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Counterion dependence of normal versus abnormal binding of triazolium salts to an iridium complex

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ABSTRACT

Reaction of 2-pyridylmethyl-substituted triazolium salts with $IrH_5(PPh_3)_2$ produces novel NHC iridium complexes. Both normal (C-5) and abnormal (C-3) binding is seen. Changing the counter-anion of the triazolium salt reactant determines the regiochemistry of binding between iridium and the triazolium ring. Bromide, being the best hydrogen bonder, favors normal binding to iridium (C-5), all other counterions tried, favor abnormal binding (C-3).

1. Introduction

Since Arduengo isolated the first crystalline carbene [1], imidazol-2-ylidene carbenes have been very widely studied both in organometallic synthesis and in catalytic applications, where they have shown useful advantages [2–7]. The triazole analogues have been far less studied, [8–11] although they are expected to be usefully different in their properties, notably in being less electron donating than the imidazole analogues [12]. Since imidazol-2-ylidenes are all much more electron-donating than conventional phosphines, PR_3, triazole versions may occupy the middle ground between the two classes of ligand in terms of electron donor power.

Because of our need to incorporate molecular recognition and other reactive functionality into these carbenes, the synthetic route from the azolium salts had to avoid high temperatures or harsh alkyllithium reagents. We have therefore looked for low temperature, mild routes to NHCs [13–16]. In the course of this work, we found a reaction of imidazolium salts with IrH_5L_2 (**1**, L = PPh_3) in which either normal C-2-bound or abnormal C-5-bound isomers, or both, could both be formed, depending on the conditions (Scheme 1). Surprisingly, the outcome was very sensitive to the choice of counterion, abnormal binding being favored by SbF_6 and normal by Br [17,18]. Prior computational work (DFT) on the imidiazolium reaction suggested that the abnormal path involves C–H oxidative addition to Ir(III) to give Ir (V) with little anion dependence. The normal path, in contrast, goes by heterolytic C–H activation with proton transfer to the adjacent hydride. The proton that is transferred is accompanied by the ion-paired counteranion in an anion-coupled proton transfer, leading to a strong anion dependence of this path, accounting for the shift in normal/abnormal selectivity [18]. In recent years there have been other reports describing new synthetic pathways and properties of abnormal carbenes [19–21].

To see if this behavior is general, we have now moved to the triazole analogues, where normal binding would occur at C-5, flanked by alkylated nitrogens at N-1 and N-4. Abnormal binding would now occur at C-3, flanked by one alkylated N at N-4 and one standard N at N-2 (see Fig. 1 for numbering scheme). This paper reports the outcome of the triazole chemistry and the counterion dependence of the normal/abnormal product ratio. We prefer the normal/abnormal terminology because the conventional numbering scheme of diazoles and triazoles produces confusing descriptions, such as C-5 binding being normal for triazoles but abnormal for imidazoles.

2. Results & discussion

2.1. Synthesis of triazolium ligands

Novel triazolium bromide salts, having two different wingtip groups **4** and **5**(Fig. 2), were made by extending the method that was used for preparation of the related imidazole ligands, which we have published in our previous articles [13,17]. Heating the 2-bromomethylpyridine

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(that was extracted from the corresponding commercial HBr salt) with methyltriazole or isopropyltriazole at reflux (overnight) in methanol or dioxane gave ligand precursors **4** and **5** in good yields (66 % and 49 %).

Formation of the ligand is unambiguously proven by ^{1}H NMR, notably the downfield signal of the C5-H which is seen at 11.86 ppm (for ligand **4**) and 11.92 ppm (for ligand **5**) in $CDCl_3$. From our previous work this shift is not only diagnostic of the corresponding ligand salt being formed, but also helps in suggesting which counterion is present since ion pairing occurs at this position with suitable anions such as bromide. Counterion exchanges have been performed with either AgX or NaX in acetone or methylene chloride. In both ligands, the C5-H shift moves upfield when counterion is exchanged from bromide to all the others tried, all of which have lower ion pairing ability [22]. With the BF_4 counterion, for example, the signal moves to 10.06 ppm (for ligand **4**) and to 9.86 ppm (for ligand **5**). Table 1 lists chemical shifts for C5-H and C3-H for several counterions. This observed change in the chemical shift of C5-H is consistent with prior work [23]. We have fully characterized ligand **4** as described in the experimental section and supplemental information. (Full NMR characterization of ligand precursor **4** was carried out in DMSO-d_6 due to its limited solubility in $CDCl_3$)

2.2. Synthesis of iridium complexes

All the metallation reactions were carried out in the same way as in our previous papers. $Ir(H)_5(PPh_3)_2$ and the appropriate pyridine functionalized ligand were suspended in a minimal amount of THF (5 ml) and vigorously refluxed for 2 h. Although the starting materials were not completely soluble in THF, almost all the products were. The reaction mixture usually turns clear after about 20 min, signaling that the reaction is occurring. All of the products were precipitated with pentane, giving either a yellow or an off-white solid. Yields for all these reactions are in the range of 70–90 %. Scheme 2 shows the reaction and the counterions used (X^-) are listed in Table 3.

