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A Tetracyclic Bis(imidazolindiylidene) Ligand and Its Diiridium and Dipalladium Complexes

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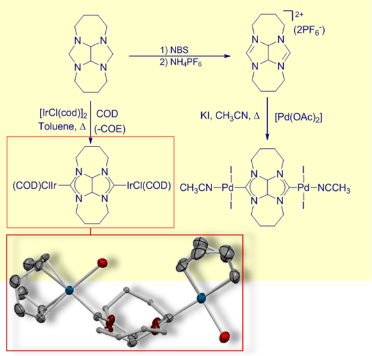
Supporting Information

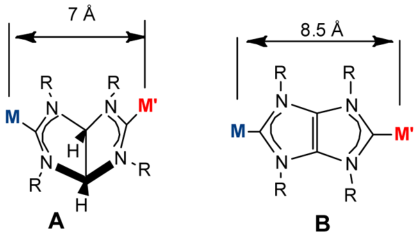
ABSTRACT: A bis(imidazolidine) with two butylene linkers between the nitrogen atoms of the adjacent heterocycles has been prepared. This tetracyclic molecule can be coordinated to iridium and palladium following two different methodologies. The coordination to iridium is achieved by double C(sp^3)−H activation of the neutral tetracyclic bis(imidazolidine), which reacts with $[IrCl(COD)]_2$ to afford the corresponding bis-NHC complex that contains two IrCl(COD) fragments. The reaction is facilitated by the addition of 1,5-cyclooctadiene, which is released from the reaction as cyclooctene. The reaction of the bis-NHC[IrCl(COD)] (bis-NHC = bis(imidazolindiylidene)) complex with CO allows the formation of the corresponding tetracarbonyl complex of diiridium. The molecular structures of the two iridium complexes have been determined by means of X-ray crystallography. The reaction of the tetracyclic bis(imidazolidine) with *N*-bromosuccinimide allows the formation of a tetracyclic bis(imidazolinium) salt, which serves as a traditional bis-NHC precursor. The reaction of this bis(imidazolinium) salt with $Pd(OAc)_2$ in the presence of KI and in acetonitrile allows the formation of the bis-NHC$[PdI_2(CH_3CN)]_2$ complex. The acetonitrile ligand can be easily replaced by reaction with 3-chloropyridine, affording the corresponding bis-NHC$[PdI_2(3\text{-Clpyr})]_2$ complex. The two palladium complexes were tested in the acylation of aryl halides with hydrocinnamaldehyde, showing moderate to low activity.



■ INTRODUCTION

In the search for new precursors to multifunctional materials, polytopic N-heterocyclic carbene ligands (NHCs) have emerged as very promising tools.[1] Among them, those featuring rigid geometrically isolated carbene moieties that prevent chelation have recently found great utility as building blocks for novel macromolecules with structurally dynamic characteristics and useful electronic properties.[2] In this regard, there is a growing interest in the development of polytopic carbenes for the design of molecular and supramolecular systems with electronically communicating metal centers.[2e,3] Typically, through-ligand metal−metal electronic communication is envisioned as taking place via the delocalized π orbitals of the bridging ligand, as a consequence of the arguable interaction between the metal d_π orbitals and the π-delocalized system of the NHC ligand through the M═C π back-bonding. However, we recently proved that the presence of an extended π-delocalized linker has little effect in the electronic communication between the metals bound to a poly-NHC ligand[4] and that the electronic interaction between NHC-bridged bimetallic complexes decays exponentially against the through-ligand metal-to-metal separation. These observations were especially relevant when comparing fused bis(imidazolinylidenes) (**A**; Scheme 1), and fused bis(imidazolylidenes) (**B**), which displayed similar electronic interactions between the metals, despite their obvious differences in terms of π-delocalization along the ligand. This fact, together with the synthetic difficulties found for the preparation of bis(imidazolylidenes) of type **B**,[5] and their coordination to metal fragments, make bis(imidazolinylidenes) of type **A** especially valuable synthons for the preparation of bimetallic complexes and metallic-based polymers with interesting applications. Additionally, we believe that the shorter intermetallic distance in bis(imidazolinylidenes) due to their folded geometry that approaches the metals, in comparison to the situation in **B**, may provide the dimetallic structure with additional benefits in terms of positive catalytic effects. It is well accepted that catalysts containing multiple metal centers in close proximity can lead to better reactivity in comparison to that for the related monometallic systems, in particular for second-order kinetic dependence on the catalyst,[6] an effect that we have already proved several times using rigid poly-NHC ligands.[7]

Scheme 1. Fused Bis(imidazolinylidenes) (A) and Bis(imidazolylidenes) (B)



