An unprecedented, figure-of-eight, dinuclear iridium(I) dicarbene and new iridium(III) 'pincer' complexes†

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An unusual dinuclear Ir(I) complex bridged by two *N*-heterocyclic biscarbene ligands, forming a 20-membered, figure-of-eight dimetallacycle, and new $C_{NHC}CC_{NHC}$ pincer complexes of Ir(III) have been obtained directly from the bis(imidazolium) precursors and $[Ir(\mu\text{-}Cl)(cod)]_2$.

N-Heterocyclic carbene (NHC) ligands have been extensively studied during the last decade and continue to be of considerable interest, notably for their contribution to coordination and organometallic chemistry and their numerous applications in homogeneous catalysis.[1] Their electron donor properties make them attractive alternatives to tertiary phosphine ligands.[2] Metal complexes containing planar, rigid, tridentate ligands which incorporate at least one NHC have been intensively investigated during the last ten years and found to exhibit unique catalytic properties.[1c,3] Their synthesis may however be more difficult than anticipated, both when monoanionic $C_{NHC}{}^{\wedge}C^{\wedge}C_{NHC}$ (C = metallated aryl, $^{\wedge}$ represents a spacer) or neutral $C_{NHC}{}^{\wedge}N^{\wedge}C_{NHC}$ (N = *e.g.* pyridine) pincer systems are considered. Indeed, metallation of the aryl carbon or coordination of the nitrogen donor may be prevented by the formation of kinetically stable dinuclear complexes in which the ligand behaves solely as a $C_{NHC}{}^{\wedge}C_{NHC}$ bridge.[2c] This has been observed with the formation of complexes of the type $[Rh_2X_2(cod)_2(\mu\text{-}C_{NHC}{}^{\wedge}C_{NHC})]$ (cod = 1,5-cyclooctadiene).[4] We have now found that an unprecedented type of dinuclear complex can also be formed when the 1,3-xylyl-bis-imidazolium carbene precursor $(^{Et}CH^{\wedge}CH^{\wedge}CH)(PF_6)_2$ **1** is reacted with $[Ir(\mu\text{-}Cl)(cod)]_2$. Indeed, in the presence of Cs_2CO_3, the air-stable complex $[Ir(cod)(\mu\text{-}{}^{Et}C_{NHC}{}^{\wedge}CH^{\wedge}C_{NHC})]_2(PF_6)_2$ **2** [eqn (1)] was obtained.†

The molecular structure of **2**·MeCN was determined by single crystal X-ray diffraction‡ and revealed the non-pincer character of the ligand (Fig. 1). Two bridging $C_{NHC}{}^{\wedge}CH^{\wedge}C_{NHC}$ ligands connect the Ir(I) centres in such a way that each metal is bonded to two mutually *cis* carbene donors (C(1)–Ir(1)–C(32) 98.1(2)° and C(14)–Ir(2)–C(19)

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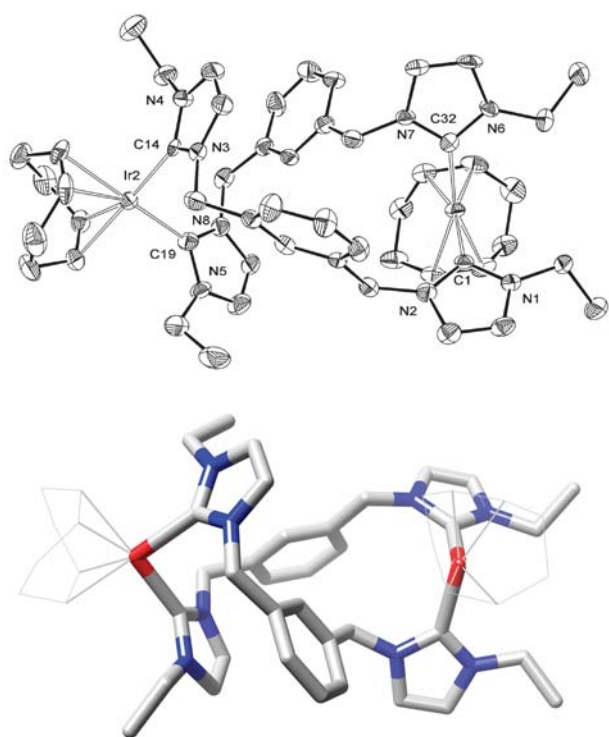

