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ARTICLE

Synthesis of New Heteroscorpionate Iridium(I) and Iridium(III) Complexes

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The reactivity of different heteroscorpionate ligands based on bis(pyrazol-1-yl)methane, with different iridium-(I) and -(III) precursors is reported. The reaction of the heteroscorpionate lithium salts “Li(bdmpza)”, [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], “Li(bdmpzdta)” [bdmpzdta = bis(3,5-dimethylpyrazol-1-yl)dithioacetate] and “Li(*S*)-mbpam” [(*S*)-mbpam = (*S*)-(-)-*N*- α -methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamidate] with 1 equivalent of [IrCl₃(THF)₃] in THF for 18 h affords high yields of neutral and anionic heteroscorpionate chloride iridium complexes [IrCl₂(bdmpza)(THF)] (**1**), [Li(THF)₄][IrCl₃(bdmpzdta)] (**2**) and [IrCl₂{(*S*)-mbpam}(THF)] (**3**). Solution of complex **3** in acetonitrile at room temperature leads to complex [IrCl₂{(*S*)-mbpam}(NCCH₃)] (**4**). Complexes **3** and **4** were isolated as enantiopure compounds. The reaction of the lithium salt “Li(bdmpza)” with [IrCl(η^4 -CH₂=C(Me)C(Me)=CH₂)]₂ in THF for 18 h gave the Ir(I) complex [Ir(bdmpza)(η^4 -CH₂=C(Me)C(Me)=CH₂)] (**5**). The reaction of complex **5** with CO (2 atm) at room temperature leads to a new complex of Ir(III), [Ir(bdmpza)(*k*²-CH₂C(Me)=C(Me)CH₂)(CO)] (**6**). Treatment of heteroscorpionate ligand precursors “Li(bdmpza)” and “Li(bdmpzdta)” with [IrCp*Cl₂]₂ in THF yielded the iridium(III) complexes [Ir₂Cp*₂Cl₂(bdmpzx)] (x = a **7**, x = dta **8**). These complexes have helical chirality due to the demands of the fixed pyrazole rings. The stereoisomerism and the self-assembly processes of these helicates have been studied in some detail in solution by NMR spectroscopy and in the solid state by X-ray diffraction. Mixtures of *M*- and *P*-handed enantiomers were obtained. Complex **7** undergoes a decarboxylation process initiated by the HCl generated in the previous step leading to the known ionic complex [IrClCp*(bdmpm)][IrCl₃Cp*] [bdmpm = bis(3,5-dimethylpyrazol-1-yl)methane] (**9**). The structures of the complexes were determined by spectroscopic methods and the X-ray crystal structures of **4**, **6**, **8** and **9** were also established.

Introduction

The heteroscorpionate ligands based on the bis(pyrazol-1-yl)methane moiety are among the most versatile types of tridentate ligands, and they can coordinate to a wide variety of elements.¹ Chemistry based on the design of this particular type of intriguing ligands has been extended considerably in terms of coordination chemistry² and catalytic applications.³ In the past decade, a number of research groups have widely contributed to this field, designing new ligands related to the bis(pyrazol-1-yl)methane system and incorporating several pendant donor arms, such as, carboxylate, dithiocarboxylate,

alkoxide, thiolate, aryloxy, sulfonate, cyclopentadienyl, acetamidate, thioacetamidate, amidate, amide, heterocyclic ring, phosphine, oxophosphine, iminophosphine and organometallic groups.⁴⁻¹⁰ The different functional groups of the heteroscorpionate ligands have influence on both the geometry around the metal center and the electronic and steric properties of their complexes, the conjunction of which directly impacts their reactivity, and broadens their scope of application. These tridentate ligands can coordinate to a wide variety of elements, from early to late transition metals. There are only a few heteroscorpionate iridium complexes reported to date,¹¹ in contrast to a large number of poly(pyrazolyl)borate or

related anionic borate-based iridium complexes with attractive catalytic uses¹² described in the literature. In particular, a series of Rh and Ir compounds with the bdmzpa ligand, exhibited good properties as catalysts for arene H/D exchange.^{11b}

In this paper we describe the synthesis and characterization of new classes of neutral and ionic iridium(I) and iridium(III) complexes containing heteroscorpionate ligands functionalized with different arms along with halide, diene or carbonyl as ancillary ligands. Some of these target complexes constitute the first examples of this class of compounds with heteroscorpionate ligands. Neutral enantiopure iridium(III) complexes that contain an acetamidate scorpionate ligand have been prepared. In addition, iridium(III) complexes with helical chirality have been isolated.

Results and discussion

Syntheses of carboxylate, dithiocarboxylate and acetamidate heteroscorpionate complexes.

The reagents [$\text{Li}(\text{bdmpza})(\text{H}_2\text{O})_4$]^{13a} [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], [$\text{Li}(\text{bdmpzda})(\text{H}_2\text{O})_4$]^{4e} [bdmpzda = bis(3,5-dimethylpyrazol-1-yl)dithioacetate], and (*S*)-mbpamH^{13b} [(*S*)-mbpamH = (*S*)-(-)-*N*- α -methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide] (see Fig. 1) were used in the complexation of a number of iridium precursors. These compounds (the latter with prior addition of ⁿBuLi) reacted with solutions of [IrCl₃(THF)₃] (1:1, THF, 18 h, reflux or room temperature for the acetamide compound) leading to reaction mixtures from which the complexes [IrCl₂(bdmpza)(THF)] (1), [Li(THF)₄][IrCl₃(bdmpzda)] (2) and [IrCl₂{(*S*)-mbpam}(THF)] (3) were isolated in moderate to good yields as yellow (1), orange (2) and brown (3) solids after the appropriate workup (Scheme 1). In one attempt to obtain crystals of complex 3 in CH₃CN, we obtained the acetonitrile adduct [IrCl₂{(*S*)-mbpam}(CH₃CN)] (4) as a crystalline solid. Accordingly, when the reaction of [IrCl₃(THF)₃] with “Li(*S*)-mbpam” was carried out in CH₃CN instead of THF complex 4 was isolated after the appropriate workup (Scheme 1). Complexes 3 and 4 were obtained as enantiopure compounds.

Insert Figure 1

Fig. 1 Heteroscorpionate ligands used in the synthesis of iridium complexes

The isolation of the neutral complex 1 after complete removal of one chloride ligand by formation of LiCl contrasts with the composition of compound 2, in which the three Cl atoms remain coordinated to iridium, and more remarkably contrasts with the results reported by Jones,^{11b} in which the hydrated salt [IrCl₃(H₂O)_n] is reported to yield [IrCl₃(bdmpza)]Li⁺ after reaction with [$\text{Li}(\text{bdmpza})(\text{H}_2\text{O})_4$] in MeOH as the solvent and at room temperature. Clearly the stronger conditions used in our case promote the LiCl to be eliminated from the compound.

Insert Scheme 1

Scheme 1. Synthesis of complexes 1-4 (isolated yields in parentheses)

In order to prepare organometallic compounds based on these heteroscorpionate ligands, we carried out some reactions starting from diene iridium complexes. Thus, the reaction of the lithium salt [$\text{Li}(\text{bdmpza})(\text{H}_2\text{O})_4$]^{13a} with the diene Ir(I) precursor, [Ir(μ -Cl)(η^4 -CH₂=C(Me)C(Me)=CH₂)₂], led to complex [Ir(bdmpza)(η^4 -CH₂=C(Me)C(Me)=CH₂)] (5), which contains both heteroscorpionate and diene ligands (Scheme 2). The Ir(I) complex 5 is structurally analogous to the hydrotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) iridium complex [IrTp^{Me2}(η^4 -CH₂=C(Me)C(Me)=CH₂)]¹⁴ and contains 2,3-dimethyl-1,3-butadiene coordinated in the η^4 mode. The Ir(I) complex 5 readily reacts with a Lewis base such as CO (25 °C, 2 atm) to afford the Ir(III) adduct of composition [Ir(bdmpza)(κ^2 -CH₂C(Me)=C(Me)CH₂)-(CO)] (6) in good isolated yield (Scheme 2). The same type of reaction has been previously observed¹⁵ for the above mentioned analogous [IrTp^{Me2}(η^4 -CH₂=C(Me)C(Me)=CH₂)].

Insert Scheme 2

Scheme 2. Synthesis of compounds 5 and 6 (isolated yields in parentheses)