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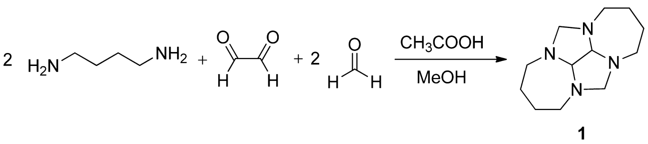
For the coordination of bis(imidazolinylidenes) to rhodium and iridium, we recently used the corresponding neutral tetraazabicyclooctane (or bis(imidazolidine)) as the bis-NHC precursor.[8] The formation of the bis-NHC implied a double geminal C−H bond activation of the methylene groups of the bis(imidazolidine), which was facilitated by the presence of an external diolefin (1,5-cyclooctadiene or norbornadiene), acting as a hydrogen acceptor. The reaction constituted one of the very rare examples of conversions of neutral N-heterocycles into NHC complexes.[9] In order to extend the coordination of this type of bis-NHC ligands to other metals, and therefore widen the scope of its applicability, we herein describe the preparation of a new series of bis(imidazolinylidene)-based complexes, using two synthetic protocols: (i) the double C−H activation methodology, starting from a neutral bis(imidazolidine) and (ii) the traditional use of a bis(azolium) salt in the presence of a base.

■ RESULTS AND DISCUSSION

As we already discussed in the Introduction, in a previous work we used a tetrabenzyl-substituted bis(imidazolidine) for the preparation of a series of Rh and Ir bis-NHC complexes by double geminal C−H bond activation of the NCH_2C groups.[8] The presence of the benzyl groups was convenient, in the sense that it facilitated the preparation of the starting ligand precursor in high yield, in comparison to the yields obtained for other starting materials, such as those containing *N*-Me or other *N*-alkyl groups. However, its coordination to the metal fragments afforded mixtures of atropisomers due to the restricted rotation of the benzyl rings about the C−N bond, therefore sometimes yielding to mixtures of complexes that were difficult to identify. In order to circumvent this problem, we decided to synthesize a bis(imidazolidine) analogue in which the N substituents have been substituted by a butylene linker between the nitrogen atoms of adjacent heterocycles (**1**, in Scheme 2). This new situation avoids the potential formation of atropisomers due to rotation of the N substituents, therefore simplifying the resulting mixture of complexes obtained after coordination. Additionally, the resulting tetracyclic ligand provides the complex with an unusual asymmetric "pocket-type" topology, in which the two faces of the ligand (inner and outer sides) may provide the metal complexes with unusual reactivity patterns.

Scheme 2. Synthesis of Tetracyclic Compound 1



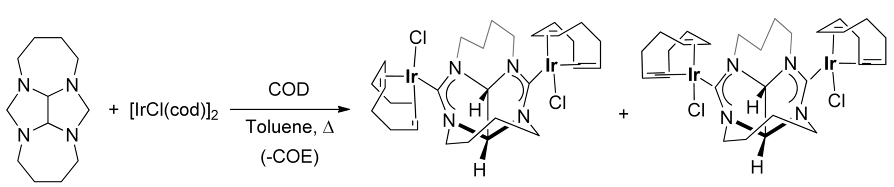
1

The tetracyclic bis(imidazolidine) **1** was prepared by condensation of formaldehyde with 1,4-diaminobutane, in a manner similar to that described in the literature for related bis(imidazolidines) containing noncyclic N substituents (Scheme 1).[2] Formaldehyde and glyoxal were subsequently added to a methanolic solution of 1,4-diaminobutane and acetic acid. After purification, the desired product could be obtained as a white crystalline solid in 50% yield.

The reaction of **1** with $[IrCl(COD)]_2$ in the presence of an excess of 1,5-cyclooctadiene in refluxing toluene afforded a 1:1 mixture of isomers **2a**,**b** (Scheme 3). Isomers **2a**,**b** were easily separated by column chromatography on silica gel (33% and 30% yields, respectively). The two isomers are two of the three possible atropisomers resulting from the two different relative orientations of the iridium fragment about the ligand, with the chlorine atom pointing toward the inner cavity or outside the cavity, which in the case of **2a**,**b** results in the formation of the anti (**2a**) and syn (**2b**) conformers. Complexes **2a**,**b** were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. Additionally, the molecular structure of isomer **2a** was unambiguously confirmed by means of X-ray analysis. The most significant resonances in the ^{13}C NMR spectra of **2a**,**b** are those assigned to the metalated carbene carbons, at 208.5 and 208.3 ppm for **2a** (the two different signals are consistent with the two different coordination environments of the two carbenes) and at 207.9 ppm for **2b**.

