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PAPER

Stepwise synthesis of a hydrido, *N*-heterocyclic dicarbene iridium(III) pincer complex featuring mixed NHC/abnormal NHC ligands†‡

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We describe a stepwise synthesis of the hydrido, *N*-heterocyclic dicarbene iridium(III) pincer complex [Ir(H)I($C_{NHC}CC_{aNHC}$)(NCMe)] (**3**) which features a combination of normal and abnormal NHC ligands. The reaction of the bis(imidazolium) diiodide [($CH_{imid}CHCH_{imid}$)]I_2 (**1**) with [Ir(μ-Cl)(cod)]$_2$ afforded first the mono-NHC Ir(I) complex [IrI(cod)($CH_{imid}CHC_{NHC}$)]I (**2**), which was then reacted with 2 equiv. of Cs_2CO_3 in acetonitrile at 60 °C for 40 h to yield **3**. These observations support our previously proposed mechanism for the formation of hydrido, *N*-heterocyclic dicarbene iridium(III) pincer complexes from the reaction of bis(imidazolium) salts with weak bases involving a mono-NHC Ir(I) intermediate. We describe the reactivity of the mono-NHC Ir(I) complex **2** under various conditions. By changing the reaction solvent from MeCN to toluene, we observed the cleavage of the imidazol-2-ylidene ring and the formation of an iminoformamide-containing mono-NHC Ir(I) complex [IrI(cod){[NHCH═CHN(Ad)CHO]CHC_{NHC}}] (**4**). Complex **4** was also prepared in high yield from the reaction of **2** with strong bases (potassium *tert*-butoxide or potassium hexamethyldisilazane), *via* the initial formation of the complex [IrI(cod)($CH_{NHC}CHC_{NHC}$)] (**5**), which contains a coordinated NHC moiety and a free carbene arm, followed by subsequent hydrolysis of the latter. The bis(imidazolium) salt **1** can be deprotonated by strong bases to form the bis(carbene) ligand $C_{NHC}CHC_{NHC}$ (**6**), which readily reacts with [Ir(μ-Cl)(cod)]$_2$ to give the dinuclear complex [{IrI(cod)}$_2$(μ-$C_{NHC}CHC_{NHC}$)] (**7**), in which the *N*-heterocyclic bis(carbene) ligand bridges the two metals through the carbene carbon atoms.

Introduction

Pincer-based metal complexes often exhibit unique reactivity due to the right combination of stability and reactivity imparted by the pincer ligands and they have provided access to a better fundamental understanding of a variety of organometallic reactions and to new catalytic applications.[1–5] The physical and chemical properties of pincer complexes can be controlled by systematic ligand modifications and/or variation of the metal centre, allowing in particular a fine tuning of the metal complex reactivity and stability.[2,3,6–11] Selected examples of pincer ligands include those with PCP,[1,12,13] PCN,[14–17] PCO,[18–20] SCS,[21] NCN,[22–27] NNN,[28] CNC,[11,29–32] and PNP donor sets.[13,33,34]

Various types of iridium pincer complexes have been employed as catalysts in important organometallic transformations, including alkane dehydrogenation (in the presence or absence of an H_2 acceptor),[12,35–42] the dehydrogenation of primary amines to nitriles,[43] the dehydrogenation of borane–amine complexes[44] and the intermolecular C–H activation of substituted aromatic compounds.[45,46] Several methods including direct cyclometallation,[2] oxidative-addition across low-valent metal precursors[47,48] and direct coordination of a neutral ligand to metal precursors[49,50] have been developed for the metallation of pincer ligands by an iridium centre. A series of PCP [PCP = $C_6H_3(CH_2PR_2)_2$-2,6, $C_6H_3(OPR_2)_2$-2,6 or anthracene-1,8-diphosphanes] pincer complexes of iridium have been prepared by direct activation of the central aryl group C–H bond.[2,37,39,42,51] The metallation reaction probably involves precoordination of both phosphorus groups of the PCP ligands to the iridium centre to give a κ^2-P,P bidentate chelating intermediate,[47] which further undergoes an intramolecular C_{aryl}–H bond activation resulting in the production of the corresponding biscyclometallated products.[52]

Attempts to develop new iridium pincer complexes with improved activity and selectivity by replacement of the P donors of the pincer arms with, for example, *N*-heterocyclic carbene (NHC) donor groups have also been made recently. Combining the reaction of the bis(imidazolium) salt ($CH_{NHC}CHCH_{NHC}$)I_2 with [$Zr(NMe_2)_4$], which leads to activation of three C–H bonds, with a transmetallation from zirconium to iridium or rhodium, successfully afforded the desired metal CCC–NHC pincer complexes.[53,54] A dinuclear Ir(III) complex metallated on the pyridine ring was formed when the 2,6-bis(imidazol-2-ylidene)pyridine-based dicarbene ligand was reacted with [Ir(μ-Cl)(cod)]$_2$. When methyl

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‡ Dedicated to Christian Bruneau, on the occasion of his 60th birthday, with our warmest wishes.

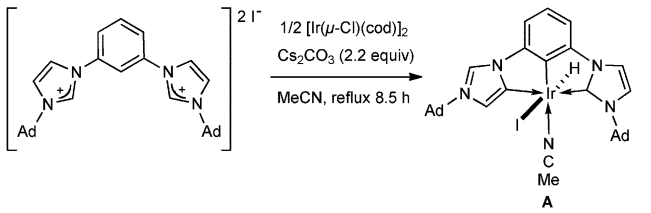
groups were introduced at the C^3 and C^5 positions of the central pyridine ring, metallation at these positions was prevented and a CNC iridium pincer complex was isolated.[55] *meta*-Phenylene-bridged bis-benzimidazolium chlorides were recently synthesized and successfully metalated by $[Ir(\mu\text{-}Cl)(cod)]_2$ under mild conditions, in the presence of excess triethylamine or of a stoichiometric amount of caesium fluoride as a base, to give neutral iridium(III) pincer complexes of formula [Ir(H)Cl(CCC)(NCMe)].[56]