$$(1)$$

95.6(2)°). This results in a dicationic 20-membered dimetallacycle which forms a figure-of-eight. There is no symmetry element relating the metal centres (the molecule has C_1 symmetry), and the C_{NHC}–Ir(1)–C_{NHC} and C_{NHC}–Ir(2)–C_{NHC} planes are approximately orthogonal and parallel, respectively, to the Ir(1)–Ir(2) axis. This is also indicated by the complexity of the ^{1}H NMR spectrum in solution. Each Ir atom is further coordinated by a cod ligand, allowing the metals to reach a 16 e environment. The metal–carbene distances (2.050(6)–2.068(6) Å) are similar to those found in other Ir(I) carbene complexes.[5]

In contrast to the reaction of eqn (1), metallation of the central aryl ligand was observed when the bis(imidazolium) carbene precursor **3** or **4** was reacted with $[Ir(\mu\text{-}Cl)(cod)]_2$ in the presence of NEt_3 and KI. This afforded the dinuclear $C_{NHC}CC_{NHC}$ pincer complexes **5** and **6**, respectively, in *ca.* 30% yields [eqn (2)].§ We are currently examining the influence of the spacer and of the base on these contrasting reactions.

$$(2)$$
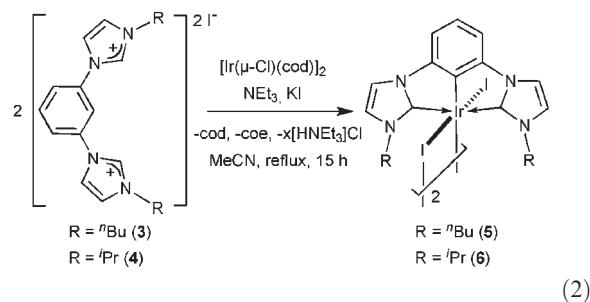
The addition of NEt_3 promotes the transformation of the bis(imidazolium) salt in the presence of the Ir(I) precursor

Fig. 1 Top: molecular structure of the dication in **2**·MeCN. H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Ir(1)–C(1) 2.050(6), Ir(1)–C(32) 2.068(6), Ir(2)–C(14) 2.059(6), Ir(2)–C(19) 2.058(6); C(1)–Ir(1)–C(32) 98.1(2), C(14)–Ir(2)–C(19) 95.6(2). Bottom: view (Chimera software) emphasizing the figure-of-eight structure generated by the 20-membered dimetallacycle.

complex, as observed in the formation of non-pincer, bis-NHC complexes of rhodium[4b,6] and iridium.[5c,7] Interestingly, we detected, by GC analysis of the reaction mixture, the presence of uncoordinated 1,5-cod and cyclooctene. The dimeric form of the bis-NHC complexes is retained in dichloromethane, where it is scarcely soluble, as shown by the observation of MALDI-TOF MS peaks at $m/z = 1407.0$ $[M − I]^+$ and $m/z = 767.8$ $[0.5\ M]^+$, which are consistent with the composition of **5**. However, the iodide bridged species can be cleaved by solvents such as MeCN and DMSO (Scheme 1). These solvento complexes have been fully characterised,§ including by X-ray diffraction analysis.‡