The different complexes were characterized spectroscopically. The IR spectra of 1, 5 and 6 show two strong bands at ca. 1690 and 1400 cm⁻¹, which are assigned to $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$, respectively. The value of $\Delta\nu_{\text{as-s}}$ (ca. 290 cm⁻¹) for these compounds is consistent with an O-coordination (monodentate) mode.¹⁶ The IR spectrum of 2 contains two strong bands at ca. 1050 and 800 cm⁻¹, which were assigned to $\nu_{\text{as}}(\text{CS}_2^-)$ and $\nu_{\text{s}}(\text{CS}_2^-)$, respectively. The IR spectrum of complex 6 shows a strong band at 2014 cm⁻¹ that is assigned to $\nu(\text{CO})$. Compared to a value of 2000 cm⁻¹ for the analogous [IrTp^{Me2}(κ^2 -CH₂C(Me)=C(Me)CH₂)-(CO)]¹⁵ this difference indicates that the bdmzpa ligand is slightly less donor than Tp^{Me2}. The ¹H and ¹³C{¹H} NMR spectra of 1 and 2 show a single set of resonances for the two pyrazole rings in each case, indicating that the pyrazoles are equivalent. These data confirm an octahedral disposition with κ^3 -NNE coordination (E = O or S) for the heteroscorpionate ligand with a THF or a Cl ligand, respectively for 1 or 2, *trans* with respect to the oxygen or sulfur atom of the bdmzpa ligands (see Scheme 1). ⁷Li NMR spectroscopy and an elemental analysis confirmed the presence of cation [Li(THF)₄]⁺ in complex 2. The structures of compounds 3 and 4 were established with the information supplied by the ¹³C NMR data of the acetamidate moiety, (*S*)-Ph(Me)CHNCO, with the ¹³C NMR signals of the carbonyl groups being good indicators of the bonding mode of this fragment. The acetamidate carbon resonance, NCO, was shifted

to lower field with respect to the one in the neutral ligand (see Experimental Section),^{3c,8b,13b,17} indicating an unprecedented *N*-coordination of the acetamidate fragment to the metal centre (see Scheme 1). All the previously known compounds containing this ligand exhibit an *O*-coordination of this moiety.^{3c,8b,13b,17} The ¹H and ¹³C{¹H} NMR spectra of **3** and **4** (with a chiral ligand) show two singlets for each of the H⁴, Me³ and Me⁵ pyrazole protons and carbons and one set of signals for the THF or CH₃CN protons. Unfortunately, no NOE signals between the coordinated Lewis base (THF or NCMe) in **3** and **4** and any other protons of the molecule were observed. Hence, due to the asymmetry of the ligand, it was not possible to unequivocally assign the position of these ligands. Nevertheless, based on the molecular structure of **4** determined by X-ray diffraction studies (see below) we propose the structure shown in Scheme 1, with the solvent molecule (THF or NCMe) *trans* to the N- of the acetamidate. ¹H-¹³C heteronuclear correlation (g-HSQC) experiments helped to assign the resonances corresponding to C⁴, Me³ and Me⁵ of the pyrazol rings and the other groups.

NMR data for **5** and **6** are in good agreement with the structures proposed and are with those of the analogous Tp^{Me2} derivatives. For the case of **5**, the two pyrazol groups are equivalent, as expected, with chemical shift values which could be anticipated for this structure with a symmetry plane. The diene ligand reflects the same situation, with a pattern (in the ¹H NMR spectrum) typical for this type of η^4 coordination. The two Me groups of the diene resonate at 1.98 ppm, and the two different protons of the two mutually equivalent =CH₂ groups give rise to resonances at 2.39 ppm (for the *syn* protons) and -0.02 ppm (for the *anti* ones), with a very small ²J_{HH} coupling constant of 4 Hz. Coordinated dienes are usually fluxional in solution and this likely occurs to compound **5**. Thus ¹³C NMR signals for the diene moiety (81.6 ppm for the quaternary carbons and 8.9 ppm for the =CH₂) are broad, suggesting that both isomers depicted in Fig. 2 are present in the solutions of this product.

Insert Figure 2

Fig. 2 Proposed isomerization in the solutions of compound **5**

For compound **6**, while the signals for the bdm₂ are very similar to those of compound **5**, the NMR data drastically change for the diene moiety, in agreement with the change in the coordination mode from η^4 to κ^2 . The diastereotopic protons of the two equivalent Ir-CH₂ moieties generate two resonances (2 H each) at 3.07 ppm and 2.21 ppm respectively (²J_{HH} = 10 Hz). A high field ¹³C NMR signal at 15.7 ppm is assigned to these Ir-CH₂ groups, and the ¹J_{CH} measured, of ca 120 Hz, matches well with the sp³ hybridization of this C atom. The olefin quaternary carbon atoms, which in **6** are not coordinated to the metal, are responsible for the resonance at 136.2 ppm.

The molecular structures of complexes **4** and **6** were determined by X-ray diffraction. The corresponding ORTEP drawings are depicted in Fig. 3. Crystallographic data and

selected interatomic distances and angles are shown in Tables 1 and 2, respectively. The molecular structures determined by X-ray

Insert Figure 3

Fig. 3 ORTEP drawing of compounds **4** (above) and **6** (below). Thermal ellipsoids are set at 50% probability and most hydrogen atoms are omitted for clarity

diffraction are in good agreement with the solution structures deduced from the NMR experiments. The heteroscorpionate ligands are attached to the iridium centres through the two nitrogen atoms of the pyrazole rings and the nitrogen atom of the acetamidate (**4**) or the oxygen nucleus of the carboxylate (**6**) moieties in a κ^3 -NNE (E = N, O) coordination mode in the expected *fac* coordination fashion. In compound **4** the iridium centre is coordinated to two chloride ligands and one CH₃CN molecule, *trans* to the nitrogen of acetamidate group, whereas in **6** the other metal sites are occupied by a 2,3-dimethylbut-2-ene-1,4-diyl ligand forming a five-membered iridacycle and a carbon monoxide molecule *trans* to the carboxylate terminus. The geometry around the metal centre is octahedral in both cases, with a minimal distortion in compound **4** and a slightly higher deformation in **6**, probably due to the steric pressure imposed by the bulkier CH₂ groups of the metalated diene with respect to the chloride ligands in **6**. The *cis*-angles containing the iridium atom in **4** lie within an ideal range between 86.8(1) and 92.7(1)°, for N(1)—Ir(1)—N(3) and N(1)—Ir(1)—Cl(1), respectively; whereas the higher distortion in **6** is evidenced by a broader range between 82.8(3) and 101.0(4)°, for C(13)—Ir(1)—C(16) and C(19)—Ir(1)—N(3), respectively. The Ir—Cl distances of 2.343(1) Å and 2.355(1) Å in **4** are in good agreement with literature data,¹⁸ as well as the Ir—C bond distances in **6**^{19a,b} (Ir(1)—C(13), 2.066(8) Å; Ir(1)—C(16), 2.066(9) Å; and Ir(1)—C(19), 1.793(11) Å for Ir—CO^{19c}), with d(Ir—CO) being slightly shorter than the average likely due to the π -donor character of its *trans* carboxylate group.²⁰ The Ir—N(pyrazolyl) bond distances in both molecular structures are similar to those in other Ir/pyrazolyl complexes, with those in **6** slightly longer than in **4** (2.15 versus 2.05 Å approximately) due to the higher *trans* influence of the CH₂ groups compared to the chloride ligands.^{11,12,15} The short Ir—N(acetamidate) bond distance in **4**, with a value of 2.037(3) Å, confirms the nitrogen atom of the acetamidate group being attached to the iridium centre.

Previous studies on the coordination ability of these scorpionate ligands have shown the adoption of coordination modes different to the facial tripodal, when interacting with other metal centres.^{1,4,17} In order to explore these possibilities for iridium, we carried out the reactions of “Li(bdm₂zx)” (x = a, dta) with [IrCl₂Cp*]₂, which yielded dinuclear complexes of composition [Ir₂Cl₂Cp*₂(μ -bdm₂zx)] (x = a **7**, dta **8**), by an unexpected and unprecedented deprotonation of the carboxylate or dithiocarboxylate ligand by C—H activation of the methyne group, which results in the formation of dianionic ligands bridging two iridium atoms in each case (Scheme 3).

Insert Scheme 3

Scheme 3. Synthesis of helical chirality complexes **7** and **8**, and evolution of **7** to compound **9** (isolated yields in parentheses)

Table 1. Crystal data and structure refinement details for **4**, **6** and **8**.

	4	6	8
Molecular formula	C ₂₂ H ₂₇ Cl ₂ IrN ₆ O	C ₁₉ H ₂₅ IrN ₄ O ₃	C ₃₂ H ₄₄ Cl ₂ Ir ₂ N ₄ S ₂ ·CH ₂ Cl ₂
Formula weight	654.62	549.65	1089.06
Temperature (K)	173(2)	173(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Trigonal
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	R-3
a(Å)	10.4264(5)	13.2553(5)	44.234(2)
b(Å)	17.4090(8)	12.9876(7)	44.234(2)
c(Å)	27.1794(12)	13.5364(10)	10.1891(6)
α(°)	90.00	90.00	90.00
β(°)	90.00	106.435(3)	90.00
γ(°)	90.00	90.00	120.00
Volume(Å ³)	4933.4(4)	2235.14(18)	17266(1)
Z	8	4	18
Density (calculated) (g/cm ³)	1.7630	1.954	1.885
Absorption coefficient (mm ⁻¹)	5.65	5.997	7.346
F(000)	2560.0	1072.0	9468
Crystal size (mm ³)	0.35 x 0.25 x 0.13	0.28 x 0.10 x 0.07	0.37 x 0.34 x 0.22
Index ranges	-14 ≤ h ≤ 14 -24 ≤ k ≤ 24 -38 ≤ l ≤ 38	-15 ≤ h ≤ 15 -7 ≤ k ≤ 15 -13 ≤ l ≤ 16	-61 ≤ h ≤ 61 -59 ≤ k ≤ 60 -11 ≤ l ≤ 13
Reflections collected	58627	9367	47196
Independent reflections	14398 [R(int) = 0.0614]	3978 [R(int) = 0.0405]	10045 [R(int) = 0.0888]
Data / restraints / parameters	14398 / 0 / 489	3978 / 0 / 250	10045 / 0 / 439
Goodness-of-fit on F ²	0.988	1.067	0.807
Final R indices [I > 2σ(I)]	R1 = 0.0307 wR2 = 0.0588	R1 = 0.0490 wR2 = 0.1541	R1 = 0.0390 wR2 = 0.0410
Largest diff. peak and hole, e.Å ⁻³	1.31 and -1.11	1.96 and -1.64	0.649 and -0.722
Flack parameter	-0.009(4)		

Table 2. Selected bond lengths [Å] and angles [°] for **4** and **6**.

