Synthesis and coordination compounds of a bis(imino)acenaphthene (BIAN)-supported N-heterocyclic carbene†‡

Kalyan V. Vasudevan,[a] Rachel R. Butorac,[a] Colin D. Abernethy[b] and Alan H. Cowley*[a]

The bis(imino)acenaphthene-supported N-heterocyclic carbene IPr(BIAN) has been prepared by deprotonation of the precursor imidazolium chloride. Treatment of IPr(BIAN) imidazolium chloride with Ag$_2$O afforded the silver complex [IPr(BIAN)]AgCl which can be converted into the corresponding gold complex [IPr(BIAN)]AuCl by reaction with (tht)AuCl (tht = tetrahydrothiophene). The iridium complex [IPr(BIAN)]Ir(COD)Cl was prepared by reaction of the imidazolium chloride with KO^{t}Bu and [Ir(COD)Cl]$_2$ and subsequently converted to the carbonyl complex [IPr(BIAN)]Ir(CO)$_2$Cl by exposure to an atmosphere of CO. All new compounds were characterized by single-crystal X-ray diffraction, multinuclear NMR, MS and HRMS data.

Introduction

In comparison with phosphines, N-heterocyclic carbenes are not particularly amenable to ligand tuning by changing the steric and electronic characteristics of the substituents. One way to extend the scope of NHC ligand tuning is by means of architectural change. In this context, there is a steadily growing interest in the annulation of NHCs with a variety of carbocyclic and heterocyclic rings.[1,2] Such ring fusions have been shown to have a significant impact on the stabilities of and bonding in the resulting annulated species. Representative examples of 4,5-fused rings include benzene,[1a] pyridine,[1b] naphthalene,[1c] phenanthrene,[1c,d] a novel benzene-supported bis(carbene),[1e] and a redox-active naphthoquinone derivative.[1f] (Fig. 1)

Ligands of the bis(imino)acenaphthene (BIAN) class seemed like promising candidates for fusion to NHCs, not only because of their structural rigidity, but also on account of their redox behavior.[3] The annulation proposed herein would result in an Arduengo-type[4] NHC (**A**). Such a carbene would also represent an interesting contrast with the saturated Wanzlick-type[5] (**B**) BIAN carbene which has been described recently.[6] Thus, **A** is anticipated to possess a planar skeleton while **B** has been shown to be bent along the saturated C–C bond. A further differentiating feature is that, in principle, the carbenic carbon of **A** is in conjugative contact with the naphthalene moiety. Examples of Group 14 homologues of **A** are confined to the germylenes (dipp-BIAN)Ge, (dtb-BIAN)Ge and (bph-BIAN)Ge (dipp = 2,6-i-Pr$_2$C$_6$H$_3$; dtb = 2,5-t-Bu$_2$C$_6$H$_3$; bph = 2-PhC$_6$H$_4$).[7]
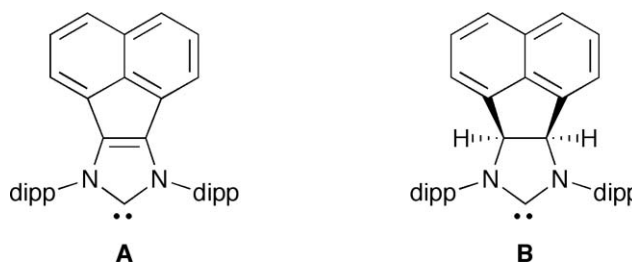
Results and discussion

Syntheses of 1–7

The BIAN imidazolium chloride **1** (Scheme 1) was prepared by heating a mixture of dipp-BIAN and methoxy(methyl) chloride in a thick-walled glass tube. Recrystallization of the resulting yellow powder from a dichloromethane–toluene mixture afforded a crop of single crystals of **1** suitable for X-ray analysis. The yield of analytically pure **1** prior to recrystallization was 86%. In some instances,[8] difficulties or failures have been reported in attempted deprotonations of annulated imidazolium salts to form the corresponding NHCs. However, in the present case, the deprotonation of **1** with KO^{t}Bu in THF solution proceeded smoothly to produce the corresponding yellow carbene, IPr(BIAN) **2** in moderate (71%) yield. X-ray quality crystals of **2** were grown from a 1:1 toluene–THF solution. Interestingly, when the deprotonation of **1** was carried out in THF solution and worked up in toluene, a red, ring-opened product **3** was also produced in low yield (19%). Compound **3** is believed to be formed by hydrolysis of **2** since yellow solutions of the latter slowly develop a red coloration upon standing. Ring-opened products have also been reported to be formed in 80–85% yields when the corresponding saturated imidazolium salts were treated with a variety of deprotonation agents in THF solution.[6] Our results further emphasize the finding that the deprotonation of annulated imidazolium salts to the corresponding carbenes is highly sensitive to the reaction conditions.[6,8]

