A nano-sized Janus di-N-heterocyclic carbene ligand based on a quinoxalinophenanthrophenazine core, and its coordination to iridium

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ABSTRACT: A Janus-type di-NHC ligand based on a quinoxalinophenanthrophenazine core has been obtained and coordinated to iridium. The electronic properties of the ligand have been determined based on the evaluation of the TEP values. The new ligand disposes the two metals at a distance of 22.4 Å, significantly longer than any of the related ligands reported so far.

INTRODUCTION

During the last two decades, N-heterocyclic carbene (NHC) chemistry has experienced an enormous development,[1] which has been boosted by the large amount of applications found in areas beyond chemistry, such as physics[2] and medicine.[2b,3] Probably, a large part of the success of NHC chemistry comes from the easy access to a large variety of azoliums, which can be considered as the most widely used NHC-precursors. Among poly-NHCs,[4] those featuring geometrically isolated carbenes bound by rigid polyaromatic systems have constituted a particularly interesting family, because they can give access to bis(NHC) structurally dynamic homopolymers,[5] and polymetallic catalysts whose properties are fundamentally different from those given by their monometallic analogues.[6] Besides their applications in catalysis and materials science, this type of compounds have found a prominent space in the field of metallosupramolecular chemistry, in which a number of poly NHC-based molecular rectangles,[7] cylinders,[8] and organometallic polymers[9] are known. Metallorganic assemblies with cavities are especially interesting because cage-like structures can be used for purely cage-catalyzed chemical transformations,[10] in which the substrate adapts to the shape of the cavity giving rise to increased reactivity and selectivity.[11] One of the most important challenges for researchers in the area is to be able to synthesize target structures with controlled length and width, for which the availability of a library of functional ligands is playing a dominant role. Bis(NHC) ligands with rigid polyaromatic linkers constitute excellent building blocks for the preparation of discrete molecular species and supramolecular assemblies, in which the shape of the molecule can be carefully controlled by the right choice of the bis-carbene ligand. Scheme 1 shows the library of known rigid-rod bis(NHCs), and illustrates the great potential of this type of ligands as building blocks for an enormous number of assemblies. While the bis(NHC) ligands reported to date allow to establish a metal-to-metal through-space separation in the range of 6-14 Å (A-D),[9e,12] in the present work we describe the preparation of a new Janus-bis(NHC) that connects the two metal fragments at a distance of 22.4 Å (E), an important qualitative leap forward that makes this nano-sized ligand the longest among all previously reported bis-carbenes. The bis-carbene E, incorporates a quinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine core, a fragment that adds a great potential to the complexes derived, because it has already found applications in the design of organic semiconductors,[13] sensors,[14] nanofibers[15] and EPR spin labels.[16]
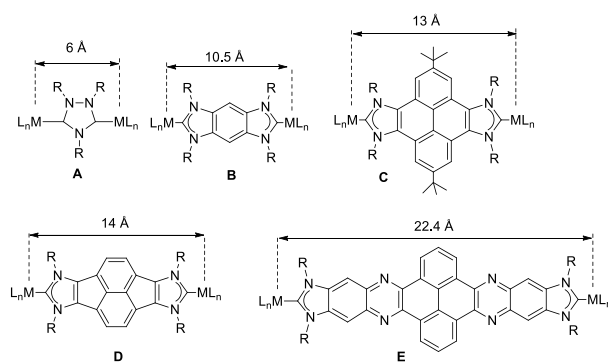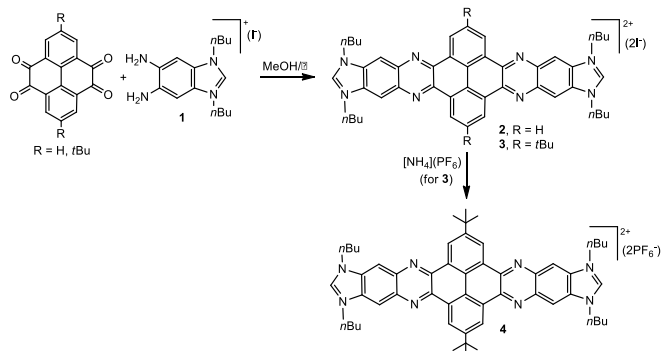