4		6	
Ir(1)-N(1)	2.049(3)	Ir(1)-N(1)	2.180(7)
Ir(1)-N(3)	2.049(3)	Ir(1)-N(3)	2.156(8)
Ir(1)-N(5)	2.037(3)	Ir(1)-O(1)	2.081(5)
Ir(1)-N(6)	2.029(4)	Ir(1)-C(19)	1.793(11)
Ir(1)-Cl(1)	2.343(1)	Ir(1)-C(16)	2.066(9)
Ir(1)-Cl(2)	2.355(1)	Ir(1)-C(13)	2.066(8)
O(1)-C(12)	1.242(5)	C(15)-C(16)	1.492(12)
N(5)-C(12)	1.344(5)	C(13)-C(14)	1.505(13)
N(6)-C(21)	1.085(6)	C(14)-C(15)	1.327(13)
N(1)-Ir(1)-N(3)	86.8(1)	N(1)-Ir(1)-N(3)	83.7(3)
Cl(1)-Ir(1)-Cl(3)	88.1(1)	C(13)-Ir(1)-C(16)	82.8(3)
N(1)-Ir(1)-N(6)	91.1(1)	C(19)-Ir(1)-O(1)	174.7(4)
N(1)-Ir(1)-N(5)	87.4(1)	N(1)-Ir(1)-C(19)	100.4(4)
N(5)-Ir(1)-N(6)	177.8(1)	N(3)-Ir(1)-O(1)	83.1(3)
Cl(1)-Ir(1)-N(6)	90.3(1)	O(1)-Ir(1)-C(13)	85.8(3)
N(3)-Ir(1)-N(6)	90.7(1)	O(1)-Ir(1)-C(16)	86.1(3)
N(3)-Ir(1)-N(5)	87.6(1)	C(19)-Ir(1)-C(13)	90.6(5)
N(1)-Ir(1)-Cl(1)	92.7(1)	C(19)-Ir(1)-C(16)	89.7(4)

Complex **8** was isolated as a yellow solid in high yield. However, complex **7** was isolated as a residual compound in a low yield because it undergoes a decarboxylation process

initiated by the HCl generated in the deprotonation step, leading to the ionic complex [IrClCp*(bdmpm)][IrCl₃Cp*] (**9**), [bdmpm = bis(3,5-dimethylpyrazol-1-yl)methane]. Compound **9** and a family of analogous iridium derivatives of the type [IrClCp*(N-N)][IrCl₃Cp*]^{21a} (or with a different anion^{21b,c}) have been previously formed by reaction of [IrCl₂Cp*]₂ with a series of bidentate ligands with sp² N-donors [N-N = bis(pyrazol-1-yl)methane, bis(1-methylimidazol-2-yl)methane]. The ¹³C{¹H} NMR signals of the carbon atom bridging the two pyrazole rings (C^a) in these complexes is indicative of the reaction that has occurred in these moieties. While the values of 68–80 ppm were appropriate for the sp³ CH atom in compounds **1–6**, the values observed for **7** (100.3 ppm) and **8** (120.4 ppm) indicate a quaternary sp² nature of the corresponding C atom, in agreement with the deprotonation process. The ¹H and ¹³C{¹H} NMR spectra of **7** and **8** show one set of singlets for the H⁴, Me³ and Me⁵ pyrazole protons and carbons and one set of signals for the methyl groups of the cyclopentadienyl rings. NOESY 1D NMR experiments enabled the unequivocal assignment of most of the ¹H NMR resonances while ¹H-¹³C heteronuclear correlation (g-HSQC) experiments allowed us to

assign the resonances corresponding to C⁴, Me³ and Me⁵ of the pyrazole rings and Cp* rings. The data obtained supported an octahedral disposition for each iridium atom, with the Cp* ligands occupying three fac positions, and the heteroscorpionate ligand bridging two iridium centres.

Compound **8** was also characterized in the solid state by X-ray crystallography (see below). The steric demands of the fixed pyrazole rings impose rigidity to the structure and give rise to a helical surface to afford overall helical chirality. Complexes **7** and **8** are generated as a racemic mixture of *P* and *M* enantiomers (Fig. 4).

Insert Figure 4

Fig. 4 Schematic illustration of the helical surface in complexes **7** and **8**.

The presence in solution of the corresponding two enantiomers of compound **8** was confirmed by adding a chiral shift reagent namely (*R*)-(-)-(9-anthryl)-2,2,2-trifluoroethanol. This gave rise to the appearance of two sets of signals for the protons of the pyrazole and Cp* rings (see Fig. 5) that correspond to the two diastereoisomers (*MR/PR*) from the corresponding two enantiomers (see Fig. 4).

Insert Figure 5

Fig. 5 (a) ¹H NMR spectrum of the complex [Ir₂Cl₂Cp*₂(μ-bdmpzda)] (**8**) in CDCl₃. (b) ¹H NMR spectrum of complex **8** with chiral shift reagent in CDCl₃

The helical surfaces for complexes **7** and **8** were characterized in the solid state by X-ray crystallography of a single crystal of complex **8**. The crystallographic data are given in Table 1. The molecular structure of complex **8** (Fig. 6) exhibits a dimeric-like arrangement that is achieved through bridging of the dianionic dithiocarboxylate heteroscorpionate ligand. This complex adopts a bimetallic helical structure in which each iridium atom is in a distorted tetrahedral geometry. Selected interatomic distances and angles are given in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] for **8**.

Bond Lengths		Angles	
Ir(1)-N(1)	2.108(4)	S(1)-Ir(1)-N(1)	85.8(1)
Ir(1)-S(1)	2.360(1)	Cl(1)-Ir(1)-N(1)	88.9(1)
Ir(1)-Cl(1)	2.412(1)	Cl(1)-Ir(1)-S(1)	85.4(1)
Ir(2)-N(4)	2.104(4)	S(2)-Ir(2)-N(4)	86.2(1)
Ir(2)-S(2)	2.358(1)	Cl(2)-Ir(2)-N(4)	88.4(1)
Ir(2)-Cl(2)	2.416(1)	Cl(2)-Ir(2)-S(2)	85.6(1)
C(1)-C(2)	1.355(6)	S(1)-C(1)-S(2)	117.2(3)
S(1)-C(1)	1.722(5)	S(1)-C(1)-C(2)	122.0(4)
S(2)-C(1)	1.749(5)	S(2)-C(1)-C(2)	120.7(4)
Cp* _{centroid} (1)-Ir(1)	1.807		
Cp* _{centroid} (2)-Ir(2)	1.801		

Cp*_{centroid}(1) refers to the centroid of the C13-C17 ring and Cp*_{centroid}(2) refer to the centroid of the C23-C27 ring

The crystals of complex **8** contained two enantiomers (*M*, *P*) in the unit cell. The pyrazole rings in each complex are located in different planes. The twist angle between the two pyrazoles is 66.3°. The geometry around the Ir centres can be described as distorted tetrahedral, with the dihedral angle between the planes defined by Cp*_{centroid}-Ir-S and N-Ir-Cl (89.1° and 91.0° for Ir1 and Ir2, respectively) consistent with a tetrahedral geometry. The C(1)-C(2) bond length, 1.355(6) Å, confirms the double bond character of this bond for these compounds. This bond is shorter than the corresponding one in previously reported metal complexes containing the bdmpzda ligand coordinated in a facial tripodal fashion.^{2i,4e} The S(1)-C(1) and S(2)-C(2) bond lengths of 1.722(5) and 1.749(5) Å respectively, corroborate the single bond character of these bonds for this complex.

Insert Figure 6

Fig. 6 ORTEP drawing for compound **8**. Thermal ellipsoids are set at the 30% probability level and hydrogen atoms are omitted for clarity

The crystal structure of complex **8** reveals that the molecules can be appropriate building blocks for the construction of single helices by weak CH-π interactions involving the methyl groups of Cp* rings and C(H)-Cl hydrogen bonds. These types of interactions are of relevance in many areas of chemistry such as the fields of conformation, supramolecular chemistry, gas-phase inclusion, chiral discrimination, solid-state reactions, molecular recognition, and polymer science and it also extends to biological science and medical chemistry or drug design.²² In complex **8** these interactions seem to be the force that builds single helicates. Complex **8** crystallizes in the trigonal R-3 space group and the helicates are generated around a crystallographic 3₁ screw axis. Self-assembly of the single helices in **8** gives rise to single-strand helicates that contain both enantiomers (*M*, *P*) formed along the *c* axis by hydrogen bonds established between the H30B atoms and the Cl2 atoms with a distance H...Cl of 2.96 Å and an angle C-H-Cl of 158.2°. Additionally, we observed the assembly of different chains through another intermolecular CH-π interaction established between the C20-H20A methyl of Cp* ring and the Cp* ring centroid of the other helix, with a distance of 2.88 Å and a degree of displacement of H20A from the center of the Cp* ring (*D*_{offset}) of 0.80 Å. A new hydrogen bond is established between H18B and Cl1 atoms. The H...Cl distances has a value of 2.81 Å and the angle C-H-Cl has a value of 162.4°. These interactions give rise to the supramolecular structure depicted in Fig. 8. Fig. 8a shows how each helicate is surrounded by another three helicates of opposite chirality in a trigonal disposition.

Concentration dependent ¹H NMR measurements in deuterated chloroform were performed on complex **8** in the concentration range of 10-300 mM. These measurements show a downfield shift of H⁴ pyrazole protons at higher concentrations (Fig. 9) accompanied by line broadening especially for the highest concentrations measured. These experiments indicate that there

are interactions involving the Cp* rings, therefore suggesting the existence of CH- π interactions and C(H)-Cl hydrogen bonds in solution that would result in a molecular aggregation as observed previously for similar complexes with aluminum centers.^{17b}

Insert Figure 7

Fig. 7 (a) Structure of single-stranded helicate in complex **8** which extend along the c axis. (b) Stick view of the intermolecular interactions for the single-stranded helicate. Red lines indicate the hydrogen bonds. The hydrogen atoms and the half part of the molecule are omitted for clarity

Insert Figure 8

Fig. 8 (a) Representation of the helicoidal supramolecular chains. The CH- π interactions are indicated by red dashed lines and the hydrogen bond are indicated by black dashed lines. The hydrogen atoms are omitted for clarity. Blue and pink triangles represent the single-strand helicates *M* and *P* respectively. (b) Schematic illustration of the adjacent *M* (blue) and *P* (red) helicates for **8**. The red and blue points represent the centroid of every molecule that joins to form the chain.

