but instead an unexpected



Scheme 2 Synthesis of *N*-heterocyclic carbene (base/reaction solvent, temperature); (i) KO^{t}Bu/THF, −78 °C (**3a**); (ii) ^{n}BuLi/pentane, −78 °C (**3b**); (iii) KO^{t}Bu/THF, −78 °C (**3b**); (iv) $KN(SiMe_3)_2$]/THF, −78 °C (**3a** and **3b**); (v) potassium pentalate/THF, −78 °C (**3a** and **3b**); (vi) ^{n}BuLi/THF, −78 °C (**3b**).

ring opening at the backbone was observed with the formation of corresponding amines; [*N*-(acenaphthylene-1-yl)-*N*-*N*-bis(2,4,6-trimethylphenyl)formamidine,**4a**] and [*N*-(acenaph-thylene-1-yl)-*N*-*N*-bis(2,6-diiso-propylphenyl)formamidine, **4b**] in high yields (>80%). (Scheme 2) After optimizing the conditions, the deprotonation of the imidazolium salt **3a** was successfully achieved by KO^{t}Bu in THF at −78 °C for 30 min. The reaction mixture was then warmed to room temperature and stirred for one hour. After work-up, the diaminocarbene **5a** was isolated as an off-white solid in 79% yield. Whereas the diaminocarbene BIAN-SIPr **5b** was synthesised by the careful deprotonation of imidazolium salt **3b** with ^{n}BuLi in pentane at −78 °C for 10 min. The reaction mixture was warmed to room temperature and stirred for 2 h. After work-up, the diaminocarbene **5b** was obtained as an off-white solid (90% yield). (Scheme 2) The isolated diaminocarbenes BIAN-SIMes **5a** and BIAN-SIPr **5b** appeared to be stable under nitrogen both in solution and in solid state. The diaminocarbene BIAN-SIMes **5a** and the decomposition product; formamidine **4b** were characterised by X-ray diffraction. The detailed synthetic protocol is provided in the Experimental.

The ^{1}H NMR spectrum of carbene **5a** shows a set of three distinctive signals for the mesityl CH_3 protons at δ 1.74, 2.21 and 2.41 ppm, respectively, while the ^{1}H NMR spectrum of carbene **5b** shows two set of two doublets at δ 0.53, 0.87, 1.06 and 1.14 ppm, respectively. This may be attributed to the hindered rotation around *N*-aryl bond in the imidazole ring. In the $^{13}C\{^1H\}$ NMR (C_6D_6) spectrum a weak downfield carbene resonances (–N$C_{(carbene)}$N–) at δ 247.3 (**5a**) and δ 241.9 (**5b**) ppm were observed and found to be in a good comparison with the chemical shift values reported for Arduengo's cyclic diaminocarbene SIMes (δ 243.8 ppm) and SIPr (δ 244.0 ppm).[28] The lower population of the carbene pπ-orbital in the cyclic diamino carbene **5a** and **5b** results in downfield chemical shifts (approximately 24 ppm downfield on average) in $^{13}C\{^1H\}$ NMR, when compared with the corresponding values observed for Arduengo's unsaturated carbene IMes (δ 219.5 ppm) and IPr (δ 220.6 ppm).[29–33] As expected no significant change in the chemical shift values for the backbone (–N*CC*N–) carbons was observed for **5a** and **5b** when compared with imidazolinium ion **3a** and **3b**.[26] Full ^{1}H and ^{13}C NMR assignments for carbenes **3a** and **3b** are given in the Experimental.

Structural study

Single crystals of the BIAN-SIMes **5a** (Fig. 2) suitable for X-ray diffraction study were grown from a saturated solution of benzene at room temperature. An ORTEP view of the molecule **5a** is depicted in Fig. 2. The structure was solved in the space group *C*2/*c* using the direct-methods program SIR92,[34] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[35] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0482$, w$R = 0.0584$. The X-ray structural analysis reveals that the unit cell contains one molecule of diaminocarbene **5b** located on a site with no crystallographic symmetry, but having an approximate local mirror plane with

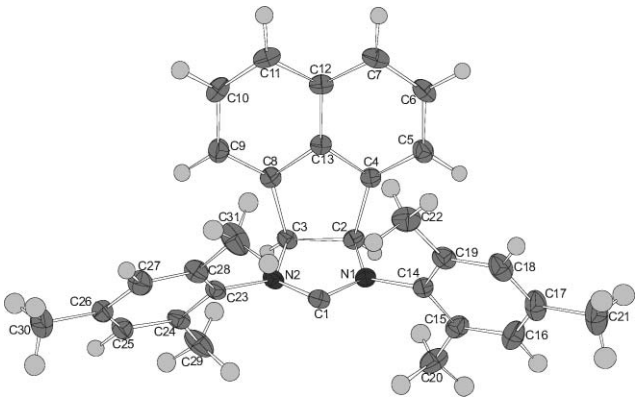


Fig. 2 ORTEP diagram of the molecular structure of the BIAN-SIMes **5a** at 40% probability (solvent molecule C_6H_6 have been omitted for clarity).

the solvent molecule on a crystallographic two-fold axis. A comparison of selected bond length and angles for imidazolinium ion **3a** and diaminocarbene **5a** along with the related structural parameters for 1,3-dimesitylimidazolinium chloride[28] and 1,3-dimesitylimidazolin-2-ylidene[28] are given in Table 1.

More interestingly, the N_1–C_1–N_2 angle at the carbene centre (106.09°) is 1.4° larger than Arduengo's cyclic diamino carbene (104.7(3)°)[28] and approximately 7.7° shorter relative to imidazolinium ion **3a** (113.8(3)°). The average C_1–N_1 and C_1–N_2 bond length (1.347 Å) observed for **5a** is increased by 0.0328 Å (3.28 pm) from the average value of 1.314 Å observed for **3a** but of the same order as that observed for Arduengo's cyclic diamino carbene (1.349 Å).[28] This increase in the bond length is due to the loss of π-delocalization over the N_1–C_1–N_2 bonds and also an indicative of carbene formation. This increase in bond lengths for average C_1–N_1 and C_1–N_2 bonds is also consistent with the Arduengo's cyclic diaminocarbene, where an increase of 0.03 Å (3.0 pm) was observed.[28] The average $N_{1(2)}$–$C_{2(3)}$ bond length observed for **5a** (1.493 Å) is 0.012 Å (1.2 pm) is significantly larger than the corresponding bond lengths (1.481 Å) observed for the SIMes[28] but of the same order as that observed for **3a** (1.495 Å) and are consistent with the single bond character between these bonds. The longer 0.0526 Å (5.26 pm) C_2–C_3 bond in **5a** (1.558 Å) when compared with Arduengo's cyclic diaminocarbene[28] (SIMes) (1.505 Å) is due to the presence of bulky naphthyl group at the backbone C_2–C_3. The average $N_{1(2)}$–$C_{2(3)}$–$C_{3(2)}$ bond angle of 101.47° is shorter than the one observed for **3a** (102.42°) is consistent with the loss of π-delocalization over nitrogen atoms bound to carbene carbon in carbene **5a**. The N_1–C_2–C_3–N_2 torsion angle is 1.29° wider relative to **3a** is also an indicative of the loss of π-delocalization over the N–C–N bonds and consistent with the carbene formation. The angle between the best planes of the dihydroimidazole ring and the naphthyl group is 60.93°. The angle between the best planes of the dihydroimdazole ring and the phenyl rings C_{15}–C_{14}–C_{19} and C_{24}–C_{23}–C_{28} are 78.22° and 63.22°, respectively, and consistent with loss of π-delocalization due the carbene formation. The remaining bond lengths and angles are unexceptional and lie within the range expected. Complete details of the single-crystal X-ray analysis are given in the ESI.†

Crystals of the *N*-(acenaphthylene-1-yl)-*N*-*N*-bis(2,6-diisopropylphenyl)formamidine, **4b** (Fig. 3) suitable for X-ray diffraction study were grown from a saturated solution of diethyl ether at –78 °C. An ORTEP view of the molecule **4b** is depicted in Fig. 3. Crystallographically interesting structures of molecule **4b** shows the presence of two conformers with respect to rotation about the tertiary nitrogen atom and the imine carbon atom. In both conformers the atoms of the acenaphthylene, amine nitrogen atoms and imine groups are all approximately co-planar with the two isopropyl groups approximately perpendicular to these planes. Details of the single-crystal X-ray analysis are given in the ESI.†

Synthesis and characterization of rhodium(I) complexes

The rhodium(I) complexes (η^4-1,5-COD)Rh(BIAN-SIMes)Cl **6a** and (η^4-1,5-COD)Rh(BIAN-SIPr)Cl **6b** were synthesised by the reaction of the free carbenes with [Rh(η^4-1,5-COD)(μ-Cl)]$_2$ in toluene at –78 °C. (Scheme 3) After work-up, the rhodium(I)

Table 1 Selected bond lengths (Å) and angles (°) in carbenium ion **3a** and diaminocarbene **5a**

Property	[(BIAN-SIMes)(H)]BF_4 **3a**[a]	BIAN-SIMes **5a**	[(SIMes)(H)]Cl[b]	SIMes[c]
Bond lengths/Å				
C_1–$N_{1(2)}$	1.315(4), 1.313(4)	1.348(2), 1.346(2)	1.327(5), 1.310(5)	1.352(5), 1.345(5)
$N_{1(2)}$–$C_{2(3)}$	1.496(4), 1.494(4)	1.491(2), 1.496(2)	1.498(6), 1.487(6)	1.475(5), 1.487(5)
C_2–C_3	1.560(4)	1.558(2)	1.518(7)	1.505(6)
$N_{1(2)}$–C_{mes}	1.442(4), 1.442(4)	1.434(2), 1.435(2)	1.432(5), 1.437(6)	1.427(5), 1.437(5)
Bond angles (*θ*)/°				
N_1–C_1–N_2	113.8(3)	106.09(14)	113.1(4)	104.7(3)
C_1–$N_{1(2)}$–$C_{2(3)}$	110.7(2), 110.7(2)	115.51(14),115.37(14)	109.7(4), 110.6(4)	115.0(3), 114.6(3)
$N_{1(2)}$–$C_{2(3)}$–$C_{3(2)}$	102.3(2), 102.5(2)	101.51(13),101.43(13)	103.0(4), 103.3(4)	101.6(4), 101.9(4)
C_1–$N_{1(2)}$–C_{mes}	126.9(2), 121.2(2)	124.01(14), 123.18(14)	127.0(4), 126.2(4)	122.9 (3), 122.5(3)
$N_{1(2)}$–$C_{2(3)}$–$C_{4(8)}$	113.2(2), 112.5(2)	113.97(14)114.30(14)	—	—
Torsion angle/°				
N_1–C_2–C_3–N_2	0.68	1.97	—	—

[a] Ref. 36. [b] Ref. 37. [c] Ref. 28.

