Dinuclear (N ∧ C ∧ N) Pincer Pt(II) Complexes with Bridged Organometallic Linkers: Synthesis, Structures, Self-Aggregation, and Photophysical Properties

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HAL Id: hal-01675266

https://hal.sorbonne-universite.fr/hal-01675266

Submitted on 4 Jan 2018

Dinuclear (N^C^N) Pincer Pt(II) Complexes with Bridged Organometallic Linkers: Synthesis, Structures, Self-Aggregation, and Photophysical Properties

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S *Supporting Information*

ABSTRACT: A new family of cationic dinuclear cyclometalated Pt(II) complexes containing an organometallic assembling ligand has been reported. The general formulas for these compounds is as follow: [R-(N^C^N)Pt—L-L—Pt(N^C^N)-R][X]$_2$, where L-L = [Cp*Ir-p-(η^4-C$_6$H$_4$S$_2$)], R = H, X = OTf (**5**); R= CF$_3$−, X = OTf (**6a**), SbF$_6$ (**6b**); L-L = [Cp*Ir-p-(η^4-C$_6$H$_4$Se$_2$)] R= CF$_3$−, X = OTf (**7a**), SbF$_6$ (**7b**). In these coordination assemblies two cyclometalated R-(N^C^N)Pt moieties are held by either η^4-dithio-p-benzoquinone complex [Cp*Ir-p-(η^4-C$_6$H$_4$S$_2$)] (**3**) or η^4-diseleno-p-benzoquinone complex [Cp*Ir-p-(η^4-C$_6$H$_4$Se$_2$)] (**4**). The molecular structures of the known complex [4-CF$_3$-(N^C^N)-PtCl] as well as two compounds of the above family [(N^C^N)Pt−Cp*Ir-p-(η^4-C$_6$H$_4$S$_2$)—Pt(N^C^N)][CF$_3$SO$_3$]$_2$ (**5**) and [CF$_3$-(N^C^N)Pt—Cp*Ir-p-(η^4-C$_6$H$_4$S$_2$)—Pt-(N^C^N)-CF$_3$][CF$_3$SO$_3$]$_2$ (**6a**) were ascertained by single crystal X-ray diffraction study and confirmed the formation of the target molecules. The solid-state packing of **5** and **6a** confirms the presence $\pi-\pi$ and short Pt···Pt interactions among individual units providing 1D supramolecular chains. To our knowledge, these are the only known examples where two cyclometalated Pt(N^C^N) units are assembled by a bridging ligand (vide infra). All compounds show phosphorescence in the bluish-green region (486−521 nm) in the solution at room temperature and exhibit higher luminescence quantum yields relative to the analogous compounds containing a Pt(terpy) chromophore in thin film.
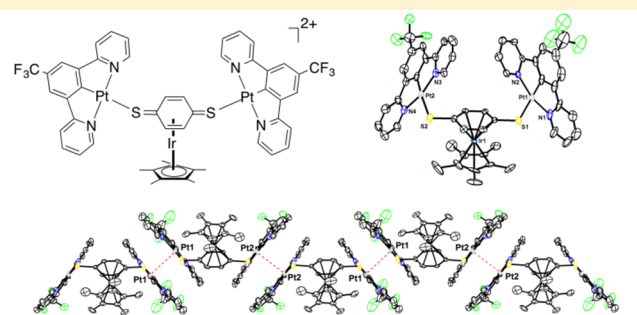
Molecular structure of **6a** showing self-aggregation due to Pt···Pt interactions.

■ INTRODUCTION

Cyclometalated platinum(II) complexes containing the pincer-type N^C^N ligands have received considerable attention.[1−4] They provide rich photophysical properties[5,6] and unusually high phosphorescence quantum yields, for example, a photoluminescence quantum yield (PLQY) of up to 0.68 in solution was reported by Williams and co-workers.[7] Such compounds form stable square-planar complexes with d^8 electronic configuration, which promotes metal−metal and $\pi-\pi$ interactions that profoundly impact the properties of the electronic excited states.[8,9] Moreover, the introduction of substituents into the aryl or pyridyl units impacts the excited state energy and eventually the color of such compounds. Due to their charge neutrality and intense phosphorescence, cyclometalated platinum(II) complexes can be viewed as attractive candidates for applications for optical devices and OLEDs.[10−13]