2.3. NMR characterization of iridium complexes

The isolated products are easily identifiable by ^{1}H NMR in $CDCl_3$, a solvent in which all the complexes were soluble. Normal or abnormal binding is recognizable in the ^{1}H NMR spectrum by the chemical shifts of the R group. For complexes **6a** and **7a**, with R = Me, the methyl group shift is diagnostic. In the normal binding mode **6a** (X = Br^-), methyl group resonance occurs around 2.8 ppm, while in the abnormal binding mode **7a** (X = BF_4^-) it appears at 3.5 ppm. For **6b** (X = Br^-), the CH_3 signal of the i-Pr group is seen at 0.48 ppm, while the CH_3 signal of the abnormal complex **7b** (X = BF_4^-) comes at 1.21 ppm. This shift in the signal of the R groups is, we think, explainable by the closer proximity of the R group to the metal center in the normal binding mode and in any case is a very useful tool in distinguishing between normal and abnormal complexes. Another way to determine the binding mode is to identify the C5-H signal in the ^{1}H NMR ($CDCl_3$). For the normal case **6a** (X = Br^-) this signal, which was at 11.86 ppm in the ligand precursor, disappears altogether because this proton is replaced by the metal in the metallation reaction. For the abnormal complex **7a** (X =BF_4), the C5-H signal is still present, appearing at 9.08 ppm, this constituting a slight expected

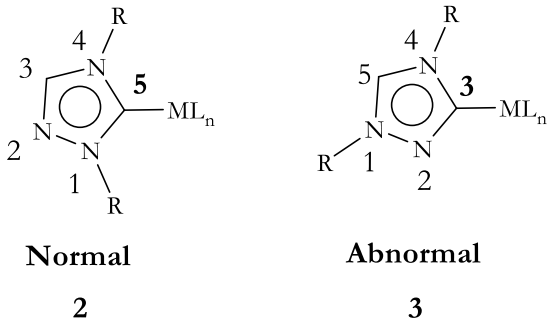


Fig. 1. Numbering scheme for triazolium ligands.

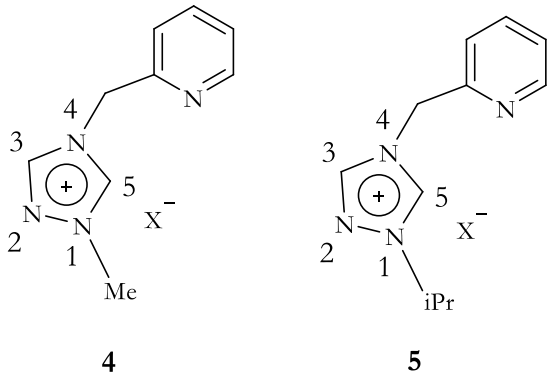
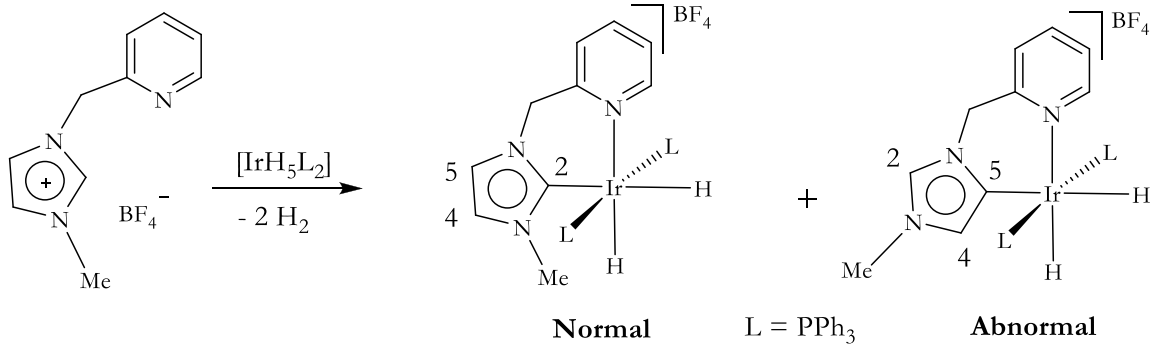