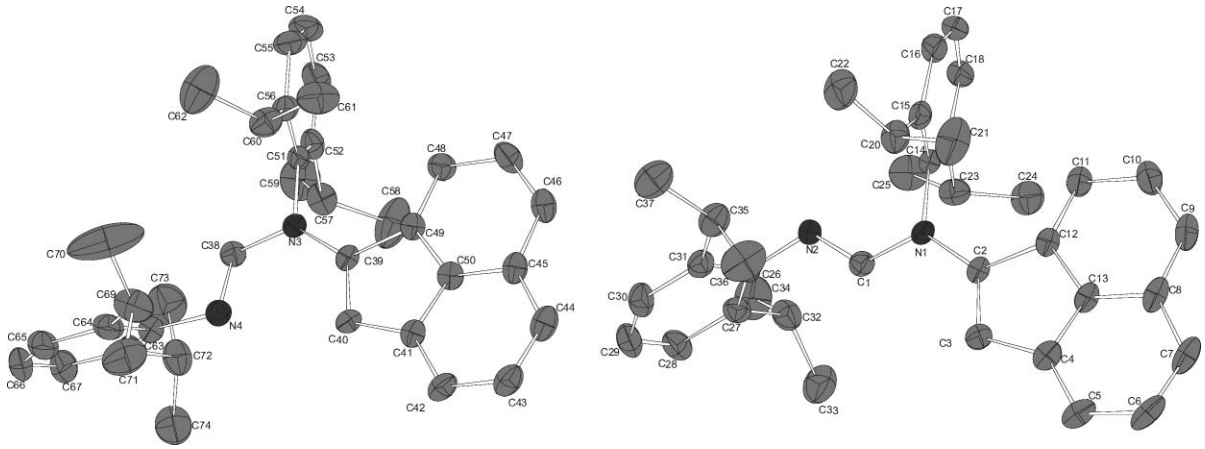
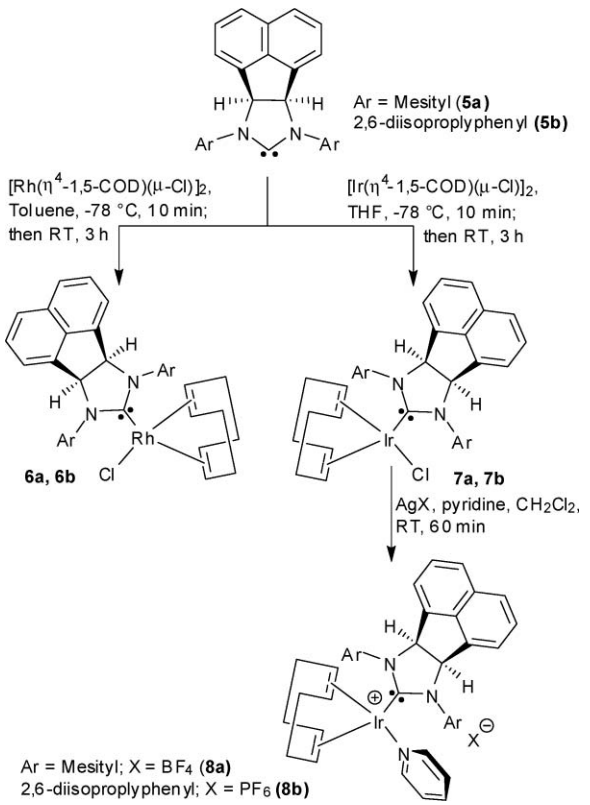


Fig. 3 ORTEP diagram of the two crystallographically distinct molecules of amine **4b** at 40% probability (hydrogen atoms have been omitted for clarity).



Scheme 3 Synthesis of Rh(I) and Ir(I) complexes.

complexes **6a** and **6b** were isolated as yellow crystalline solids, which were characterised by elemental analysis, mass spectrometry (ES^+), ^1H and $^{13}C\{^1H\}$ NMR spectroscopy using gCOSY, HMBC, HMQC, ROESY and TOCSY experiments.

The ^1H NMR spectra for complexes **6a** and **6b** were well resolved. The chemical shifts observed for the *N*-aromatic substituents on the imidazole ring for **6a** and **6b** indicates the slightly different chemical environment with hindered rotation on either side of imidazole ring. The backbone (–N*CHCH*N–) protons resonate as a set of singlets at δ 5.93 ppm and δ 6.02 ppm for (**6a**) and δ 6.15 ppm (**6b**), upfield of those observed for carbene **5a** (δ 5.70) and **5b** (δ 6.15), respectively. All the COD-CH protons appear as broad singlet at δ 3.32 (2H), 3.41 (1H) and 4.40 (1H) ppm for complex **6a** and at δ 3.35 (2H) and δ 4.59 (2H) ppm for complex **6b**. In the $^{13}C\{^1H\}$ NMR spectrum of **6a** the signal for the $C_{(carbene)}$ is upfield at δ 213.3 ppm ($J_{Rh-C} = 46.2$ Hz) relative to the free diaminocarbene **5a** which appears at δ 247.3 ppm and consistent with data reported for (η^4-1,5-COD)Rh(SIMes)Cl[38] (δ 212.0, $J_{Rh-C} = 48.1$ Hz). No signal for the $C_{(carbene)}$ in rhodium complex **6b** was observed and may be attributed to a slight fluxional behaviour of the molecule in solution as evidenced by the broader peaks in the ^1H NMR spectrum. The COD C_{CH} for rhodium complex **6a** appears as doublets at δ 67.7 ($J_{Rh-C} = 14.6$ Hz, *trans* to chlorine) and δ 95.9 ($J_{Rh-C} = 7.4$ Hz, *trans* to carbene) while the corresponding resonances for rhodium complex **6b** appear as broad singlets at δ 69.6 and δ 94.9 ppm and further confirms the fluxional nature of the molecule. These chemical shifts for the COD C_{CH} are also consistent with the reported data for (η^4-1,5-COD)Rh(SIMes)Cl[38] and (η^4-1,5-COD)Rh(tmiy)Cl[39] complexes; where tmiy = 1,3-bis(4-tolylmethyl)imidazol-2-ylidene.

Structural study

To establish the structure for rhodium complexes **6a** and **6b**, a single-crystal X-ray diffraction study was performed on crystals grown from slow diffusion of pentane into a saturated dichloromethane solution. The ORTEP views of the molecule **6a** and **6b** is shown in Fig. 4 and the crystal data is summarised in Table 4. The absolute configuration of rhodium complexes **6a** and **6b** as determined by X-ray analysis confirms the distorted square planar geometry at the rhodium(I) centre. Interestingly, the asymmetric unit cell of rhodium complex **6b** contains two different molecules with no crystallographic symmetry and differs slightly in their conformations. Both molecules have similar geometries for coordinated diaminocarbenes whereas the cycloctadiene of one molecule is reflected about the $C_1Rh_1Cl_1$ plane with respect to the other molecule. The Flack enantiopole parameter[40] gave the value of 0.01(2) showing the crystal consists of a single enantiomer despite the achiral nature of the molecule. As expected for cyclic diaminocarbene, the Rh–$C_{(carbene)}$ bond lengths are 2.042(4) Å **6a** and 2.078(4) Å **6b**, respectively, confirming the single bond character of the bond. These observed bond lengths are somewhat longer than the corresponding bond lengths observed for unsaturated heterocyclic carbene complexes[41–47] but comparable to that found