[a] Department of Chemistry and Biochemistry, University of Texas at Austin, 1 University Station, A5300, Austin, TX 78712, USA. E-mail: cowley@mail.utexas.edu; Tel: +1 512 471-7484
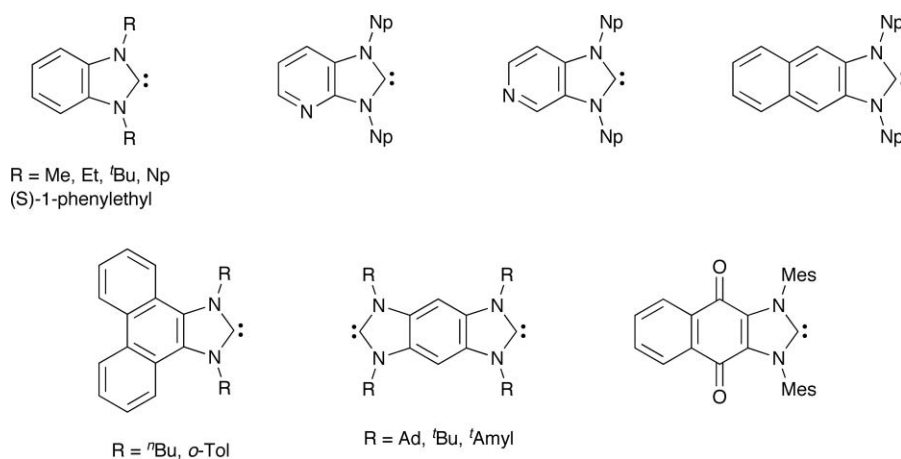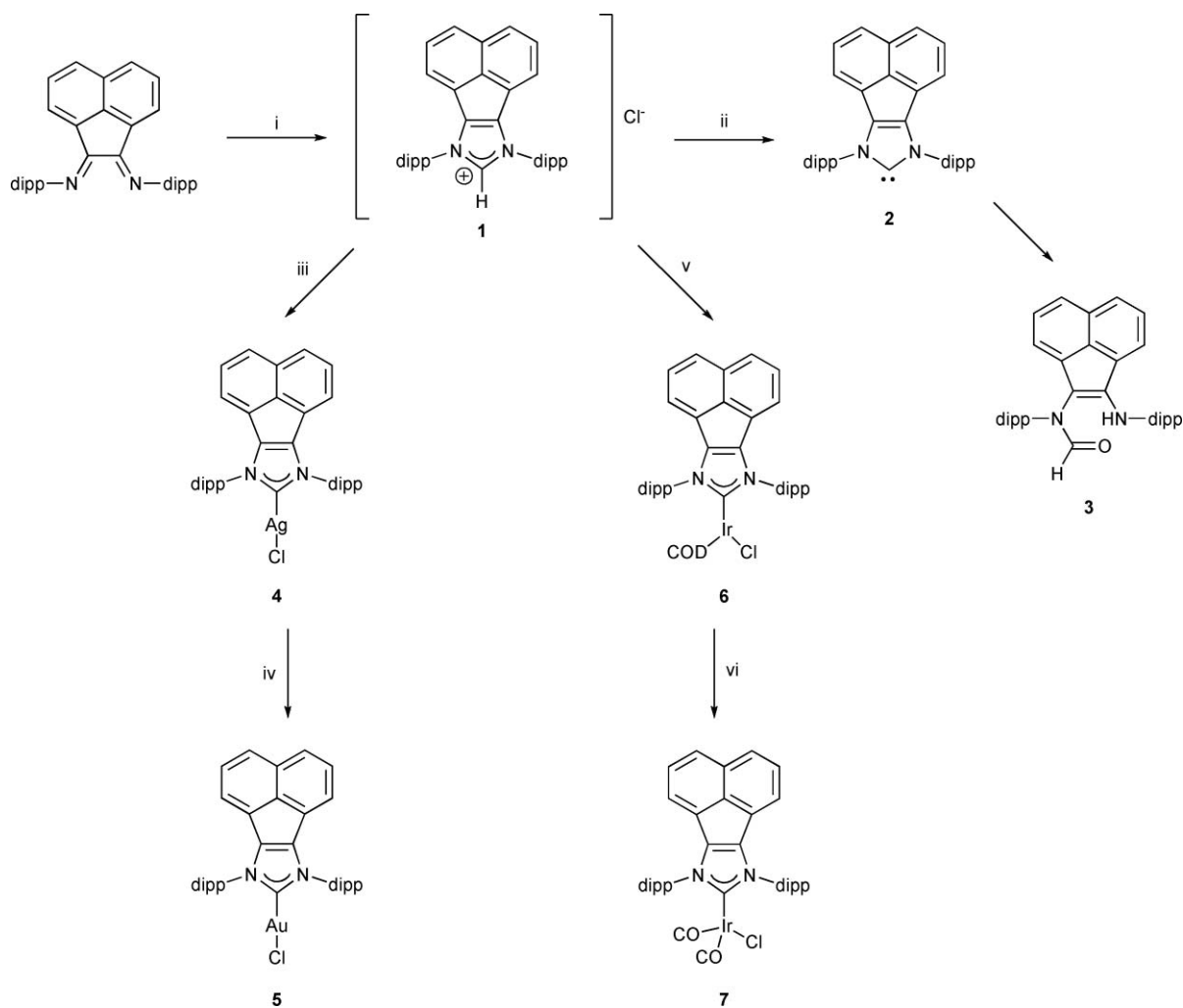[b] Department of Chemistry, Sarah Lawrence College, 1 Mead Way, Bronxville, NY, 10708, USA

Fig. 1 Representative examples of N-heterocyclic carbenes annulated at the 4 and 5 positions.

Scheme 1 Synthesis of IPr(BIAN) and metal complexes (i) MeOCH$_2$Cl, 100 °C, 16 h; (ii) KO^{t}Bu, THF, 25 °C, 12 h; (iii) Ag$_2$O, CH$_2$Cl$_2$–THF, 25 °C, 16 h; (iv) (tht)AuCl, CH$_2$Cl$_2$, 25 °C, 12 h; (v) KO^{t}Bu, [Ir(COD)Cl]$_2$, tol, 25 °C, 2 h; (vi) CO(atm), CH$_2$Cl$_2$, 25 °C, 1 h.