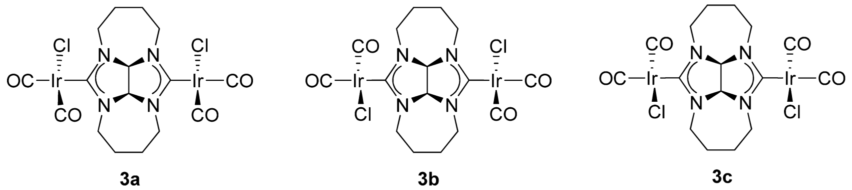
In order to shed some light on the electron-donating ability of the new ligand, the dimetallic complexes **2a**,**b** were transformed into their corresponding carbonyl derivatives. The displacement of the COD ligand by CO was carried out by bubbling carbon monoxide into a solution of the complex **2a** (or **2b**) in CH_2Cl_2 at 0 °C. Regardless of the starting complex used (**2a** or **2b**), the carbonylation always led to a mixture of the same two isomers in a 62:38 molar ratio, which we attributed to the restricted rotation about the M−C carbene bond. As a consequence of the ligand exchange, the formation of three different isomers (Scheme 4) should be expected, resulting from two possible orientations of the chloride ligand relative to the bicyclic bis-NHC. However, only two isomers were clearly observed by NMR spectroscopy in both reactions. Variable-temperature NMR experiments showed that these atropisomers do not interconvert on the NMR time scale. Unfortunately, we were unable to separate the two isomers by column chromatography, and therefore we could not discard the notion that the two isomers may interconvert at a lower reaction rate. However, we were able to obtain single crystals of **3a**, which allowed us to unambiguously determine its molecular structure by means of X-ray diffraction (vide infra). The ^{13}C NMR of the mixture of the two isomers of **3** reveals the presence of three signals due to metalated carbene carbons (201.9, 200.7, and 200.3 ppm) and six signals attributed to the CO ligands (181.1, 181.0, 180.9, 167.9, 167.2, and 166.6 ppm). The number of signals is in agreement with the presence of the two isomers. In one of the isomers observed (**3a**), the two metal fragments are expected to be symmetry related; therefore,

Scheme 3. Synthesis of 2a,b



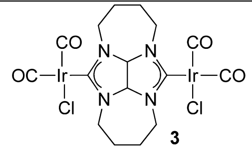
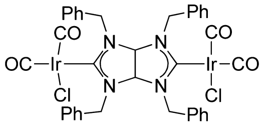
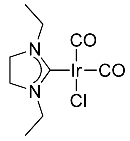
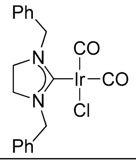
1 **2a** **2b**

Scheme 4. The Three Expected Isomers for the Carbonyl Derivatives of 3[a]



[a]Only **3a,b** were obtained.

Table 1. Carbonyl Stretching Frequencies of Ir(NHC)Cl(CO)$_2$ Complexes Related to 3

Complex	ν(CO)(cm^{-1})[a]	ν$_{av}$(CO)(cm^{-1})	TEP(cm^{-1})[b]
 **3**	2073, 1990	2032	2057
	2071, 1986[8]	2029	2054
	2057, 2001[11]	2029	2055
	2051, 2001[12]	2026	2052

[a]IR data obtained in CH_2Cl_2. [b]Value calculated by linear regression from the experimentally measured ν_{av}(CO) value of the [LIrCl(CO)$_2$] complex using TEP = 0.847[ν_{av}(CO)] + 336.[10c]

one signal due to the metalated carbons and two signals due to the CO ligands can be assigned to **3a**. The molecular structure of this complex confirmed this assumption and allowed us to assess that this 2-fold symmetry spectrum should be assigned to **3a** and not to **3c** (also presenting symmetry-related metal fragments but not detected by NMR).

The existence of the different isomers has little effect on the local symmetry about the metals and on the electron-donating power of the ligands, and this justifies why the IR spectrum of **3** displays only two CO stretching bands at 2073 and 1990 cm^{-1}, consistent with the cis disposition of the carbonyl ligands. Table 1 shows the IR data corresponding to relevant Ir(I) complexes with saturated NHCs. In comparison to our previously reported tetrabenzylated analogue,[8] compound **3** exhibits a higher ν_{av}(CO) value by about 3 cm^{-1}, which reveals its lower σ-donor strength. The same tendency is observed when the *N*-benzyl group is replaced by an *N*-ethyl group in mono(imidazolinylidenes), as can be seen by comparing the data shown in Table 1. In comparison to the related monocarbenes, the ν_{av}(CO) values of the bis(carbenes) reveal their lower electron donicity, most likely due to the relative inductive effect promoted by the presence of the second metal fragment. Although it is now well accepted that the TEP values can be obtained from the appropriate correlations using the ν_{av}(CO) frequencies of [Ir(L)Cl(CO)$_2$] complexes,[10] the value of 2057 cm^{-1} that we have estimated for the TEP value of **3** must be considered with caution, both because it corresponds to a mixture of atropisomers and because it refers to a binuclear tetracarbonylated complex, for which the correlations are not known to be accurate.