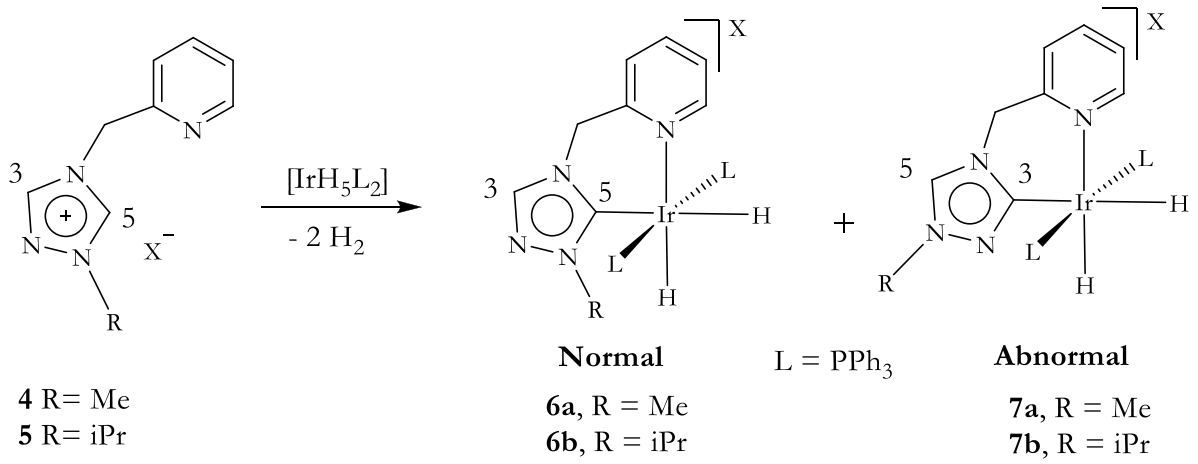
Fig. 2. Pyridine functionalized triazolium ligands with the numbering scheme.

Table 1
C5-H and C3-H ^{1}H NMR chemical shift for several counterions in $CDCl_3$ (ligands **4** and **5**).

R	X	C5-H Chemical Shift (ppm)	C3-H Chemical Shift (ppm)
Methyl	Br	11.86	8.96
Methyl	BF_4	10.06	8.72
Methyl	SbF_6	9.59	8.68
Methyl	PF_6	9.65	8.67
Isopropyl	Br	11.92	8.95
Isopropyl	BF_4	9.86	8.73
Isopropyl	SbF_6	9.53	8.69
Isopropyl	PF_6	9.77	8.74



Scheme 1. Normal and abnormal binding in pyridine functionalized imidazolium ligands.



Scheme 2. Synthesis of the normal and abnormal iridium complexes of pyridine functionalized 1,2,4-triazolium salts.

upfield shift from the ligand precursor as the result of metal coordination. It is also interesting to note that the Ir-C carbene signals in the ^{13}C NMR spectrum are very similar in both normal and abnormal complexes, the normal carbene signal is seen at 172.4 ppm (**6a**) while the abnormal carbene signal comes at 170.2 ppm (**7a**). This is in contrast with the corresponding imidazolium ligands, studied previously, where normal (~170 ppm) and abnormal (~150 ppm) carbene signals were significantly different form each other and could be used as a diagnostic shift to determine the binding mode [14]. The similarity of carbene chemical shifts for triazolium ligands can be explained by similar electronic environment of the two carbon positions, with both being flanked by two nitrogens, which was not the case in the imidazolium ring. Full characterization of the representative complexes, normal and abnormal (**6a** and **7a**) is reported in the experimental section and supplemental information.