Despite these advances, cationic cyclometalated Pt(N^C^N) compounds are less known; the synthesis and luminescent properties of some mononuclear cationic species have been reported by Che and co-workers and others.[14−17] Moreover, luminescent coordination assemblies containing two cationic Pt(N^C^N) units are even more scarce.[16] Thus, we sought to design novel classes of luminescent coordination assemblies where appropriate bridging linkers are capable to attach two (N^C^N)Pt units, in the hopes that such novel compounds might promote strong intermolecular Pt···Pt and $\pi-\pi$ interactions which in turn would affect the luminescent properties. In a previous work, the synthesis of luminescent heterotrinuclear coordination assemblies, [Pt(terpy){Cp*Ir-p-(η^4-C$_6$H$_4$E$_2$)}Pt(terpy)][OTf]$_4$ was reported, in which an organometallic linker [Cp*Ir(η^4-C$_6$H$_4$E$_2$)] (E = S, Se) holds two Pt(terpy) units through coordination via the sulfur or selenium centers (Figure 1).[18,19] The molecular structures showed that individual units exhibit $\pi-\pi$ and Pt···Pt interactions to give a 1D chain in the solid state. The heterotrinuclear coordination assembly showed unusual UV−vis absorption and luminescence properties at low temperature,
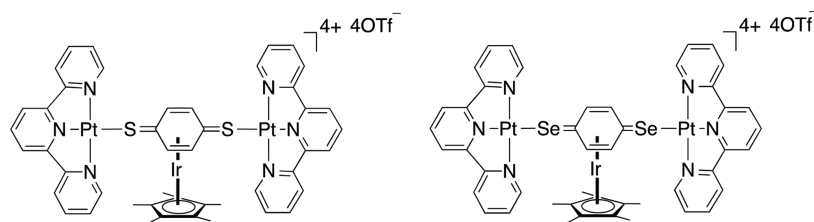
Figure 1. $[Pt(terpy)\{Cp*Ir-p-(\eta^4-C_6H_4S_2)\}Pt(terpy)][OTf]_4$ and $[Pt(terpy)\{Cp*Ir-p-(\eta^4-C_6H_4Se_2)\}Pt(terpy)][OTf]_4$ reported previously.[18,19]
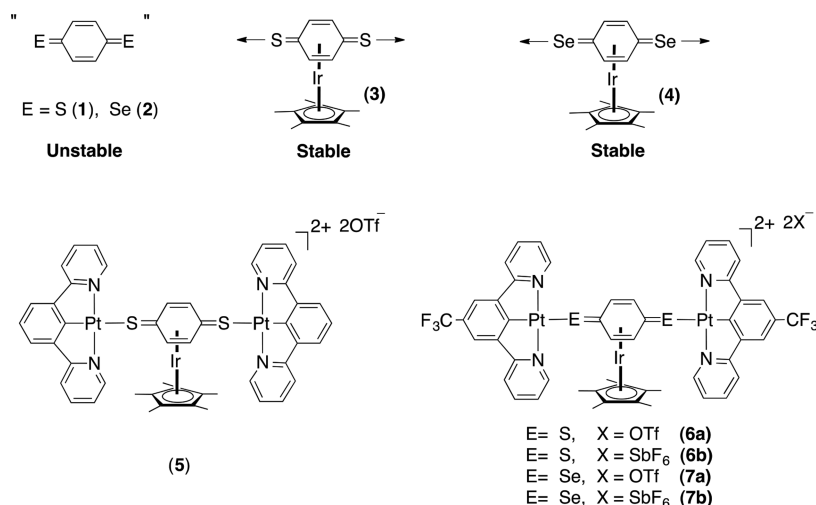

Figure 2. Schematic drawings of the thio- and seleno-quinone intermediates (**1** and **2**), the isolated metalated thio- and seleno-quinones (**3** and **4**), and the luminescent cyclometalated platinum salts (**5**, **6a**, **6b**, **7a**, and **7b**).

imparted from self-aggregation of the individual subunits mediated by π–π and Pt···Pt interactions.

Pursuing our research in this area, we wish to report the synthesis and luminescent properties of rare examples where two cyclometalated Pt chromophores are now attached to a thio- or seleno- organometallic linker p-[Cp*Ir(η^4-C_6H_4E_2)], E = S (**3**) and Se (**4**) (Figure 2). To the best of our knowledge, these are the first dicationic Pt(N^C^N) compounds to be prepared displaying quinonoid π-complexes as assembling ligands. The reason for the scarcity of such compounds is that unlike quinones which are a prominent class of compounds that play an important role in chemistry and biology the related thio- and seleno-quinones "C_6H_4Se_2" (**1**) (Figure 2), are in contrast, unstable[20–22] and consequently do not exist in nature; hence, their chemical properties remain little known.

Thus, we anticipated that metalated thio- and seleno-quinone might be appropriate assembling ligands for a new class of luminescent Pt(II) cyclometalated complexes (Figure 2). The latter represents a novel strategy to obtain cationic luminescent coordination assemblies containing cyclometalated Pt(N^C^N) chromophores.

Pursuing our research program in the area of metal-stabilized reactive intermediates, we demonstrated that the Cp*Ir fragment is a powerful stabilizing entity.[23–26] For instance, in 1998 we reported the synthesis of the first stable *ortho*-quinone methide metal complex, in which the Cp*Ir unit is attached to the internal diene moiety through η^4-coordination.[27–29] Later, in 2006 we described the synthesis of the first stable iridium *p*-dithiobenzoquinone complex, p-[Cp*Ir(η^4-C_6H_4S_2)], and the related *ortho* congener, o-[Cp*Ir(η^4-C_6H_4S_2)].[30,31] Both compounds were used as successful organometallic linkers to construct functional coordination assemblies.[32,33] Moreover, we

reported the synthesis and the X-ray molecular structure of the *p*-diselenobenzoquinone (**2**) as a metal complex, p-[Cp*Ir(η^4-C_6H_4Se_2$)] (**4**) (Figure 2).[34]