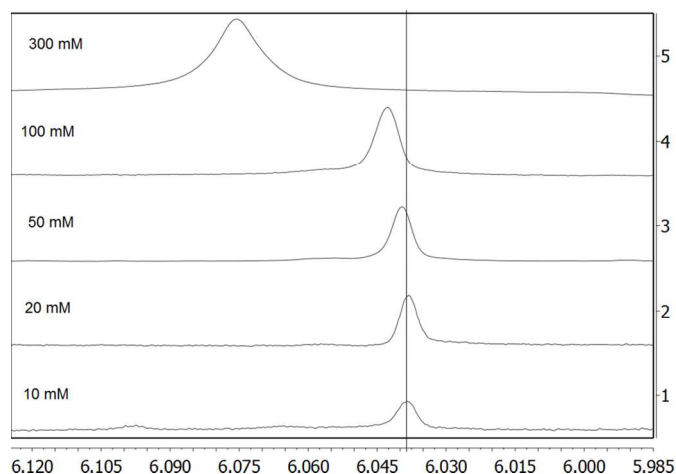


Fig. 9 Concentration-dependent ¹H NMR spectra of complex **8** (⁴H pyrazole protons) in CDCl₃ at 25°C.

Focused on understanding whether the interaction involving the Cp* protons is due to the presence of aggregates in solution, ¹H Pulsed field-gradient spin-echo (PFGSE) NMR experiments were carried out on the same samples, to investigate whether there is a variation in the diffusion coefficient (*D*_t) of the molecules in solution with the change in concentration.²³ Hence, PFGSE NMR experiments were carried out for complex **8** in deuterated chloroform at 25°C using TMS as internal standard for the progressive concentration experiments from 10 mM to 300 mM. Remarkably, the value of the diffusion coefficient extracted from these PFGSE NMR experiments led to a roughly twofold concomitant decrease (Table 4), supporting the self-assembly of the single-molecular species of complex **8** in solution and providing, in itself, important

information about the strength of intermolecular interactions. This behaviour is in agreement with the self-assembly phenomenon observed in solid state, which lead to the formation of a helicate through intermolecular CH- π interactions and C(H)-Cl hydrogen bonds.

Table 4. Concentrations (*C*, mM) and Diffusion Coefficients (10^{-10} *D*_t, m²·s⁻¹) for complex **8** in CDCl₃ at 25°C.

<i>C</i>	<i>D</i> _t
10	8.7±0.02
50	7.4±0.02
100	7.0±0.02
300	3.8±0.02

Conclusions

In conclusion, we have shown that heteroscorpionate ligands bearing different groups as pendant donor arm, including carboxylate, dithiocarboxylate and acetamidate moieties, are versatile in stabilizing iridium metallic complexes with chloride or diene ligands. Starting from “Li(*S*)-mbpam” [(*S*)-mbpam = (*S*)-(-)-*N*- α -methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamidate], complexes **3** and **4** were isolated as enantiopure compounds. The η^4 -dimethylbutadiene derivative of the [Ir(bdmpza)] moiety behaves similarly to the corresponding [IrTp^{Me2}] one when reacting with a Lewis base (CO), yielding the κ^2 -dimethyl-2-butene-1,4-diyl heteroscorpionate iridium(III) compound **6**. When reacting with [IrCl₂Cp*]₂, the two ligands bdmpza and bdmpzda experience (in the presence of LiCl) an unprecedented double deprotonation of the carboxylate or dithiocarboxylate ligand by C-H activation of the methyne group resulting in the formation of dianionic ligands bridging two iridium(III) atoms in each case. The steric demands of the fixed pyrazole rings impose rigidity to the structure and give rise to a helical surface to afford overall helical chirality. This has proved to be a novel and straightforward approach to prepare single-helical dinuclear iridium complexes able to act as building block to build up single-stranded iridium helicate self-assembled by CH/ π interactions. This has been characterized by X-ray diffraction study. Additionally, NMR experiments confirmed the existence of intermolecular interactions and thereby corroborates the tendency of the single-helical species to self-assemble also in solution.

Experimental

All manipulations were performed under nitrogen, using standard Schlenk techniques. The solvents employed were dried before use. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. The elemental analyses of the new compounds were carried out at the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla) (Perkin-Elmer Series II CHNS/O 2400). IR spectra were recorded on a Perkin-Elmer

system 2000 FT-IR (KBr). ^1H , ^{13}C NMR and ^7Li NMR spectra were recorded on Bruker models DPX-300, DRX-400, DRX-500 and a Varian Innova FT-500 spectrometer and referenced to the residual deuterated solvent and to LiCl for ^7Li NMR. The NOESY-1D spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard BRUKER-FT and VARIANT-FT softwares. Two-dimensional NMR spectra were acquired using standard BRUKER-FT and VARIANT-FT software. The specific rotation $[\alpha]_{\text{D}}^{22}$ was measured at 22 °C using a Perkin-Elmer 241 polarimeter equipped with a Na Lamp operating at 589 nm with a light path length of 10 cm. $[\text{IrCp}^*\text{Cl}_2]_2$ was used as purchased (Strem), $[\text{IrCl}_3(\text{thf})_3]_2$, $[\{\text{Li}(\text{bdmpza})(\text{H}_2\text{O})\}_4]$, ^{13}a $[\{\text{Li}(\text{bdmpzda})(\text{H}_2\text{O})\}_4]^{4\text{e}}$ and (S) -mbpamH $^{13\text{b}}$ were prepared according to literature procedures.

Synthesis of $[\text{IrCl}_2(\text{bdmpza})(\text{THF})]$ (1). To a THF (20 mL) solution of $[\text{IrCl}_3(\text{THF})_3]$ (0.210 g, 0.567 mmol) was added an equimolar quantity of $[\{\text{Li}(\text{bdmpza})(\text{H}_2\text{O})\}_4]$ (0.154 g, 0.142 mmol). The reaction mixture was stirred for 18 h under reflux. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2 . A yellow solid was obtained after removal of the solvent, and this was crystallized from a mixture of THF/hexane. Yield: (0.24 g), 75%. Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{Cl}_2\text{IrN}_4\text{O}_3$: C, 33.0; H, 4.0; N, 9.6. Found: C, 33.1; H, 4.1; N, 9.4. IR (cm^{-1}): 1561 $\nu(\text{C}=\text{N})$, 1691 $\nu_{\text{as}}(\text{CO}_2^-)$, 1464 $\nu_{\text{s}}(\text{CO}_2^-)$. ^1H NMR ($\text{DMSO}-d_6$, 297 K): δ = 6.56 (s, 1 H, CH), 6.22 (s, 2 H, H^4), 3.60 (m, 4 H, THF), 2.66 (s, 6 H, Me^3), 2.56 (s, 6 H, Me^5), 1.76 (m, 4 H, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 297 K): δ = 166.2 (CO_2^-), 156.5, 142.5 ($\text{C}^{3\text{or}5}$), 108.9 (C^4), 73.3 (CH), 67.3 (thf), 25.5 (thf), 14.2 (Me^5), 10.9 (Me^3).

Synthesis of $[\text{Li}(\text{thf})_4][\text{IrCl}_3(\text{bdmpzda})]$ (2). The synthetic procedure was the same as for complex 1, using $[\text{IrCl}_3(\text{THF})_3]$ (0.210 g, 0.567 mmol) and $[\{\text{Li}(\text{bdmpzda})(\text{H}_2\text{O})\}_4]$ (0.173 g, 0.142 mmol), to give 2 as an orange solid. Yield: (0.34 g), 70%. Anal. Calcd for $\text{C}_{28}\text{H}_{47}\text{Cl}_3\text{IrLiN}_4\text{O}_4\text{S}_2$: C, 38.5; H, 5.4; N, 6.4. Found: C, 38.6; H, 5.5; N, 6.4. IR (cm^{-1}): 1586 $\nu(\text{C}=\text{N})$, 1039 $\nu_{\text{as}}(\text{CS}_2^-)$, 798 $\nu_{\text{s}}(\text{CS}_2^-)$. ^1H NMR ($\text{DMSO}-d_6$, 297 K): δ = 7.53 (s, 1 H, CH), 6.03 (s, 2 H, H^4), 4.50 (m, 16 H, THF), 2.76 (s, 6 H, Me^3), 2.49 (s, 6 H, Me^5), 2.12 (m, 16 H, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 297 K): δ = 233.9 (CS_2^-), 152.5, 142.8 ($\text{C}^{3\text{or}5}$), 108.2 (C^4), 80.5 (CH), 74.7 (THF), 25.6 (THF), 15.0 (Me^3), 11.6 (Me^5). ^7Li NMR ($\text{DMSO}-d_6$, 297 K): 1.50 (s).