2.4. *Structure determination of **6a** and **7a***

X-ray quality crystals were grown by layering a solution of **6a** or **7a** (Fig. 3) in chloroform with pentane and the complexes were fully characterized by X-ray diffraction. The crystal structure of **6a** showed chloroform molecules hydrogen-bonded to the bromide counterions as well as the presence of two conformers of the iridium complex which differed significantly only by having different orientations of the phenyl groups in one of the trans phosphines with the remainder of the complex being essentially the same. For complex **7a**, the structure also contained a single $[BF_4]^-$ anion and a single chloroform molecule, each disordered over two distinct orientations. The *N*-methyl-*N*'-(2-pyridyl-methyl)triazole-3-ylidene ligand of the complex cation was also disordered over two orientations, effectively superimposing the 5-membered triazole ring of the minor component (~10 % occupancy) on the major-

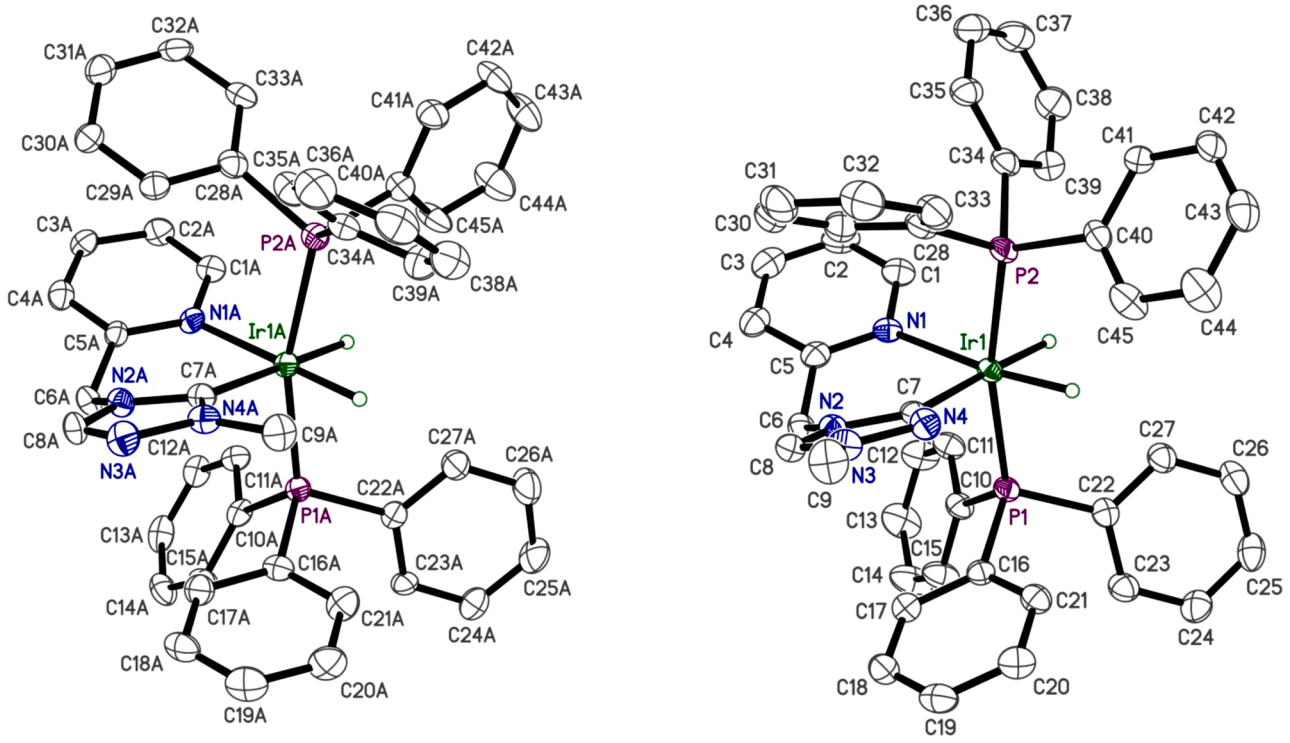


Fig. 3. A diagram of one conformer of 6a (left) with 30 % probability ellipsoids. The other conformer differs in the orientations of the phenyls attached to P2. Bromide anions, solvent and hydrogens (other than the two attached to Ir1A) were removed to enhance clarity. A diagram of **7a** (right) with 50 % probability ellipsoids. A minor (~10 %) disorder component, a [BF4]- anion, solvent and hydrogens (other than the two attached to Ir1) were removed to enhance clarity.

component (~90 %) 6-membered pyridine ring, and vice versa.

The triazole-pyridine complex in **6a** deviates from planarity with a dihedral angle of 31.6° between the plane of the pyridine and triazole rings in one conformer and 32.3° in the other. The analogous dihedral angle between triazole and pyridine rings in **7a** is 42.8 (2)°. Iridium carbon bond distances in both complexes are similar. In the normal compound **6a** the of Ir-C7 (crystallographic numbering) bond length is 2.086 Å and 2.061 Å and in the abnormal complex **7a**, the Ir-C7 bond length is 2.072 Å. This again contrasts with what was seen in the imidazolium counterparts, where the iridium carbon bond length was significantly different between the two complexes [14]. This is not unexpected, since the two carbon atoms are now much more similar. Selected bond distances and angles are listed in Table 2.