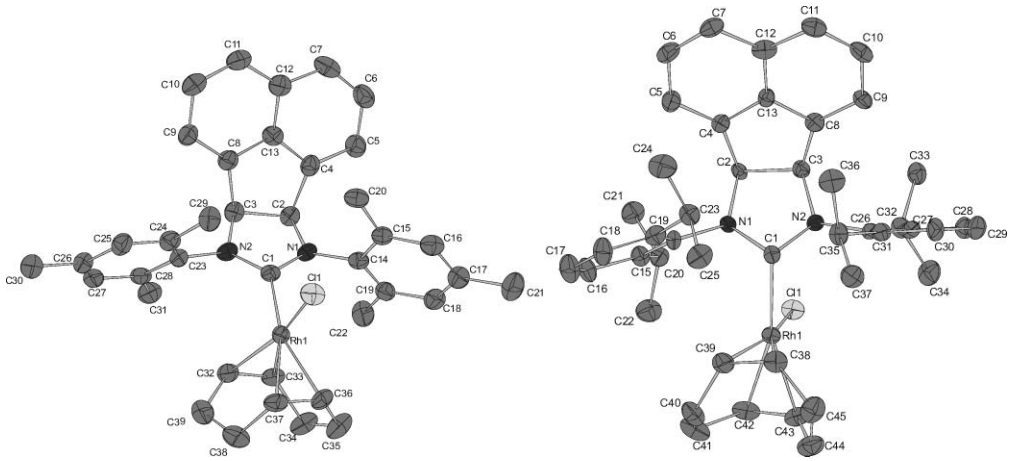


Fig. 4 ORTEP representation of molecular structure of the rhodium complexes **6a** (left) and **6b** (right) Thermal ellipsoids drawn at 40% probability.

in analogous diaminocarbene complexes.[38] The Rh–$C_{(carbene)}$ for **6b** is 0.036 Å (3.6 pm) longer when compared with **6a** and this may be due to the greater steric interactions of bulky isopropyl groups. The average Rh–$C_{(COD)}$ distance is 2.114 Å **6a** and 2.094 Å **6b** *trans* to chlorine and 2.205 Å **6a** and 2.192 Å **6b** *trans* to diaminocarbene, respectively, and found to be consistent with the greater *trans* influence of diaminocarbene when compared to chlorine. A large N_1–C_2–C_3–N_2 torsion angle 9.48° was observed for rhodium complex **6a**, when compared with 1.97° observed for **5a** and 3.38° for rhodium complex **6b**.

The angle between the best planes of the dihydroimidazole ring and the naphthyl group is 58.38° **6a** and 50.55° **6b**,respectively. The angle between the best planes of the dihydroimidazole ring and the phenyl rings C_{15}–C_{14}–C_{19} and C_{24}–C_{23}–C_{28} are 81.44° and 68.28° for **6a** and 79.64° and 69.73° for **6b**, respectively. The angle between the best planes of the dihydroimidazole ring and the coordination plane is 77.70° **6a** and 79.96° **6b**. The remaining bond lengths and bond angles are normal and lie within the expected range.

Synthesis and characterization of iridium(I) complexes

The reaction of the free carbenes **5a** and **5b** with [Ir(η^4-1,5-COD)(μ-Cl)]$_2$ in THF at −78 °C yields the neutral iridium(I) complexes **7a** and **7b**, which were isolated as orange-yellow crystalline solids in high yields 78% **7a** and 77% **7b**, respectively. (Scheme 3) Reaction of iridium(I) complexes **7a**and **7b** with $AgBF_4$ or $AgPF_6$ in the presence of pyridine as a coordinating ligand in CH_2Cl_2 at room temperature results in formation of cationic iridium(I) complexes [(η^4-1,5-COD)Ir(BIAN-SIMes)Py]BF_4 **8a** and [(η^4-1,5-COD)Ir(BIAN-SIPr)Py]PF_6 **8b** (Py = pyridine), respectively. The complexes **8a** and **8b** were isolated as bright red crystalline solids in high yields (>75%). The ^{1}H NMR spectrum (CD_2Cl_2) of the iridium complex **7b** at room temperature shows the absence of characteristic resonances for isopropyl protons and the COD-CH protons appear as broad singlets, suggesting that molecule is fluxional, *via* rotation about the Ir–$C_{(carbene)}$ bond. At 273 K peaks started to appear as broad resonances and complete freezing of the fluxional process was achieved at 213 K (−60 °C). At this temperature assignment of the NMR data was made with the help of ^{1}H-^{1}H COSY, ^{1}H-^{1}H TOCSY and ^{1}H-^{1}H ROESY NMR spectroscopy. At 213 K four doublets (δ 0.01 (6H), δ 0.88 (6H), δ 1.35 (6H), δ 1.45 (6H) ppm, respectively) for isopropyl-CH_3, two septets (δ 2.33 (2H) and δ 4.05 (2H)) for isopropyl-CH groups and two singlets (δ 2.33 (2H) and δ 4.05 (2H)) for COD-CH protons were carefully assigned.

The ^{1}H NMR spectrum (CD_2Cl_2, room temperature) of the cationic iridium complex **8a** shows three resonances (δ 1.49 (6H), δ 1.71 (6H) and δ 2.63 (6H)) for the mesityl CH_3 protons while five resonances (δ 1.49 (6H), δ 1.71 (3H), δ 2.38(6H), δ 2.58 (3H) and δ 2.73 (3H), respectively) for the corresponding mesityl CH_3 protons were observed for iridium complex **7a** (CD_2Cl_2, room temperature). The backbone protons (–NC*HCH*N–) resonate downfield at δ 6.01 ppm for complex **7a** and δ 6.10 ppm (233 K, CD_2Cl_2) for iridium complex **7b**, respectively, when compared with BIAN-H_2IMes **5a**, which resonate as singlets at δ 5.70 ppm. The COD-CH protons appear as multiplets at δ 3.12–3.20 and δ 3.82–3.98 ppm for complex **7a**, singlets (213 K, CD_2Cl_2) at δ 2.33 and δ 4.05 ppm for complex **7b**, singlets at δ 2.98 and δ 3.92 ppm for cationic iridium complex **8a** and singlets at δ 3.12 and δ 4.22 ppm for cationic complex **8b**, respectively. The downfield signals for COD-CH protons at δ 3.82–3.98 **7a**, δ 4.23 **7b**, δ 3.92 **8a** and δ 4.22 **8b** ppm were assigned to the vinyl hydrogens *trans* to carbene with the help of a ^{1}H-^{1}H ROESY NMR experiment and confirm its similarity with the very well studied Crabtree catalyst[48–51] Ir(COD)(py)L]PF_6; where L= tertiary phosphine. This is also found to be consistent with the longer Ir–$C_{(COD)}$ bond lengths *trans* to carbene ligand (*vide infra*). In the ^{13}C NMR spectrum of **7a** the signal for the $C_{(carbene)}$ is upfield at δ 201.9 ppm relative to iridium complex **6a** (δ 208.4) and free carbene **3a**, which appears at δ 247.3 ppm. This characteristic upfield shift of $C_{(carbene)}$ is consistent with coordination of carbene with the iridium centre.[52,53] The important ^{1}H and ^{13}C {^{1}H} NMR resonances for iridium complexes **7a**, **b** and **8a**, **b** are summarised in Table 3. Full ^{1}H and ^{13}C assignments are given in the Experimental.

Structural study

Single crystals for iridium complex **7b** and **8b**, suitable for X-ray study were grown by slow diffusion of pentane into a saturated dichloromethane solution. The ORTEP views of the molecule

Table 2 Selected bond lengths (Å) and angles (°) for rhodium and iridium complexes

Property	6a	6b	7b	8b
Bond lengths/Å				
C_1–$N_{1(2)}$	1.342(5), 1.362(5)	1.351(5), 1.358(5)	1.353(4), 1.351(4)	1.348(6), 1.376(7)
$N_{1(2)}$–$C_{2(3)}$	1.495(5),1.478(5)	1.489(5), 1.495(5)	1.487(4), 1.492(4)	1.496(7), 1.477(8)
C_2–C_3	1.555(5)	1.552(6)	1.548(4)	1.538(7)
C=$C_{(COD,trans\ to\ carbene)}$	1.370(6)	1.369(8)	1.390(5)	1.402(17)
C=$C_{(COD,trans\ to\ X)}$	1.390(6)	1.365(7)	1.412(5)	1.404(11)
M–C_1	2.042(4)	2.078(4)	2.070(3)	2.098(5)
M–X	2.3836(11)	2.3821(11)	2.3587(7)	2.109(6)
M–$C_{(COD,trans\ to\ X)}$	2.102(4), 2.120(4)	2.083(5), 2.105(4)	2.104(3), 2.131(3)	2.156(6), 2.167(7)
M–$C_{(COD,trans\ to\ carbene)}$	2.189(4), 2.220(4)	2.189(5), 2.194(4)	2.158(3), 2.195(3)	2.180(5), 2.171(6)
Bond angles (θ)/°				
N_1–C_1–N_2	107.6(3)	107.3(3)	108.0(2)	107.1(5)
C_1–$N_{1(2)}$–$C_{2(3)}$	114.0(3), 113.5(3)	114.2(3), 113.0(3)	112.8(2), 113.0(2)	113.4(4), 112.8(5)
$N_{1(2)}$–$C_{2(3)}$–$C_{3(2)}$	101.4(3), 102.5(3)	101.5(3), 102.8(3)	102.6(2), 101.2(2)	101.3(4), 103.1(4)
C_1–M–X	96.84(10)	83.53(11)	82.97(8)	101.9(2)
C_1–M–$C_{(COD,trans\ to\ X)}$	91.18(16), 88.55(15)	98.92(18), 101.93(18)	101.16(12), 102.98(12)	83.5(2), 90.8(3)
C_1–M–$C_{(COD,trans\ to\ carbene)}$	154.06(16), 168.41(16)	158.29(18), 162.25(18)	155.55(13), 163.51(14)	165.4(5), 153.9(2)
Torsion angle/°				
N_1–C_2–C_3–N_2	9.48	3.38	12.58	13.56

M = Rh (**6a**, **6b**), Ir (**7b**, **8b**); X = Cl (**6a**, **6b**, **7b**), pyridine (**8b**)