Synthesis of $[\text{IrCl}_2\{\text{(S)-mbpam}\}(\text{thf})]$ (3). To a cooled (−30 °C) solution of (S) -mbpamH (0.069 g, 0.194 mmol) in dry THF (25 mL) was added a 1.6 M solution of Bu^nLi in hexane (0.12 mL, 0.194 mmol). After 5 min, a solution of $[\text{IrCl}_3(\text{THF})_3]$ (0.071 g, 0.194 mmol) in THF (10 mL) was added and the reaction mixture stirred for 18 h at room temperature. The solvent was removed under vacuum and the solid was extracted with CH_2Cl_2 . A brown solid was obtained after removal of the solvent, and this was crystallized from a mixture of THF/hexane. Yield: (0.097 g) 73%. $[\alpha]_{\text{D}}^{22} = -22.3^\circ$ (c 0.10, THF). Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{Cl}_2\text{IrN}_5\text{O}_2$: C, 42.0; H, 4.7; N, 10.2. Found: C, 42.2; H, 4.9; N, 10.0. IR (cm^{-1}): 1563 $\nu(\text{C}=\text{N})$, 1632 $\nu(\text{C}=\text{O})$, ^1H NMR (CD_2Cl_2 , 297 K): δ = 7.64 [d, $^3J_{\text{H-H}} = 7.0$ Hz, 2H, $\text{H}^p\text{-NCH}(\text{CH}_3)\text{Ph}$], 7.26 [t, $^3J_{\text{H-H}} = 7.0$ Hz, 2H, $\text{H}^m\text{-$

$\text{NCH}(\text{CH}_3)\text{Ph}$], 7.12 [t, $^3J_{\text{H-H}} = 6.9$ Hz, 1H, $\text{H}^p\text{-NCH}(\text{CH}_3)\text{Ph}$], 6.53 (s, 1 H, CH), 6.08 (s, 2 H, $\text{H}^{4,4'}$), 5.42 [m, 1H, $\text{NCH}(\text{CH}_3)\text{Ph}$], 3.88 (m, 4H, THF), 2.68, 2.59 (s, 6H, $\text{Me}^{3,3'}$), 2.45, 2.40 (s, 6H, $\text{Me}^{5,5'}$), 1.92 (m, 4H, THF), 1.59 [d, $^3J_{\text{H-H}} = 7.9$ Hz, 3H, $\text{NCH}(\text{CH}_3)\text{Ph}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 297 K): δ = 163.2 ($\text{NC}=\text{O}$), 152.1, 150.3, 149.7, 147.6, 145.4 [$\text{C}^{3,3'}$ or $^{5,5'}$, $\text{C}^{\text{ipso-NCH}(\text{CH}_3)\text{Ph}}$], 128.3 [$\text{C}^m\text{-NCH}(\text{CH}_3)\text{Ph}$], 127.3 [$\text{C}^o\text{-NCH}(\text{CH}_3)\text{Ph}$], 126.4 [$\text{C}^p\text{-NCH}(\text{CH}_3)\text{Ph}$], 107.4 ($\text{C}^{4,4'}$), 71.6 (CH), 54.6 [$\text{NCH}(\text{CH}_3)\text{Ph}$], 24.4 [$\text{NCH}(\text{CH}_3)\text{Ph}$], 13.1, 12.8 ($\text{Me}^{3,3'}$), 10.9, 10.5 ($\text{Me}^{5,5'}$).

Synthesis of $[\text{IrCl}_2\{\text{(S)-mbpam}\}(\text{NCCH}_3)]$ (4). The synthetic procedure was the same as for complex 3, using CH_3CN as solvent. Yield: (0.051 g) 40%. $[\alpha]_{\text{D}}^{22} = -25.1^\circ$ (c 0.10, CH_3CN). Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{Cl}_2\text{IrN}_6\text{O}$: C, 40.4; H, 4.2; N, 12.8. Found: C, 40.6; H, 4.5; N, 12.5. IR (cm^{-1}): 1562 $\nu(\text{C}=\text{N})$, 1630 $\nu(\text{C}=\text{O})$, ^1H NMR (CD_2Cl_2 , 297 K): δ = 7.22 [d, $^3J_{\text{H-H}} = 7.0$ Hz, 2H, $\text{H}^p\text{-NCH}(\text{CH}_3)\text{Ph}$], 7.12 [m, 2H, $\text{H}^m\text{-NCH}(\text{CH}_3)\text{Ph}$], 7.05 [m, 1H, $\text{H}^p\text{-NCH}(\text{CH}_3)\text{Ph}$], 6.23 (s, 1 H, CH), 6.10 (s, 2 H, $\text{H}^{4,4'}$), 4.91 [m, 1H, $\text{NCH}(\text{CH}_3)\text{Ph}$], 2.77 (s, 3H, CH_3CN), 2.71, 2.70 (s, 6H, $\text{Me}^{3,3'}$), 2.52, 2.47 (s, 6H, $\text{Me}^{5,5'}$), 1.69 [d, $^3J_{\text{H-H}} = 7.8$ Hz, 3H, $\text{NCH}(\text{CH}_3)\text{Ph}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 297 K): δ = 161.0 ($\text{NC}=\text{O}$), 155.2, 155.1, 146.9, 141.9, 1414.8 [$\text{C}^{3,3'}$ or $^{5,5'}$, $\text{C}^{\text{ipso-NCH}(\text{CH}_3)\text{Ph}}$], 127.2 [$\text{C}^o\text{-NCH}(\text{CH}_3)\text{Ph}$], 126.7 [$\text{C}^m\text{-NCH}(\text{CH}_3)\text{Ph}$], 125.8 [$\text{C}^p\text{-NCH}(\text{CH}_3)\text{Ph}$], 118.0 (CH_3CN), 109.0, 108.9 ($\text{C}^{4,4'}$), 71.7 (CH), 58.6 [$\text{NCH}(\text{CH}_3)\text{Ph}$], 18.8 [$\text{NCH}(\text{CH}_3)\text{Ph}$], 13.8 ($\text{Me}^{3,3'}$), 11.3 ($\text{Me}^{5,5'}$), 3.9 (CH_3CN).

Synthesis of $[\text{Ir}(\text{bdmpza})(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]$ (5). To a solution of $[\text{IrCl}(\text{coe})_2]_2$ (0.100 g, 0.105 mmol) in THF (5 mL) was added 0.2 mL of 2,3-dimethylbutadiene. The reaction mixture was stirred at room temperature. After 3 h, a solution of $[\{\text{Li}(\text{bdmpza})(\text{H}_2\text{O})\}_4]$ (0.057 g, 0.053 mmol) in THF (10 mL) was added and the reaction mixture was stirred for 18 h at room temperature. The solvent was removed under vacuum and the solid was extracted with CH_2Cl_2 . A brown solid was obtained after removal of the solvent, and this was crystallized from a mixture of THF/hexane. Yield: (0.99 g) 91%. Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{IrN}_4\text{O}_2$: C, 41.4; H, 4.8; N, 10.7. Found: C, 41.6; H, 5.1; N, 10.4. IR (cm^{-1}): 1560 $\nu(\text{C}=\text{N})$, 1645 $\nu_{\text{as}}(\text{CO}_2^-)$, 1463 $\nu_{\text{s}}(\text{CO}_2^-)$. ^1H NMR (CDCl_3 , 297 K): δ = 6.75 (s, 1 H, CH), 5.86 (s, 2 H, H^4), 2.39 (s, 6 H, Me^5), 2.38 [d, $^1J_{\text{H-H}} = 4.0$ Hz, 2H, $\text{H}^p\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$], 2.19 (s, 6 H, Me^3), 1.98 [s, 6H, $\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$], −0.02 [d, $^1J_{\text{H-H}} = 4.0$ Hz, 2H, $\text{H}^b\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 297 K): δ = 166.9 (CO_2^-), 153.2, 141.2 ($\text{C}^{3\text{or}5}$), 107.8 (C^4), 81.6 [$\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$], 68.3 (CH), 17.9 [$\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$], 9.5 [$\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$], 14.7 (Me^3), 11.9 (Me^5).

Synthesis of $[\text{Ir}(\text{bdmpza})(\eta^4\text{-CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2)(\text{CO})]$ (6). A solution of $[\text{Ir}(\text{bdmpza})(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]$ (5) (0.100g, 0.190 mmol) in 10 mL of THF was placed in a reactor with CO (2 atm). The reaction mixture was stirred for 18 h at 90 °C. The solvent was removed under vacuum and the solid was crystallized in a 1:1 mixture of CH_2Cl_2 -hexane to give 6 as an orange crystalline solid. Yield: (0.75 g) 72%. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{IrN}_4\text{O}_3$: C, 41.5; H, 4.6; N, 10.2. Found: C, 41.7; H, 4.7; N, 10.0. IR (cm^{-1}): 2014 $\nu(\text{CO})$, 1561 $\nu(\text{C}=\text{N})$, 1669

$v_{as}(\text{CO}_2^-)$, 1462 $v_s(\text{CO}_2^-)$. ^1H NMR (CD_2Cl_2 , 297 K): δ = 6.39 (s, 1 H, CH), 6.06 (s, 2 H, H^4), 3.07 [m, 2H, $\text{CH}_2\text{-C}(\text{Me})=\text{C}(\text{Me})\text{-CH}_2$], 2.43 (s, 6 H, Me^5), 2.34 (s, 6 H, Me^3), 2.21 [m, 2H, $\text{CH}_2\text{-C}(\text{Me})=\text{C}(\text{Me})\text{-CH}_2$], 1.69 [s, 6H, $\text{CH}_2\text{-C}(\text{Me})=\text{C}(\text{Me})\text{-CH}_2$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 297 K): δ = 167.3 (CO), 164.9 (CO_2^-), 152.5, 141.4 ($\text{C}^{3\text{or}5}$), 136.2 [$\text{CH}_2\text{-C}(\text{Me})=\text{C}(\text{Me})\text{-CH}_2$], 108.1 (C^4), 69.3 (CH), 18.1 [$\text{CH}_2\text{-C}(\text{Me})=\text{C}(\text{Me})\text{-CH}_2$], 15.7 [$\text{CH}_2\text{-C}(\text{Me})=\text{C}(\text{Me})\text{-CH}_2$], 14.1 (Me^3), 11.4 (Me^5).