The molecular structures of **2a** and **3a** were unambiguously confirmed by means of X-ray diffraction analysis. The molecular structure of **2a** (Figure 1) confirms that the tetracyclic bis-NHC is bridging two iridium fragments, each of which complete their coordination spheres with a chloride and a COD ligand. The relative conformation of the two metal fragments is anti, with one of the chloride ligands pointing toward the inner cavity of the ligand and the other chloride pointing out of the cavity. The average Ir−C$_{carbene}$ distance is 2.019 Å. Due to the folded geometry of the NHC ligand, the through-space distance between the two metals is 6.885 Å, significantly shorter than that of the dimetallic Ir(I) complex bearing a benzyl-substituted bis(imidazolinylidene) ligand reported by our group (7.17 Å).[8] The two planes defined by the backbone-connected azole rings are at an angle of 64.89°, and the distance between the two carbene carbon atoms is 3.691 Å.

The molecular structure of the tetracarbonylated complex **3a** is shown in Figure 2. The structure shows that the bis(imidazolinylidene) ligand is bridging the two iridium fragments, which complete their coordination sphere with a

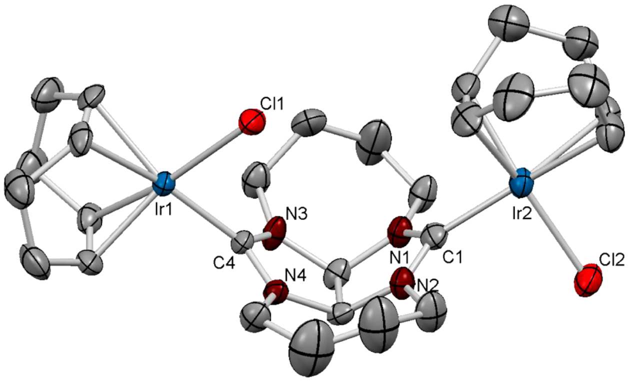


Figure 1. Molecular structure of compound **2a**. Solvent ($CHCl_3$ and CH_2Cl_2) and hydrogen atoms have been omitted for clarity. Ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): Ir(1)−C(4) = 2.017(7), Ir(1)−Cl(1) = 2.368(19), Ir(2)−C(1) = 2.021(8), Ir(2)−Cl(2) = 2.366(2); C(4)−Ir(1)−Cl(1) = 85.2(2), C(1)−Ir(2)−Cl(1) = 89.2(2), N(3)−C(2)−N(1) = 113.1(7), N(2)−C(3)−N(4) = 113.2(6).

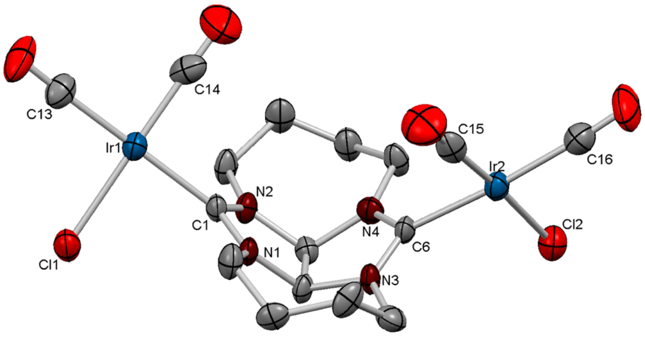
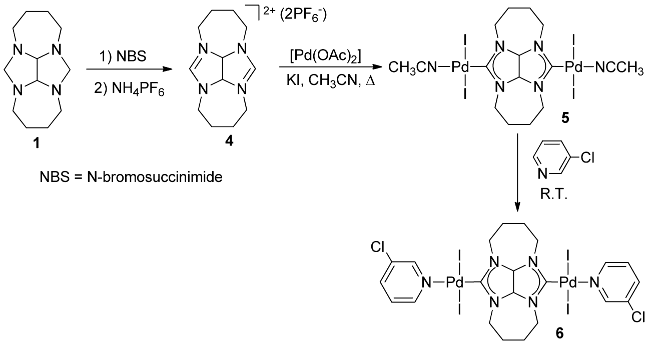


Figure 2. Molecular structure of compound **3a**. Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) = 2.080(14), Ir(1)−Cl(1) = 2.342(4), Ir(1)−C(14) = 1.83(2), Ir(1)−C(13) = 1.918(17), Ir(2)−C(6) = 2.081(14), Ir(2)−Cl(2) = 2.344(4), Ir(2)−C(15) = 1.86(2), Ir(2)−C(16) = 1.913(19); C(1)−Ir(1)−Cl(1) = 86.8(4), C(1)−Ir(1)−C(13) = 176.6(7), C(6)−Ir(2)−Cl(2) = 88.9(4), C(6)−Ir(2)−C(16) = 174.4(7).