We have recently reported the direct synthesis of iridium(III) $C_{NHC}CC_{NHC}$ pincer complexes from bis(imidazolium) precursors containing a xylylene moiety as spacer between the imidazolium rings, and $[Ir(\mu\text{-}Cl)(cod)]_2$ in the presence of NEt_3 or Cs_2CO_3 as bases in refluxing acetonitrile.[57,58] The influence of the nature of the weak base used to deprotonate the imidazolium salt and of the reaction conditions on the formation of the NHC complexes have been discussed in detail.[58,59] On the basis of the nature of the intermediates isolated during the synthesis of hydrido, *N*-heterocyclic dicarbene iridium(III) pincer complexes, we postulated a reaction mechanism for the formation of the pincer hydride complexes, which would involve (*a*) formation of a mono-NHC Ir(I) complex, (*b*) oxidative addition of the C–H bond at the C2 position of the aromatic to the Ir(I) centre, (*c*) base-assisted HI elimination from the Ir(III) complex, and (*d*) oxidative addition of the second imidazolium moiety to the Ir(I) centre.[58]

We recently found that the reaction of (4,6-dimethyl-1,3-phenylene)bis(1-adamantylimidazolium) diiodide with $[Ir(\mu\text{-}Cl)(cod)]_2$ in the absence of base afforded a hydrogen-bonded compound where two isolated units, the $[(CH_{imid}CHCH_{imid})I]$ cation and the [IrXI(cod)] (X = Cl or I) anion, are held together in the solid state by intermolecular hydrogen bonds which involve one of the iridium-bound halides as multiple hydrogen bond acceptor to the two bis(imidazolium) (C2-)H donors.[60] By using either weak or strong bases, these hydrogen-bonded salts could be converted to the corresponding mono-metallated NHC Ir(I) complexes, such as **2** (Scheme 1).[60]

In the present study, we investigate the reaction of the *N*,*N*-adamantyl-substituted mono-NHC Ir(I) complex **2** (Scheme 1) with excess Cs_2CO_3, which successfully and selectively afforded a hydrido, *N*-heterocyclic dicarbene iridium(III) pincer complex possessing both an NHC and an abnormal NHC ligand. The stepwise formation of such mixed normal/abnormal NHC pincer hydride complexes provides experimental support for our previously proposed mechanism for the formation of hydrido, *N*-heterocyclic dicarbene Ir(III) pincer complexes.[58] Mixed normal/abnormal NHC hydride pincer complexes of Ir(III) have recently been obtained by the reaction shown in Scheme 2, but without intermediates being isolated.[61]

Ligands in which the aryl spacer is further substituted in the 4- and 6-positions by methyl groups, as in **2**, were used with the



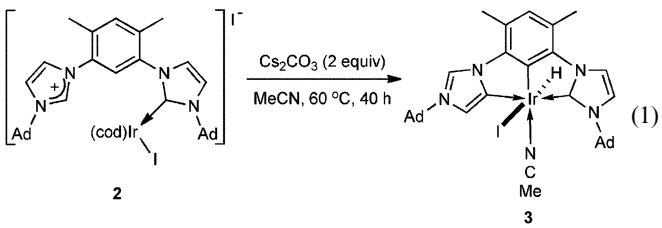
Scheme 2 Direct formation of the Ir(III) mixed normal/abnormal NHC pincer hydride complex **A**.[61]

objective to prevent direct aryl metallation at these positions, a reaction that has been previously found to occur readily.[58] Here we will show how experimental conditions such as the nature and the amount of the base used, the reaction solvent, the temperature, *etc.*, significantly influence the formation of the final products, with different reaction conditions leading to the isolation of different metal complexes.

Results and discussion

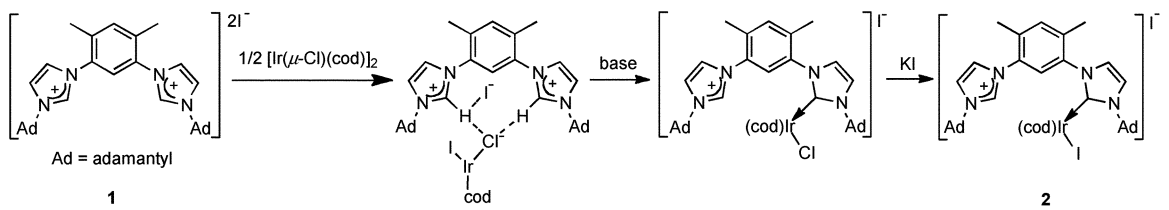
1. Synthesis of the hydride Ir(III) pincer complex $[Ir(H)I(C_{NHC}CC_{aNHC})(NCMe)]$ (3)

Heating a mixture of complex **2** with 2 equiv. Cs_2CO_3 in acetonitrile at 60 °C for 40 h yielded the new complex **3** as a yellow, air-stable solid after crystallization from the mixture of toluene/Et_2O (eqn (1)).



(1)

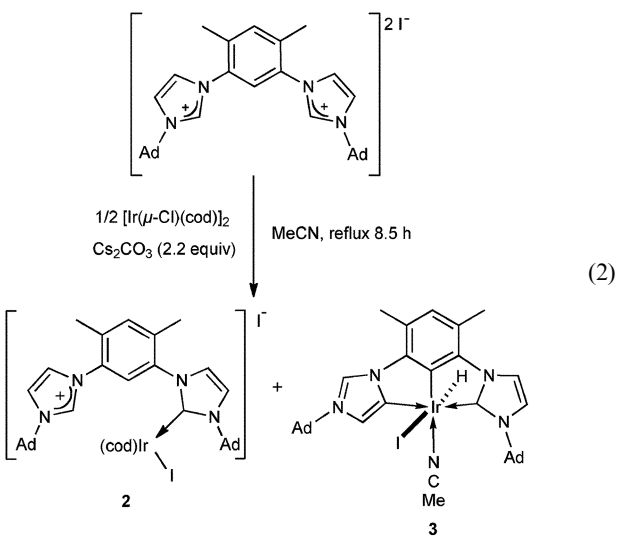
The identity of this product was suggested by its spectroscopic data (298 K), particularly by ^{1}H NMR spectroscopy in CD_3CN where the low field doublet at 8.50 ppm is assigned to the imidazole-2 proton, while the imidazole-4 proton of the same heterocycle resonates at 6.89 ppm, with a ^4J(HH) coupling constant of 1.5 Hz. Related iridium complexes featuring an abnormal carbene coordination show similar NMR spectroscopic features.[61–63] The ^{1}H NMR resonances in the normally bound NHC ligand appear as two doublets at 7.20 and 7.71 ppm, with a ^3J(HH) coupling constant of 2.4 Hz. The ^{1}H NMR spectrum of **3** also exhibits a singlet resonance in the hydride region at δ –23.9 ppm, which is assigned to the hydride ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the metallated carbene carbon atoms