Synthesis of $[\text{Ir}_2\text{Cp}^*_2\text{Cl}_2(\text{bdmpza})]$ (7) and $[\text{IrClCp}^*(\text{bdmpm})][\text{IrCl}_3\text{Cp}^*]$ (9). To a THF (20 mL) solution of $[\text{IrCp}^*\text{Cl}_2]_2$ (0.200 g, 0.240 mmol) was added an equimolar quantity of $[\{\text{Li}(\text{bdmpza})(\text{H}_2\text{O})\}_4]$ (0.065 g, 0.060 mmol). The reaction mixture was stirred for 18 h at room temperature. The solvent was removed under vacuum and the solid contains a mixture of complexes 7 and 9. Complex 7 was extracted with hexane and a yellow solid was obtained after removal of the solvent, and this was crystallized from a mixture of THF/hexane, yield: (0.058 g), 25%. Complex 9 was extracted with CH_2Cl_2 and an orange solid was obtained after removal of the solvent, and this was crystallized from a mixture of $\text{CH}_2\text{Cl}_2/\text{THF}$, yield: (0.180 g), 75%. *For complex 7:* Anal. Calcd for $\text{C}_{32}\text{H}_{44}\text{Cl}_2\text{Ir}_2\text{N}_4\text{O}_2$: C, 39.5; H, 4.6; N, 5.8. Found: C, 39.8; H, 4.9; N, 5.5. IR (cm^{-1}): 1555 $\nu(\text{C}=\text{N})$, 1598 $\nu_{as}(\text{CO}_2)$, 1495 $\nu_s(\text{CO}_2)$. ^1H NMR (CDCl_3 , 297 K): δ = 6.06 (s, 2 H, H^4), 2.43 (s, 6 H, Me^3), 1.78 (s, 30 H, Me-Cp^*), 1.53 (s, 6 H, Me^5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 297 K): δ = 155.5, 153.2, 142.3 ($\text{C}^{3\text{or}5}$ or CO_2), 108.1 (C^4), 100.3 (C^a), 89.3 (C-Cp^*), 15.1 (Me^3), 11.4 (Me^5), 9.5 (Me-Cp^*). *For complex 9:* Anal. Calcd for $\text{C}_{31}\text{H}_{46}\text{Cl}_4\text{Ir}_2\text{N}_4$: C, 37.2; H, 4.6; N, 5.6. Found: C, 37.4; H, 4.9; N, 5.4. IR (cm^{-1}): 1556 $\nu(\text{C}=\text{N})$. ^1H NMR (CDCl_3 , 297 K): δ = A 7.07, B 5.85 (AB, J_{AB} = 16.0 Hz, 2 H, CH_2), 5.98 (s, 2 H, H^4), 2.66 (s, 6 H, Me^5), 2.36 (s, 6 H, Me^3), 1.67 (s, 15 H, $\text{Me-Cp}^*\text{Ir}^+$), 1.56 (s, 15 H, $\text{Me-Cp}^*\text{Ir}^-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 297 K): δ = 153.3, 144.1 ($\text{C}^{3\text{or}5}$), 108.4 (C^4), 100.3 (C^a), 88.5, 83.9 (C-Cp^*), 14.7 (Me^3), 12.7 (Me^5), 9.6 ($\text{Me-Cp}^*\text{Ir}^+$), 9.0 ($\text{Me-Cp}^*\text{Ir}^-$).

Synthesis of $[\text{Ir}_2\text{Cp}^*_2\text{Cl}_2(\text{bdmpzda})]$ (8). To a THF (20 mL) solution of $[\text{IrCp}^*\text{Cl}_2]_2$ (0.200 g, 0.240 mmol) was added an equimolar quantity of $[\{\text{Li}(\text{bdmpzda})(\text{H}_2\text{O})\}_4]$ (0.073 g, 0.060 mmol). The reaction mixture was stirred for 18 h at room temperature. The solvent was removed under vacuum and the solid was extracted with CH_2Cl_2 . A yellow solid was obtained after removal of the solvent, and this was crystallized from a mixture of $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Yield: (0.181 g), 75%. Anal. Calcd for $\text{C}_{32}\text{H}_{44}\text{Cl}_2\text{Ir}_2\text{N}_4\text{O}_2$: C, 38.3; H, 4.4; N, 5.6. Found: C, 38.3; H, 4.5; N, 5.2. IR (cm^{-1}): 1545 $\nu(\text{C}=\text{N})$, 934 $\nu_{as}(\text{CS}_2)$, 730 $\nu_s(\text{CS}_2)$. ^1H NMR (CDCl_3 , 297 K): δ = 6.01 (s, 2 H, H^4), 2.58 (s, 6 H, Me^3), 1.64 (s, 30 H, Me-Cp^*), 1.53 (s, 6 H, Me^5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 297 K): δ = 155.5, 140.9 ($\text{C}^{3\text{or}5}$), 154.9 (CS_2), 120.4 (C^a), 109.3 (C^4), 88.6 (C-Cp^*), 17.3 (Me^3), 11.1 (Me^5), 9.7 (Me-Cp^*).

X-ray crystallographic structure determination

A single crystal of suitable size, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173 K and 296 for compound 8] to the goniometer head. Data collection was performed on three different Bruker APEX-II CCD diffractometers, using

monochromatic radiation $\lambda(\text{Mo K}\alpha_1) = 0.71073 \text{ \AA}$ generated by a fine-focus sealed tube (8 and 9) or by a tube microfocus source (4 and 6) by means of ω and ϕ scans. Data collection of structures 4 and 6 were obtained at the Centro de Investigaciones, Tecnología e Innovación Universidad de Sevilla (CITIUS), for 9 at the Instituto de Investigaciones Químicas (Sevilla) and for 8 at Facultad de Ciencias y Tecnologías Químicas (Ciudad Real). The data were reduced (SAINT)²⁵ and corrected for Lorentz polarization effects and absorption by multiscan method applied by SADABS.²⁶ The structures were solved by direct methods and refined against all F^2 data by full-matrix least-squares techniques using the SHELXTL package (v. 6.14).²⁷ All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with C-H = 0.95 Å or C-H = 0.98 Å for methyl H atoms, and $U_{iso}(\text{H}) = 1.2 U_{eq}(\text{C})$ or $U_{iso}(\text{H}) = 1.5 U_{eq}(\text{C})$ for methyl H atoms. Compound 4 contains two independent iridium molecules in the asymmetric unit showing identical geometric parameters within experimental error. The solid structure of complex 6 contains six water molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.²⁸ It was not possible to model them by assigning peaks in the Fourier electron density map. These solvent molecules are allocated in four accessible voids of 77 Å³ (1.5 molecules per void). Compound 8 co-crystallized with a dichloromethane solvent molecule whose chloride atoms were modeled over two positions using the PART instruction (52:48 ratio). The solid state structure of 9 has already been reported,^{21a} however, at variance with the previous report, we observe in this case that 9 crystallizes as a dichloromethane solvate whose crystallographic details are included in the Supporting Information. CCDC-1012291 (4), CCDC-1012292 (6), CCDC-1012294 (8) and CCDC-1012293 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes and references

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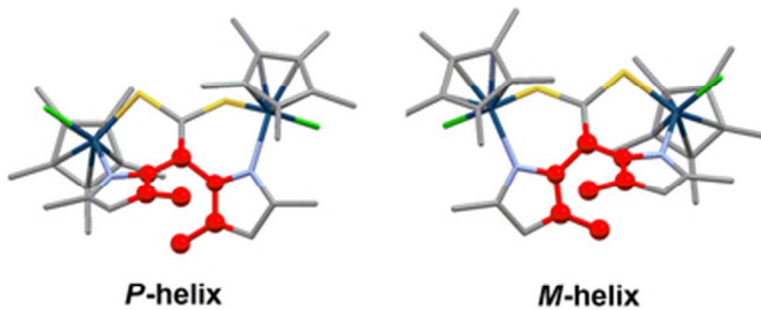
† Electronic Supplementary Information (ESI) available: X-ray data for compound **9**. CCDC reference numbers 1012291 (**4**), 1012292 (**6**), 1012294 (**8**) and 1012293 (**9**). See DOI: 10.1039/b000000x/