2.5. Counterion dependence

We have tried a wide variety of counterions for this paper with the results shown in Table 3. Only the bromide ligands give the normal carbene complex as a major product. All other counterions gave the abnormal carbene as major product. The only counterion that showed clear evidence of both forms of binding was BF_4 (R = Me) with 88 % abnormal and 12 % normal carbene (by ^{1}H NMR). In the prior imidazole case, this ratio was more equal, 55 % abnormal and 45 % normal [17]. Moving to a larger R group (iPr) biases the ratio of **6** to **7** in favor of the abnormal product, with ligand **5** (X = BF_4) giving only abnormal product **7b** All other reactions gave only one type of binding within experimental error (~1 %). In addition, we did not observe any interconversion of **6** to **7** or vice versa. The products appear very stable in air and in solution with no changes observed after weeks of standing.

A comparison between the triazolium results reported here and those obtained in the prior work on the imidazolium analogues [17,18] shows that the former has a higher preference for abnormal binding. We ascribe this to the greater electronic similarity of the two binding sites in the triazolium case where both sites have flanking ring nitrogens, compared with the imidazolium ligand where only the normal binding site has two such flanking ring nitrogens, the abnormal site having just one such ring nitrogen. The results in Table 3 are consistent with our prior explanation [18] as well as illustrating the effects of sterics in the case of the iPr substituted tetrafluoroborate, which gives the abnormal NHC while the methyl substituted ligand gave a mixture of normal and abnormal.

Previous work on the pyridine functionalized imidazolium salts, showed that the normal and abnormal carbenes formed from the reaction with $Ir(H)_5(PPh_3)_2$ occur via different paths, C2 (N path) and C5 (AN path) depending on the anion involved [18]. Tight ion pairing between the cationic complex and the anion account for the different outcomes. Similar reasoning can be used here in the reactions of pyridine functionalized triazolium salts with $Ir(H)_5(PPh_3)_2$. It is again likely that formation of the normal and abnormal carbenes occur via different mechanisms as mentioned above. The bromide ion can accelerate proton transfer from the triazolium moiety to the iridium metal center due to its strong H—Br interaction. This leads to the formation of the normal triazolium carbene. Other counterions that were used promote the abnormal pathway that involves oxidative addition step, which shows little anion dependance.

Table 2
Bond Distances (Å) and Angles (°) for 6a and 7a.

	6a (mol A)	6a (mol B)	7a[a]
Ir1-P1	2.2859(16)	2.2881(16)	2.2814(7)
Ir1-P2	2.3096(16)	2.3185(17)	2.3160(7)
Ir1-N1	2.186(4)	2.213(5)	2.221(3)
Ir1-C7	2.086(6)	2.061(6)	2.072(3)
P1-Ir-P2	163.03(6)	163.45(6)	165.77(2)
N1-Ir-C7	89.2(2)	89.5(2)	88.79(11)

[a] Major disorder component [90.4(3)%] only.

Table 3
Ratio of abnormal and normal products from scheme 2 for various alkyl groups, R and anions, X.

R	X	Normal (**6a, 6b**)	Abnormal (**7a, 7b**)
Methyl	Br	>99	<1
Methyl	BF_4	12	88
Methyl	SbF_6	<1	>99
Methyl	PF_6	<1	>99
Methyl	Tosylate	<1	>99
Methyl	$B(Ph)_4$	<1	>99
Methyl	Acetate	<1	>99
Methyl	Triflate	<1	>99
Isopropyl	Br	>99	<1
Isopropyl	BF_4	<1	>99
Isopropyl	SbF_6	<1	>99
Isopropyl	PF_6	<1	>99
Isopropyl	Tosylate	<1	>99
Isopropyl	Triflate	<1	>99

3. Conclusions

We have shown that the counter-anion effect on the azole binding mode is not only limited to imidazole, but it also extends to triazoles with the same pattern holding as before. The best H-bonder, bromide anion, favors the formation of the normal carbene, while the other weaker H-bonders favor abnormal binding. By analogy with prior work, the origin of this phenomenon can be traced to an interaction of the bromide ion with the acidic H substituent at the C-5 position of the azole ring.