Scheme 1

RESULTS AND DISCUSSION

The quinoxalinophenanthrophenazine-bis-imidazolium iodides **2** and **3** were obtained from the direct condensation of pyrene-4,5,9,10-tetraone (or 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone) with 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (**1**)[17] in methanol, in 70 and 74 % yield, respectively. Anion metathesis of **3** with

[NH$_4$](PF$_6$) allowed the preparation of the corresponding hexafluorophosphate salt, **4** (Scheme 2). All salts were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Due to its high insolubility, the ^{13}C NMR spectrum of the bisazolium salt with the unsubstituted pyrene core (**2**, R = H), could not be obtained.
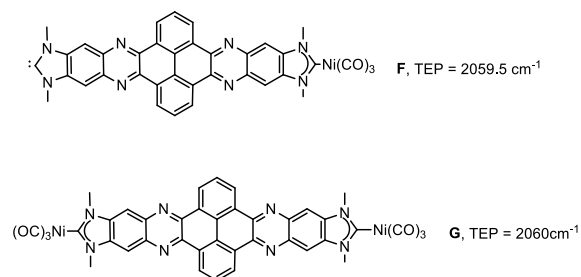

Scheme 2

Due to the higher solubility of the di-*tert*-butyl-substituted bisazoliums **3** and **4**, we considered them as more suitable bis-NHC precursors than **2**, and therefore used them for the coordination to metals. The reaction of the bisazolium di-hexafluorophosphate **4** with [IrCl(COD)]$_2$ in THF in the presence of potassium *tert*-butoxide, allowed the formation of the di-iridium complex **5**, in 39% yield. By following a similar procedure, but with the addition of an excess of KI, the reaction of **3** with [IrCl(COD)]$_2$ afforded the iodide analogue complex **6**, in 42% yield. Both ^{1}H and ^{13}C NMR spectra of **5** and **6** are consistent with the twofold symmetry of the molecules, as exemplified by the appearance of only one ^{1}H signal due to the four protons of the pyrene core, or to the four protons of the two benzenes that connect the imidazolylidenes with the pyrene. The ^{13}C NMR spectra display the distinctive carbene-carbon resonances at δ 202.2 and 202.8, for **5** and **6**, respectively.
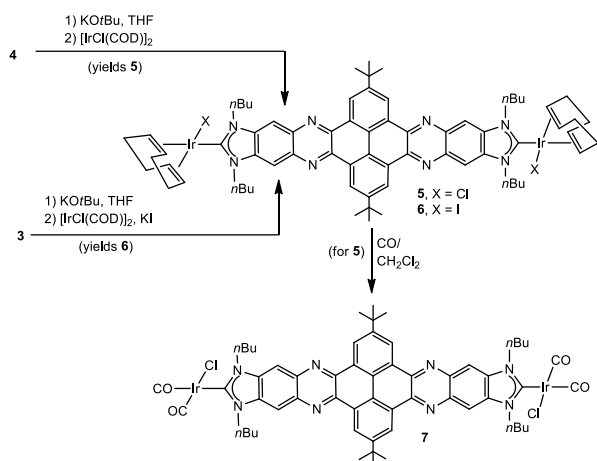
Scheme 3

The reaction of **5** with carbon monoxide in CH$_2$Cl$_2$, allowed the preparation of the tetracarbonyl-di-iridium complex **7**. The analysis of the CO stretching frequencies of the complex (bands at 1989 and 2072 cm^{-1}, from a solution of the complex in CH$_2$Cl$_2$) allows quantifying the electrondonating character of the ligand, by calculating a TEP value of 2056 cm^{-1}, from the well-known correlations.[18] This value differs in +2 cm^{-1} compared to the related pyrene-based bis-imidazolylidene **C** (Scheme 1), indicating that the presence of the two pyrazine rings results in a slight decrease of the electrondonating power of the ligand. Interestingly, the CO stretching frequencies of the complex are modified by the addition of π-stacking additives to CH$_2$Cl$_2$ solutions of **7**. The addition of pyrene results in a decrease of the TEP value to 2054 cm^{-1}, while the addition of C$_6$F$_6$ makes the TEP to raise up to 2057 cm^{-1}, therefore indicating that the addition of the suitable π-stacking additive may post-modify the electron-donating ligand by increasing or decreasing its electron-donating character. We have recently observed the same type of effect for a series of Ir-carbonyl complexes with NHC ligands decorated with extended polyaromatic systems.