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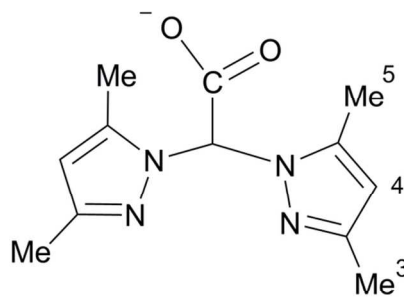
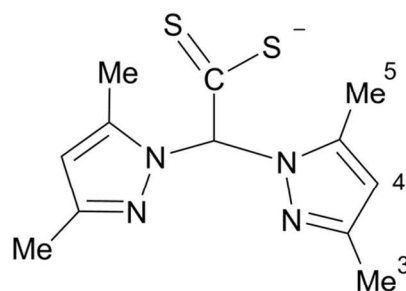
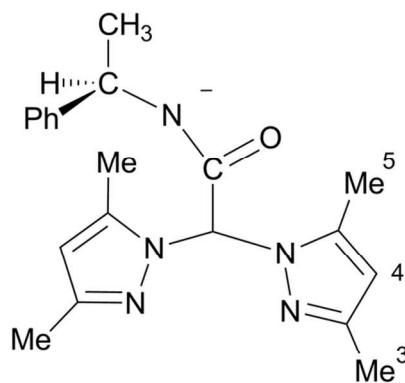
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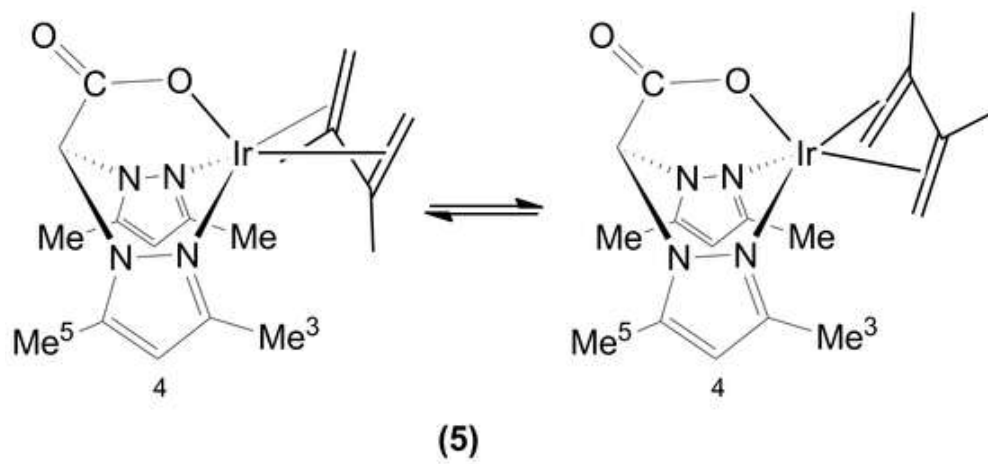
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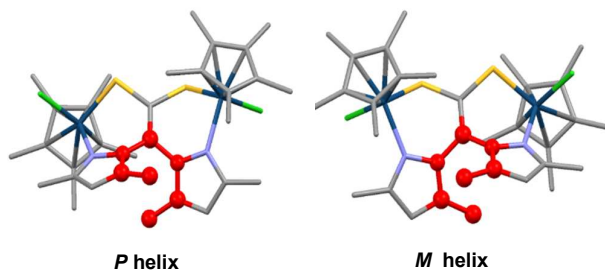
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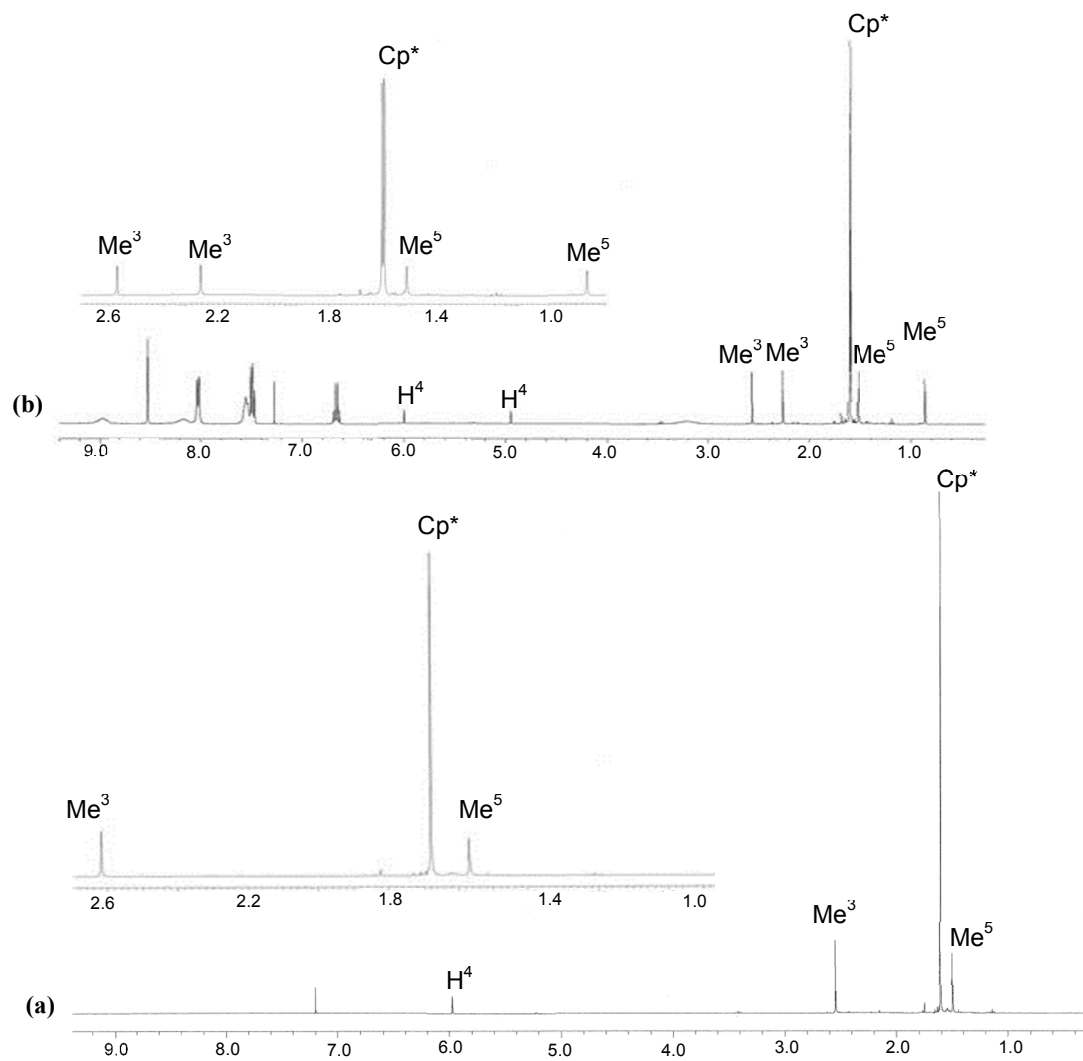
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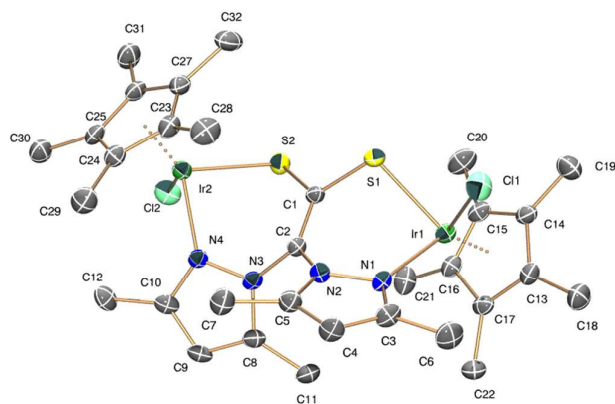
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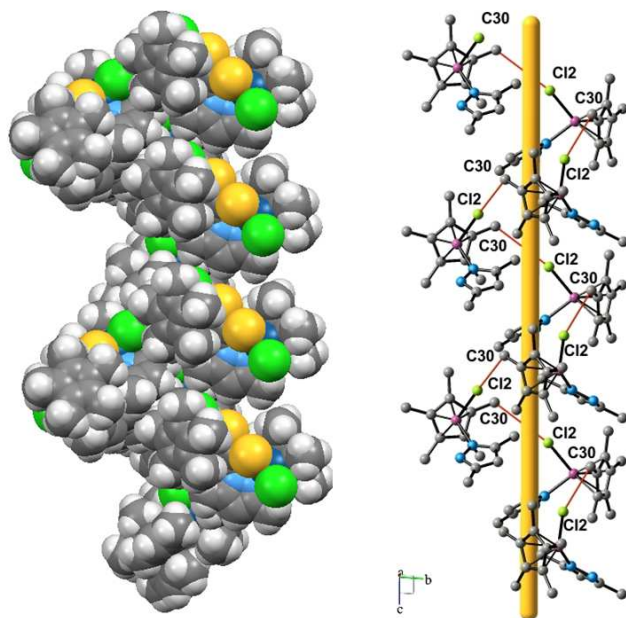
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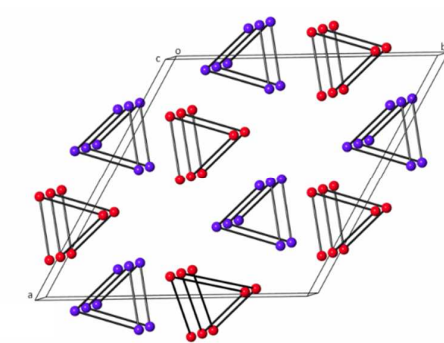
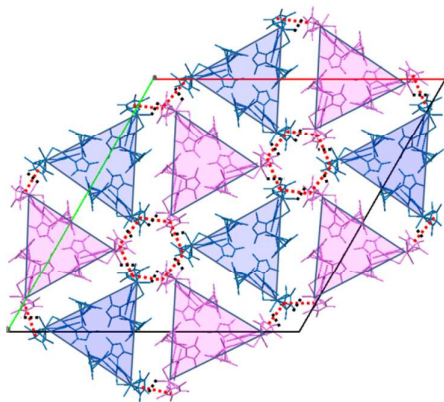