The reaction of imidazolium chloride **1** with Ag$_2$O in CH$_2$Cl$_2$–THF solution at ambient temperature afforded an excellent (92%) yield of the anticipated IPr(BIAN) silver chloride complex **4**. Yellow crystals of **4** appropriate for single-crystal X-ray analysis were grown from a saturated solution of **4** in 3 : 1

dichloromethane–hexane. In turn, treatment of **4** with (tht)AuCl afforded the corresponding AuCl complex **5**. X-ray quality crystals of **5** were grown from a saturated THF–hexanes solution. The Ir(COD)Cl complex of IPr(BIAN) (**6**) was produced by treatment of imidazolium chloride **1** with KO^{t}Bu and [Ir(COD)Cl]$_2$ in

Table 1 Selected crystal data, data collection and refinement parameters for compounds **1**, **2**, **4–7**

	1	**2**	**4**	**5**	**6**	**7**
Formula	$C_{53}H_{61}Cl_5N_2$	$C_{37}H_{40}N_2$	$C_{37}H_{40}AgClN_2$	$C_{45}H_{56}AuClN_2O_2$	$C_{45}H_{52}ClIrN_2$	$C_{39}H_{40}ClIrN_2O_2$
Formula weight	903.29	512.71	656.03	889.33	848.60	796.38
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Cc	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Pnma$
a/Å	12.958(3)	9.823(5)	12.027(2)	15.007(3)	19.933(4)	12.468(3)
b/Å	17.012(3)	14.604(5)	15.592(3)	17.331(4)	12.719(3)	18.494(4)
c/Å	21.450(4)	21.114(5)	18.241(4)	17.298(4)	15.990(3)	14.718(3)
α (°)	90.0	90.0	83.15(3)	90.0	90.0	90.0
β (°)	98.35(3)	101.882(5)	83.04(3)	115.01(3)	112.63(3)	90.0
γ (°)	90.0	90.0	82.24(3)	90.0	90.0	90.0
Z	4	4	4	4	4	4
D_c/g cm^{-3}	1.283	1.149	1.302	1.449	1.506	1.559
$F(000)$	1912	1104	1360	1808	1720	1592
Crystal size/nm	$0.13 \times 0.12 \times 0.05$	$0.33 \times 0.20 \times 0.12$	$0.10 \times 0.07 \times 0.06$	$0.43 \times 0.46 \times 0.16$	$0.14 \times 0.08 \times 0.05$	$0.29 \times 0.27 \times 0.11$
Θ range/°	1.53–27.49	3.42–27.48	1.72–27.46	3.00–26.00	1.95–25.00	2.20–26.25
Collected reflections	19190	13027	21840	43245	11443	6370
Independent reflns	10713	3398	15211	8003	6582	3529
R_{int}	0.0859	0.0367	0.0268	0.0286	0.0593	0.0693
R_1 [$I > 2\sigma(I)$]	0.0774	0.0707	0.0463	0.0248	0.0395	0.0436
wR_2 (all data)	0.1764	0.1819	0.0849	0.0592	0.0594	0.0751

Table 2 Selected bond distances (Å) and angles (°) for compounds **1**, **2**, **4–7**

	1	**2**	**4**	**5**	**6**	**7**
Bond distances/Å						
C(1)–N(1)	1.345(4)	1.379(5)	1.363(4) [1.372(4)]	1.362(3)	1.392(6)	1.371(6)
C(1)–N(2)	1.336(4)	1.377(5)	1.376(3) [1.370(4)]	1.356(3)	1.382(7)	1.371(6) [C(1)–N(1)i]
C(2)–C(3)	1.354(4)	1.373(5)	1.349(4) [1.365(4)]	1.358(4)	1.359(7)	1.348(11) [C(2)–C(2)i]
C(2)–N(1)	1.378(4)	1.387(5)	1.377(3) [1.384(4)]	1.374(4)	1.389(7)	1.388(7)
C(3)–N(2)	1.374(4)	1.389(5)	1.383(3) [1.378(3)]	1.379(3)	1.388(7)	1.388(7) [C(2)i–N(1)i]
Bond angles/°						
N(1)–C(1)–N(2)	109.4(3)	103.0(3)	105.5(2) [105.1(2)]	105.7(2)	104.9(5)	105.7(6) [N(1)–C(1)–N(1)i]
N(1)–C(2)–C(3)	107.4(3)	106.8(3)	107.4(2) [107.2(2)]	107.3(2)	108.2(5)	107.5(3) [N(1)–C(2)–C(2)i]
C(2)–C(3)–N(2)	107.9(3)	106.0(3)	107.7(2) [107.0(3)]	106.9(2)	107.1(5)	107.5(3) [C(2)–C(2)i–N(1)i]
C(1)–N(1)–C(2)	107.6(2)	111.9(3)	110.2(2) [110.1(3)]	110.0(2)	109.4(5)	109.6(5)
C(1)–N(2)–C(3)	107.7(2)	112.3(3)	109.3(2) [110.6(2)]	110.1(2)	110.5(4)	109.6(5) [C(1)–N(1)i–C(2)i]

toluene solution. Orange-red **6** was isolated in 78% yield and a small crop of single crystals suitable for X-ray analysis was grown from a saturated hexanes solution. Finally, the yellow IPr(BIAN)[Ir(CO)$_2$Cl] complex **7** was produced by exposure of a dichloromethane solution of **6** to an atmosphere of CO for 1 h. A few crystals of X-ray quality were produced from a saturated solution of **7** in hexanes.

Characterization of 1–7

Compounds **1**, **2**, and **4–7** were characterized on the basis of ^{1}H and ^{13}C NMR, MS, HRMS, and single-crystal X-ray diffraction. The ^{1}H, ^{13}C, MS and HRMS data are presented in the Experimental section. Compound **3** was characterized solely by X-ray crystallography.