We previously suggested that the DFT evaluation of the TEP values of di-NHC ligands connected by extended polyaromatic systems may be used for the estimation of the electronic communication between the metals bound to the ligand.[19] For this purpose, we calculated the TEP value for the di-NHC ligand bound to a single Ni(CO)$_3$ fragment, while keeping the other carbene unbound (**F** in Chart 2, note that for this ligand, the 2,7-*t*Bu substituents were replaced by hydrogens, and N-Me groups were used instead of N-*n*Bu). The resulting TEP value is 2059.5 cm^{-1}. The calculated TEP value for the system in which the di-NHC ligand is bound to two Ni(CO)$_3$ fragments (**G**) is 2060 cm^{-1}. This small TEP-shift, indicates that the two metals are basically disconnected, despite being apparently linked by a very effective π-delocalized system.[19]


Scheme 4

We wanted to quantify the π-stacking interaction between **7** and other polyaromatic substrates and, for that reason, we decided to perform an experiment consisting of the titration of **7** with pyrene and the evaluation of the changes produced in the resulting ^{1}H NMR spectra. The first indication that the π-stacking between **7** and pyrene is produced, is the shifting of the signals at 9.8 and 8.5 ppm toward lower frequencies, upon addition of increasing amounts of pyrene, indicating that the interaction

between pyrene and **7** is mainly produced at the pyrazine part of the ligand in **7**. By assuming a 1:1 molar stoichiometry for the formation of the π-stacking adducts, we were able to estimate the association constant between pyrene and **7**, by using the Benesi-Hildebrand treatment (see ESI for all details).[20] The resulting association constant is K_a = 11.6 M^{-1}, higher than the association constants that we found for the interaction of pyrene with other mono-NHCs decorated with polyaromatic ligands.[21]

The molecular structure of **6** was unambiguously determined by single crystal X-ray diffraction. The molecule consists of a quinoxalinophenanthrophenazine-bis-imidazole-di-ylidene, bridging two iridium fragments, which complete their coordination spheres with a iodide and a 1,5-cyclooctadiene ligand. The relative orientation of the two metal fragments is *anti*, with the two iodide ligands pointing at opposite directions. The average Ir-C$_{carbene}$ bond distance is 2.01 Å. The molecule displays a remarkably long metal-to-metal through-space distance of 22.37 Å (the longest reported so far for a Janus-type di-NHC ligand), which is slightly shorter than the through-ligand distance of 22.61 Å as a consequence of the bow-shaped conformation adopted by the ligand. The crystal packing reveals that the molecules are associated in pairs, in which the convex parts of the molecules are approaching each other by one of their pyrazine heterocycles.
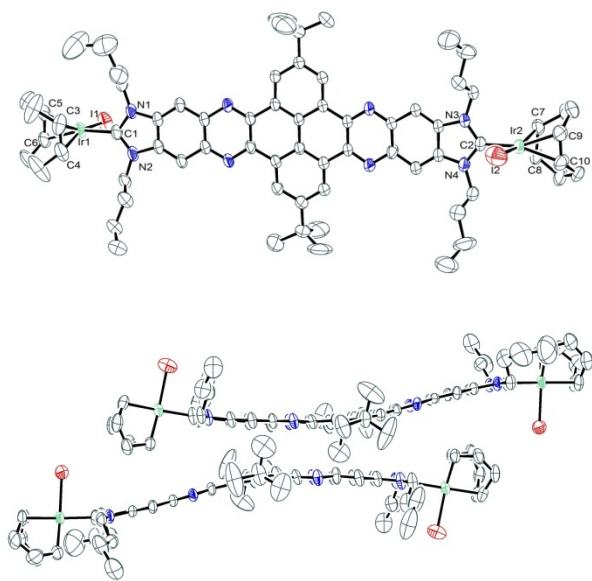
Figure 1. Two perspectives of the molecular structure of **6**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% level of probability. The figure below shows a side-on perspective of the molecule, and illustrates the π-stacking between two molecules. Selected bond distances (Å) and angles (º): Ir1-I1 2.6153(9), Ir1-C1 2.013(9), Ir1-C3 2.083(13), Ir1-C4 2.082(12), Ir1-C5 2.188(10), Ir1-C6 2.185(9), Ir2-I2 2.6057(10), Ir2-C2 2.000(10), Ir2-C7 2.082(11), Ir2-C8 2.078(10), Ir2-C9 2.199(10), Ir2-C10 2.191(10), C1-Ir1-I1 86.6(3), C2-Ir2-I2 87.9(4).