chloride and two carbonyl ligands. The two chloride ligands are pointing toward the outer side of the ligand, in a syn conformation relative to the two metal fragments, although the two metal fragments deviate from a fully eclipsed conformation by 68.9° (as measured by the torsion angle C(14)−Ir(1)−Ir(2)−C(15)). The average Ir−$C_{carbene}$ distance is 2.08 Å, and the through-space distance between the two metals is 7.11 Å, significantly longer than the distance between the two iridium centers in **2a**. The angle established between the planes of the azole rings is 64.42°, and the distance between the carbene carbon atoms is 3.708 Å; therefore, both parameters are very similar to those shown by **2a** and indicate that the differences in the metal-to-metal distances should be ascribed to the longer Ir−C bond distances in **2a** rather than to topological changes in the bis-NHC ligand.

In order to extend the coordination of bis(imidazolinylidenes) of type **A** (Scheme 1) to other metals for which the double C−H activation of bis(imidazolidines) may not be possible, we decided to use a more traditional synthetic protocol starting from the corresponding bis(imidazolinium) salts. The bis(azolium) salt **4** was obtained by oxidation of the bis(imidazolidine) **1** using *N*-bromosuccinimide (NBS), following previously described methods reported in the literature for other imidazolidines.[13] The desired dicationic salt was isolated as a white solid in 64% yield (Scheme 5). The ^1H NMR spectrum of **4** reveals the appearance of a signal at 8.99 ppm, which may be assigned to the acidic protons of the NC*H*N group.

Scheme 5. Synthesis of Bis(imidazolinium) Salt 4 and Pd(II) Complexes 5 and 6

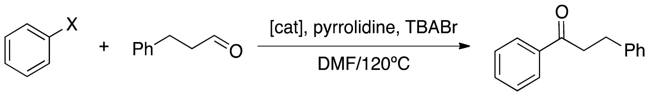


The reaction of the bis(azolium) salt **4** with $[Pd(OAc)_2]$ in refluxing acetonitrile in the presence of KI afforded the dipalladium complex **5**, which was obtained in 33% yield after purification by column chromatography. In the presence of 3-chloropyridine, the acetonitrile ligands in **5** were readily replaced, allowing the formation of complex **6** in 82% yield. Both complexes (**5** and **6**) were fully characterized by NMR spectroscopy, mass spectroscopy, and elemental analysis. The molecular structure of complex **5** was confirmed by an X-ray diffraction study, although the quality of the crystal did not allow us to obtain a molecular structure with the accuracy needed for publication. In order to supply additional information that could be used to assess the characterization of **5**, we have included an ORTEP diagram of the complex in the Supporting Information. The ^{13}C NMR spectra of **5** and **6** display signals due to the metalated carbons at 181.6 and 184.4 ppm, respectively.

We undertook a preliminary exploration of the catalytic activity of the new palladium complexes **5** and **6**. As an important benchmark reaction, we chose the acylation of aryl halides. Such a methodology, originally reported by Xiao and co-workers,[14] is of keen interest as a direct route to alkyl aryl ketones. It offers expanded scope over the classic Friedel−Crafts approach (which fails for electron-deficient arenes), while also minimizing the requirement for hazardous reagents. Perhaps surprisingly, given this potential importance, only a small number of examples have been reported to date,[15] a few of which include intermolecular processes.[7i,14,15c,d]

We tested the catalytic activity of complexes **5** and **6**, at 120 °C in DMF, in the presence of pyrrolidine, and using almost equimolecular amounts of aryl halide (0.5 mmol) and hydrocinnamaldehyde (0.6 mmol), in order to simulate the most atom-efficient conditions. As seen from the data shown in Table 2, both complexes afford very modest outcomes, especially in comparison to other catalysts previously described.[9,14,16] The activity of the 3-chloropyridine-supported catalyst **6** is higher than that of the acetonitrile-based complex **5**, in agreement with other published results.[7i]

Table 2. . Acylation of Aryl Halides with Hydrocinnamaldehyde[a]



entry	catalyst	X	yield (%)
1	**5**	I	35
2	**6**	I	45
3	**5**	Br	12
4	**6**	Br	15

[a]Reactions were carried out with XAr (0.5 mmol), hydrocinnamaldehyde (0.6 mmol), pyrrolidine (1 mmol), 4 Å MS (1 g), and catalyst (2 mol %) in DMF (2 mL) at 120 °C for 16 h. Yields were obtained by GC analysis using anisole as internal reference.

■ CONCLUSIONS

A set of metal complexes bearing a tetracyclic back-to-back bis(imidazolinylidene) ligand have been prepared. The complexes were obtained by two methodologies, namely the double C−H activation of the C−H bond of a neutral N-heterocycle (iridium) and the classical route implying the deprotonation of a bis(imidazolinium) salt (palladium). The combination of this new ligand with the two coordination strategies widens the applicability of this scaffold with its unique folded topology to the preparation of new di- and polymetallic structures whose stereochemical properties may give rise to interesting applications in the field of homogeneous catalysis and materials chemistry. Studies on the preparation of extended two- and three-dimensional structures using **1** are underway.