Scheme 1 Formation of a hydrogen-bonded complex and its conversion to the mono-NHC Ir(I) complex **2**.[60]

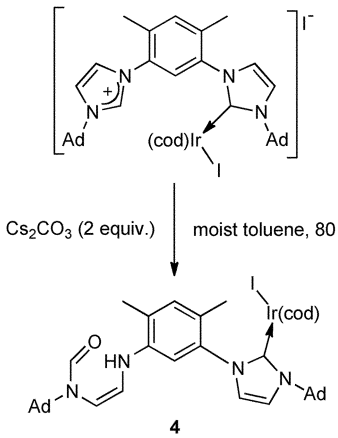
resonates at δ 169.8 and 172.6 ppm, respectively, values which are in the typical range of normal and abnormal carbene carbon atoms.[64] FT-IR analysis also indicated the presence of a hydride ligand with a ν(IrH) vibration at 2016 cm^{-1}. By comparison with its non-dimethyl-substituted analogue **A**[61] and on the basis of the NMR and FT-IR data and MALDI TOF-MS analysis (peak at m/z = 740.3 $[M - I]^+$), we suggest for **3** the structure drawn with a pincer ligand featuring both C-bound isomers of the NHC ligands. The coordination mode of one carbene ligand corresponds to a normal binding through the C2 carbene carbon, whereas the other NHC ligand binds "abnormally" *via* C4 to the Ir(III) centre. The lack of any other product in the reaction mixture, as revealed by NMR spectroscopy, indicated that the mono-NHC iridium complex **2** has been readily converted to **3**. All these observations are consistent with our previously proposed hypothesis that the formation of the pincer Ir(III) hydride complex proceeds in a stepwise manner *via* a mono-NHC Ir(I) intermediate complex **2**.[58] Accordingly, the steric bulk of the adamantyl groups in this intermediate favors the formation of the abnormal NHC binding. Complex **3** is air-stable at room temperature in CD_3CN solution overnight, even in the presence of H_2O. When compared to **A**, complex **3** shows improved stability and solubility in usual solvents.[61]

The nature and quantity of the base used have pronounced effects on this reaction. The reactivity of complex **2** contrasts markedly with that of related precursors featuring an *n*-Bu substituent in place of adamantyl.[58] In that case, NEt_3 was a strong enough base to transform the mono-NHC Ir(I) intermediate into the corresponding pincer Ir(III) complex, whereas in the case of **2**, no reaction was observed with NEt_3, even when it was used in large excess. Moreover, when Cs_2CO_3 was used as the base, its quantity also played an important role, less base usually leading to incomplete reaction while excess base facilitating side reactions and the formation of several unknown compounds. Refluxing the mixture of bis(imidazolium) salt **1** with 2.2 equiv. of Cs_2CO_3 in MeCN mainly yielded the mono-NHC Ir(I) complex **2** and only a small quantity of **3** (about 10% based on ^{1}H NMR analysis) whereas the analog of **2** was not observed during the synthesis of **A** (Scheme 2),[61] thus implying that the dimethyl-substitution in the central aryl group deactivates the ligand (eqn (2)).



(2)

The influence of the reaction solvent on the formation of the pincer complex was also studied. When the reaction mixture was heated in toluene at 80 °C for 8.5 h, cleavage of the uncoordinated imidazolium ring occurred to form the iminoformamide derivative [IrI(cod){[NHCH═CHN(Ad)CHO]CHC_{NHC}}] (**4**) whose structure was established by NMR and X-ray analyses (eqn (3)). In particular, the ^{1}H NMR spectrum of **4** in CD_2Cl_2 contains the signal of the formyl proton at 8.44 ppm. We shall come back to the formation of this complex below.



(3)

Single crystals of **4** suitable for X-ray diffraction were grown by slow evaporation of a saturated chloroform solution at ambient temperature (Fig. 1, Table 1). Considering the midpoints of the C═C double bonds of the coordinated cod ligand and the mutually *cis* iodide and carbon (NHC) atoms, the iridium centre is in a slightly distorted square-planar coordination environment. The Ir–carbene bond length of 2.05(1) Å is similar to that in complex **2**[60] and to those found in other Ir(I) carbene complexes.[65–69] The imidazole-2-ylidene ring forms an angle of 76.6° with the aryl ring. In the iminoformamide group, the atoms are not coplanar and the oxygen atom is oriented in such a way that it forms a H-bond with one of the aryl methyl protons (3.006 Å). This may be responsible, at least in part, for the orientation of the iminoformamide group which also minimizes intramolecular steric repulsions (Fig. 1). As a result of the cleavage of the heterocyclic imidazole-2-ylidene ring,

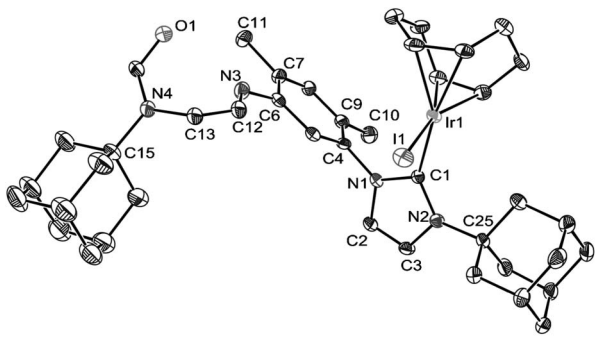


Fig. 1 ORTEP of the molecular structure of **4**. H atoms are omitted for clarity. Ellipsoids are represented at the 40% probability level. Selected bond distances (Å) and angles (°): Ir(1)–I(1) 2.68(1), Ir(1)–C(1) 2.05(1), C(1)–N(2) 1.38(1), N(2)–C(3) 1.39(2), C(3)–C(2) 1.32(2), C(2)–N(1) 1.39(2), N(3)–C(12) 1.40(1), C(12)–C(13) 1.36(2), C(13)–N(4) 1.41(2); C(1)–Ir(1)–I(1) 89.4(3), N(1)–C(1)–N(2) 103.2(8), N(2)–C(3)–C(2) 109.1(9), C(3)–C(2)–N(1) 106.0(9), N(3)–C(12)–C(13) 123.1(2), C(12)–C(13)–N(4) 126.2(2).