CONCLUSIONS

In summary, in this work we have prepared and successfully coordinated a new Janus di-N-heterocyclic-carbene ligand based on a quinoxalinophenanthrophenazine core. The preparation of this type of ligand may serve as a scaffold for the preparation of sophisticated metallorganic structures, which may include molecular squares, cages and organometallic polymers. The π-stacking abilities of the molecules based on this new ligand have been demonstrated, and may introduce interesting benefits for the selective recognition of polyaromatic substrates, if the related metallosupramolecules derived were obtained. Efforts aiming to obtain molecular cages based on this new ligand are underway in our lab.

EXPERIMENTAL SECTION

General methods. 1,3-Dibutyl-5,6-dinitro-benzimidazolium iodide,[17] pyrene-4,5,9,10-tetraone,[22] and 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone[22] were prepared according to literature methods. All reactions were carried out under nitrogen standard Schlenk techniques unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased and degassed prior to use by purging with nitrogen and kept over molecular sieves. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using CDCl$_3$ or DMSO-d_6 as solvents. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. Infrared spectra (FTIR) were performed on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000-600 cm^{-1}.

Synthesis of 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (1). Hydrazine (8.2 mL of 64% of aqueous solution, 108.19 mmol) was added dropwise to a solution of 1,3-dibutyl-5,6-dinitrobenzimidazolium iodide (1.6 g, 3.57 mmol) and Pd/C (0.4 g of 10% wt. Pd, 0.38 mmol) in 80 mL of deoxygenated ethanol. After 5 minutes, 25 mL of a 1 M solution of HCl were added dropwise. The reaction mixture was stirred and heated at 80ºC for 4h. Then, the solution was cooled to room temperature and filtered thought Celite. The clear solution was concentrated under vacuum and the precipitated white solid was filtered, washed with water and abundant diethyl ether. Yield: 1.24 g (90%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.29 (s, 1H, NC*H*N), 6.89 (s, 2H, C*H*$_{Ar}$), 5.27 (s, 4H, N*H*$_2$), 4.25 (t, $^3J_{H-H}$ = 6.7 Hz, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.96-1.73 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.43-1.19 (m, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.90 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 137.2 (N*C*HN), 135.5 (*C*$_{Ar}$), 123.8 (*C*$_{Ar}$), 94.0 (*C*H$_{Ar}$), 45.8 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 30.2 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 19.0 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.3 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, *m/z*): 261.3 [M]$^+$. Anal. Calcd. for C$_{15}$H$_{25}$IN$_4$ (388.3): C, 46.40; H, 6.49; N, 14.43. Found: C, 46.40; H, 6.47; N, 14.84.

Synthesis of bisazolium salts. General procedure. A mixture of **1** (2.2 eq.) and the corresponding tetraone (1

eq.) in methanol (50 mL) was refluxed overnight. Then, the reaction mixture was cooled to room temperature and concentrated under vacuum. The solid so formed was separated by filtration and washed subsequently with a little amount of ethanol and diethyl ether.