X-ray crystallographic studies

Compounds **1–7** were structurally authenticated on the basis of single-crystal X-ray diffraction studies. A summary of data collection details appears in Table 1 and a selection of pertinent metrical parameters is presented in Table 2. Further details are available as electronic supplementary information (ESI).[1]

The average C(1)–N(1,2) bond length of 1.341(4) Å for the imidazolium cation **1** is 0.037 Å shorter than that observed in the case of the corresponding carbene **2** (Fig. 2) for which this distance is 1.378(5) Å. As discussed elsewhere,[6] bond shortening of this magnitude is attributable to the loss of π-delocalization across the N(1)–C(1)–N(2) moiety of the imidazolium salt and is also consistent with carbene formation. A similar trend is evident in the corresponding non-annulated imidazolium chloride and IPr for which the pertinent average bond lengths are 1.339(5) and 1.366(3) Å, respectively.[9]

Structural comparisons between our Arduengo-type NHC (**A**) and the related, saturated Wanzlick-type NHC (**B**)[6] are also of interest. The major architectural difference between these two annulated carbenes relates to the fact that carbon atoms C(2) and C(3) adopt trigonal planar and tetrahedral geometries in **A** and **B**, respectively. Accordingly, the C(2)–C(3) separation in **B** (1.558(2) Å) corresponds to that of a single bond while **A**, with a bond distance of 1.373(5) Å, clearly possesses some double bond character—albeit less than that in the precursor imidazolium salt (**1**) or IPr[9] where these distances are 1.354(4) and 1.336(3) Å, respectively. Further comparison of the structure of **2** with that of IPr[9] is also instructive since it reveals the other structural changes that take place upon annulation. In terms of bond distances, the
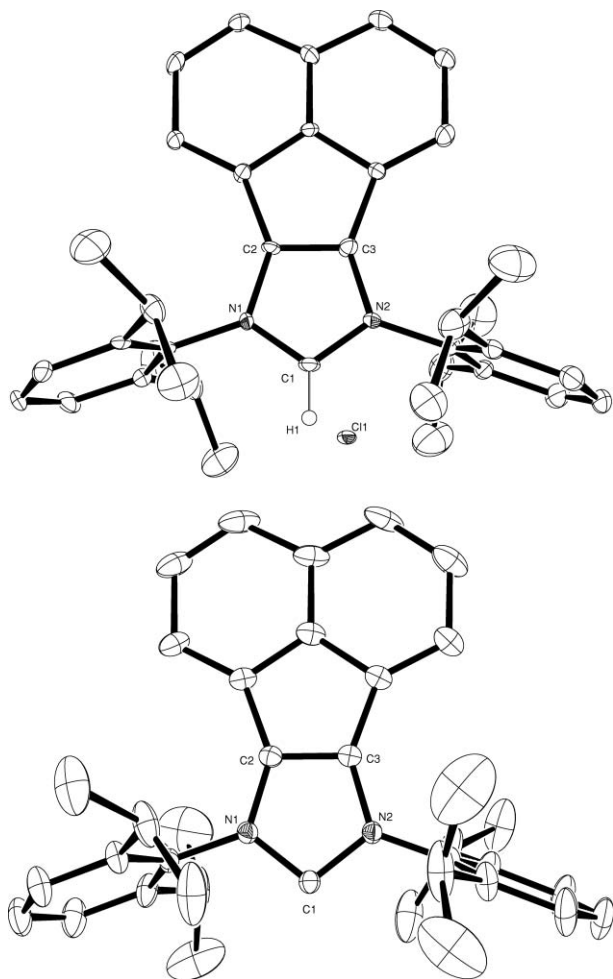
Fig. 2 ORTEP diagrams of **1** (top) and **2** (bottom) with 35% probability thermal ellipsoids. Hydrogen atoms except H1 of **1** are omitted for clarity.
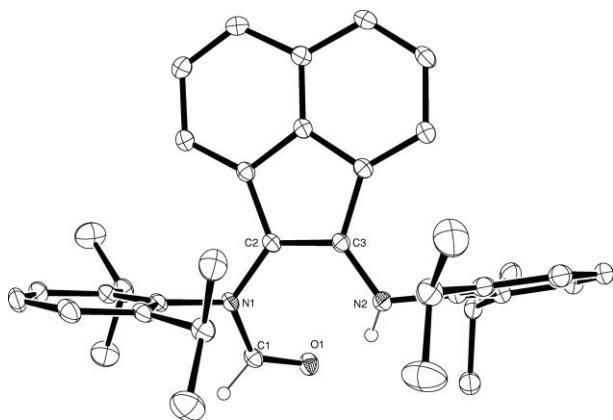

Fig. 3 ORTEP diagram of **3** with 35% probability thermal ellipsoids. Hydrogen atoms except H1 and H2n are omitted for clarity.

major changes comprise an average decrease of 0.041 Å in C(2,3)–N(1,2) and an average increase of 0.012 Å in C(1)–N(1,2). From the standpoint of bond angles, the major change is an increase in the N(1)–C(1)–N(2) bond angle from 101.5(2)° to 103.0(3)° and a decrease of ~1° in the average C–N–C angle.

As pointed out earlier, the red, crystalline compound **3** apparently originates from hydrolysis of carbene **2**. Complete details of the X-ray analysis of **3** are provided in the ESI‡. A database search revealed that there is no structure that is exactly analogous to that of **3**. A noteworthy feature of the structure (Fig. 3) is the C(2)–C(3) distance of 1.383(2) Å which corresponds to that of a somewhat long C=C bond. Although C(2)–N(1) and C(3)–N(2) are both single bonds, the latter is ~0.05 Å shorter than the former. Moreover, the N(1)–C(1) distance is shorter than the N(1)–C(2) separation which is suggestive of a modicum of delocalization across the O(1)–C(1)–N(1) fragment.

The IPr(BIAN)AgCl complex **4** crystallizes with two independent molecules in the asymmetric unit. However, the metrical parameters for both molecules are very similar hence only one molecule is displayed in Fig. 4. The C–Ag and Ag–Cl bond distances and the C–Ag–Cl bond angles (averaged over the crystallographically independent molecules) of 2.067(3) Å, 2.314(1) Å and 175.84(9)°, respectively, are very similar to those reported for the non-annulated complex (IPr)AgCl, namely 2.056(6) Å, 2.316(17) Å and 175.2(2)°, respectively.[10] The coordination of IPr(BIAN) **2** to AgCl prompts some significant changes in the metrical parameters of the NHC ring. Thus, the C–C distance of 1.357(4) Å (averaged over the two crystallographically independent molecules) is somewhat shorter than that for the unligated IPr(BIAN) carbene (1.373(5) Å). Other noteworthy changes that accompany the coordination of the AgCl unit are widening of the N–C–N angle by 2.3° and narrowing of the average C(carbene)–N–C bond angles by ~2.1° and widening of the N–C–C bond angles by ~1°.