7b and **8b** are shown in Fig. 5 and 6, respectively, and crystal data is summarised in Table 4. Selected bond lengths (Å) and bond lengths (°) are given in Table 2. For iridium complex **8b**, the refinement on the Flack enantiopole parameter[40] gave a value of 0.384(8) showing the crystal to be twinned by inversion. The structure of the complexes **7b** and **8b** confirm the coordination is distorted square planar at the iridium(I) centre, with coordinated C=C (cyclooctadiene) midpoints as vertexes. The angle between the best planes of the dihydroimidazole ring and the coordination plane is 70.14° **7b** and 60.29° **8b**, respectively. The iridium–$C_{(carbene)}$ distance of 2.070(3) Å in **7b** and 2.098(5) Å in **8b** is slightly longer than the corresponding bond lengths observed for Crabtree's[39] and Nolan's saturated carbene-iridium systems.[52]

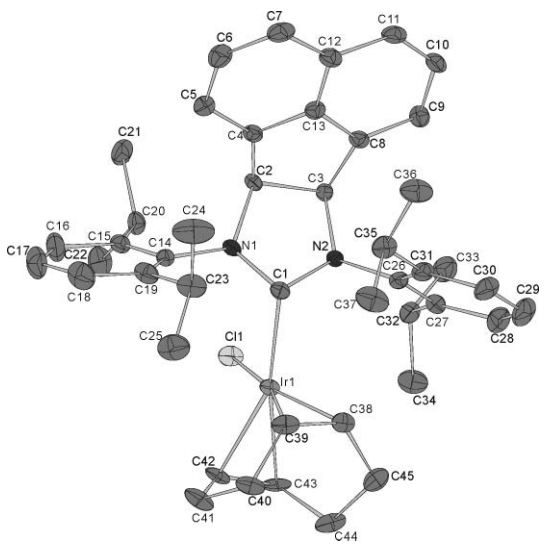


Fig. 5 ORTEP representation of molecular structure of **7b** (thermal ellipsoids drawn at 40% probability and hydrogen atoms are omitted for clarity).

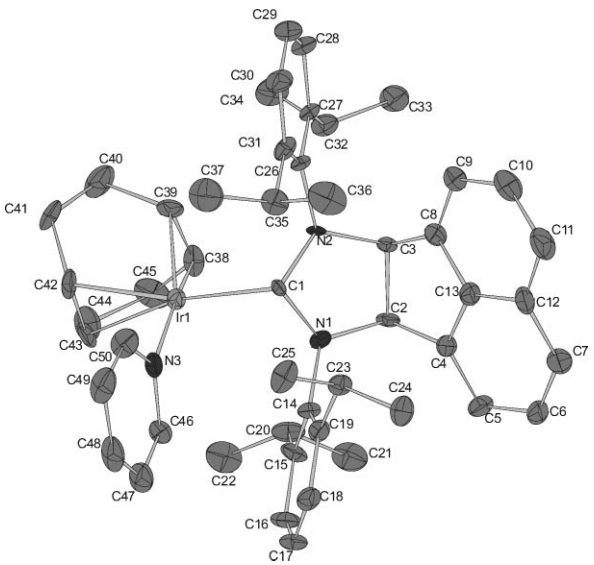


Fig. 6 ORTEP representation of molecular structure of **8b** (thermal ellipsoids drawn at 40% probability and hydrogen, solvent of crystallisation (CH_2Cl_2) and PF_6 are omitted for clarity).

These relatively longer bond lengths for the iridium–$C_{(carbene)}$ bond is presumably due to the greater steric interactions of diaminocarbene **5b** on coordination and also suggests the single bond character for the cyclic diaminocarbenes. For complex **7b**, the mean iridium–$C_{(COD)}$ bond distances of 2.176(8) Å (*trans* to carbene) and 2.117(8) Å (*trans* to chlorine) are in agreement

Table 3 Selected NMR chemical shifts for iridium complexes **7–8**

	^{1}H NMR Chemical Shifts (δ)/ppm	^{13}C{^{1}H} NMR Chemical Shifts (δ)/ppm	
Compound	COD-CH *trans* to $C_{(carbene)}$	COD-CH *trans* to $C_{(carbene)}$	$C_{(carbene)}$
7a	3.82–3.89 [m, 2H]	82.4, 83.4	208.4
7b	3.92 [m, 2H]	83.5	201.9
8a	4.23 [s, 2H]	80.5	Not observed
8b	4.22 [s, 2H]	83.82	202.6

Table 4 Crystal structure refinement data for carbene **5a**, rhodium complexes **6a** and **6b** and iridium complexes **7b** and **8b**

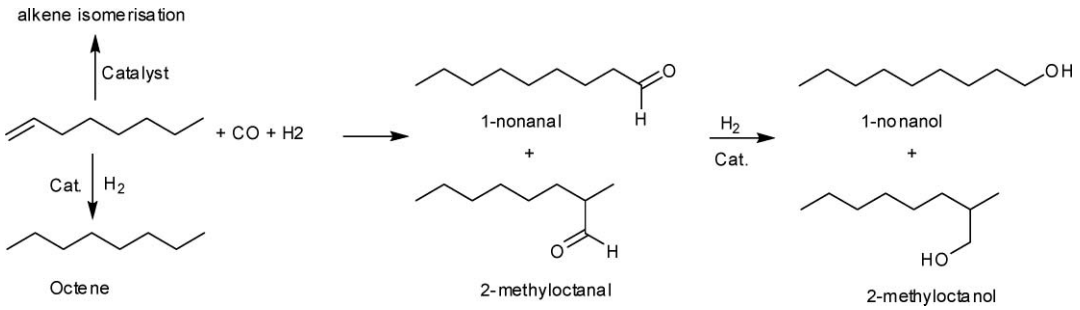
	Compound **5a**	Compound **6a**	Compound **6b**	Compound **7b**	Compound **8b**
Chemical formula	$C_{34}H_{33}N_2$	$C_{39}H_{42}ClN_2Rh$	$C_{45}H_{54}ClN_2Rh$	$C_{45}H_{54}ClIrN_2$	$C_{51}H_{61}Cl_2F_6IrN_3P$
Formula weight	469.65	677.13	761.29	850.61	1124.15
T/K	150	150	150	150	150
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1$	$P2_1/c$	Cc
a/Å	25.9142(4)	9.0034(2)	12.5115(2)	11.6520(2)	18.6624(3)
b/Å	11.0550(2)	17.0287(5)	12.2042(2)	28.9269(3)	15.6085(2)
c/Å	19.0937(3)	21.0890(5)	24.8139(5)	11.7784(2)	16.6277(3)
α/°	90	90	90	90	90
β/°	105.1595(8)	93.5968(15)	90.4245(9)	106.6717(5)	90.0100(6)
γ/°	90	90	90	90	90
V/Å^3	5279.64(15)	3226.92(14)	3788.80(12)	3803.10(10)	4843.52(13)
Z	8	4	4	4	4
D_{calcd}/Mg m^{-3}	1.182	1.394	1.335	1.486	1.542
μ/mm^{-1}	0.068	0.642	0.555	3.615	2.961
F_{000}	2008	1408	1600	1728	2272
Crystal size/mm	0.16 × 0.24 × 0.40	0.14 × 0.18 × 0.18	0.08 × 0.12 × 0.14	0.08 × 0.14 × 0.14	0.12 × 0.16 × 0.24
Description of crystal	Colourless block	Yellow fragment	Yellow block	Orange fragment	Orange fragment
Absorption correction	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections
Transmission coefficients (min/max)	0.97/0.99	0.89/0.91	0.93/0.96	0.60/0.75	0.49/0.72
θ range for data collection/°	$5.0 \le \theta \le 27.5$	$5.0 \le \theta \le 27.5$	$5.0 \le \theta \le 27.5$	$5.0 \le \theta \le 27.5$	$5.0 \le \theta \le 27.5$
Index ranges	$-33 \le h \le 32, 0 \le k \le 14, 0 \le l \le 24$	$-11 \le h \le 11, 0 \le k \le 22, 0 \le l \le 27$	$-16 \le h \le 16, -15 \le k \le 13, 0 \le l \le 32$	$-15 \le h \le 14, 0 \le k \le 37, 0 \le l \le 15$	$-24 \le h \le 24, 0 \le k \le 20, 0 \le l \le 21$
Reflections measured	32 188	26 281	46 131	39 394	22 099
Unique reflections	6309	7519	14 962	8609	10 569
R_{int}	0.051	0.064	0.072	0.041	0.047
Observed reflections ($I > 3\sigma(I)$)	3638	4293	10 770	6115	9261
Refinement method	Full-matrix least-squares on F	Full-matrix least-squares on F	Full-matrix least-squares on F	Full-matrix least-squares on F	Full-matrix least-squares on F
Parameters refined	326	404	916	458	594
Weighting scheme	Chebychev 3-term polynomial	Chebychev 3-term polynomial	Chebychev 3-term polynomial	Chebychev 3-term polynomial	Chebychev 3-term polynomial
Goodness of fit	1.0758	1.1352	1.0788	1.0769	1.1069
R	0.0482	0.0386	0.0385	0.0218	0.0378
wR	0.0584	0.0415	0.0385	0.0226	0.0423
Residual electron density (min/max)/e Å^{-3}	−0.32/0.29	−0.45/0.65	−0.49/0.35	−0.62/0.49	−1.48/1.80
Flack parameter	—	—	−0.01 (2)	—	0.384 (8)
Structure details	—	—	5983, Friedel-Pairs	—	4865, Friedel-Pairs

with the reported Crabtree's unsaturated carbene-iridium (η^4-1,5-COD)Ir(tmiy)Cl[39] systems and confirms the greater *trans* influence of cyclic diaminocarbenes when compared with chlorine.[39] For iridium complex **8b**, the average Ir–$C_{(COD)}$, *trans* to pyridine bond distance is 0.014 Å shorter than that *trans* to carbene, due to the higher *trans* influence of carbene. This also confirms the ^{1}H NMR assignments for COD vinyl protons (*vide supra*). In contrast, very large torsion angles of 12.58° and 13.56. Were observed for iridium complexes **7b** and **8b**, respectively, when compared with 2.44° and 3.38° observed for imidazolium salt **3b**[26] and rhodium complex **6b**. The angle between the best planes of the dihydroimidazole ring and the naphthyl group at the backbone decreases from 59.80° for **3b**[26] to 54.28° and 54.72° for **7b** and **8b**, respectively. Whereas, the angles between the best planes of the dihydroimidazole ring and the 2,6-diisopropylphenyl rings are 61.81° and 88.07° for **7b** and 63.66° and 85.78° for **8b**, respectively. The remaining bond lengths and bond angles are normal and lie within the expected range.