Synthesis of 2. Compound **2** was prepared by reacting **1** (163 mg, 0.42 mmol) with pyrene-4,5,9,10-tetraone (50 mg, 0.19 mmol). Yield: 143.2 mg (75%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.18 (br s, 2H, NC*H*N), 9.48-9.24 (m, 4H, C*H*$_{Ar}$), 8.91 (s, 4H, C*H*$_{Ar}$), 8.40-8.12 (m, 2H, C*H*$_{Ar}$), 4.63 (br s, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.06 (br s, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.69-1.31 (br m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.05 (br s, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). Attempts to record the ^{13}C NMR spectrum of **2** were unsuccessful due to the low solubility of the compound. Electrospray MS (20 V, m/z): 356.4 [M]$^{2+}$. Anal. Calcd. for C$_{46}$H$_{48}$I$_2$N$_8$·2H$_2$O (1002.8): C, 55.10; H, 5.23; N, 11.17. Found: C, 55.63; H, 5.30; N, 11.09.

Synthesis of 3. Compound **3** was prepared by reacting **1** (300 mg, 0.77 mmol) with 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (131 mg, 0.35 mmol). Yield: 276.7 mg (73%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.19 (s, 2H, NC*H*N), 9.72 (s, 4H, C*H*$_{Ar}$), 9.19 (s, 4H, C*H*$_{Ar}$), 4.72 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.18-1.99 (m, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.76 (s, 18H, C(CH$_3$)$_3$), 1.65-1.43 (m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.05 (t, $^3J_{H-H}$ = 7.4 Hz, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, DMSO-d_6): δ 151.0 (C_{Ar}), 146.4 (NCHN), 142.6 (C_{Ar}), 138.5 (C_{Ar}), 133.3 (C_{Ar}), 128.6 (C_{Ar}), 125.3 (C_{Ar}), 124.8 (CH_{Ar}), 112.5 (CH_{Ar}), 47.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 35.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.4 (*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 19.2 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.5 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, m/z): 412.4 [M]$^{2+}$. Anal. Calcd. for C$_{54}$H$_{64}$I$_2$N$_8$ (1078.9): C, 60.11; H, 5.98; N, 10.39. Found: C, 60.00; H, 6.02; N, 10.31.

Synthesis of 4. NH$_4$PF$_6$ (77.3 mg, 0.48 mmol) was added to a solution of **3** (255.9 mg, 0.24 mmol) in a mixture 3:1 methanol/CH$_2$Cl$_2$. The reaction mixture was stirred at room temperature overnight. Then, the yellow solid so formed was separated by filtration and washed with methanol and diethyl ether. Yield: 252.7 mg (93%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.17 (s, 2H, NC*H*N), 9.69 (s, 4H, C*H*$_{Ar}$), 9.12 (s, 4H, C*H*$_{Ar}$), 4.83-4.56 (m, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.21-1.97 (m, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.77 (s, 18H, C(CH$_3$)$_3$), 1.64-1.45 (m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.05 (t, $^3J_{H-H}$ = 7.3 Hz, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.9 (C_{Ar}), 148.0 (C_{Ar}), 142.3 (C_{Ar}), 138.3 (C_{Ar}), 133.1 (C_{Ar}), 128.2 (C_{Ar}), 124.9 (C_{Ar}), 124.6 (CH_{Ar}), 112.2 (CH_{Ar}), 47.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 35.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.5 (*C*(CH$_3$)$_3$), 30.4 (C(*C*H$_3$)$_3$), 19.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.5 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (20 V, m/z): 412.3 [M]$^{2+}$. Anal. Calcd. For C$_{54}$H$_{64}$F$_{12}$N$_8$P$_2$·2H$_2$O (1151.1): C, 56.34; H, 5.95; N, 9.73. Found: C, 56.57; H, 5.92; N, 9.73.

General procedure for the synthesis of the Ir(I) complexes. A mixture of the corresponding bisazolium salt (1eq.), potassium *tert*-butoxide (2.2 eq.) and [IrCl(cod)]$_2$ (1 eq.) in THF (10 mL) was stirred overnight at room temperature. After removal of the volatiles, the crude solid

was purified by column chromatography using CH$_2$Cl$_2$ as eluent.