The metrical parameters for the NHC ring of the IPr(BIAN)–AuCl complex (**5**) (Fig. 4) are almost identical with those of the corresponding AgCl complex **4**. Moreover, these bond lengths and angles are very similar to those reported for non-annulated (IPr)AuCl.[11]

The structures of the Ir(COD)Cl (**6**) and Ir(CO)₂Cl (**7**) complexes of the IPr(BIAN) carbene **2** are displayed in Fig. 5. The Ir–C(1) bond distance for **6** of 2.040(6) Å is similar to the value reported for the corresponding Wanzlick-type BIAN carbene (2.070(3) Å).[6] Furthermore, both values fall within the range of 1.99–2.091 Å reported in the literature for other (NHC)Ir(COD)Cl complexes.[1f] Likewise, the Ir–C(1) bond distance of 2.089(7) Å for **7** is also encompassed by the range of literature values of 2.065–2.122 Å cited for this parameter.[12] Additionally, the *cis* and *trans* Ir-carbonyl distances of 1.850(10) and 1.849(9) Å, respectively are close to the literature values of 1.827(4)–1.888(4) and 1.877(4)–1.900(5) Å, respectively. Overall, the geometries, bond distances and bond angles for the Ir(COD)Cl and Ir(CO)₂Cl moieties are very similar to those reported for the corresponding IPr complexes.[12] Similarly, the metrical parameters for the NHC rings of **6** and **7** differ from those of the corresponding IPr complexes in only a minor way.

Assessment of the donor character of 2

Over the years, several methods have been proposed for determination of the electronic characteristics of the carbenic ligands in metal complexes. While no attempt has been made here to review the merits of the various approaches, we opted to use the recently proposed method of Nolan *et al.*[12,13] to estimate the donor
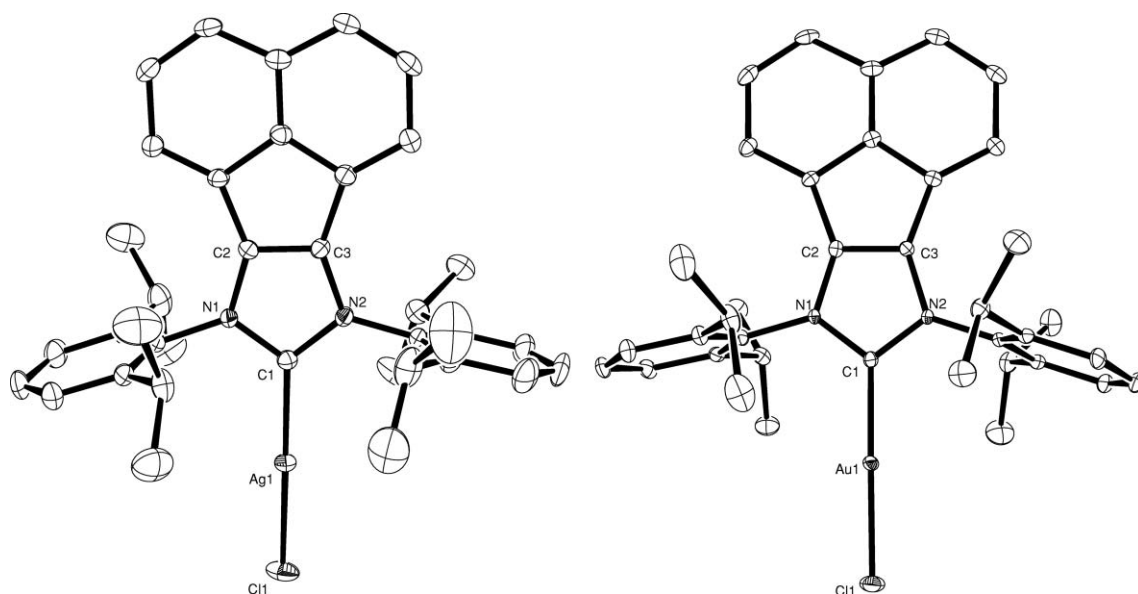
Fig. 4 ORTEP diagrams of **4** (left) and **5** (right) with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.
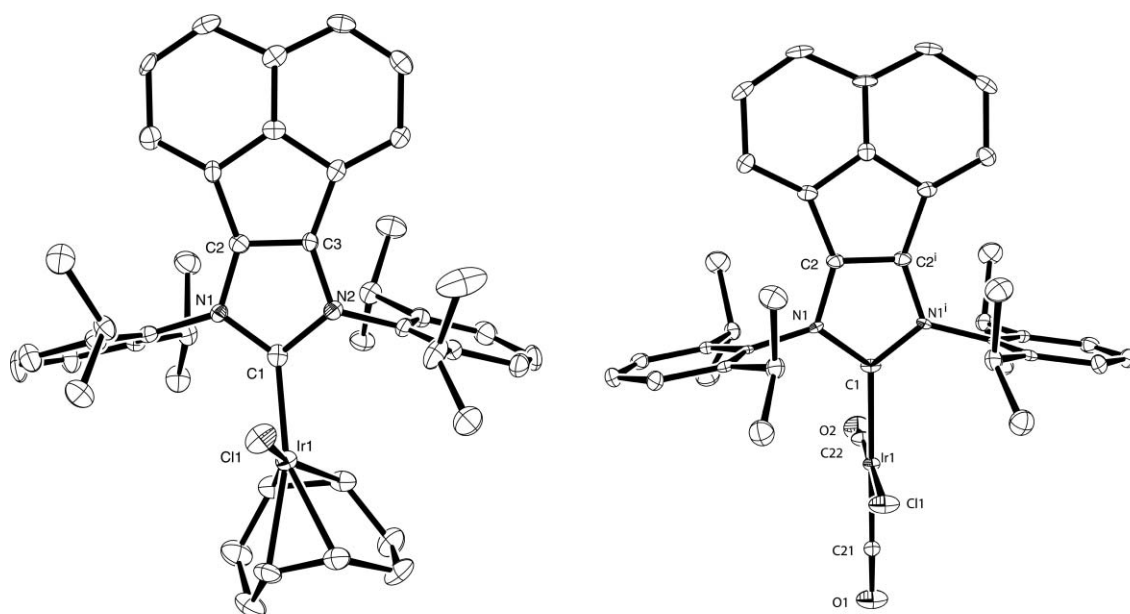
Fig. 5 ORTEP diagrams of **6** (left) and **7** (right) with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