Table 1 Crystal data and structure refinement for **4** and **7**

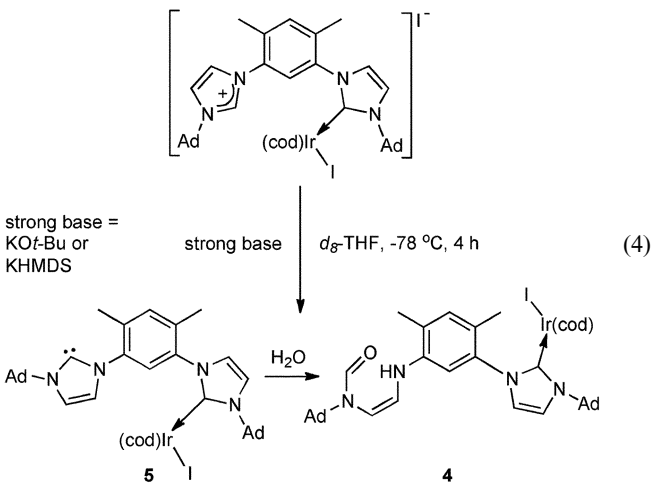
	4	**7**
Chemical formula	$C_{42}H_{55}IIrN_4O$	$C_{50}H_{66}Cl_{0.25}I_{1.75}Ir_2N_4$
Formula mass	951.00	1338.41
Crystal system	Monoclinic	Monoclinic
a/Å	19.6758(13)	14.3334(5)
b/Å	12.2455(5)	17.8209(8)
c/Å	16.8436(10)	19.0291(5)
β/°	93.658(2)	106.637(2)
V/Å^3	4050.0(4)	4657.2(3)
T/K	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
μ/mm^{-1}	4.095	6.922
No. of reflns measd	13 359	17 895
No. of indep reflns	7510	10 267
R_{int}	0.0615	0.0675
Final R_1 ($I > 2\sigma(I)$)	0.0623	0.0531
Final $wR(F^2)$ ($I > 2\sigma(I)$)	0.1604	0.1223
Final R_1 (all data)	0.1110	0.1249
Final $wR(F^2)$ (all data)	0.1803	0.1462
Goodness of fit on F^2	0.940	0.989

the N(4)–C(13), C(12)–C(13) and C(12)–N(3) bond lengths are slightly longer than their counterparts in the coordinated NHC ligand [1.41(2) Å for N(4)–C(13) *vs.* 1.39(2) Å for N(2)–C(3); 1.36(2) Å for C(13)–C(12) *vs.* 1.32(2) Å for C(3)–C(2); 1.40(1) Å for C(12)–N(3) *vs.* 1.39(2) Å for C(2)–N(1), respectively], but remain in the usual range for such bonds.

We found that among a series of organonitrile solvents, the formation of complex **3** could only be optimized in MeCN since under otherwise identical reactions, solvents such as isobutyronitrile, 2-chloroacetonitrile or benzonitrile yielded a mixture of unknown compounds. This is consistent with our proposed mechanism for the formation of pincer hydride complexes, where MeCN could not only act as solvent but also as ligand, by initial replacement of the cyclo-octadiene ligand of the mono-NHC Ir(I) intermediate, followed by oxidative addition of the second imidazolium C2–H bond to the iridium centre.[58] Other reaction parameters for eqn (1), such as temperature and time, were also found to be important, higher reaction temperatures facilitating side reactions while at lower temperatures, no reaction occurred. Enough time is required to achieve complete conversion, however upon prolonged reaction periods, side reactions begin to dominate.

2. Formation of ring-opened complex [IrI(cod){[NHCH═CHN(Ad)CHO]CHC$_{NHC}$}] (4)

Knowing that deprotonation of the imidazolium salt by strong bases and *in situ* coordination of the free carbene is an efficient method to form NHC complexes, we reckoned that using an external base to deprotonate the imidazolium arm in complex **2** and generate the carbene ligand could facilitate its coordination to the already present metal, and thus allow the synthesis of a bis(carbene) chelate complex. Such a complex could behave similarly to bis(phosphine) analogues and possibly undergo an intramolecular C_{aryl}–H bond activation yielding the corresponding dicarbene iridium(III) pincer complex. Starting from a solution of complex **2** in anhydrous d_8-THF (same results were obtained in d_8-toluene), one equivalent of KO*t*-Bu was added at −78 °C, and after 4 h reaction, a new compound **5** was formed for which ^{1}H and ^{13}C NMR data indicated the presence of two chemically different heterocyclic moieties in the molecule (eqn (4)).