4. Experimental

4.1. General methods

$IrH_5(PPh_3)_2$ (**1**) [24] and 1-isopropyl-1,2,4-triazole [25] were prepared according to literature methods and all other reagents were commercially available and were used as received. All NMR spectra were recorded at room temperature on Bruker spectrometers operating at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), or JEOL spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR) and referenced to $SiMe_4$ (in ppm, J in Hz). Assignments are based on COSY and HMQC spectroscopy. Elemental analyses were performed by Atlantic Microlab, Inc; residual solvent molecules have been identified by ^{1}H NMR.

4.2. Synthesis of N-Methyl-N'-(2-pyridylmethyl) triazolium bromide (4) and N-Isopropyl-N'-(2-pyridylmethyl) triazolium bromide (5)

2-Bromomethylpyridine hydrobromide (1.00 g, 4.0 mmol) was neutralized with saturated sodium carbonate, and extracted into 3 × 30 ml diethyl ether at 0 °C. The solution was then dried with $MgSO_4$ and added to a solution of 1-methyl-1,2,4-triazole (0.332 g, 4.00 mmol) in 150 mL methanol (anhydrous) or to a solution of 1-isopropyl-1,2,4-triazole (0.445 g, 4.00 mmol) in 30 mL 1,4-dioxane (anhydrous). Diethyl ether was then removed under reduced pressure and the resulting methanol or dioxane solutions were refluxed for 24 h. The solution of **4** in methanol turned red after a few hours and solution of **5** turned yellow with a dark precipitate also forming after a few hours. After 24 h, the solutions were cooled to room temperature and methanol or dioxane were removed in vacuo to give an oil. Both **4** and **5** can be purified by repetitive precipitation with methanol/diethyl ether. Analytically pure crystals can be grown from by diffusion of methanol into diethyl ether. Yield: 0.670 g (66 %) for **4** and 0.550 mg (49 %) for **5**.

Full characterization of ***4***: ^{1}H NMR (DMSO, 298 K): δ 10.17 (s, 1H, H_{trz}), δ 9.29 (s, 1H, H_{trz}), δ 8.55 (d, 1H, $^3J_{HH}$ 4.8 Hz, H_{py}), δ 7.91 (t, 1H, $^3J_{HH}$ 7.7 Hz, H_{py}), δ 7.57 (d, 1H, $^3J_{HH}$ 7.8 Hz, H_{py}), δ 7.42 (t, 1H, $^3J_{HH}$ 4.9 Hz,H_{py}), δ 5.70 (s, 2H, CH_2), δ 4.12 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (DMSO,

298 K): δ 152.06 (C_{py}), 148.80 (C_{py}), 145.28 (C_{tz}), 143.53 (C_{trz}), 138.58 (C_{py}), 124.14 (C_{py}), 123.12 (C_{py}), 50.70 (CH_2), 39.73 (CH_3); Anal. Calcd. for $C_9H_{11}BrN_4$ (255.12) x H_2O: C, 39.58; H, 4.80; N, 20.51. Found: C, 39.27; H, 4.76; N, 20.19.

4.3. Anion exchange procedure

A measured amount of the bromide ligand precursor (~100 mg) was combined with either one equivalent of the silver anion salt or ten equivalents of the sodium anion salt in 20 mL CH_2Cl_2 or acetone. This suspension was then stirred overnight at room temperature in the dark and the product filtered off. Yields were usually quantitative.

4.4. Synthesis of (η^2-C,N)(N-Methyl-N'-(2-pyridyl-methyl)triazole-5-ylidene)bis(hydrido)-bis(triphenylphosphine)iridium(III) bromide **(6a)** and (η^2-C,N)(N-Isopropyl-N'-(2-pyridyl-methyl)triazole-5-ylidene)bis(hydrido)-bis(triphenylphosphine)iridium(III) bromide **(6b)**

A mixture of ligand **4** with $X = Br^-$ (20 mg, 0.08 mmol) or ligand **5** with $X = Br^-$ (23 mg, 0.08 mmol) and $Ir(H)_5(PPh_3)_2$ (55 mg, 0.08 mmol) in THF (5 mL) was vigorously refluxed in air. After 20 min. solution turned yellow. Refluxing is continued for 2 more hours. After the reaction mixture had cooled to room temperature, 50 mL pentane was added to the clear solution. This resulted in formation of an off-white precipitate which was collected and dried under vacuum. Yield: 63 mg (81 %) for **6a** and 60 mg (75 %) for **6b** The complex can be recrystallized from $CHCl_3$/pentane.