character of the IPr(BIAN) carbene **2**. The method is based on the magnitude of the average CO stretching frequency v_{av} for each particular [(NHC)Ir(CO)$_2$Cl] complex. The Tolman Electronic Parameter (TEP) is derived from the equation TEP = $0.847 \times v_{av}$ + 336 cm^{-1}.[12,13] In the case of **7** the *trans* CO stretching frequencies appear at 2053.95 and 2061.54 cm^{-1}, while the *cis* CO stretching frequencies appear at 1966.40 and 1973.90 cm^{-1} (doublets due to Fermi resonance). These values are close to the ranges of 2055–2072 and 1971–1989 cm^{-1} reported for other (NHC)Ir(CO)$_2$Cl complexes.[11] The computed TEP value of 2042 cm^{-1} for **2** suggests that it is a relatively strong donor. Unfortunately, despite several attempts, it was not possible to record the ^{13}C chemical shift for

the carbenic carbon of **2** due to low solubility and relaxation effects.

Summary and conclusions

The first example of an "Arduengo-type" bis(imino)acenaphthene (BIAN)-supported N-heterocyclic carbene, IPr(BIAN), has been prepared and structurally authenticated. The AgCl, AuCl, Ir(COD)Cl and Ir(CO)$_2$Cl complexes of IPr(BIAN) have also been synthesized, each of which was characterized on the basis of single-crystal X-ray diffraction, multinuclear NMR, MS and HRMS data. The magnitudes of the *cis* and *trans* infrared carbonyl

stretching frequencies for IPr(BIAN)Ir(CO)$_2$Cl and the TEP value suggest that the carbenic carbon of IPr(BIAN) is a relatively strong donor.

Experimental

General procedures

All manipulations and reactions were performed under a dry, oxygen-free, catalyst scrubbed argon atmosphere using a combination of standard Schlenk techniques or in an M-Braun or Vacuum Atmospheres drybox. All glassware was oven-dried and vacuum- and argon flow-degassed before use. All reagents were obtained commercially and used without further purification. The starting materials dipp-BIAN[14] and (tht)AuCl[15] were synthesized according to published procedures. Toluene, THF, hexanes and diethyl ether were dried over Na and freshly distilled prior to use. The dichloromethane was dried over CaH$_2$ and freshly distilled prior to use.

Physical measurements

Low-resolution CI mass spectra were obtained on a Thermo Scientific TSQ Quantum GC mass spectrometer and high-resolution CI mass spectra were recorded on a magnetic sector Waters Autospec Ultima instrument. MS analysis of compound **2** was performed on a sample that had been sealed in a glass capillary under an argon atmosphere. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 295 K in the indicated solvent on a Varian Unity 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or a Varian AS400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz) immediately following sample preparation and, in the cases of **2** and **3**, removal of the sample from the drybox. Deuterated solvents were obtained from Cambridge Isotopes and stored over 4 Å molecular sieves prior to use. ^{1}H and ^{13}C{^{1}H} chemical shift values are reported in parts per million (ppm) relative to SiMe$_4$ (δ 0.00), using solvent resonances as internal standards. The FTIR spectrum of **7** was obtained on a Perkin–Elmer Spectrum BX system.

X-ray crystallography

For compounds **1** and **4–7**, a crystal of suitable quality was removed from a vial, covered with mineral oil and mounted on a nylon thread loop. In the cases of compounds **2** and **3**, the selected crystal was removed from a vial that had been stored in a drybox, then covered immediately with mineral oil and mounted on a nylon thread loop. The X-ray diffraction data were collected on either a Nonius Kappa CCD diffractometer with an Oxford Cryostream low-temperature device at 153 K or a Rigaku AFC-12 with Saturn 724+ CCD diffractometer with a Rigaku XStream low temperature device at 100 K. Both instruments were equipped with a graphite-monochromated Mo-Kα radiation source (λ = 0.71073 Å). Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods and refined by full-matrix least-squares cycles on F^2 using the Siemens SHELXTL PLUS 5.0 (PC) software package[16] and PLATON.[17] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in fixed, calculated positions using a riding model.

Preparations

IPr(BIAN) imidazolium chloride (1). IPr(BIAN) (1.00 g, 0.002 mol) and methoxy(methyl)chloride (3.22 g, 0.040 mol) were added to an argon-flushed thick-walled reaction vessel. The vessel was sealed and the reaction mixture was stirred at 100 °C for 16 h, during which time the mixture changed from a murky brown suspension to a clear red solution. Cooling of the reaction mixture to ambient temperature and the subsequent addition of 10 mL of diethyl ether resulted in the formation of a yellow precipitate. The resulting solid was filtered off and washed with 50 mL of diethyl ether and dried *in vacuo* to afford **1** as an analytically pure yellow powder (0.92 g, 83.9%). Crystals of **1** suitable for X-ray diffraction experiments were obtained from a saturated solution of **1** in a 3 : 1 dichloromethane–toluene solvent mixture following 3 days of storage at –40 °C.