In this work, the preparation of several luminescent cationic dinuclear cyclometalated Pt(II) complexes containing an organometallic linker is described. For instance, [(N^C^N)-Pt−Cp*Ir-p-(η^4-C_6H_4S_2)−Pt(N^C^N)][OTf]_2 (**5**) and those containing CF_3-cyclometalated platinum counterparts, [CF_3-(N^C^N)Pt−L−L−Pt(N^C^N)-CF_3][X]_2, with L-L = [Cp*Ir-p-(η^4-C_6H_4S_2)], X = OTf (**6a**), SbF_6 (**6b**); L-L = [Cp*Ir-p-(η^4-C_6H_4Se_2)], X = OTf (**7a**), SbF_6 (**7b**). The molecular structures of **5** and **6a** were determined by single crystal X-ray diffraction, which confirmed the formation of the target complexes. Remarkably, the crystal packing shows the presence of π–π and short Pt···Pt interactions among individual units, which induce the formation of 1D supramolecular chains. These complexes exhibit interesting luminescent properties in the solid state and in thin film matrix at room temperature and showed higher luminescence quantum yields compared to those obtained with Pt(terpy) chromophores. This behavior might arise from the nature of the cyclometalated Pt(N^C^N) luminophore.[19] To the best of our knowledge, our compounds are the first examples of dicationic luminescent Pt(N^C^N) complexes bearing an ancillary ligand coordinated through sulfur and selenium centers.[3]

■ RESULTS AND DISCUSSION

Synthesis of the Cationic (N^C^N)Pt(II) Complexes with the Organometallic Linkers (5, 6ab and 7ab). The pincer-type cyclometalated starting material (N^C^N)Pt−Cl was first prepared by Cardenas and co-workers[35] in 1999 and the high emission quantum yield was revealed by Williams and

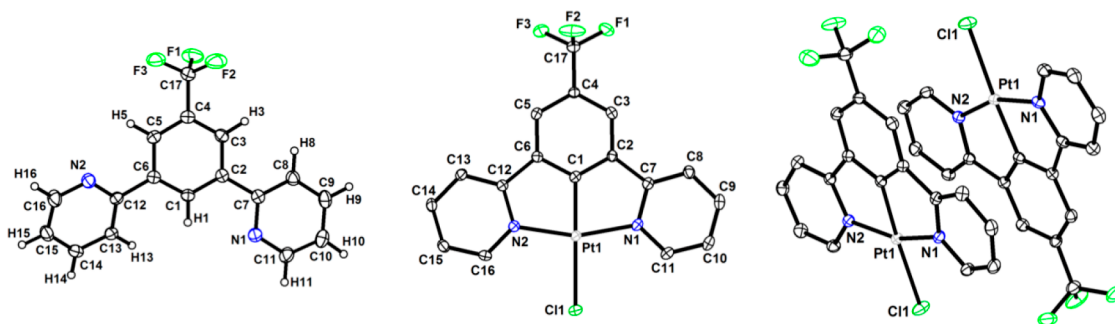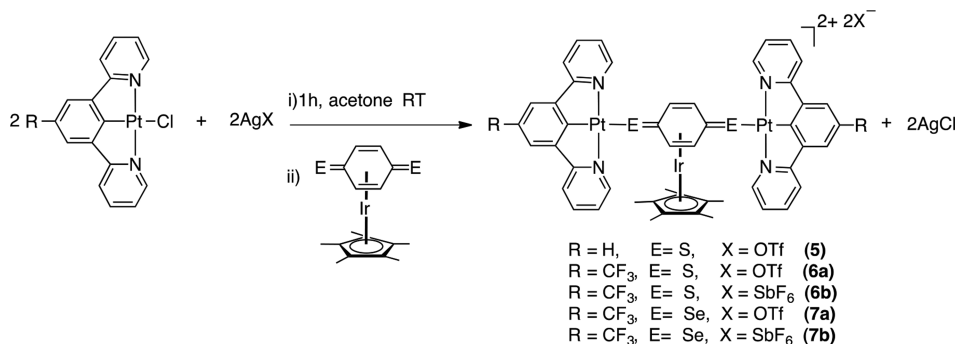**Scheme 1. General Synthesis Procedure to Luminescent Heterotrinuclear Species 5, 6a, 6b, 7a and 7b**

R = H, E= S, X = OTf (**5**)
R = CF$_3$, E= S, X = OTf (**6a**)
R = CF$_3$, E= S, X = SbF$_6$ (**6b**)
R = CF$_3$, E= Se, X = OTf (**7a**)
R = CF$_3$, E= Se, X = SbF$_6$ (**7b**)

Figure 3. Molecular structures of the free ligand 4-CF$_3$-N^CH^N, metal complex [(4-CF$_3$-N^C^N)PtCl], and the related head-to-tail dimer.

co-workers[7] in 2003, while the synthesis and luminescent properties of the functionalized cyclometalated platinum complex [(4-CF$_3$-N^C^N)PtCl] was reported by Che et al. in 2009.[14]