Table 5 Hydroformylation of 1-octene using rhodium complexes **6a** and **6b**

Entry	Catalyst/mol%		T/°C	p^a/bar	t/h	Aldehyde^b l/b (%)	Alcohol^b l/b (%)
1	**6b**	1	40	40	12	1.45 (20)	—
2		1	100	55	20	1.47 (≥ 99)	—
3	**6a**	0.1	100	55	24	0.85 (95)	2.66 (3)
4	**6b**	0.5	100	40	22	1.72 (≥ 99)	—
5	**6a**	0.1	100	30	24	0.58 (96)	2.57 (3)
6	**6b**	0.1	100	30	20	0.75 (96)	1.7 (1)
7		0.01	100	20	24	0.54 (85)	1.57 (10)
8	**6a**	0.1	100	20	24	0.76 (60)	0.87 (30)

^{a} $CO–H_2$, 33 : 67. ^{b} Conversion to linear and branched aldehydes and alcohols, as determined by GC and an average of two runs.



Scheme 4 Possible side reaction in the hydroformylation of 1-octene.

Catalytic hydroformylation

The rhodium complexes **6a** and **6b** were tested for the hydroformylation of 1-octene and the data is summarised in Table 5. The catalytic reaction is sensitive to the reaction conditions as well as the ligand employed. A series of possible side reaction in the rhodium catalysed hydroformylation of 1-octene is described below (Scheme 4). The hydroformylation reactions were carried out in toluene using varying pressures of CO + H_2 (33% CO balanced with H_2) at 100 °C unless otherwise stated. Cyclohexane was used as an internal standard. All the reaction conditions are optimised as reported in Table 5. The greatest yields of aldehyde at 100 °C were obtained with higher pressures of H_2/CO (>20 bar), while the linear *versus* branched ratio varied from 0.85 to 1.72. The catalytic activities for catalysts **6a** and **6b** is comparable (TOF and TON) to that of closely related systems.[54–56] No measurable hydrogenation or isomerisation was observed for catalysts **6a** and **6b**, as commonly observed for rhodium-phosphine based catalytic systems which under hydroformylation conditions produced a mixture of aldehydes.[57–61] The detailed hydroformylation procedure is given in the ESI.†

Conclusion

In conclusion we describe the synthesis and isolation of first two members of a new family of annulated cyclic diaminocarbenes ligands BIAN-SIMes, **5a** and BIAN-SIPr, **5b**, which have been structurally characterised (**5a**). Such carbenes were previously thought to be impossible to synthesise due their rigid tetracyclic imidazole skeleton. The imidazolinium precursors show the base selectivity for the synthesis of such carbenes. The decomposition of imidazolinium salt *via* the ring opening at the backbone during carbene synthesis was also observed and decomposition products were isolated and structurally characterised. The rhodium(I) and iridium(I) complexes were obtained by the reaction of free carbene with suitable metal precursors. The rhodium(I) complexes show activity for the hydroformylation of 1-octene.

Experimental

General procedures

All manipulations were performed under dinitrogen using standard Schlenk vessel techniques or in an inert atmosphere glove box. All solvents were dried by passage through an alumina column under a positive pressure of dinitrogen and deoxygenated by bubbling dry dinitrogen through the dried solvents for twenty minutes before use. NMR spectra were recorded on either a Varian Unity Plus 500 (^{1}H at 500 MHz, ^{13}C at 125.7 MHz) or on a Varian Mercury 300 (^{1}H at 300 MHz, ^{13}C at 75.5 MHz) spectrometer at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances and chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Electrospray mass spectra were recorded in acetonitrile on a Micromass LC TOF spectrometer. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford. Gas Chromatographs were recorded using Perkin Elmer XL 1100 instrument with Perkin Elmer NCI 900 Network Chromatography Interface using fused silica, non-polar SGE column 25QC2/BP1 1.0.

All reagents were purchased from Aldrich, metal precursors from Johnson-Matthey and used as received unless otherwise stated. The reagents Ar-BIAN,[24,25] [(BIAN-SIMes)(H)]BF_4,[36] [(BIAN-SIPr)(H)]BF_4,[36] $[Rh(COD)Cl]_2$[62] and $[Ir(COD)Cl]_2$[51] were prepared using published procedures. The bases KO^{t}Bu and

$KN(SiMe_3)_2$ were triply sublimed and kept in the inert atmosphere glove box.

Synthesis of 7,9-bis(2,4,6-trimethylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylidene (5a)

The imidazolinium salt **3a** (0.3 g, 0.58 mmol) was suspended in THF (5.0 mL) and cooled to −78 °C. The KO^{t}Bu (65.0 mg, 0.60 mmol) was separately dissolved in THF (5.0 mL) and cooled to −78 °C and added dropwise with constant stirring to the imidazolinium salt over the period of 5.0 min, stirred for 30 min and gradually warmed to room temperature. The reaction mixture was further stirred for 1 h, during which time the colour of the reaction mixture changed from off-white to light orange yellow. The mixture was then filtered, evaporated to dryness and washed with pentane (2 × 10 mL) at −78 °C and dried in vacuum. The product was isolated as off white solid. Yield: 0.19 g, 79%.

^{1}H NMR (300 MHz, 291.6 K, C_6D_6): 7.47 (d, J = 7.5 Hz, 2H, backbone ring CH), 7.11 (t, J = 7.6 Hz, 2H, backbone ring CH), 6.94 (s, 2H, mesityl-*m*-CH), 6.78 (s, 2H, mesityl-*m*-CH), 6.75 (d, J = 6.9 Hz, 2H, backbone ring CH), 5.70 (s, 2H, –NC*HCH*N–), 2.41 (s, 6H, mesityl-CH_3), 2.21 (s, 6H, mesityl-CH_3), 1.74 (s, 6H, mesityl-CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 293 K, C_6D_6): 247.3 (s, $C_{(carbene)}$), 136.4, 138.3, 141.6 (s, $C_{(Backbone\ ring\ aromatic)}$), 131.9, 135.4, 136.8, 138.0 (s, $C_{(Mesityl\ aromatic)}$), 129.5, 129.7 (s, $C_{(Mesityl\text{-}m\text{-}CH)}$), 120.7, 124.8, 128.1 (s, $C_{(Backbone\ ring\ aromatic\ CH)}$), 71.6 (s, –N*CHCH*N–), 18.4, 19.9, 21.1 (s, $C_{(Mesityl\text{-}CH_3)}$).

Mass Spectrometry (ES+, C_6H_6): m/z = 431.2501 $[M + H]^+$, (100%).

Elemental analysis (%): found (calcd): C 85.98 (86.47), H 6.92 (7.02), N 6.34 (6.51).

Synthesis of 7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylidene (5b)

To a stirred suspension of imidazolium tetrafluoroborate **3b** (0.26 g, 0.43 mmol) in pentane (15.0 mL) at −78 °C was added dropwise a solution of 1.6 M ^{n}BuLi in hexane (0.27 mL, 0.43 mmol) with the help of syringe, stirred for 10 min and gradually warmed to room temperature. The reaction mixture was further stirred for 2 h at room temperature, during which time the mixture changed from off-white to light orange with the dissolution of imidazolium precursor in pentane. The mixture was then filtered, evaporated to dryness and washed with pentane at −78 °C and dried in vacuum. The product was isolated as off white solid. Yield: 0.19 g, 90%.

^{1}H NMR (300 MHz, 293 K, C_6D_6): 7.18 (d, J = 8.21 Hz, 2H), 6.73–7.10 (m + br, 8H), 6.36 (d, J = 6.9 Hz, 2H), 5.38 (s, 2H, –NC*HCH*N–), 3.19 (sept, J = 6.9 Hz, 2H, ^{i}Pr-CH), 2.28 (sept, J = 6.9 Hz, 2H, ^{i}Pr-CH), 1.14 (d, J = 6.9 Hz, 3H, ^{i}Pr-CH_3), 1.06 (d, J = 6.7 Hz, 6H, ^{i}Pr-CH_3), 0.87 (d, J = 6.7 Hz, 6H, ^{i}Pr-CH_3), 0.53 (d, J = 6.8 Hz, 6H, ^{i}Pr-CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 293 K, C_6D_6): 241.9 (s, $C_{(carbene)}$), 137.4, 146.5, 148.8 (s, $C_{(Phenyl\ aromatic)}$), 131.7, 136.3, 140.8 (s, backbone $C_{(aromatic)}$), 124.7 (s, $C_{(Backbone\ ring\ aromatic\ CH)}$), 123.7, 123.8 (s + br, $C_{(Phenyl\ CH)}$), 121.0 (s, $C_{(Backbone\ ring\ aromatic\ CH)}$), 73.9 (s, –N*CHCH*N–), 28.7, 29.1 (s, ^{i}Pr-CH), 21.9, 23.4, 25.2, 26.6 (s, ^{i}Pr-CH_3).