■ EXPERIMENTAL SECTION

The tetracyclic compound **1** was synthesized by condensation of formaldehyde and a diamine, in a manner similar to that reported in the literature.[16] Iridium-based complexes **2a,b** were synthesized by a method similar to that reported by us.[8] All reactions were carried out under nitrogen with standard Schlenk techniques unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS MBraun) or purchased from Aldrich 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 Varian Innova 300 and 500 MHz spectrometers, using $CDCl_3$, CD_3CN, or DMSO-d_6 as solvent. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as the drying and nebulizing gas. Infrared spectra (FTIR) were performed on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000−600 cm^{-1}.

Synthesis of 1. To a solution of 1,2-diaminobutane (4 mL, 40 mmol) and a few drops of acetic acid in methanol at 0 °C was added dropwise formaldehyde (3.3 mL of a 37% aqueous solution, 44 mmol). Glyoxal (2.5 mL of a 40% aqueous solution, 22 mmol) was then added dropwise over 30 min, while the temperature was kept at 0 °C. The solution was stirred for 7 days at room temperature. After this time, the solution was concentrated under reduced pressure, giving a red oil. The oil was then extracted 10 times with diethyl ether (10 × 10 mL). The combined organic layers were concentrated and washed with cold acetone, giving the desired product as a white crystalline solid. Yield: 2.2 g (50%). ^1H NMR (300 MHz, $CDCl_3$): δ 4.14 (s, 2H, CH_{bridge}), 3.43 (d, $^2J_{H-H}$ = 3.0 Hz, 2H, NCH_2N), 3.27 (d, $^2J_{H-H}$ = 3.0 Hz, 2H, NCH_2N), 2.78−2.74 (m, 4H, NCH_2), 2.63−2.60 (m, 4H, NCH_2), 1.74−1.73 (m, 8H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.6 (CH_{bridge}), 74.4 (NCH_2N), 50.4 (NCH_2), 28.0 (CH_2). Electrospray MS (20 V, *m*/*z*): 223.4 $[M + H]^+$. Anal. Calcd for $C_{12}H_{24}N_4$ (222.3): C, 64.83; H, 9.97; N, 25.20. Found: C, 65.30; H, 9.86; N, 25.53.

Synthesis of Isomers 2a,b. A mixture of **1** (82.6 mg, 0.37 mmol), $[IrCl(COD)]_2$ (250 mg, 0.37 mmol), and 1,5-cyclooctadiene (457 μL, 3.7 mmol) was refluxed in dry toluene (10 mL) overnight. After removal of the volatiles, the crude solid was dissolved in CH_2Cl_2 and purified by column chromatography using silica gel. Using mixtures of CH_2Cl_2/acetone afforded the separation of two yellow bands that contained **2a** (95:5) and **2b** (75:25). Yield: 107.2 mg (33%) for **2a** and 98.3 mg (30%) for **2b**. Overall yield: 205.5 mg (62%).

*Isomer **2a**.* ^1H NMR (500 MHz, $CDCl_3$): δ 5.47 (s, 2H, CH_{brigde}), 4.87−4.82 (m, 4H, NCH_2), 4.49−4.47 (m, 4H, CH_{COD}), 3.50−3.45 (m, 2H, NCH_2), 3.34−3.29 (m, 2H, NCH_2), 2.94−2.93 (m, 4H, CH_{COD}), 2.10−2.08 (m, 8H, $CH_{2\ COD}$), 2.01−1.94 (m, 4H, CH_2), 1.91−1.83 (m, 4H, CH_2), 1.71−1.65 (m, 4H, $CH_{2\ COD}$), 1.62−1.53 (m, 4H, $CH_{2\ COD}$).^{13}C NMR (126 MHz, $CDCl_3$): δ 208.5 (Ir-$C_{carbene}$), 208.3 (Ir-$C_{carbene}$), 86.6 (CH_{COD}), 85.9 (CH_{COD}), 81.5 (CH_{bridge}), 54.3 (CH_{COD}), 51.9 (CH_{COD}), 50.1 (NCH_2), 50.0 (NCH_2), 33.4 ($CH_{2\ COD}$), 33.3 ($CH_{2\ COD}$), 29.2 ($CH_{2\ COD}$), 28.1 (CH_2), 26.8 (CH_2). Electrospray MS (20 V, *m*/*z*): 896.2 $[M - Cl + CH_3CN]^+$.