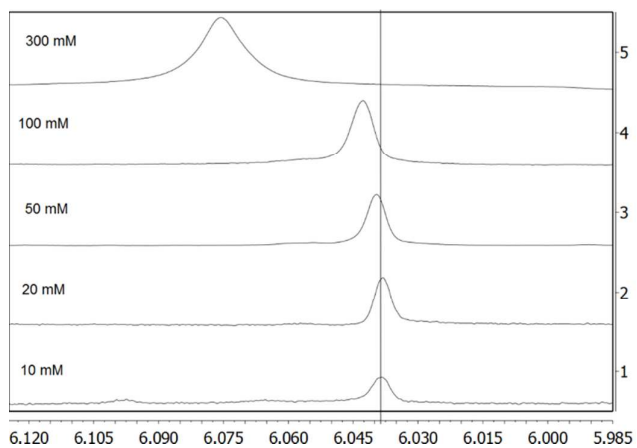


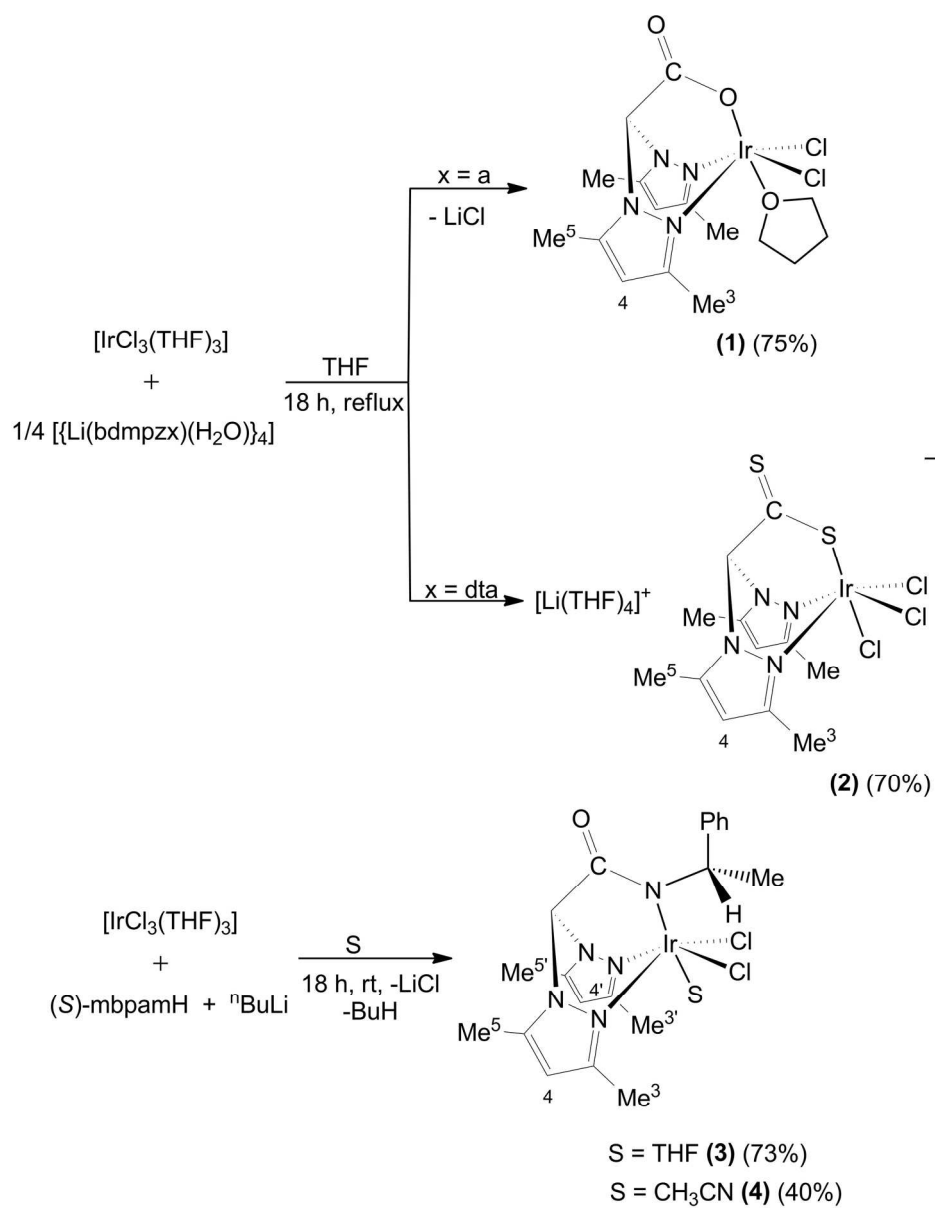


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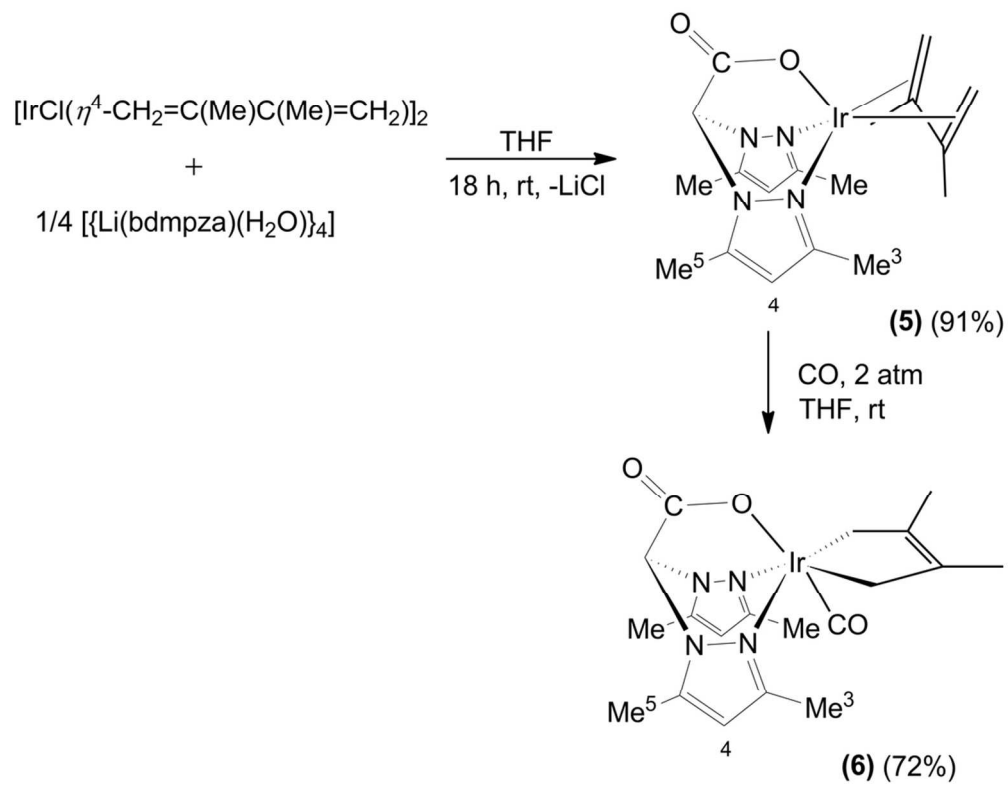




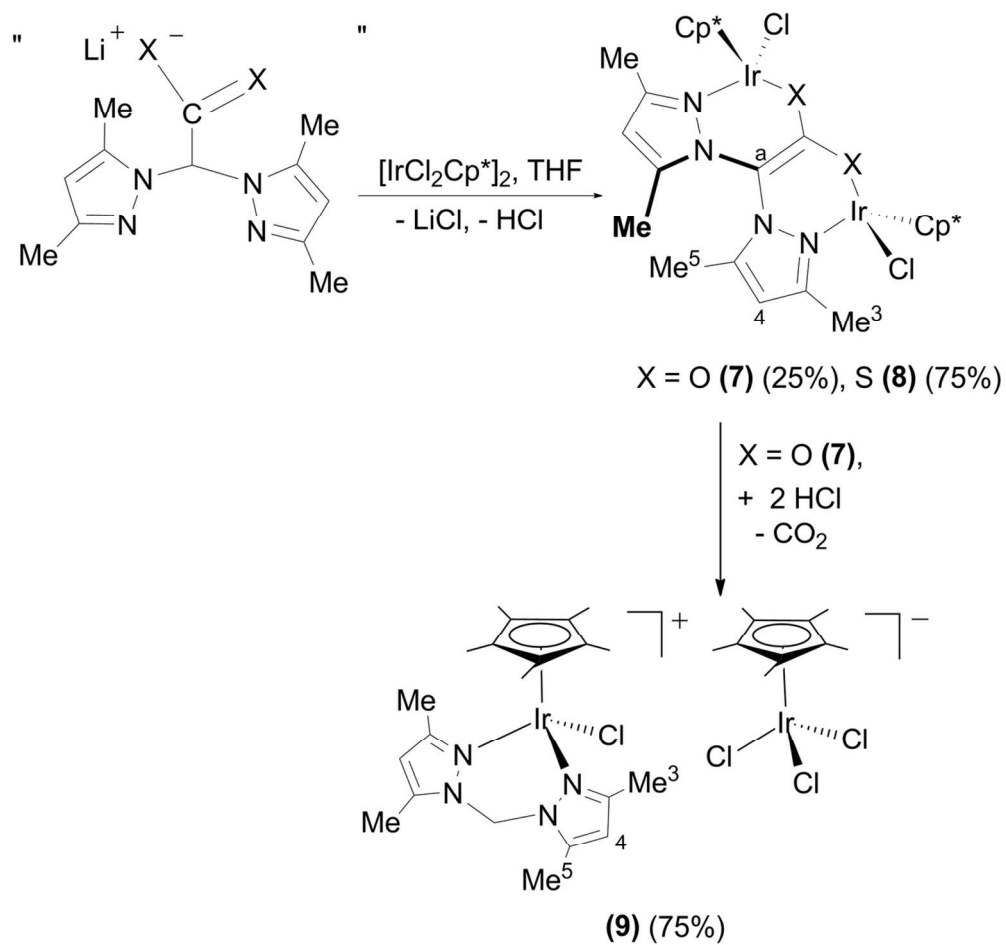




173x212mm (300 x 300 DPI)



99x77mm (300 x 300 DPI)



115x108mm (300 x 300 DPI)