Mass Spectrometry (ES+, C_6H_6): m/z = 515.3409 $[M + H]^+$, (100%).

Elemental analysis (%): found (calcd): C 85.89 (86.33), H 8.15 (8.22), N 5.20 (5.27).

Synthesis of (η^4-1,5-COD)-7,9-bis(2,4,6-trimethylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylidenerhodium(I) chloride (6a)

The carbene **5a** (0.53 g, 1.28 mmol) in toluene (5.0 mL) was dropwise added to a stirred solution of $[Rh(COD)Cl]_2$ (0.30 g, 0.61 mmol) in toluene (5.0 mL) at −78 °C and mixture was stirred for 10 min, warmed to room temperature and stirred for further 3 h. The colour of the reaction mixture changed to orange yellow and the reaction mixture was then filtered through Celite and the volatiles were *in vacuo*. The crude was washed with pentane (2 × 5.0 mL) to give the product as yellow solid which was further extracted with warm ether (3 × 10.0 mL). Evaporation of diethyl ether solution gave an orange yellow crystalline solid. Yield: 0.61 g, 81%.

^{1}H NMR (300 MHz, 293 K, C_6D_6): 7.76 (d, J = 7.5 Hz, 1H, backbone ring CH), 7.74 (d, J = 7.8 Hz, 1H, backbone ring CH), 7.38 (m, 2H, backbone ring CH), 7.12 (s, 1H, mesityl-*m*-CH), 7.08 (s, 1H, mesityl-*m*-CH), 7.03 (s, 1H, mesityl-*m*-CH), 6.91 (s, 1H, mesityl-*m*-CH), 6.86 (d, J = 6.9 Hz, 1H, backbone ring CH), 6.81 (d, J = 6.9 Hz, 1H, backbone ring CH), 6.02 (s, 1H, –NC*HCH*N–), 5.93 (s, 1H, –NC*HCH*N–), 4.40 (s + br, 2H, COD-CH), 3.41 (s + br, 1H, COD-CH), 3.32 (s + br, 1H, COD-CH), 2.82 (s, 3H, mesityl-CH_3), 2.54 (s + br, 3H, mesityl-CH_3 + 1H, CODCH_2), 2.39 (s + br, 6H, mesityl-CH_3 + 1H, COD CH_2), 1.87 (s, 3H, mesityl-CH_3), 1.43–1.82 (m + br, 6H, COD-CH_2), 1.41 (s, 3H, mesityl-CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 293 K, C_6D_6): 213.3 [d, $J_{Rh\text{-}C}$ = 46.2, Rh–$C_{(carbene)}$], 137.7, 137.8, 137.9, 139.4, 139.5, 139.9 [s, $C_{(aromatic)}$], 131.5, 134.3, 134.8, 137.1, 137.2, [s, $C_{(aromatic)}$], 128.5, 128.6, 130.1, 130.3 [s, mesityl CH], 121.6, 121.8, 125.3, 125.4, 127.9, [s, $C_{(Backbone\ ring\ aromatic\ CH)}$], 97.1 (d, J = 7.1 Hz, $C_{(COD\text{-}CH)}$), 70.8, 71.1 (s, –N*CHCHCH*N–), 95.9 (d, J = 7.4 Hz, $C_{(COD\text{-}CH)}$), 67.7 (d, J = 14.6 Hz, $C_{(COD\text{-}CH)}$), 67.0 (d, J = 14.6 Hz, $C_{(COD\text{-}CH)}$), 28.1, 32.5 (s + br, $C_{(COD\text{-}CH2)}$), 19.2, 19.3, 20.4, 21.1, 21.3 (s, $C_{(Mesityl\text{-}CH3)}$).

Mass Spectrometry (ES+, CH_3CN): m/z = 641.2415 $[M\text{-}Cl]^+$, (100%),

Elemental analysis (%): found (calcd): C 68.91 (69.18), H 6.32 (6.25), N 4.19 (4.14).

Synthesis of (η^4-1,5-COD)-7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylidenerhodium(I) chloride (6b)

The carbene **5b** (0.63 g, 1.22 mmol) in toluene (5.0 mL) was dropwise added to a stirred solution of $[Rh(COD)Cl]_2$ (0.28 g, 0.58 mmol) in toluene (5.0 mL) at −78 °C and mixture was stirred for 10 min, warmed to room temperature and stirred for further 3 h, during which time reaction mixture changed to pale yellow. The reaction mixture was then filtered through Celite and solvent was removed *in vacuo*. It was then washed with pentane (2 × 5.0 mL) to give the product as yellow solid. The crude product was then dissolved in CH_2Cl_2 (2.0 mL) and precipitated with pentane (10.0 mL), filtered and dried in vacuum. The product was obtained as pale yellow crystalline solid. Yield: 0.68 g, 78%.

^{1}H NMR (300 MHz, 291.8 K, CD_2Cl_2): 7.71 (d, J = 8.3 Hz, 2H, backbone ring CH), 7.50 (d, J = 4.6 Hz, 4H, phenyl-*p*-CH),

7.29 (t, $J = 7.6$ Hz, 2H, backbone ring CH), 7.22 (t, $J = 4.5$ Hz, 2H, phenyl-*p*-CH), 6.51 (s + br, 2H, backbone ring CH), 6.15 (s, 2H, –NC*HCH*N–), 4.59 (s + br, 2H, COD-CH), 4.25 (s + br, 2H, ^{i}Pr-CH), 3.35 (s + br, 2H, COD-CH), 2.53 (s + br, 2H, ^{i}Pr-CH), 1.85 (m, 2H, COD-CH_2), 1.68 (m, 2H, COD-CH_2), 1.58 (d, $J =$ 6.4 Hz, 6H, ^{i}Pr-CH_3), 1.44 (d, $J = 6.8$ Hz, 6H, ^{i}Pr-CH_3), 1.40–1.55 (m, 4H, COD-CH_2), 1.03 (d, $J = 5.6$ Hz, 3H, ^{i}Pr-CH3), 0.09 (s + br, 6H, ^{i}Pr-CH_3).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, 293 K, CD_2Cl_2): 135.9, 148.7 [s + br, $C_{(Phenyl\ aromatic)}$), 132.1, 136.8, 139.4 [s, $C_{(Backbone\ aromatic)}$), 124.6, 125.9, 129.2 (s + br, $C_{(Phenyl\ CH)}$), 122.9, 125.9, 128.4 (s, $C_{(Backbone\ ring\ aromatic\ CH)}$), 72.5 (s, –N*CHCH*N–), 69.6, 94.9 (s + br, $C_{(COD\text{-}CH)}$), 28.4, 29.4 (s, ^{i}Pr-CH), 28.5, 32.8 (s, $C_{(COD\text{-}CH2)}$), 22.5, 25.5, 26.1 (s + br, ^{i}Pr-CH_3).

Mass Spectrometry (ES+, CH_3CN): $m/z = 725.3323$ $[M - Cl]^+$, (100%),

Elemental analysis (%): found (calcd): C 70.76 (71.00), H 7.25 (7.15), N 3.61 (3.68).

Synthesis of (η⁴-1,5-COD)-7,9-bis(2,4,6-trimethylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylideneiridium(I) chloride (7a)

The compound $[Ir(COD)Cl]_2$ (0.37 g, 0.55 mmol) was dissolved in THF (5.0 mL) and cooled to −78 °C. A solution of carbene **5a** (0.50 g, 1.13 mmol) in THF (5.0 mL) was then added dropwise. The solution was stirred for 10 min at −78 °C and then warmed to room temperature, stirred for 3 h. The colour of the reaction mixture changed to orange yellow. The reaction mixture was then filtered through Celite and solvent was reduced to dryness. The addition of ice cold pentane (5.0 mL) gave the product as yellow solid. The crude product was then extracted with warm diethyl ether (2 × 5 mL). Evaporation of diethyl ether solution gave the orange yellow crystals. Yield: 0.66 g, 77%.

^{1}H NMR (300 MHz, 291.6 K, CD_2Cl_2): 7.80 (d, $J = 8.2$ Hz, 2H, backbone ring CH), 7.41 (m, 2H, backbone ring CH), 7.10 (s + br, 2H, mesityl-*m*-CH), 6.94 (s + br, 2H, mesityl-*m*-CH), 6.82 (d, $J = 7.0$ Hz, 1H, backbone ring CH), 6.79 (d, $J = 6.9$ Hz, 1H, backbone ring CH), 3.82–3.98 (m, 2H, COD-CH), 6.01 (s, 2H, –NC*HCH*N–), 3.12–3.20 (m, 2H, COD-CH), 2.73 (s, 3H, mesityl-CH_3), 2.58 (s, 3H, mesityl-CH_3), 2.38 (s, 6H, mesityl-CH_3), 1.71 (s, 3H, mesityl-CH_3), 1.50–1.63 (m + br, 4H, COD-CH_2), 1.49 (s, 3H, mesityl-CH_3), 1.21–1.32 (m + br, 4H, COD-CH_2).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, 293 K, CD_2Cl_2): 208.4 (s, Ir–$C_{(carbene)}$), 137.7, 137.8, 138.1, 138.2, 139.7, 139.9 (s, $C_{(aromatic)}$), 131.8, 134.9, 135.2, 135.3, 137.5 (s, $C_{(aromatic)}$), 128.9, 129.2, 130.1 (s, $C_{(Mesityl\text{-}m\text{-}CH)}$), 122.0, 122.4, 125.7, 128.3, 128.4, (s, $C_{(Backbone\ aromatic\ CH)}$), 82.4, 83.4 (s, $C_{(COD\text{-}CH)}$), 71.4, 71.5(s, –N*CHCH*N–), 51.7, 52.4 (s, $C_{(COD\text{-}CH)}$), 28.8, 33.5, 33.7 [s, $C_{(COD\text{-}CH_2)}$), 19.5, 19.8, 20.3, 21.2 (s, $C_{(Mesityl\text{-}CH_3)}$).