The ^{1}H NMR spectrum of **7** in CD₃CN indicated the coordination of an acetonitrile molecule in the equatorial position (*trans* to metallated aryl) because of the magnetic equivalence of the CH₂ linked to the NHC (triplet at 4.39 ppm). We also observed equivalent carbene carbons at 164.1 ppm, at rather low field compared to what is reported for unsaturated NHC bound to 18 electron iridium(III).[7,8] The metallated carbon was unambiguously associated with the signal at 136.1 ppm, which is comparable to data reported by Peris and coworkers[9] for cyclometallated Cp*–Ir–NHC complexes (141–145 ppm). The structure of **7** was confirmed by X-ray diffraction on a single crystal (Fig. 2).‡ The Ir–carbene bond lengths are similar to those in **2**·MeCN whereas the covalent bond involving the metallated aryl ring is shorter (Ir(1)–C(6) 1.987(9) Å). The crystal structure of **8**·MeCN is similar and details are provided in the ESI.‡
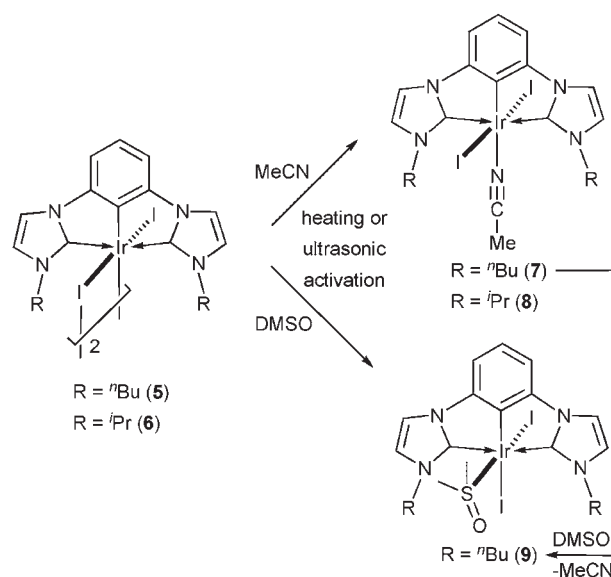
Scheme 1

The ^{1}H NMR spectrum of **9** in CD₂Cl₂ confirmed that DMSO remains coordinated in solution as indicated by the presence of the CH₃ resonance at 3.12 ppm (deshielded compared to free DMSO). A DMSO ligand occupies an apical position (*cis* to the metallated aryl) leading to diastereotopic CH₂ protons (multiplets at 4.33–4.43 and 5.33–5.42 ppm). The ^{13}C NMR spectrum contains signals at 155.7 ppm for the two carbene carbon atoms and at 138.6 ppm for the cyclometallated carbon. The ligand arrangement was confirmed by an X-ray diffraction study on **9** (Fig. 3).‡

The fact that MeCN coordinates in a position *trans* to the metallated carbon atom whereas DMSO coordinates *trans* to an iodide is important to bear in mind when discussing the structure and reactivity of such mononuclear complexes resulting from solvent-induced halide bridge-splitting reactions. The reaction of **7** with DMSO leads to displacement of the acetonitrile ligand
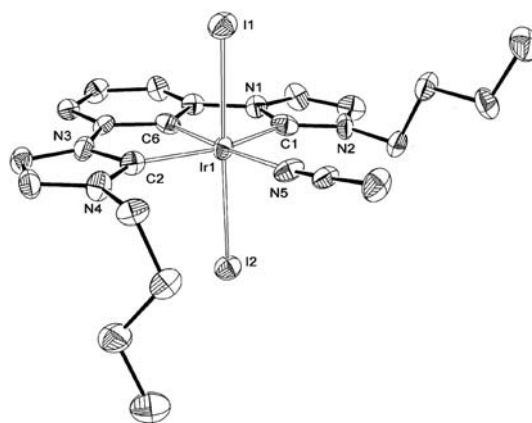

Fig. 2 ORTEP plot of the molecular structure of **7** in **7**·MeCN. H atoms omitted for clarity. Ellipsoids are represented at 50% probability level. Selected bond distances (Å) and angles (°): Ir(1)–C(1) 2.053(10), Ir(1)–C(2) 2.047(10), Ir(1)–C(6) 1.987(9), Ir(1)–I(1) 2.6692(8), Ir(1)–I(2) 2.6835(8), Ir(1)–N(5) 2.120(8), C(1)–Ir(1)–C(6) 77.8(4), C(2)–Ir(1)–C(6) 78.8(4).
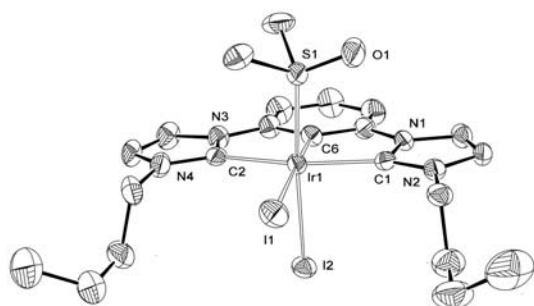
Fig. 3 ORTEP plot of the molecular structure of one of the two crystallographically independent molecules of **9** in **9**·1/2CH₂Cl₂. H atoms omitted for clarity. Ellipsoids are represented at 50% probability level Selected bond distances (Å) and angles (°): Ir(1)–C(1) 2.065(5), Ir(1)–C(2) 2.082(5), Ir(1)–C(6) 1.979(5), Ir(1)–I(1) 2.7947(4), Ir(1)–I(2) 2.7141(4), Ir(1)–S(1) 2.2405(14), C(1)–Ir(1)–C(6) 77.7(2), C(2)–Ir(1)–C(6) 77.8(2).

and quantitative formation of **9** (Scheme 1). In contrast, DMSO is not displaced from **9** by acetonitrile.