Treatment of [(N^C^N)PtCl] or [(4-CF$_3$-N^C^N)PtCl] in acetone with silver salt AgX and subsequent reaction with the organometallic linkers, [Cp*Ir-p-(η^4-C$_6$H$_4$E$_2$)] (E = S (**3**) or Se (**4**)), provided an orange-red solution which after workup gave target compounds **5**, **6a**, **6b**, **7a** and **7b** (Scheme 1). For instance, the ^{1}H NMR spectrum of **5** recorded in CD$_3$CN shows the presence of a singlet at δ 7.23 ppm attributed to the metalated p-quinonoid unit and a singlet at δ 1.92 ppm assigned to the Cp*Ir moiety. Furthermore, we note the presence of several multiplets in the range of δ 7.72–9.10 ppm assigned to the protons of the fragment "(N^C^N)Pt". We noticed however that upon standing at room temperature in CD$_3$CN solution the complex undergoes changes and decoordination of the chromophore occurs slowly on the NMR time-scale. Perhaps this is due to the σ-trans effect of the carbon center, which weakens the coordination of the sulfur ligands in **5**. Such behavior had also been reported in cyclometalated Pt(II) complexes containing a sulfur coligand.[3] We anticipated that the related CF$_3$-cyclometalated platinum compounds would be more stable since the electron-withdrawing inductive effect of the CF$_3$– group might alleviate the trans effect of the carbon center trans to the sulfur or selenium nucleophile in **6a**, **6b**, **7a** and **7b**. Complex **5** was fully characterized and in addition its X-ray molecular structure was determined (vide infra). Compounds **6a**, **6b**, **7a** and **7b** gave pattern in the ^{1}H NMR spectra similar to that of **5** and turned out to be more stable in solution. Moreover, the presence of the CF$_3$– functional group is observed in the ^{19}F NMR spectra (Experimental Section). The infrared data of the above compounds confirm the presence of the respective counteranion (Experimental Section).

X-ray Molecular Structures of 4-CF$_3$-N^CH^N Ligand, [(4-CF$_3$-N^C^N)PtCl], and [R-(N^C^N)Pt−Cp*Ir-p-(η^4-C$_6$H$_4$S$_2$)−Pt(N^C^N)-R][CF$_3$SO$_3$]$_2$ (R = H (5) and CF$_3$ (6a)). Convenient crystals of 4-CF$_3$-N^CH^N ligand for X-ray analysis were obtained by slow diffusion of diethyl ether into CH$_3$CN solution of the ligand. The crystal structure of the 2,2′-(5-trifluoromethyl-1,3-phenylene)dipyridine (dpyb-CF$_3$) shows a head−tail arrangement of the two pyridyl rings in a similar fashion to that reported for the analogous 2,2′-(5-bromo-1,3-phenylene)dipyridine (dpyb-Br) (Figure 3). Moreover, one of the nitrogen atoms displays weak C−H⋯N intermolecular interaction [C16−H16⋯N1 = 3.551(4) Å] with a carbon of the pyridyl moiety of another ligand which might favor the transoid configuration.[36] We also note that the three aromatic rings are not coplanar with angles of 3.30(8) and 22.53(9)° between the two pyridyl units and the central benzene ring, mainly, the pyridyl unit pointing toward the CF$_3$– group displaying the larger angle.

Crystals of the starting material [(4-CF$_3$-N^C^N)PtCl] were also obtained from DMSO/MeOH mixture. The structure shows that the complex displays a distorted square planar geometry around the platinum center as expected for this type of N^C^N compounds (Figure 3).[36] The Pt1−C1 bond distance is 1.909(3) Å which is short and typical of such compounds suggesting higher rigidity of the molecular skeleton compared to the related Pt(N^N^C) and Pt(N^N^N) related compounds.[37] Examining the crystal packing showed the formation of a dimer species through π−π interaction; however, the Pt⋯Pt distance, 5.086(1) Å, is long to suggest any interaction.[8,9,36]