*Isomer **2b**.* ^1H NMR (500 MHz, $CDCl_3$) δ 5.55 (s, 2H, CH_{bridge}), 4.74−4.70 (m, 4H, NCH_2), 4.62−4.60 (m, 4H, CH_{COD}), 3.52−3.49 (m, 4H, NCH_2), 2.59−2.62 (m, 4H, CH_{COD}), 2.21−2.17 (m, 8H, $CH_{2\ COD}$), 1.99−1.94 (m, 8H, CH_2), 1.81−1.78 (m, 4H, $CH_{2\ COD}$), 1.71−1.65 (m, 4H, $CH_{2\ COD}$).^{13}C NMR (126 MHz, $CDCl_3$): δ 207.9 (Ir-$C_{carbene}$), 87.4 (CH_{COD}), 81.4 (CH_{bridge}), 52.9 (CH_{COD}), 50.2 (NCH_2), 50.1 (NCH_2), 33.4 ($CH_{2\ COD}$), 29.2 ($CH_{2\ COD}$), 27.8 (CH_2). Electrospray MS (20 V, *m*/*z*): 896.1 $[M - Cl + CH_3CN]^+$. Anal. Calcd for $C_{28}H_{42}Cl_2Ir_2N_4$ (890.00): C, 37.79; H, 4.76; N, 6.30. Found: C, 38.20; H, 4.65; N, 6.37.

Synthesis of 3a,b. CO gas was bubbled through a solution of isomer **2a** (or **2b**) in dichloromethane (5 mL) at 0 °C over 20 min. After the addition of hexanes, a light yellow solid precipitated. The solid obtained contained a mixture of complexes **3a,b** in a 62:38 ratio. Yield: 19.0 mg (71%). ^1H NMR (500 MHz, $CDCl_3$): δ 5.82 (s, 2H), 5.79 (s, 2H), 4.75−4.64 (m, 4H), 3.60−3.48 (m, 4H), 2.09−1.97 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 201.9, 200.7, 200.3, 181.1, 181.0, 180.9, 167.9, 167.2, 166.6, 82.2, 82.1, 51.1, 51.0, 50.9, 50.8, 26.9, 26.6. IR (KBr): ν(CO) 2073, 1990 cm^{-1}. Electrospray MS (20 V, *m*/*z*): 824.9 $[M + K]^+$. Anal. Calcd for $C_{16}H_{22}Cl_2Ir_2N_4O_4$ (789.71): C, 24.33; H, 2.81; N, 7.09. Found: C, 24.76; H, 2.72; N, 7.26.

Synthesis of 4. To a solution of **1** (500 mg, 2.25 mmol) in 1,2-dimethoxyethane (DME, 10 mL) was added dropwise a solution of *N*-bromosuccinimide (800 mg, 4.5 mmol) in DME (5 mL). The reaction mixture was stirred at room temperature for 3 h under the exclusion of light. After this time, the white solid that formed was separated by filtration and solubilized in methanol (10 mL). NH_4PF_6 (734 mg, 4.5 mmol) was then added in one portion to the methanolic solution, and the resulting suspension was stirred for 30 min at room temperature. The white solid that formed was separated by filtration and subsequently washed with cold methanol, yielding the desired dicationic salt. Yield: 483 mg (42%). ^1H NMR (300 MHz, DMSO-d_6): δ 8.99 (s, 2H, $NCHN$), 6.66 (s, 2H, CH_{bridge}), 3.91−3.86 (m, 4H, NCH_2), 3.64−3.59 (m, 4H, NCH_2), 2.07−2.00 (m, 4H, CH_2), 1.92−1.85 (m, 4H, CH_2). ^{13}C NMR (126 MHz, DMSO-d_6): δ 160.41 (NCHN), 80.47 (CH_{bridge}), 48.13 (NCH_2), 25.41 (CH_2). Electrospray MS (20 V, *m*/*z*): 110.3 $[M]^{2+}$, 365.13 $[M + PF_6]^+$. Anal. Calcd for $C_{12}H_{20}N_4P_2F_{12}$: C, 28.25; H, 3.95; N, 10.98. Found: C, 28.53; H, 4.21; N, 10.65.

Synthesis of 5. A mixture of **4** (202 mg, 0.396 mmol), $[Pd(OAc)_2]$ (175 mg, 0.782 mmol), and KI (275 mg, 1.65 mmol) was refluxed in acetonitrile (10 mL) for 2 h. After removal of the volatiles, the crude solid was dissolved in CH_2Cl_2/CH_3CN (97/3) and purified by column chromatography using silica gel. Elution with CH_2Cl_2/CH_3CN (97/3) afforded the separation of an orange band that contained compound **5**. Yield: 76 mg (19%). ^1H NMR (300 MHz, CD_3CN): δ 5.88 (m, 2H, CH_{bridge}), 4.53−449 (m, 4H, NCH_2), 3.57−3.52 (m, 4H, NCH_2), 1.99−1.95 (m, 8H, CH_2). ^{13}C NMR (126 MHz, CD_3CN): δ 181.6 (Pd-$C_{carbene}$), 79.3 (CH_{bridge}), 51.2 (NCH_2), 25.8 (CH_2). Anal. Calcd for $C_{16}H_{24}N_6Pd_2I_4 \cdot CHCl_3$: C, 17.91; H, 2.21; N, 7.37. Found: C, 17.53; H, 2.23; N, 6.89.