MS (CI$^+$, CH$_4$): m/z 513 [M + H]$^+$ (–Cl); HRMS (CI$^+$, CH$_4$): calcd for C$_{37}$H$_{41}$N$_2$ m/z 513.3270; found, 513.3262; ^{1}H NMR (CD$_2$Cl$_2$): δ 1.20 (d, 12H, CH$_3$), 1.41 (d, 12H, CH$_3$), 2.75 (sept, 4H, –CH), 7.18–7.29 (d of d, 4H, Ar–H), 7.48 (d, 2H, Naph-H), 7.60 (t, 2H, Ar–H), 7.68 (t, 2H, Naph-H), 8.02 (d, 2H, Naph-H), 12.23 (s, 1H, C–H); ^{1}H NMR (CD$_2$Cl$_2$): δ 1.45 (d, 12H, CH$_3$), 1.59 (d, 12H, CH$_3$), 2.97 (sept, 4H, –CH), 7.55 (d, 2H, Naph-H), 7.80 (d, 4H, Ar–H), 7.92 (t, 2H, Ar–H), 8.03 (t, 2H, Naph-H), 8.35 (d, 2H, Naph-H), 11.32 (s, 1H, C–H); ^{13}C NMR (CD$_2$Cl$_2$): δ 23.51, 24.84, 29.75, 123.37, 123.46, 125.46, 128.74, 129.43, 130.40, 130.87, 132.68, 138.08, 142.51, 145.44, 206.83 (C–H); mp (decomp): 286–290 °C.

IPr(BIAN) (2). Chilled THF (20 mL) was added to a 100 mL Schlenk flask containing **1** (0.10 g, 0.182 mmol) and K(^{t}BuO) (0.028 g, 0.273 mmol). The reaction mixture was stirred at ambient temperature for 12 h, after which the solvent was removed under reduced pressure. The crude solid was digested in toluene, filtered and the solvent was stripped from the filtrate thereby leaving a mixture of red-orange and yellow solids. The crude material was washed with cold hexanes to remove the red-orange product. The remaining yellow solid was dried under vacuum to afford a moderate yield of analytically pure **2** (0.066 g, 70.8%). A single crystal of **2** was grown from a saturated 1 : 1 toluene–THF solution of **2** that had been stored at –40 °C for 3 days.

MS (CI$^+$, CH$_4$): m/z 513 [M + H]$^+$ (+ H); HRMS (CI$^+$, CH$_4$): calcd for C$_{37}$H$_{40}$N$_2$ m/z 513.3270; found, 513.3283; ^{1}H NMR (C$_6$D$_6$): δ 1.13 (d, 12H, CH$_3$), 1.36 (d, 12H, CH$_3$), 3.38 (sept, 4H, –CH), 6.91 (d, 2H, Ar–H), 6.94 (d, 2H, Naph-H), 7.24 (d, 2H, Naph-H), 7.29 (t, 2H, Ar–H), 7.31 (d, 2H, Ar–H), 3.38 (t, 2H, Naph-H); ^{13}C NMR (C$_7$D$_8$): δ 23.35, 24.70, 29.05, 119.89, 123.97, 124.74, 127.01, 127.23, 129.35, 130.35, 131.76, 140.30, 146.34; mp: 299–302 °C.

IPr(BIAN)[AgCl] (4). A 1 : 1 dichloromethane–THF solution (30 mL) was added to a 50 mL round bottom flask that had been covered with aluminium foil, then charged with **1** (0.10 g, 0.182 mmol) and Ag$_2$O (0.20 g, 0.863 mmol). The reaction mixture was stirred for 16 h at ambient temperature, following which it was filtered and the solvent stripped from the filtrate under reduced pressure to afford **4** as an analytically pure yellow solid (0.110 g, 92.1%). X-ray quality crystals of **4** were grown by storage of a saturated solution of **4** in dichloromethane–hexanes at –40 °C for 5 days in the dark.

MS (CI⁺, CH₄): m/z 656 [M + H]⁺; HRMS (CI⁺, CH₄): calcd for C₃₇H₄₀N₂AgCl m/z 654.1931; found, 654.1922; ¹H NMR (CDCl₃): δ 1.09 (d, 12H, CH₃), 1.30 (d, 12H, CH₃), 2.80 (sept, 4H, –CH), 7.00 (d, 2H, Naph-H), 7.38 (d of d, 4H, Ar–H), 7.43 (t, 2H, Naph-H), 7.58 (t, 2H, Ar–H), 7.80 (d, 2H, Naph-H); ¹³C NMR (CDCl₃): δ 23.81, 24.78, 28.85, 121.11, 124.63, 125.10, 127.82, 128.49, 129.86, 130.82, 130.96, 133.22, 139.26, 145.54; mp (decomp): 305–310 °C.

IPr(BIAN)[AuCl] (5). Dichloromethane (30 mL) was added to a 50 mL aluminium foil-wrapped round bottom flask containing **4** (0.051 g, 0.079 mmol) and (tht)AuCl (0.025 g, 0.078 mmol). The reaction mixture was stirred for 12 h at ambient temperature, after which the solvent was removed under reduced pressure. The crude product was digested in toluene, filtered and the solvent stripped under reduced pressure to afford analytically pure **5** as a bright yellow solid (0.0511 g, 86.8%). A suitable crystal for X-ray diffraction analysis was grown from a saturated THF–hexanes solution of **5** stored at –40 °C for 5 days.