On the other hand, crystals of our target molecules **5** and **6a** were successfully obtained. The crystal structure of **5** shows indeed that the p-dithiobenzoquinone iridium complex bridges two Pt(N^C^N) units through the two sulfur centers with Pt−S bond distances of 2.421(2) Å (Pt1−S1) and 2.410(2) Å (Pt2−
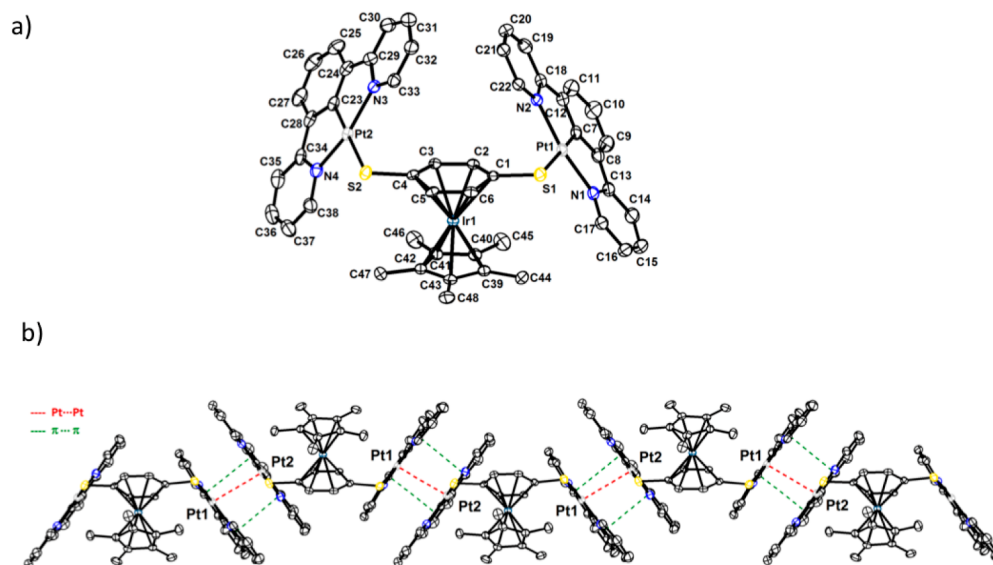
Figure 4. (a) View of the cationic part of complex **5**. Selected bond distances (Å) and angles (deg) for **5**: Ir1···C1 = 2.348(4), Ir1···C2 = 2.220(4), Ir1···C3 = 2.218(4), Ir1···C4 = 2.343(4), Ir1···C5 = 2.234(4), Ir1···C6 = 2.219(4), C1···S = 1.720(4) C4···S2 = 1.719(5), S1···Pt1= 2.421(2), S2···Pt2 = 2.410(2), C7···Pt1 = 1.930(5), C23···Pt2 = 1.919(5) N1−Pt1−N2 = 160.4(2), N3−Pt2−N4 = 160.7(2). (b) 1D supramolecular chain formed through π−π (3.53 Å) and Pt···Pt (3.300 Å) contacts between individual molecules.
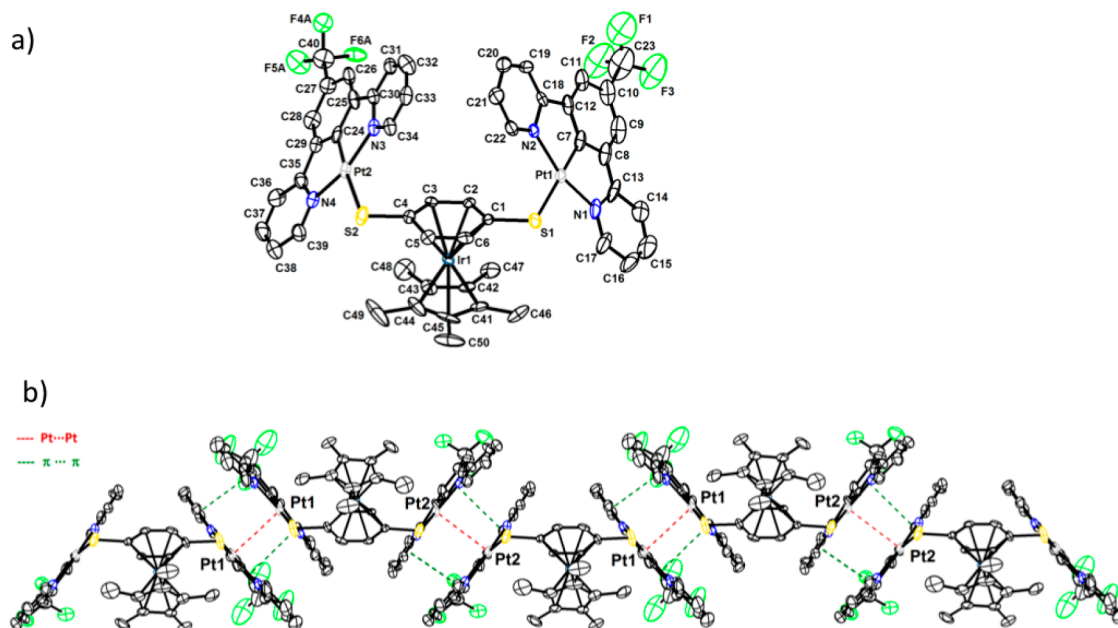

Figure 5. (a) View of the cationic part of complex **6a**. Selected bond distances (Å) and angles (deg) for **6a**: Ir1···C1 = 2.328(11), Ir1···C2 = 2.229(10), Ir1···C3 = 2.221(10), Ir1···C4 = 2.316(12), Ir1···C5 = 2.197(11), Ir1···C6 = 2.221(12), C1···S1 = 1.728(11), C4···S2 = 1.744(12), S1···Pt1= 2.410(5), S2···Pt2 = 2.413(4), C7···Pt1 = 1.917(16), C24···Pt2 = 1.889(17), N1−Pt1−N2 = 161.7(6), N3−Pt2−N4 = 160.8(5). (b) 1D supramolecular chain formed through π−π (3.40 Å), Pt1···Pt1 (3.306(1) Å) and Pt2···Pt2 (3.355(1) Å) contacts between individual molecules.

S2) (Figure 4a). The coordination geometry around each Pt center is a distorted square planar, formed by two nitrogen atoms of the two lateral pyridyl units, one carbon of the central arene ring and one sulfur center from bridging organometallic linker **3**. The Pt1−C7 bond distance is 1.930(5) Å, while Pt2−C23 = 1.919(5) Å, Pt1−N1 = 2.049(4) Å, Pt1−N2 = 2.048(4) Å, Pt2−N3 = 2.037(4) Å, and Pt2−N4 = 2.039(4) Å, respectively. The aromatic ring of the organometallic linker is almost planar, with the thioquinone carbons bent out of the diene plane (hinge angles $\theta1$ = 7.98°, $\theta2$ = 7.66°) while acting as a bidentate ligand and connecting two Pt(N^C^N) units.