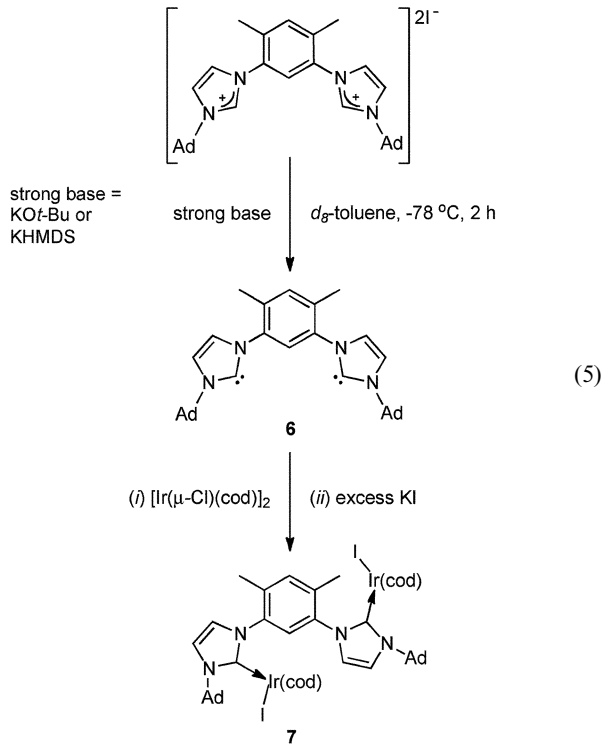


One set of ^{1}H NMR signals corresponds to the protons of a coordinated imidazole (at 7.22 and 7.29 ppm). The metallated carbene carbon resonates in ^{13}C NMR at a chemical shift similar to that in complex **2** (179.0 ppm for **5** in d_8-THF *vs.* 178.4 ppm for **2** in CD_2Cl_2). The other set of signals is assigned to an uncoordinated NHC group, with two ^{1}H NMR signals at 7.52 and 7.65 ppm, which are upfield shifted when compared to those found in the imidazolium arm in **2**, but are in the typical range for protons of uncoordinated NHC moieties.[70,71] In the ^{13}C NMR spectrum, the resonance at δ 217.0 ppm is characteristic for the carbene carbon of a free NHC.[70,71]

Inspection of the NMR spectra of this sample after the NMR tube was stored overnight revealed that the solution now contained **4** as the major species, which may originate from the reaction of the free carbene ligand of **5** with traces of water. If the concentration of **5** in d_8-THF is high enough, nice crystals of complex **4** form directly in the NMR tube stored overnight. That complex **4** resulted from hydrolysis of the free carbene of **5** is supported by the observation that addition of water considerably increased the reaction rate, whereas in rigorously dry solvents, complex **5** is stable for *ca.* 2 days. Unfortunately, we were not able to crystallize complex **5**. Similar hydrolysis of imidazole-2-ylidenes has been reported previously.[72,73] Recent studies indicate that in the presence of a suitable quantity of H_2O, the free carbene is protonated and the resulting imidazolium hydroxide acts as an intermediate in the formation of the ring-opened hydrolysis product, the (solvated) hydroxide ion undergoing nucleophilic attack of the imidazolium ion.[74]

3. Formation of Dinuclear Complex [IrI(cod)]$_2$(μ-C$_{NHC}$CHC$_{NHC}$) (7)

Deprotonation of ligand **1** by KHMDS at −78 °C in d_8-toluene for 2 h resulted in the formation of the free bis(carbene) $C_{NHC}CHC_{NHC}$ (**6**), which could be analyzed by ^{1}H NMR at room temperature (similar results can be obtained when using potassium *tert*-butoxide as the base) (eqn (5)).



(5)

In the ^{1}H NMR spectrum of **6**, only one set of signals was observed for the imidazole moieties, thus suggesting a symmetric conformer for **6** in solution. The imidazole protons show two doublet resonances at 6.69 and 6.80 ppm, which are significantly upfield shifted with respect to the corresponding resonances of the bis(imidazolium) precursor. Compound **6** was found to be stable for 4 h at −78 °C in the reaction medium, but it begins to decompose after prolonged storing. Addition of [Ir(μ-Cl)(cod)]$_2$ to the d_8-toluene solution of **6** followed by treatment with excess KI resulted in the formation of the dinuclear complex [IrCl(cod)]$_2$(μ-$C_{NHC}CHC_{NHC}$) (**7**). The same product was obtained when either 1 or 2 equiv. [Ir(μ-Cl)(cod)]$_2$ was used. In the ^{1}H NMR spectrum (CD_2Cl_2) of **7**, four doublets (6.99 and 7.37 ppm with ^3J(HH) = 1.7 Hz; 7.15 and 7.40 ppm with ^3J(HH) = 1.7 Hz) corresponding to two sets of NHC moieties were observed. In the $^{13}C\{^1H\}$ NMR spectrum, the metallated carbene carbons appear at 178.7 and 180.2 ppm, similar to the values observed in analogous complexes.[58] Complex **7** could also be synthesized in a stepwise manner in high yield by addition of a stoichiometric amount of [Ir(μ-Cl)(cod)]$_2$ to a THF solution of **5**.

Single crystals of the dinuclear complex **7** suitable for X-ray diffraction were grown by slow diffusion of Et_2O into its $ClCH_2CH_2Cl$ solution for one week (Table 1). The molecular structure of **7** shown in Fig. 2 consists of a dimetallic unit bridged by the μ-$C_{NHC}CHC_{NHC}$ ligand through the carbene carbon atoms C1 and C2. Both iridium centres adopt a distorted square-planar coordination geometry including a terminal halide, a chelating cod molecule and a NHC ligand. Consistent with the NMR data in solution, the molecular structure of **7** in the solid state has no symmetry element and the Ir(cod) fragments occupy opposite positions with respect to the bridging ligand, which allows to minimize steric repulsions. The iridium–carbon bond lengths involving the two NHC ligands are not significantly different [2.08(1) Å for Ir(1)–C(1) and 2.05(1) Å for Ir(2)–C(2)], and are

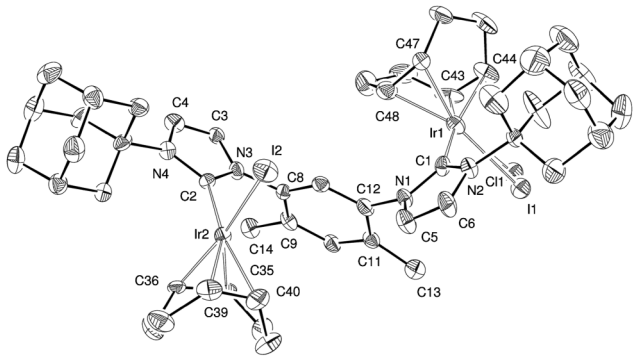


Fig. 2 ORTEP of the molecular structure of **7**. H atoms are omitted for clarity. Ellipsoids are represented at the 40% probability level. A chloride [Cl(1)] and an iodine [I(1)] were found occupying almost the same coordinate with a mutual occupancy factor of 0.25/0.75. Selected bond distances (Å) and angles (°): Ir(1)–I(1) 2.70(1), Ir(1)–Cl(1) 2.32(2), Ir(1)–C(1) 2.08(1), Ir(2)–I(2) 2.67(1), Ir(2)–C(2) 2.05(1); C(1)–Ir(1)–I(1) 91.6(3), Cl(1)–Ir(1)–Cl(1) 98.9(6), N(1)–C(1)–N(2) 104.3(8), N(3)–C(2)–N(4) 104.1(8).