MS (CI⁺, CH₄): m/z 745 [M + H]⁺; HRMS (CI⁺, CH₄): calcd for C₃₇H₄₀N₂AuCl m/z 744.2546; found, 744.2548; ¹H NMR (CD₂Cl₂): δ 1.12 (d, 12H, CH₃), 1.38 (d, 12H, CH₃), 2.83 (sept, 4H, –CH), 7.04 (d of d, 2H, Naph-H), 7.46 (t, 2H, Naph-H), 7.47 (d, 4H, Ar–H), 7.68 (t, 2H, Ar–H), 7.85 (d of d, 2H, Naph-H); ¹³C NMR (CD₂Cl₂): δ 23.91, 24.59, 29.35, 121.70, 125.00, 125.62, 128.26, 128.96, 130.56, 131.33, 133.12, 138.41, 146.11; mp (decomp): 337–340 °C.

IPr(BIAN)[Ir(COD)Cl] (6). Toluene (40 mL) was added to a 50 mL Schlenk flask that contained **1** (0.10 g, 0.182 mmol), KOᵗBu (0.028 g, 0.273 mmol) and [Ir(COD)Cl]₂ (0.61 g, 0.0091 mmol). The resulting yellow suspension was stirred for 2 h, during which time the solution assumed a clear red color. The reaction mixture was filtered and the volatiles were removed under reduced pressure thereby leaving an orange-red solid residue. The crude product was washed with cold pentane (10 mL) leaving 0.121 g of analytically pure **6** (78.4% yield). Single crystals of **6** were grown from a saturated hexanes solution that had been stored at –40 °C for 5 days. The resulting orange plates were suitable for single-crystal X-ray diffraction experiments.

MS (CI⁺, CH₄): m/z 848 [M + H]⁺; HRMS (CI⁺, CH₄): calcd for C₄₅H₅₂N₂ClIr m/z 846.3440; found, 848.3447; ¹H NMR (CDCl₃): δ 0.96 (b, 12H, CH₃), 1.10 (d, 4H, COD), 1.35 (d, 12H, CH₃), 1.42 (d, 4H, COD), 1.66 (sept, 2H, –CH), 1.94 (b, 1H, –CH), 3.26 (sept, 1H, –CH), 3.12 (m, 2H, COD), 4.29 (m, 2H, COD), 6.80 (d, 2H, Naph-H), 7.29 (d, 2H, Naph-H), 7.40 (m, 3H, Ar–H), 7.45 (d, 1H, Ar–H), 7.51–7.66 (m, 4H, Ar–H, Naph-H); ¹³C NMR (C₆D₆): δ 23.73, 23.92, 24.54, 25.93, 28.71, 28.95, 29.45, 33.57, 50.76, 83.59, 121.58, 122.92, 123.26, 124.39, 124.99, 126.62, 127.13, 127.56, 128.25, 128.28, 129.01, 129.42, 129.59, 130.05, 130.39, 132.24, 134.75, 140.35, 144.97, 191.03 (C–Ir); mp (decomp): 255–260 °C.

IPr(BIAN)[Ir(CO)₂Cl] (7). A Schlenk flask was charged with **6** (0.030 g, 0.035 mmol) followed by the addition of 20 mL of dichloromethane. The orange colored reaction mixture was stirred under a CO atmosphere for 1 h, during which time it gradually assumed a yellow color. Evaporation of the solvent under an argon atmosphere resulted in the formation of a bright yellow solid. The crude product was washed with pentane (50 mL) and subsequently dried under argon to afford air-stable, analytically pure **7** (0.025 g,

88.8%). Crystals of **7** suitable for X-ray diffraction study were grown from a saturated hexanes solution that had been stored at –40 °C for 3 days.

MS (CI⁺, CH₄): m/z 761 [M + H]⁺; HRMS (CI⁺, CH₄): calcd for C₃₉H₄₀N₂IrO₂ m/z 761.2719; found, 761.2724; ¹H NMR (CDCl₃): δ 0.98 (d, 5H, CH₃), 1.16 (d, 7H, CH₃), 1.42 (d, 12H, CH₃), 2.74 (sept, 3H, –CH), 3.17 (sept, 1H, –CH), 6.84 (d, 1H, Naph-H), 7.29 (d, 1H, Naph-H), 7.40 (t, 1H, Ar–H), 7.45–7.55 (d of d, 4H, Ar–H), 7.63 (t, 2H, Naph-H), 7.68–7.79 (m, 2H, Naph-H, Ar–H), 8.06 (d, 1H, Naph-H); ¹³C NMR (CDCl₃): δ 23.52, 24.06, 24.16, 25.63, 29.01, 29.43, 122.13, 123.02, 123.17, 124.59, 125.09, 125.80, 127.43, 128.34, 129.06, 129.66, 130.12, 130.65, 130.83, 132.37, 133.46, 137.69, 138.25, 140.35, 140.92, 144.95, 146.16, 167.57 (CO), 168.80 (CO), 215.10 (C–Ir); IR (KBr pellet) (v_{max}/cm⁻¹: 2061.54 and 2053.95 (CO, *trans*), 1973.90 and 1966.40 (CO, *cis*); mp (decomp): 217–220 °C.

Isolation of N-(2,6-diisopropyl)-N-[(2,6-diisopropyl-phenyla-mino)acenaphthylen-l-yl]-formamide (3). As noted in the Results and discussion section, yellow toluene solutions of the IPr(BIAN) carbene **2** gradually assume a red coloration when stored under an argon atmosphere for ~12 h in a sealed reaction vessel at ambient temperature. In a typical procedure, filtration of the reaction mixture, followed by solvent stripping under reduced pressure, afforded a mixture of red-orange and yellow solids. The crude reaction mixture was then stirred with 20 mL of hexanes for 10 min, after which the red hexanes solution was cannulated into a Schlenk flask, leaving the yellow IPr(BIAN) carbene **2** as an analytically pure solid. The extracted red hexanes solution was filtered and the solvent was removed under reduced pressure to afford **3**. Large red crystals of **3** suitable for X-ray diffraction study were grown by slow evaporation of a saturated benzene solution. The yield was 19.0%.

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