*Full characterization of **6a**.* ^{1}H NMR ($CDCl_3$, 298 K): δ 8.95 (s, 1H, H_{trz}), δ 8.04 (d, 1H, $^3J_{HH}$ 7.9 Hz, H_{py}), δ 7.98 (d, 1H, $^3J_{HH}$ 5.60 Hz, H_{py}), δ 7.53 (t, 1H, $^3J_{HH}$ 7.6 Hz, H_{py}), δ 7.35–7.19 (m, 30H_{ph}), δ 6.18 (t, 1H, $^3J_{HH}$ 6.6 Hz, H_{py}), δ 5.49 (s, 2H, CH_2), δ 2.80 (s, 3H, CH_3), δ −10.76 (dt, 1H, $^2J_{HP}$ 19.6 Hz, $^2J_{HH}$ 5.2 Hz, Ir-H), δ −21.09 (dt, 1H, $^2J_{HP}$ 17.2 Hz, $^2J_{HH}$ 5.4 Hz, Ir-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 172.45 (t, J_{PC} = 6.8 Hz, $C_{carbene}$), 160.93 (C_{py}), 152.91 (C_{trz}), 143.34 (C_{py}), 138.14 (C_{py}) 133.87 (t, J_{PC} = 27.1 Hz, C_{ph}), 133.31 (t, J_{PC} = 5.9 Hz, C_{ph}), 130.50 (C_{ph}), 128.46 (t, J_{PC} = 5.0 Hz, C_{ph}), 127.44 (C_{py}), 124.04 (C_{py}), 52.37 (CH_2), 38.36 (CH_3); $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K): δ 16.72; Anal. Calcd. for $C_{45}H_{42}BrIrN_4P_2$ (972.93) 1/2$CHCl_3$: C, 52.92; H, 4.15; N, 5.43. Found: C, 53.12; H, 4.17; N, 5.47.

4.5. Synthesis of (η^2-C,N)(N-Methyl-N'-(2-pyridyl-methyl)triazole-3-ylidene)bis(hydrido)-bis(triphenylphosphine)iridium(III) tetrafluoroborate **(7a)** and (η^2-C,N)(N-Isopropyl-N'-(2-pyridyl-methyl)triazole-3-ylidene)bis(hydrido)-bis(triphenylphosphine)iridium(III) tetrafluoroborate **(7b)**

A mixture of ligand **4** with $X = BF_4^-$ (21 mg, 0.08 mmol) or ligand **5** with $X = BF_4^-$ (23 mg, 0.08 mmol) and $Ir(H)_5(PPh_3)_2$ (55 mg, 0.08 mmol) in THF (5 mL) was vigorously refluxed in air. After 20 min. a clear solution was obtained. Heating under reflux was continued for 2 more hours. After the reaction mixture had cooled down to room temperature, 50 mL pentane was added to the clear solution. This resulted in formation of an off-white precipitate which was collected and dried under vacuum. Yield: 59 mg (75 %) for **7a** and 60 mg (74 %) for **7b** The complex can be recrystallized from $CHCl_3$/pentane.

*Full Characterization of **7a**.* ^{1}H NMR ($CDCl_3$, 298 K): δ 9.10 (s, 1H, H_{trz}), 8.09 (d, 1H, $^3J_{HH}$ = 5.5 Hz, H_{py}), 7.52–7.41 (m, 2H, H_{py}), 7.31–7.17 (m, 30H, H_{ph}), 6.21 (t, $^3J_{HH}$ = 6.6 Hz, H_{py}), 4.72 (s, 2H, CH_2), 3.46 (s, 3H, CH_3), −10.69 (dt, $^2J_{PH}$ = 20.1 Hz, $^2J_{HH}$ = 5.0 Hz, Ir-H), −20.94 (dt, $^2J_{PH}$ = 17.1 Hz, $^2J_{HH}$ = 5.2 Hz, Ir-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 170.25 (t, J_{PC} = 7.7 Hz, $C_{carbene}$), 161.71 (C_{py}), 152.41 (C_{trz}), 139.20 (C_{py}), 137.80 (C_{py}) 134.88 (t, J_{PC} = 26.9 Hz, C_{ph}), 133.69 (t, J_{PC} = 6.1 Hz, C_{ph}), 129.93 (C_{ph}), 128.03 (t, J_{PC} = 4.5 Hz, C_{ph}), 126.40 (C_{py}), 124.40 (C_{py}), 52.13 (CH_2), 37.21 (CH_3); $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K): δ 18.54; Anal. Calcd. for $C_{45}H_{42}BF_4IrN_4P_2$ (979.83) 1/2$CHCl_3$: C, 52.57; H, 4.12; N, 5.39. Found: C, 53.01; H, 4.12; N, 5.41.