Mass Spectrometry (ES+, CH_3CN): $m/z = 729.2792$ $[M - Cl]^+$, (100%).

Elemental analysis (%): found (calcd): C 61.06 (61.12), H 5.50 (5.52), N 3.73 (3.66).

Synthesis of (η⁴-1,5-COD)-7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylideneiridium(I) chloride (7b)

The compound $[Ir(COD)Cl]_2$ (0.49 g, 0.73 mmol) was dissolved in THF (5.0 mL) and cooled to −78 °C. A solution of carbene **5b** (0.78 g, 1.53 mmol) in THF (5.0 mL) was then added dropwise and mixture was stirred for 10 min at −78 °C and then warmed to room temperature, stirred for 3 h. The colour of the reaction mixture changed to orange-yellow. The reaction mixture was filtered through Celite and reduced to dryness. Addition of ice cold pentane (5.0 mL) gave the product as yellow solid. The crude product was then extracted with warm pentane (5 × 10 mL) and evaporation of yellow pentane solution gave the product as orange-yellow crystalline solid. Yield: 1.05 g, 87%.

^{1}H NMR (500 MHz, 213 K, CD_2Cl_2): 7.72 (d, $J = 8.3$ Hz, 2H, backbone ring proton), 7.40–7.52 (m + br, 4H, Ph-*m*-CH + Ph-*p*-CH), 7.28 (t, $J = 7.62$ Hz, 2H, backbone ring proton), 6.45 (d, $J =$ 6.5 Hz, 2H, Ph-*m*-CH), 6.36 (d, $J = 6.4$ Hz, 2H, backbone ring proton), 4.23 (s + br, 2H, COD-CH_2), 6.10 (s, 2H, –NC*HCH*N–), 4.05 (d, $J = 6.5$ Hz, 3H, ^{i}Pr-CH_3), 2.33 (sept, $J = 6.5$ Hz, 2H, ^{i}Pr-CH), 2.92 (s + br, 2H, COD-CH_2), 1.69 (s + br, 2H, COD-CH_2), 1.45 (d, $J = 6.1$ Hz, 3H, ^{i}Pr-CH_3), 1.35 (d, $J = 6.5$ Hz, 3H, ^{i}Pr-CH_3), 1.19 (m, 4H, COD), 1.02 (m, 2H, COD-CH), 0.88 (d, $J = 6.1$ Hz, 3H, ^{i}Pr-CH_3), 0.01 (d, $J = 6.5$ Hz, 3H, ^{i}Pr-CH_3).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, 293 K, CD_2Cl_2): 136.7, 138.3, 147.8 (s + br, $C_{(phenyl\ aromatic)}$), 130.9, 135.5 (s + br, $C_{(Backbone\ aromatic)}$), 128.55, 130.32 (s, $C_{(Phenyl\ CH)}$), 123.5, 124.6, 128.1 (s + br, $C_{(Phenyl\ CH)}$), 121.8, 124.9, 127.3 (s, $C_{(Backbone\ ring\ CH)}$), 71.6 (s + br, –N*CHCH*N–), 52.6, 80.5 (s + br, $C_{(COD\text{-}CH)}$), 32.6 (s + br, $C_{(^{i}Pr\text{-}CH)}$), 27.4, 27.6, 28.5 (s + br, $C_{(COD\text{-}CH_2)}$), 0.0, 23.4, 24.0, 25.1 (s, $C_{(^{i}Pr\text{-}CH_3)}$).

Mass Spectrometry (ES+, CH_3CN): $m/z = 850.1475$ $[M]^+$, (100%)

Elemental analysis (%): found (calcd): C 63.49 (63.54), H 6.71 (6.40), N 3.09 (3.29).

Synthesis of (η⁴-1,5-COD)(pyridine)-7,9-bis(2,4,6-trimethyl phenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylideneiridium(I) tetrafluoroborate (8a)

The iridium complex **6a** (0.50 g, 0.65 mmol) and pyridine (80.0 μL, 0.98 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and a solution of $AgBF_4$ (0.12 g, 0.65 mmol) in CH_2Cl_2 (5.0 mL) was added then dropwise, solution was stirred for 1 h in dark at room temperature. The precipitated silver chloride was separated by filtration and volume was reduced to 3.0 mL, pentane (10.0 mL) was added to precipitate the product. This was then washed with pentane (2 × 5.0 mL) and dried in vacuum. The product was obtained as a bright red solid. Yield: 0.42 g, 73%.

^{1}H NMR (300 MHz, 291.6 K, CD_2Cl_2): 8.49 (s + br, 2H, Py H_4), 7.69 (d + br, $J_{HH} = 8.0$ Hz, 2H, Py $H_{2,6}$), 7.56 (d, 2H, $J =$ 5.9 Hz, backbone ring CH), 7.27 (t + br, $J = 6.9$ Hz, 2H, Py $H_{3,5}$), 7.21 (s + br, 2H, mesityl-*m*-CH), 7.06 (t + br, $J = 6.6$ Hz, 2H, backbone ring CH), 6.77 (s + br, 2H, mesityl-*m*-CH), 6.50 (d, 2H, $J = 6.9$ Hz, backbone ring CH), 6.00 (s, 2H, –NC*HCH*N–), 3.92 (s + br, 2H, COD-CH), 2.98 (s + br, 2H, COD-CH), 2.63 (s, 6H, mesityl-CH_3), 1.71 (s, 6H, mesityl-CH_3 + 2H, COD-CH_2), 1.81 (m + br, 2H, COD-CH_2), 1.21–1.74 (m + br, 4H, COD-CH_2), 1.49 (s, 6H, mesityl-CH_3).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, 293 K, CD_2Cl_2: 201.9 (s, Ir–$C_{(carbene)}$), 130.1, 130.4 (s, $C_{(Mesityl\text{-}m\text{-}CH)}$), 136.3, 137.2, 137.3, 137.8, 138.0 (s, $C_{(aromatic)}$), 131.3, 131.5, 133.9, 135.8, 136.2 (s, $C_{(aromatic)}$), 125.6, 125.8, 139.2, 149.8, 151.1 (s, $C_{(Py\text{-}CH)}$), 121.9, 124.0, 128.2 (s, $C_{(Backbone\ ring\ CH)}$), 70.9 (s, –N*CHN*CH–),65.4, 83.5 (s, $C_{(COD\text{-}CH)}$), 29.1, 32.3 (s, $C_{(COD\text{-}CH_2)}$), 18.59, 18.9, 20.9, 21.0 (s, $C_{(Mesityl\text{-}CH_3)}$).

Mass Spectrometry (ES+, CH_3CN): $m/z = 810.35$ $[M]^+$, (100%).

Elemental Analysis (%): found (calcd): C 58.77 (58.92), H 5.34 (5.28), N 4.71 (4.69).

Synthesis of (η^4-1,5-COD)(pyridine)-7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydroacenaphtho[1,2-d]imidazolin-2-ylideneiridium(I) hexafluorophosphate (8b)

The iridium complex **7b** (0.80 g, 0.94 mmol) and pyridine (92.0 μL, 1.12 mmol) was dissolved in CH_2Cl_2 (7.0 mL). A solution of $AgPF_6$ (0.24 g, 0.94 mmol) in CH_2Cl_2 (5.0 mL) was added then dropwise and mixture was stirred for 1 h in the dark at room temperature. Precipitated silver chloride was separated by filtration and volume was reduced to 3.0 mL, pentane (10.0 mL) was added to precipitate the product. A bright red solid was filtered, washed with pentane (2 × 5.0 mL) and dried in vacuum. The product was obtained as bright red crystalline solid. Yield: 0.86 g, 87%.

^{1}H NMR (300 MHz, 293 K, CD_2Cl_2): 6.35 (d, $J = 8.2$ Hz, 2H, backbone ring proton). 7.55–7.65 (br, 2H, Py $H_{2,6}$ + 2H phenyl CH), 7.41–7.52 (br, 1H, Py H_4 + 2H phenyl CH), 7.29 (t, $J =$ 6.9 Hz, 2H, backbone ring proton), 6.96–7.09 (br, 2H, Py H3,5 + 2H phenyl CH), 6.35 (d, $J = 6.9$ Hz, 2H, backbone ring proton), 6.16 (s, 2H, –NC*H*C*H*N–), 4.22 (s + br, 2H, COD-CH), 3.63 (sept, $J = 6.7$ Hz, 2H ^{i}Pr-CH), 3.12 (s + br, 2H, COD-CH), 2.10 (br, 4H COD-CH_2 + 2H ^{i}Pr-CH), 1.65 (d, $J = 6.8$ Hz, 3H, ^{i}Pr-CH_3), 1.59 (br, 4H, COD-CH_2)), 1.55 (d, $J = 6.8$ Hz, 3H, ^{i}Pr-CH_3), 0.57 (d, $J = 6.1$ Hz, 3H, ^{i}Pr-CH_3), 0.02 (d, $J = 6.6$ Hz, 3H, ^{i}Pr-CH_3).