These angles are slightly bigger than those reported for the free organometallic linker $[Cp^*Ir\text{-}p\text{-}(\eta^4\text{-}C_6H_4S_2)]$ (**3**). The C−S bond distances in **5** are 1.720(4) and 1.719(4) Å, slightly longer than those reported for **3**.[30]

The two Pt(N^C^N) units in **5** are not linearly disposed but are puckered and lean backward with Pt···Pt distance in $[(N^\wedge C^\wedge N)Pt\text{-}Cp^*Ir\text{-}p\text{-}(\eta^4\text{-}C_6H_4S_2)\text{—}Pt(N^\wedge C^\wedge N)][CF_3SO_3]_2$ (**5**) of 7.838(1) Å. Analysis of the crystal packing of **5** reveals important information such as the molecules being stacked in a head-to-tail fashion with a set of π−π/Pt1···Pt2 interactions occurring at each side of one Pt(N^C^N) arm with the adjacent

Table 1. Photophysical Data for 6a,b and 7a,b

complex	λ_{abs} [nm] (ε [dm^3 mol^{-1}cm^{-1}])[a]	medium (T [K])	λ_{em} [nm] (τ_0 [μs])	Φ_{lum}[b]
6a	358 (19230), 375 (19180), 400 sh (13650), 474 (750)	acetone (298)	485, 517 (3.9)	0.014
		solid (298)	680 (0.2)	0.004
		solid (77)	625 (0.5)	c
		thin film (298)[d]	486	0.35
6b	358 (19570), 374 (19720), 400 sh (14130), 474 (750)	acetone (298)	485, 517 (3.5)	0.016
		solid (298)	648 (0.2)	0.002
		solid (77)	623 (0.5)	c
		thin film (298)[d]	486	0.40
7a	362 sh (18880), 374 (19240), 402 sh (12360), 430 sh (7560)	acetone (298)	485, 517 (4.0)	0.032
		solid (298)	685 (0.2)	0.005
		solid (77)	652 (<0.1)	c
		thin film (298)[d]	486	0.37
7b	362 sh (19210), 374 (19860), 402 sh (13020), 430 sh (7960)	acetone (298)	485, 517 (3.6)	0.018
		solid (298)	685 (0.3)	0.002
		solid (77)	640 (<0.1)	c
		thin film (298)[d]	486	0.37

[a]Measured in acetone at 298 K. [b]The luminescence quantum yield, measured at room temperature using quinine sulfate in 0.5 M H$_2$SO$_4$ as the reference (excitation wavelength = 365 nm, Φ_{lum} = 0.55). [c]Not determined. [d]A 5% complex was doped into 1,3-bis(carbazole-9-yl)benzene (MCP), excitation wavelength at 340 nm.

molecule. The Pt1···Pt2 distance is 3.300(1) Å suggesting a strong interaction.[9] These Pt···Pt/π−π interactions among individual subunits of **5** construct a 1D supramolecular chain (Figure 4b). Similar examples of Pt(N^C^N) complexes showing a combination of π−π/Pt···Pt interactions among the individual units were previously reported.[9,16]

The crystal structure of complex **6a** was similar to that **5** suggesting little influence of CF$_3$ group on the packing. The structure of **6a** shows similar features to that observed for **5**, i.e., the organometallic linker [Cp*Ir-p-(η^4-C$_6$H$_4$S$_2$)] (**3**) holds two 4-CF$_3$-(N^C^N)Pt units through the two sulfur centers (Figure 5a). The 4-CF$_3$-(N^C^N)Pt units also lean backward in an analogous fashion to that of **5** with Pt···Pt distance of 7.922(1) Å. The crystal packing of **6a** also shows the formation of 1D chain as seen for complex **5**; however, head-to-head and tail-to-tail arrangements are visible. Thus, two combinations of π−π/ Pt1···Pt1 and π−π/Pt2···Pt2 interactions occur among individual 4-CF$_3$-(N^C^N)Pt units. The crystal structure shows π−π interactions with distances of 3.40 Å and strong metal−metal interactions with Pt1···Pt1 3.306(1) Å and Pt2··· Pt2 at 3.355(1) Å, respectively (Figure 5b).[9] Although we were able to obtain only two molecular structures of the above series with and without the CF$_3$ functional group, it is obvious that the same OTf counterion provides a similar packing of these molecules in the solid state. We then examined their optical and luminescent properties.

Photophysical Properties of 6a, 6b, 7a and 7b. The photochemistry of all compounds was investigated except for **5** due to its limited stability in solution. The electronic absorption spectra of **6a**, **6b**, **7a** and **7b** in acetone at room temperature showed an intense absorption band at 358−375 nm (ε > 10^4 dm^3 mol^{-1} cm^{-1}) with vibrational progressional spacings of ca. 1300 cm^{-1}, corresponding to the skeletal vibrational frequency of the N^C^N ligand in the excited state. In addition, a shoulder at 400−430 nm (ε > 10^3 dm^3 mol^{-1} cm^{-1}) and weak bands at 446−476 nm (ε = 140−750 dm^3 mol^{-1} cm^{-1}) are observed. The photophysical data are summarized in Table 1,

and the electronic absorption of these complexes are depicted in Figure 6. With reference to previous spectroscopic studies on
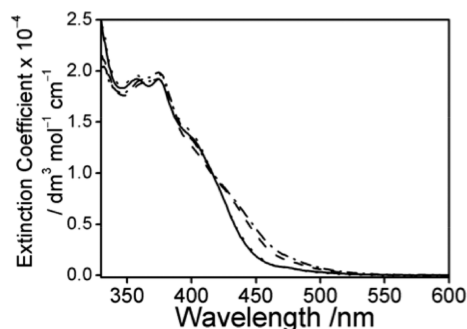