Synthesis of 6. A mixture of **5** (50 mg, 0.0489 mmol) and 3-chloropyridine (0.3 mL) was stirred at room temperature for 30 min. After this time, the solvent was evaporated under vacuum, giving a red solid. Compound **6** was obtained as a red solid after precipitation in a mixture of dichloromethane and hexanes. Yield: 28 mg (82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.01 (d, $^4J_{H-H}$ = 3 Hz, 2H, CH_{py}), 8.90 (d, $^3J_{H-H}$ = 6 Hz, 2H, CH_{py}), 7.73 (d, $^3J_{H-H}$ = 9 Hz, 2H, CH_{py}), 7.27 (t, $^3J_{H-H}$ = 6 Hz, 2H, CH_{py}), 5.76 (s, 2H, CH_{bridge}), 4.86–4.78 (m, 4H, NCH_2), 3.73–3.68 (m, 4H, NCH_2), 2.32–2.21 (m, 4H, CH_2), 2.07–1.95 (m, 4H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.4 (Pd-$C_{carbene}$), 152.8 (CH_{pyr}), 151.8 (CH_{pyr}), 137.8 ($Cq_{\ pyr}$), 132.4 (CH_{pyr}), 124.7 (CH_{pyr}), 79.6 (CH_{bridge}), 51.6 (NCH_2), 26.4 (CH_2). Anal. Calcd for $C_{22}H_{26}Cl_2I_4N_6Pd_2$ (1165.58): C, 22.66; H, 2.25; N, 7.21. Found: C, 22.08; H, 1.91; N, 7.43. Although the results of the microanalytical analysis of the compound are outside the limit viewed as establishing analytical purity (% C deviates by 0.66%), they are provided to illustrate the best values obtained to date.

General Procedure for the Acylation of Aryl Halides. In a 50 mL high-pressure Schlenk were added molecular sieves (1 g), tetrabutylammonium bromide (16 mg, 0.05 mmol), catalyst (2 mol %), aryl halide (0.5 mmol), hydrocinnamaldehyde (0.080 mg, 0.6 mmol), pyrrolidine (0.071 g, 1 mmol), and DMF (2 mL). The mixture was stirred and heated to 120 °C for 16 h. The yield of the reaction were calculated by GC, using anisole as internal standard.

X-ray Diffraction Studies. Crystals suitable for X-ray studies of compounds **2a** and **3a** were obtained by slow diffusion of hexanes into concentrated solutions of the complexes in chloroform. Diffraction data were 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. The crystals were kept at 200 K during data collection. Absorption corrections based on the multiscan method were applied.[17] The structures were solved by direct methods in ShelXS-97[18] and refined by the full-matrix method based on F^2 with the program ShelXL-97[18] using WinGX[19] (**3a**) and Olex2[20] (**2a**) software packages.

*Crystal data and structure refinement for complex **2a**:* crystal system, monoclinic; space group $I2/a$ (No. 15); a = 15.1391(2) Å, b = 15.5045(3) Å, c = 31.8334(5) Å; β = 98.9181(16)°; V = 7381.7(2) Å^3; Z = 4; T = 200.00(10) K; μ(Mo Kα) = 7.664 mm^{-1}; D_{calcd} = 1.893 g/mm^3; 41054 reflections measured ($5.86 \leq 2\theta \leq 58.392$), 9199 unique ($R_{int}$ = 0.0520), which were used in all calculations. The final R1 value was 0.0500 ($I > 2\sigma(I)$), and wR2 was 0.1376 (all data).

*Crystal Data and Structure Refinement for Complex **3a**:* crystal system, monoclinic; space group $P2_1/n$; a = 9.2720(3) Å, b = 22.7873(8) Å, c = 9.7352(3) Å; β = 94.710(3)°; V = 2049.94(12)Å^3; Z = 4; T = 200.00(10) K; μ(Mo Kα) = 13.261 mm^{-1}; D_{calcd} = 2.546 g/mm^3; 22303 reflections measured, 5062 unique (R_{int} = 0.0668), which were used in all calculations. The final R1 value was 0.0663 ($I > 2\sigma(I)$), and wR2 was 0.1604 (all data).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, figures, and a table giving spectroscopic data for the new complexes (**1**–**6**), X-ray diffraction data for complexes **2a** and **3a**, and an ORTEP diagram of complex **5**. 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 interest.

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