similar to those in related iridium NHC complexes.[65–69,75] Similar to our previous observations, owing to the chloride/iodide anion exchange at one of the two Ir–I sites, a disorder involves an iridium-bound halide, whose site is occupied by a chlorine and an iodine atom with occupancy factors of 0.25/0.75, respectively (see Experimental part).[60,61]

The formation of complex **7** indicates that coordination of the free carbene to iridium proceeds faster than its hydrolysis provided that the iridium fragments can move freely. Since in the case of eqn (5) the coordination of the carbene moieties proceeds smoothly, while in complex **5** the generated free carbene failed to react with the neighbouring iridium atom, it is possible that the specific geometry of complex **5**, and in particular the steric hindrance of the adamantyl groups, is detrimental to the intramolecular coordination reaction. This hypothesis is consistent with the formation of abnormal NHC ligand in **3** and a similar steric bulk effect of the adamantyl group has also been observed in the synthesis of **A**.[61]

Conclusions

The hydrido, *N*-heterocyclic dicarbene iridium(III) complex **3** has been prepared by first reacting the bis(imidazolium) salt **1** with [Ir(μ-Cl)(cod)]$_2$. The intermediate mono-NHC Ir(I) complex **2** was isolated and further reacted with excess Cs_2CO_3 in MeCN to form **3**. Varying the reaction conditions, such as the nature and quantity of base, the reaction solvent, the reaction temperature and time has demonstrated their significant influence on the formation of the final products. In solvents such as isobutyronitrile, 2-chloroacetonitrile or benzonitrile and under otherwise identical conditions, the pincer hydride complexes of iridium(III) were not accessible, while in toluene a new imidazol-2-ylidene ring-opened complex **4** was readily formed. Complex **4** was shown to be formed by hydrolysis of the free carbene moiety in complex **5**, which was generated by deprotonation of the imidazolium arm of **2** by strong bases. The reaction of [Ir(μ-Cl)(cod)]$_2$ with the bis(carbene) ligand **6**, generated *in situ* by deprotonation of the bis(imidazolium) salt **1** with strong bases (KO*t*-Bu or KHMDS) afforded the dinuclear

complex **7**, in which both carbene ligands are coordinated to the metal in the usual mode. Future work is aimed at studying the catalytic reactivity of complex **3** as precatalyst for alkane C–H activation.

Experimental section

General procedures

All operations were carried out using standard Schlenk techniques under an inert atmosphere. Solvents were dried and degassed, and freshly distilled prior to use. THF and Et_2O were dried over sodium/benzophenone and CH_2Cl_2, $ClCH_2CH_2Cl$ and MeCN were distilled from CaH_2. d_6-DMSO and CD_3CN were degassed and stored over 4 Å molecular sieves. Commercial d_8-THF and d_8-toluene were used as received. CD_2Cl_2 was dried over 4 Å molecular sieves, degassed by freeze–pump–thaw cycles and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.47 MHz) and referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance. Assignments are based on ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-HMQC and ^{1}H, ^{13}C-HMBC experiments. IR spectra were recorded in the region 4000–100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a micro-TOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulising gas. The salt (4,6-dimethyl-1,3-phenylene)bis(1-adamantylimidazolium) diiodide (**1**) and the complex (4,6-dimethyl-1,3-phenylene)-(1-adamantylimidazolium)-(3-adamantylimidazol-2-ylidene) iodide (η^4-1,5-cyclooctadiene)iridium(I) iodide (**2**) were prepared as reported.[60]

Synthesis of (4,6-dimethyl-1,3-phenylene-*k*C^2)(1-adamantylimidazol-2-ylidene)(3-adamantylimidazol-5-ylidene)(acetonitrile)(hydrido)(iodo)iridium(III), [Ir(H)I($C_{NHC}CC_{aNHC}$)(NCMe)] (3).

A mixture of (4,6-dimethyl-1,3-phenylene)-(1-adamantylimidazolium)-(3-adamantylimidazol-2-ylidene) iodide (η^4-1,5-cyclooctadiene)iridium(I) iodide (**2**, 0.05 g, 0.047 mmol) and Cs_2CO_3 (0.03 g, 0.093 mmol) in MeCN (30 mL) was heated at 60 °C for 40 h. The resulting suspension was then allowed to cool to room temperature and the solvent was removed *in vacuo*. The residue was extracted with toluene (20 mL) and then the solution was concentrated to a total volume of 10 mL. Slow diffusion of Et_2O into the solution at room temperature for 24 h afforded pure complex **3** as a yellow solid. ^{1}H NMR (CD_3CN): δ –23.9 (s, 1H, Ir–H), 1.63 (br s, 12H, CH_2 adam.), 2.06–2.11 (m, 18H, CH and CH_2 adam.), 2.25 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 6.42 (s, 1H, CH arom.), 6.89 [d, ^4J(HH) = 1.5 Hz, 1H, CH of abnormal NHC(C4–H)], 7.20 (d, ^3J(HH) = 2.4 Hz, 1H, CH imid.), 7.71 (d, ^3J(HH) = 2.4 Hz, 1H, CH imid.), 8.50 [d, ^4J(HH) = 1.5 Hz, 1H, CH of abnormal NHC(C2–H)]. The CH_3CN ligand is displaced by CD_3CN, and accordingly only a singlet is observed for uncoordinated CH_3CN. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 20.1, 22.7 (CH_3), 30.1, 30.7 (CH adam.), 36.2, 36.5, 43.5 and 43.6 (CH_2 adam.), 57.8 and 58.4 (C adam.), 116.0 and 116.7 (CH imid.), 117.3 [CH of abnormal NHC(C2)], 126.5 (CH arom.), 127.3 [CH of abnormal NHC(C4)], 138.7, 141.1, 141.3, 142.7 and 143.7 (C arom.), 169.8 and 172.6 (NC–Ir). ESI-MS (CH_3CN, 50 V, *m*/*z*): 740.3 [M – I]$^+$. IR (pure, orbit diamond): 2904 s, 2850 m, 2016 m ($\nu_{Ir–H}$), 1666 m, 1594 w, 1520 m, 1450 m, 1418 m, 1350 w, 1326 m, 1307 m, 1261 m, 1229 w, 1153 m, 1102 m, 1082 w, 1025 w, 937 m, 829 w, 800 m, 730 m, 688 m. Anal. Calcd for $C_{36}H_{45}IIrN_5$ (866.9): C, 49.88; H, 5.23; N, 8.08. Found: C, 49.74; H, 5.32; N, 8.15%.