Figure 6. Electronic absorption spectra of **6a** (—), **6b** (······), **7a** (- - -), and **7b** (-·-·-) in acetone at room temperature.

the organometalloligands Cp*Ir(η^4-dithiobenzoquinone)[18] and Cp*Ir(η^4-diselenobenzoquinone)[19] as well as [Pt(N^C^N)-Cl],[7] the high-energy bands are attributed to admixtures of π → π* intraligand (IL) transitions of Cp*Ir(η^4-dithiobenzoquinone)/Cp*Ir(η^4-diselenoenzoquinone) and metal-perturbed IL transitions of the N^C^N ligand, while the shoulders are tentatively assigned as admixtures of dπ(Pt) → π*(N^C^N) metal-to-ligand charge transfer (MLCT) transitions and metal-perturbed π → π* IL transitions of Cp*Ir(η^4-dithiobenzoquinone)/Cp*Ir(η^4-diselenobenzoquinone) systems.

An additional low-energy absorption shoulder at 430 nm is observed for **7a** and **7b**. On the basis of the strong electron-donating behavior of the diselenobenzoquinone group, such a low-energy absorption shoulder is assigned to the pπ(Se) → π*(N^C^N) ligand-to-ligand charge transfer (LLCT) transition with mixing of MLCT character.[19] Compared to their p-dithiobenzoquinone analogues, **6a** and **6b**, no such additional low-energy absorption shoulder is observed, probably due to the lower electron-donating ability of the dithiobenzoquinone

counterparts.[19] In contrast, the low-energy weak absorption band at 474 nm for **6a** and **6b** is unlikely to be due to d−d transitions, since the N^C^N ligand is a strong σ donor and it is unlikely that they would occur at such low energies. In view of the large spin−orbital coupling resulting from the presence of heavy Pt atom, a $^3\pi \rightarrow \pi^*(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})$ IL transition is suggested.[7] Similar assignments have also been reported for the related platinum(II) complexes.[38,39]

Upon excitation at $\lambda > 350$ nm, these complexes show vibronically structured emission with emission maximum of 485 nm in acetone at room temperature (Figure 7). The vibronic
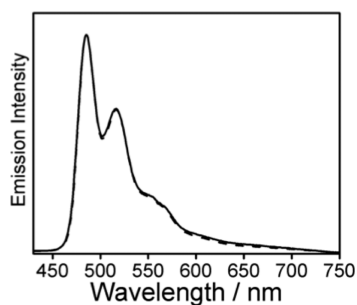

Figure 7. Normalized emission spectra of **6b** (—) and **7b** (- - -) in acetone at room temperature.

progression of 1300 cm^{-1} is in agreement with the skeletal vibrational frequency of the N^C^N ligand in the ground state. The pronounced vibronic structure is typical of emission from a $\pi \rightarrow \pi^*$ excited state, indicating that the emission originates from a state of primarily ^{3}IL $\pi \rightarrow \pi^*$ character. The relatively long lifetimes of several microseconds are typical of the phosphorescence of complexes of this class. These emissions, which are also observed in the related Pt(N^C^N) complexes are tentatively assigned as derived from states of metal-perturbed ^{3}IL $\pi \rightarrow \pi^*(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})$ origin.[38,39] Solid-state emission of cyclometalated Pt(II) complexes could be significantly affected by the packing of molecules in their crystal structures.[40,41] Figure 8 shows the normalized emission spectra
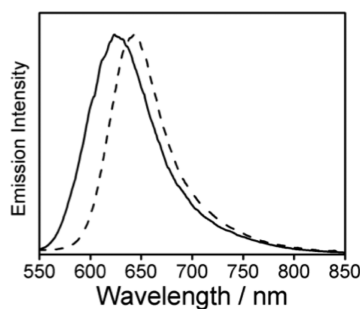

Figure 8. Normalized emission spectra of **6b** (—) and **7b** (- - -) in the solid state at 77 K.

of **6b** and **7b** in the solid state at 77 K. Compounds **6a**, **6b**, **7a** and **7b** were found to give emission at 623−685 nm in the solid state. The structureless emission is attributed to ^{3}MMLCT excited states associated with Pt···Pt interactions,[42] which are further confirmed by the solid-state packing of **6a** in the X-ray crystallography. Higher luminescence quantum yields of up to 40% are observed in the thin film samples of the complexes doped in 1,3-bis(carbazole-9-yl)benzene (MCP), which could

be attributed to the reduced nonradiative decay as a result of the increased rigidity in the film.