^{13}C{^{1}H} NMR (75.5 MHz, 293 K, CD_2Cl_2): 202.62 (s, Ir–$C_{(Carbene)}$], 126.7, 138.05, 150.93 (s, $C_{(py)}$), 135.09, 146.64, 148.21 (s, $C_{(Phenyl\ aromatic)}$), 131.96, 137.43, 137.54 (s, $C_{(Backbone\ aromatic)}$), 128.55, 130.32 (s, $C_{(Phenyl\ CH)}$), 126.1–126.38 (br, $C_{(Backbone\ ring\ CH)}$ + $C_{(Phenyl\ CH)}$), 123.26 (s, $C_{(Backbone\ ring\ CH)}$), 72.19 (s, –N*C*H*C*HN–), 66.47, 83.82 [s, $C_{(COD\text{-}CH)}$), 30.22, 31.85 (s, $C_{(COD\text{-}CH_2)}$), 28.63, 29.47b (s, $C_{(^iPr\text{-}CH)}$), 23.58, 24.66, 25.25, 26.312 [s, $C_{(^iPr\text{-}CH_3)}$).

Mass Spectrometry (ES+, CH_3CN): $m/z = 815.3959$ $[M - py]^+$, (100%), 815.3959 $[M - py + CH_3CN]^+$, 70%).

Elemental analysis (%): found (calcd): C 57.74 (57.79), H 5.62 (5.72), N 3.91 (4.04).

Acknowledgements

We thank the Royal Society for a University Research Fellowship (K. S. C.), the Ministry of Science and Technology (MOST), the Government of Pakistan and Lady Margaret Hall, University of Oxford for Graduate funding (S. D.) and Dr Nick Rees, Central Research Labs, Department of Chemistry, University of Oxford, for his help in the NMR studies and for useful discussions.

References

1 H. W. Wanzlick and H. J. Schoenherr, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 141.
2 K. Öfele and M. Herberhold, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 739.
3 A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
4 W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290.
5 R. H. Crabtree, *J. Organomet. Chem.*, 2005, **690**, 5451.
6 W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162.
7 D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.
8 D. M. Khramov, V. M. Lynch and C. W. Bielawski, *Organometallics*, 2007, **26**, 6042.
9 C. A. McAuliffe, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford Editon edn., 1987, vol. 2, pp. 989–1066.
10 F. Ullah, M. K. Kindermann, P. G. Jones and J. Heinicke, *Organometallics*, 2009, **28**, 2441.
11 F. E. Hahn, *Angew. Chem., Int. Ed.*, 2006, **45**, 1348.
12 W. A. Herrmann, D. Baskakov, E. Herdtweck, S. D. Hoffmann, T. Bunlaksananusorn, F. Rampf and L. Rodefeld, *Organometallics*, 2006, **25**, 2449.
13 C. Metallinos, F. B. Barrett, J. L. Chaytor and M. E. A. Heska, *Org. Lett.*, 2004, **6**, 3641.
14 S. Saravanakumar, M. K. Kindermann, J. Heinicke and M. Köckerling, *Chem. Commun.*, 2006, 640.
15 F. E. Hahn, L. Wittenbecher, D. Le Van and R. Frohlich, *Angew. Chem., Int. Ed.*, 2000, **39**, 541.
16 D. Tapu, C. Owens, D. VanDerveer and K. Gwaltney, *Organometallics*, 2009, **28**, 270.
17 K. S. Coleman, H. T. Chamberlayne, S. Turberville, M. L. H. Green and A. R. Cowley, *Dalton Trans.*, 2003, **14**, 2917.
18 K. S. Coleman, S. Dastgir, G. Barnett, M. J. P. Alvite, A. R. Cowley and M. L. H. Green, *J. Organomet. Chem.*, 2005, **690**, 5591.
19 K. S. Coleman, S. Turberville, S. I. Pascu and M. L. H. Green, *Tetrahedron Lett.*, 2004, **45**, 8695.
20 K. S. Coleman, S. Turberville, S. I. Pascu and M. L. H. Green, *J. Organomet. Chem.*, 2005, **690**, 653.
21 S. Dastgir, K. S. Coleman, A. R. Cowley and M. L. H. Green, *Organometallics*, 2006, **25**, 300.
22 S. Saravanakumar, A. I. Oprea, M. K. Kindermann, P. G. Jones and J. Heinicke, *Chem.–Eur. J.*, 2006, **12**, 3143.
23 H. Türkmen, O. Şhin, O. Büyükgüngör and B. Çetinkaya, *Eur. J. Inorg. Chem.*, 2006, **2006**, 4915.
24 A. Paulovicova, U. El-Ayaan, K. Shibayama, T. Morita and Y. Fukuda, *Eur. J. Inorg. Chem.*, 2001, **10**, 2641.
25 P. Preishuber-Pflugl and M. Brookhart, *Macromolecules*, 2002, **35**, 6074.
26 S. Dastgir, K. S. Coleman, A. H. Cowley and M. L. H. Green, *Manuscripts in preparation*, 2009.
27 E. Despagent-Ayoub and R. H. Grubbs, *J. Am. Chem. Soc.*, 2004, **126**, 10198.
28 A. J. Arduengo III, J. R. Goerlich and W. J. Marshall, *J. Am. Chem. Soc.*, 1995, **117**, 11027.
29 R. W. Alder, P. R. Allen, M. Murray and A. G. Orpen, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1121.
30 A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523.
31 A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913.
32 A. J. Arduengo III, S. F. Gamper, M. Tamm, J. C. Calabrese, F. Davidson and H. A. Craig, *J. Am. Chem. Soc.*, 1995, **117**, 572.
33 M. K. Denk, T. Avinash, K. Hatano and A. J. Lough, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2607.
34 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
35 P. W. Betteridge, R. J. Cooper, C. K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.
36 S. Dastgir, K. S. Coleman, A. H. Cowley and M. L. H. Green, *Organometallics*, 2009, *manuscript in preparation*.
37 A. J. Arduengo III, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.
38 K. Denk, P. Sirsch and W. A. Herrmann, *J. Organomet. Chem.*, 2002, **649**, 219.
39 A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, *Organometallics*, 2003, **22**, 1663.
40 H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.*, 2000, **33**, 1143.
41 N. Imlinger, K. Wurst and M. R. Buchmeiser, *J. Organomet. Chem.*, 2005, **690**, 4433.
42 G. A. Grasa, Z. Moore, K. L. Mertin, E. D. Stevens, S. P. Nolan, V. Paquet and H. Lebel, *J. Organomet. Chem.*, 2002, **658**, 126.
43 W. A. Herrmann, M. Elison, J. Fischer, C. Koecher and G. R. J. Artus, *Chem.–Eur. J.*, 1996, **2**, 772.
44 W. A. Herrmann, L. J. Gooßen and M. Spiegler, *J. Organomet. Chem.*, 1997, **547**, 357.

45 K. H. Park, S. Y. Kim, S. U. Son and Y. K. Chung, *Eur. J. Inorg. Chem.*, 2003, **2003**, 4341.
46 M. Poyatos, E. Mas-Marzá, J. A. Mata, M. Sanaú and P. Eduardo, *Eur. J. Inorg. Chem.*, 2003, **2003**, 1215.
47 M. Poyatos, P. Uriz, J. A. Mata, C. Claver, E. Fernandez and E. Peris, *Organometallics*, 2003, **22**, 440.
48 R. H. Crabtree, *Acc. Chem. Res.*, 1979, **12**, 331.
49 R. H. Crabtree, H. Felkin, T. Fillebeen-Khan and G. E. Morris, *J. Organomet. Chem.*, 1979, **168**, 183.
50 R. H. Crabtree, H. Felkin and G. E. Morris, *J. Organomet. Chem.*, 1977, **135**, 205.
51 R. H. Crabtree and G. E. Morris, *J. Organomet. Chem.*, 1977, **135**, 395.
52 A. C. Hillier, H. M. Lee, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 4246.
53 H. M. Lee, T. Jiang, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 1255.
54 J. M. Praetorius and C. M. Crudden, *Dalton Trans.*, 2008, 4079.
55 A. Neveling, G. R. Julius, S. Cronje, C. Esterhuyse and H. G. Raubenheimer, *Dalton Trans.*, 2005, **1**, 181.
56 S. Dastgir, DPhil. Thesis, University of Oxford, 2005.
57 A. Albers, E. Dinjus, S. Pitter and O. Walter, *J. Mol. Catal. A: Chem.*, 2004, **219**, 41.
58 M. Bortenschlager, M. Mayr, O. Nuyken and M. R. Buchmeiser, *J. Mol. Catal. A: Chem.*, 2005, **233**, 67.
59 A. Buhling, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. W. Elgersma, K. Goubitz and J. Fraanje, *Organometallics*, 1997, **16**, 3027.
60 C. Kunze, D. Selent, I. Neda, R. Schmutzler, A. Spennenberg and A. Borner, *Heteroat. Chem.*, 2001, **12**, 577.
61 L. A. Vander der Veen, P. C. J. Kamer and P. W. N. Van Leeuwen, *Organometallics*, 1999, **18**, 4765.
62 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1986, 4735.