Synthesis of (4,6-dimethyl-1,3-phenylene)(1-*N*-(2-(amino)vinyl)-*N*-adamantylformamide)(3-adamantylimidazol-2-ylidene)(iodido)(η^4-1,5-cyclooctadiene)iridium(I), [IrI(cod){[NHCH═CHN(Ad)CHO]CHC_{NHC}}] (4)

(a) Use of a strong base. A solution of **2** (0.10 g, 0.94 mmol) and 0.023 g of KHMDS (1.13 mmol) in THF (20 mL) were stirred at –78 °C for 3 h and then the mixture was further stirred at room temperature for 12 h. The solution was concentrated to a total volume of 1 mL, and single crystals suitable for X-ray diffraction studies were obtained after the solution was kept overnight. ^{1}H NMR (CD_2Cl_2): when this compound was dissolved in CD_2Cl_2, it decomposed slowly and as a result ^{13}C{^{1}H} NMR analysis could not be carried out. Here only ^{1}H NMR data are provided. The CH_2 resonances of the cod ligands were poorly resolved and partly overlapped with other signals. δ 0.83–1.59 (m, CH_2 cod), 1.70 (br s, 6H, CH_2 adam.), 1.79 (br s, 6H, CH_2 adam.), 2.01 (br s, 6H CH_2 adam. and 3H CH_3), 2.15 (br s, 3H, CH adam.), 2.21 (s, 3H, CH_3), 2.30 (br s, 3H, CH adam.), 2.47 (m, 1H, CH cod), 2.65 (m, 6H, CH_2 adam.), 3.02 (m, 1H, CH cod), 4.39 (m, 1H, CH cod), 4.64 (m, 1H, CH cod), 5.12 (d, ^3J(HH) = 6.3 Hz, 1H, NCH═CH), 6.83 (d, ^3J(HH) = 6.3 Hz, 1H, NCH═CH), 6.96 (s, 1H, arom.), 7.03 (br s, 1H, CH imid.), 7.34 (br s, 1H, CH imid.), 8.06 (s, 1H, CH arom.), 8.44 (s, 1H, CHO). IR (pure, orbit diamond): 3107 w, 2904 vs, 2849 s, 2830 sh, 1623 m, 1510 m, 1577 w, 1448 m, 1428 sh, 1390 w, 1377 w, 1355 w, 1306 w, 1244 w, 1190 w, 1158 m, 1097 m, 1044 m, 993 w, 935 w, 900 m, 838 w, 834 m, 737 m, 711 m, 690 w. ESI-MS (CH_3CN, 50 V, *m*/*z*): 825.4 [M – I]$^+$. Anal. Calcd for $C_{42}H_{56}IIrN_4O$ (952.0): C, 52.99; H, 5.93; N, 5.88. Found: C, 54.52; H, 6.22; N, 5.43%.

(b) Use of Cs_2CO_3 as a base. A mixture of (4,6-dimethyl-1,3-phenylene)-(1-adamantylimidazolium)-(3-adamantylimidazol-2-ylidene)(iodide)(η^4-1,5-cyclooctadiene)iridium(I) iodide (**2**, 0.05 g, 0.047 mmol) and Cs_2CO_3 (0.03 g, 0.093 mmol) in toluene (30 mL) was heated at 80 °C for 8.5 h. The resulting suspension was then allowed to cool to room temperature and filtered and the solid was discarded. The filtrate was evaporated *in vacuo* and the resulting solid was analyzed by ^{1}H NMR (CD_2Cl_2), which indicated that complex **4** was the main component (more than 70%) of the mixture. Isolation of **4** from this mixture was not carried out.

Synthesis of (4,6-dimethyl-1,3-phenylene)(1-adamantylimidazol-2-ylidene)(3-adamantylimidazol-2-ylidene)(iodo)(η^4-1,5-cyclooctadiene)iridium(I), [IrI(cod)($CH_{NHC}CHC_{NHC}$)] (5)

A mixture of **2** (0.10 g, 0.94 mmol) and KHMDS (0.023 g, 1.13 mmol) in d_8-THF (1 mL) was stirred at –78 °C for 4 h and then the solution was transferred to a NMR tube. Both ^{1}H and ^{13}C NMR analyses indicated the formation of complex **5**. ^{1}H NMR: one CH cod proton could not be identified owing to overlapping

signals. δ 0.95, 1.29 and 1.48 (m, 6H, CH_2 cod), 1.78 (br s, 12H, CH_2 adam.), 1.99 (m, 2H, CH_2 cod), 2.11 (s, 3H, CH_3), 2.21 and 2.24 (br s, 12H, CH and CH_2 adam.), 2.47 (s, 3H, CH_3), 2.67 (br s, 6H, CH_2 adam.), 2.99 (m, 1H, CH cod), 4.42 (m, 1H, CH cod), 4.59 (m, 1H, CH cod), 7.20 (s, 1H, CH arom.), 7.22 (br s, 1H, CH imid.), 7.29 (br s, CH imid.), 7.52 (br s, CH imid.), 7.65 (br s, 1H, CH imid.), 8.48 (s, 1H, CH arom.). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.4 (CH_3), 20.2 (CH_3), 31.1 (CH_2 cod), 31.6 (CH adam.), 31.8 (CH adam.), 33.1 (CH_2 cod), 34.3 (CH_2 cod), 37.4 (CH_2 adam.), 37.8 (CH_2 adam.), 45.1 (CH_2 adam.), 45.7 (CH_2 adam.), 55.9 (CH cod), 57.2 (C adam.), 61.3 (C adam.), 76.8 (CH cod), 79.9 (CH cod), 115.9 (CH imid.), 120.8 (CH imid.), 121.1 (CH imid.), 124.5 (CH imid.), 129.2 (CH arom.), 133.7 (CH arom.), 134.5 (C arom.), 140.2 (C arom.), 140.7 (C arom.), 179.0 (NC–Ir), 217.0 (C–free carbene).