Despite their anticipated potential in catalysis, N-heterocyclic carbene 'pincers' of group 9 metals are scarce.[4b,10] Hollis and co-workers reported the synthesis of the first $C_{NHC}CC_{NHC}$ pincer complex of rhodium(III) via transmetallation of a zirconium(IV) intermediate with [Rh(μ-Cl)(cod)]₂.[11]

While this communication was being prepared, this group also reported the first iridium(III) $C_{NHC}CC_{NHC}$ pincer complex, obtained by a similar method.[12] The ¹³C NMR chemical shifts of the carbene and metallated aryl atoms are surprisingly different to those for complexes **7–9** and their $C_{NHC}CC_{NHC}$ rhodium pincer complex.[11] Their reaction mechanism has not been clarified and half of the metal(I) precursor was reduced into an undefined compound.[11] In contrast, our method provides a more direct route, with no need for an additional transmetallation step, which could therefore become of more general applicability. The synthesis and structural characterisation of these new dicarbene complexes will be followed by an investigation of their catalytic properties.

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Notes and references

§ Selected analytical data: **5**: MALDI TOF-MS (CH₂Cl₂, m/z): 1407.0 [M − I]⁺, 768.0 [0.5 M]⁺. **6**: MALDI TOF-MS (CH₂Cl₂, m/z): 1351.9 [M − I]⁺, 739.4 [0.5 M]⁺. **7**: ¹H NMR (CD₃CN): δ 4.39 (t, ³J(HH) = 7.5 Hz, 4H, NCH₂), 6.93 (t, ³J(HH) = 8.2 Hz, 1H, CH arom.) and 7.16 (d, ³J(HH) = 8.2 Hz, 2H, CH arom.) second order signals, 7.25 (d, ³J(HH) = 2.1 Hz, 2H, CH imid.), 7.71 (d, ³J(HH) = 2.1 Hz, 2H, CH imid.). ¹³C{¹H} NMR (CD₃CN): δ 136.1 (metallated C arom.), 164.1 (C–Ir). ESI-MS (CH₃CN, 70 V, m/z): 682.1[M − I]⁺, 556.2 [M − 2I + H]⁺. **8**: ¹H NMR (CD₃CN): δ 5.13 (septet, ³J(HH) = 6.8 Hz, 2H, (CH₃)₂CH), 6.93 (t, ³J(HH) = 8.2 Hz, 1H, CH arom.) and 7.16 (d, ³J(HH) = 8.2 Hz, 2H, CH arom.) second order signals, 7.35 (d, ³J(HH) = 2.1 Hz, 2H, CH imid.), 7.75 (d, ³J(HH) = 2.1 Hz, 2H, CH imid.). ¹³C{¹H} (CD₃CN): δ 135.6 (metallated C arom.), 163.7 (C–Ir). ESI-MS (CH₃CN, 30 V, m/z): 741.0 [M − CH₃CN + H]⁺, 654.1 [M − I]⁺, 528.2 [M − 2I + H]⁺. **9**: ¹H NMR (CD₂Cl₂): δ 3.12 (s, 6H, CH₃, coord. DMSO), 4.33–4.43 (m, 2H, CH₂), 5.33–5.42 (m, 2H, CH₂), 7.18–7.28 (m, 5H, 3 × CH arom. + 2 × CH imid.), 7.66 (d, ³J(HH) = 2.1 Hz, 2H, CH imid.). ¹³C{¹H} (CD₂Cl₂): δ 48.0 (CH₃ coord. DMSO), 138.6 (metallated C arom.), 155.7 (C–Ir). MALDI TOF-MS (THF, m/z): 767.8 [M − DMSO]⁺, 718.9 [M − I]

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