Synthesis of 5. Compound **5** was prepared by reacting the bisazolium salt **4** (100.0 mg, 0.09 mmol), potassium *tert*-butoxide (21.4 mg, 0.19 mmol) and [IrCl(cod)]$_2$ (58.4 mg, 0.09 mmol). Yield: 52.8 (39%). ^{1}H NMR (300 MHz,CDCl$_3$): δ 9.81 (s, 4H, C*H*$_{Ar}$), 8.20 (s, 4H, C*H*$_{Ar}$), 5.14-4.73 (m, 12H, 4H C*H*$_{COD}$ and 8H NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.10 (br s, 4H, C*H*$_{COD}$), 2.36 (br s, 16H, 8H CH$_2$ $_{COD}$ and 8H NCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.24-1.65 (m, 34H, 8H CH$_2$ $_{COD}$, 8H NCH$_2$CH$_2$C*H*$_2$CH$_3$ and 18H C(CH$_3$)$_3$), 1.19 (t, $^3J_{H-H}$ = 7.3 Hz, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 202.2 (Ir-$C_{carbene}$), 151.2 (C_{Ar}), 142.7 (C_{Ar}), 138.7 (C_{Ar}), 137.7 (C_{Ar}), 129.6 (C_{Ar}), 125.8 (C_{Ar}), 124.7 (CH_{Ar}), 106.8 (CH_{Ar}), 88.9 (CH_{COD}), 53.3 (CH_{COD}), 49.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.1 (*C*(CH$_3$)$_3$), 33.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.1 (C(*C*H$_3$)$_3$), 31.4 (CH$_2$ $_{COD}$), 29.5 (CH$_2$ $_{COD}$), 20.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.1 (NCH$_2$CH$_2$CH$_2$CH$_3$). HRMS ESI-TOF-MS (positive mode): m/z calcd. : 1500.6188 [M-Cl+CH$_3$CN]$^+$ (monoisotopic peak); found: 1500.6385. Anal. Calcd. for C$_{70}$H$_{86}$Cl$_2$Ir$_2$N$_8$·3H$_2$O (1548.9): C, 54.28; H, 5.99; N, 7.23. Found: C, 54.37; H, 5.95; N, 7.35.

Synthesis of 6. Compound **6** was prepared by reacting the bisazolium salt **3** (70 mg, 0.06 mmol), potassium *tert*-butoxide (16.0 mg, 0.14 mmol), KI (59.76 mg, 0.36 mmol) and [IrCl(cod)]$_2$ (43.6 mg, 0.06 mmol). Yield: 45.2 mg (42%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.81 (s, 4H, C*H*$_{Ar}$), 8.12 (s, 4H, C*H*$_{Ar}$), 5.08 (br s, 4H, C*H*$_{COD}$), 4.99-4.65 (m, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.04 (br s, 4H, C*H*$_{COD}$), 2.50-2.16 (m, 16H, 8H CH$_2$ $_{COD}$ and 8H NCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.16-1.88 (m, 8H, CH$_2$ $_{COD}$), 1.84 (s, 18H, C(C*H*$_3$)$_3$), 1.77-1.63 (m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.19 (t, $^3J_{H-H}$ = 7.4 Hz, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 202.8 (Ir-$C_{carbene}$), 151.1 (C_{Ar}), 142.5 (C_{Ar}), 138.6 (C_{Ar}), 137.8 (C_{Ar}), 129.5 (C_{Ar}), 125.6, (C_{Ar}) 124.6 (CH_{Ar}), 106.7 (CH_{Ar}), 86.9 (CH_{COD}), 56.5 (CH_{COD}), 48.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.2 (*C*(CH$_3$)$_3$), 33.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.1 (C(*C*H$_3$)$_3$), 30.8 (CH$_2$ $_{COD}$), 30.3 (CH$_2$ $_{COD}$), 20.8 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.1 (NCH$_2$CH$_2$CH$_2$CH$_3$). HRMS ESI-TOF-MS (positive mode): m/z calcd : 1592.5544 [M-I+CH$_3$CN]$^+$ (monoisotopic peak); found: 1592.5741. Anal. Calcd. For C$_{70}$H$_{86}$I$_2$Ir$_2$N$_8$ (1677.7): C, 50.11; H, 5.17; N, 6.68. Found: C, 49.83; H, 5.04; N, 6.68.