4.6. Crystal structure determination

*Crystal data for **(6a)**.* Single crystals of $C_{102}H_{110}Br_2Cl_6Ir_2N_8P_4$ were obtained upon crystallization from a mixture of chloroform and pentane. A suitable crystal was selected and data collected on a Nonius Kappa CCD diffractometer. The crystal was kept at 183 K during data collection. Using Olex2 [26], the structure was solved with the SHELXT [27] structure solution program and refined with the SHELXL [28] refinement package using Least Squares minimization. Chloroform molecules were also found in the structure. Voids were found consistent with inclusion of pentane and a solvent mask was included using BYPASS/SQUEEZE [29,31] to account for two pentanes per formula unit (including two iridium complexes, two bromides and two chloroforms). Additional information can be found in the full details of the X-ray structure determination (CIF). CCDC number 2426143 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

$C_{102}H_{110}Br_2Cl_6Ir_2N_8P_4$ (M = 2328.77 g/mol): triclinic, space group P-1 (no. 2), a = 17.2507(4) Å, b = 17.2726(4) Å, c = 18.3147(4) Å, α = 81.5338(9)°, β = 70.1510(10)°, γ = 86.0290(10)°, V = 5075.9(2) Å^3, Z = 2, T = 183 K, μ(MoKα) = 3.676 mm^{-1}, $Dcalc$ = 1.524 g/cm^3, 32,891 reflections measured (3.588° ≤ 2Θ ≤ 54.966°), 22,392 unique (R_{int} = 0.0513, R_{sigma} = 0.1299) which were used in all calculations. The final R_1 was 0.0541 ($I > 2\sigma(I)$) and wR_2 was 0.1063 (all data).

*Crystal data for **(7a)**.* Single crystals of $C_{46}H_{43}BCl_3F_4IrN_4P_2$ were grown from a mixture of chloroform and pentane. A suitable specimen was mounted using polyisobutane oil at 100 K for data collection on a Bruker D8 Venture dual-microsource diffractometer. The structure was solved using the dual-space direct methods program SHELXT [27] and refined by full-matrix least-squares using SHELXL [28]. Model building and refinement were carried out within ShelXle [30]. The hydrogen atoms directly attached to iridium in **7a** were refined, subject to distance and angle-distance restraints. In addition to the main cation of interest, the structure also contained a single $[BF_4]^-$ anion and a single chloroform molecule, each disordered over two distinct orientations. The *N*-methyl-*N'*-(2-pyridyl-methyl)triazole-3-ylidene ligand of the complex cation was also disordered over two orientations, effectively superimposing the 5-membered triazole ring of the minor component (~10 % occupancy) on the major-component (~90 %) 6-membered pyridine ring, and vice versa. Additional information can be found in the full details of the X-ray structure determination (CIF). CCDC number 2435325 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

$C_{46}H_{43}BCl_3F_4IrN_4P_2$ (M = 1099.14 g/mol): triclinic, space group P-1 (no. 2), a = 11.0358(2) Å, b = 11.2428(2) Å, c = 18.9064(3)Å, α = 74.110(1)°, β = 88.153(1)°, γ = 84.507(1)°, V = 2245.74(7) Å^3, Z = 2, T = 100.0(2) K, μ(MoKα) = 3.277 mm^{-1}, $Dcalc$ = 1.625 g/cm^3, 99,928 reflections measured (3.71° ≤ 2Θ ≤ 55.00°), 10,325 unique (R_{int} = 0.0591, R_{sigma} = 0.0327), which were used in all calculations. The final R_1 was 0.0232 ($I > 2\sigma(I)$) and wR_2 was 0.0471 (all data).

CRediT authorship contribution statement

Anes Kovacevic: Writing – review & editing, Writing – original draft, Resources, Project administration, Investigation, Formal analysis, Data curation, Conceptualization. **J.W. Faller:** Resources, Investigation, Formal analysis. **Sean Parkin:** Investigation, Resources, Formal analysis.

Declaration of competing interest

There are no competing interests to declare.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2025.123681.

Data availability

The data supporting the findings of this study are available within the article and its supplementary materials. Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk/structures).

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