Synthesis of 1,3-bis(adamantylimidazol-2-ylidene)-4,6-dimethylbenzene, $C_{NHC}CHC_{NHC}$ (6)

A mixture of **1** (0.02 g, 0.26 mmol) and KHMDS (0.014 g, 0.67 mmol) was cooled to −78 °C, and then 2 mL of cold d_8-toluene was added. This mixture was further stirred at −78 °C for 2 h and the solution was transferred to a NMR tube. Due to the low solubility of the product and the progressive decomposition in the NMR tube, $^{13}C\{^1H\}$ NMR analysis could not be performed and we only indicate the ^{1} H NMR chemical shifts. ^{1}H NMR (d_8-toluene): δ 1.63 (br s, 12H, CH_2 adam.), 2.05 (br s, 6H, CH adam.), 2.23 (br s, 12H, CH_2 adam.), 2.37 (s, 6H, CH_3), 6.69 (d, ^3J(HH) = 1.5 Hz, 2H, CH imid.), 6.80 (d, ^3J(HH) = 1.5 Hz, 2H, CH imid.), 7.00 (s, 1H, CH arom.), 7.46 (s, 1H, CH arom.).

Synthesis of (4,6-dimethyl-1,3-phenylene)bis-(1-adamantylimidazol2-ylidene)- bis[(η^4-1,5-cyclooctadiene)-iridium(ι)iodide], [IrI(cod)]$_2$(μ-$C_{NHC}CHC_{NHC}$) (7)

A mixture of **1** (0.11 g, 0.15 mmol) and KHMDS (0.072 g, 0.36 mmol) was stirred in THF (20 mL) at −78 °C for 2 h, and a solution of [Ir(μ-Cl)(cod)]$_2$ (0.10 g, 0.15 mmol) in THF (10 mL) was added dropwise. The mixture was further stirred at room temperature for 12 h. Solid KI (0.25 g, 1.5 mmol) was then added to the solution and the mixture was further stirred for 12 h. The solvent was removed *in vacuo* and CH_2Cl_2 (10 mL) was added to extract the iridium complex. Slow diffusion of pentane into this solution at room temperature for 3 days afforded yellow crystals (0.11 g, 53.9%). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of Et_2O into a concentrated $ClCH_2CH_2Cl$ solution for one week. ^{1}H NMR (CD_2Cl_2): δ 0.88–1.57 (m, 12H, CH_2 cod), 1.78 (br s, 12H, CH_2 adam.), 2.00 (m, 4H, CH_2 cod), 2.18 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.29 (s, 6H, CH adam.), 2.60 (br s, 14H, 6×CH_2 adam. and 2×CH cod), 2.99 (m, 1H, CH cod), 3.08 (m, 1H, CH cod), 3.23 (m, 1H, CH cod), 4.15 (m, 1H, CH cod), 4.44 (m, 2H, CH cod), 6.99 (d, ^3J(HH) = 1.7 Hz, 1H, CH imid.), 7.15 (d, ^3J(HH) = 1.7 Hz, 1H, CH imid.), 7.23 (s, 1H, CH arom.), 7.37 (d, ^3J(HH) = 1.7 Hz, 1H, CH imid.), 7.40 (d, ^3J(HH) = 1.7 Hz, 1H, CH imid.), 8.87 (s, 1H, CH arom.). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.1 (CH_3), 20.8 (CH_3), 28.1, 30.0, 30.5 and 30.6 (CH_2 cod), 30.7 (CH adam.), 32.7, 32.8, 32.9 and 35.2 (CH_2 cod), 36.4, 44.8 and 44.9 (CH_2 adam.), 55.5, 55.7, 56.5 and 57.4 (CH cod), 60.5 and 60.6 (C adam.), 75.2, 76.7, 78.7 and 80.4 (CH cod), 119.2, 119.3, 122.6 and 123.1 (CH imid.), 130.8, 137.3, 137.9 and 138.4 (C arom.), 178.7 and 180.2 (NC–Ir). ESI-MS (CH_3CN, 50V, m/z): 1235.37 $[M - I]^+$. IR (pure, orbit diamond): 2905 s, 2849 m, 2824 sh, 1508 m, 1447 m, 1428 sh, 1396 w, 1373 w, 1329 m, 1306 w, 1273 w, 1101 m, 1068 w, 1042 w, 991 m, 975 m, 903 m, 887 m, 868 m, 825 m, 784 w, 742 w, 682 w. Anal. Calcd for $C_{50}H_{66}I_2Ir_2N_4$ (1361.3): C, 44.11; H, 4.89; N, 4.12. Found: C, 44.06; H, 4.90; N, 4.01%.

X-Ray data collection, structure solution and refinement for all compounds

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected on a Kappa CCD diffractometer[76] (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å) at 173(2) K. Crystallographic and experimental details for the structures are summarized in Table 1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[77] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms. In **4**, one of the two adamantyl groups (C15–C24) was found disordered in, at least, two positions, having C15 in common. One of the two images of the disorder was dominant. It was not possible to refine the second one, due to its low occupancy factor and to its proximity with the major component. This group was then refined with restrained C–C distances and anisotropic thermal parameters. A solvent molecule, probably toluene, was found disordered around the symmetry centre. Any attempt to locate its atomic coordinates failed. A PLATON-SQUEEZE procedure was then applied, resulting in improved refinement parameters for the main residue. In **7**, a disorder involved one of the halogens coordinating to the metal centre. A chloride and an iodine were found occupying almost the same coordinate with a mutual occupancy factor of 0.25/0.75. These atoms were refined with equal anisotropic parameters. A related disorder involved the adamantyl substituent which was disordered over two very close positions. Attempts to fully refine this disorder failed. Instead, the group was refined with restrained anisotropic parameters. For all compounds, a MULTISCAN absorption correction was applied.[78,79]

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