Synthesis of 7. CO gas was bubbled through a solution of complex **5** (50 mg, 0.03 mmol) in dichloromethane (5 mL) at 0°C during 20 min. The solution was concentrated under reduced pressure, and hexane was added to give carbonyl derivative **7** as a yellow solid. Yield: 45.0 mg (96%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.85 (s, 4H, C*H*$_{Ar}$), 8.45 (s, 4H, C*H*$_{Ar}$), 5.10-4.87 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.87-4.65 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.42-2.07 (m, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.80 (s, 18H, C(C*H*$_3$)$_3$), 1.73-1.48 (m, , NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.23-0.99 (m, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 192.2 (Ir-$C_{carbene}$), 181.2 (Ir-CO), 168.2 (Ir-CO), 151.5 (C_{Ar}), 143.5 (C_{Ar}), 138.8 (C_{Ar}), 136.5 (C_{Ar}), 129.4 (C_{Ar}), 126.2 (C_{Ar}), 125.4 (CH_{Ar}), 109.1 (CH_{Ar}), 49.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.2 (*C*(CH$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 31.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.1 (NCH$_2$CH$_2$CH$_2$CH$_3$). HRMS ESI-TOF-MS (positive mode): m/z calcd. : 1391.3608 [M+H]$^+$(monoisotopic peak); found:

1391.3599. Anal. Calcd. for $C_{58}H_{62}Cl_2Ir_2N_8O_4 \cdot 3H_2O$ (1444.6): C, 48.22; H, 4.74; N, 7.76. Found: C, 48.32; H, 4.78; N, 7.65.

X-Ray Crystallography

Suitable crystals for X-Ray study of complex **6** were obtained by slow diffusion of chloroform into a concentrated solution of the complex in methanol. Diffraction data was collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.[23] Using Olex2,[24] the structure of complex **5**-H was solved using Charge Flipping[25] in Superflip[26] and refined with ShelXL refinement package using Least Squares minimisation.[27]

Disorder solvent is present in two voids per unit cell. Solvents used in synthesis and crystallization (methanol and chloroform) could not be recognized in the disordered electron density. The contribution of the disordered solvent to the diffraction pattern was therefore incorporated in the model using Squeeze in Platon v1.17.[28] A total of 1171 electrons were found in two voids of 497 and 674 Å^3, located at (0.000, 0.000, 0.000) and (0.054, 0.446, 0.500), respectively.

Key details of the crystals and structure refinement data are summarized in the Supplementary Table S2. Further crystallographic details may be found in the CIF which was deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The reference number for **6** was assigned as 1048774.

Computational details

The DFT calculations presented in this work were carried out as reported in the literature.[29]

ASSOCIATED CONTENT

Supporting Information

CIF files of the molecular structures of complex **6**, NMR spectra of the new complexes, relevant sections of the ^{1}H NMR spectra for the application of the Method of Continuous Variations (MCV), computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interests.

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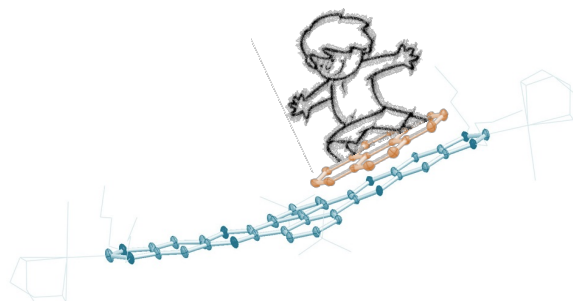
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A Janus-type di-NHC ligand based on a quinoxalinophenanthrophenazine core has been obtained and coordinated to iridium. The new ligand disposes the two metals at a distance of 22.4 Å, significantly longer than any of the related ligands reported so far.