■ CONCLUDING REMARKS

In conclusion, we reported the synthesis of the first series of binuclear Pt(N^C^N) compounds with π-bonded thio- and seleno-quinone as bridging ligands. The organic ligand 4-CF$_3$-N^CH^N and two of the platinum(II) complexes have also been structurally characterized by X-ray crystallography. Vibronic-structured emission bands in the bluish-green region have been observed for these platinum(II) complexes that are indicative of the involvement of the cyclometalated ligand in the excited state in solution at room temperature. Interestingly, these complexes are red emitters in their solid state, and their photophysical properties are attributed to ^{3}MMLCT excited states that are associated with Pt···Pt interactions, which have been further confirmed by the solid-state packing of **6a** in the X-ray crystallography. These interesting behaviors might open up a new strategy to develop new photoluminescent materials.

■ EXPERIMENTAL SECTION

All experimental manipulations were carried out under argon using Schlenk tube techniques except the chlorides/anions metathesis workup witch was performed under aerobic conditions. All solvents were purified by standard techniques. The ^{1}H NMR and ^{13}C NMR spectra were recorded in CD$_3$NO$_2$ using a Bruker Avance 300 NMR or 400 NMR spectrometer. Infrared spectra were recorded from neat samples on a Bruker FT-IR spectrometer Tensor 27 equipped with an Attenuated Total Reflection (ATR) Harrick accessory. The organometallic linkers η^4-[Cp*Ir(p-C$_6$H$_4$S$_2$)],[30] η^4-[Cp*Ir(p-C$_6$H$_4$Se$_2$)][34] (**2**), [Pt(N^C^N)Cl], and [(4-CF$_3$-N^C^N)Pt−Cl] were prepared according to published procedures.[14,35] UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state excitation and emission spectra in the solid state (298 and 77 K) and in solution at room temperature were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. Solid-state photophysical studies were carried out with solid samples contained in a quartz tube inside a quartz-walled Dewar flask. Measurements of the solid-state sample at 77 K were similarly conducted with liquid nitrogen filled in the optical Dewar flask. All solutions for photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Telflon stopper. The solutions were rigorously degassed with at least four successive freeze−pump−thaw cycles. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150−10 pulsed Nd:YAG laser. Luminescence decay signals were recorded on a Tektronix model TDS620A digital oscilloscope and analyzed using a program for exponential fits. Relative luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.[43] The solid and thin films at room temperature were measured on a Hamamatsu C9920−03 Absolute Photoluminescence Yield Measurement System.

Synthesis of [(N^C^N)$_2$Pt$_2${Cp*Ir-η^4-(p-C$_6$H$_4$S$_2$)}][OTf]$_2$ (5). To a solution of [(N^C^N)PtCl] (90 mg, 0.19 mmol) in acetone (30 mL) was added a solution of AgOTf (50 mg, 0.19 mmol), and the mixture was stirred for 18 h. The resulting solution was filtered into a dry Schlenk tube kept under argon, and the AgCl salt was removed. To this solution was added p-[Cp*Ir(η^4-C$_6$H$_4$S$_2$)] (**3**) (50 mg, 0.11 mmol) in CH$_2$Cl$_2$ (10 mL) and the mixture was stirred for 2 h at room temperature. The solvent was then reduced to roughly 5 mL and distilled Et$_2$O (30 mL) was added. The orange-red precipitate was recovered on a glass frit and washed three times with Et$_2$O (15 mL), then dried under vacuum to give [(N^C^N)$_2$Pt${Cp*Ir-$\eta^4$-($p$-C$_6H_4S_2$)}][OTf]$_2$ as an orange microcrystalline solid (48 mg, 0.03

mmol). Yield: 31%. The compound was not very stable; hence, no elemental analyses were obtained. X-ray molecular structure was determined. ^{1}H NMR (300.13 MHz, CD$_3$NO$_2$): δ 9.01 (d, J = 5.8 Hz, $^3J_{Pt-H}$ = 34 Hz, 4H; H$_a$), 8.17 (td, J = 7.7 and 1.4 Hz, 4H; H$_c$), 7.94 (dd, J = 6.9 and 0.6 Hz, 4H; H$_d$), 7.65 (d, J = 7.7 Hz, 4H; H$_e$), 7.39 (td, J = 6.1 and 2.0 Hz, 4H; H$_b$), 7.36 (t, J = 7.4 Hz, 2H; H$_f$), 6.98 (s, 4H; arene), 1.98 (s, 15H; Cp*).^{13}C {^{1}H} NMR (75.4 MHz, CD$_3$NO$_2$): δ 166.6, 151.0, 150.3, 146.4, 141.4, 140.1, 139.2, 130.8, 123.3, 119.3, 99.9, 90.8, 6.6. IR (neat ATR Harricks, cm^{-1}): ν(CF$_3$SO$_3$) 1254; 1025.

Synthesis of [(4-CF$_3$-N^C^N)$_2$Pt$_2${Cp*Ir-η^4-(p-C$_6$H$_4$S$_2$)}][OTf]$_2$ (6a). This compound was prepared following the procedure described for **5** but using [(4-CF$_3$-N^C^N)PtCl] instead of [(N^C^N)PtCl].

6a was obtained as orange microcrystalline solid (149 mg, 0.084 mmol). Yield: 90% starting with [(CF$_3$-N^C^N)PtCl] (100 mg, 0.186 mmol), AgOTf (48 mg, 0.186 mmol). and p-[Cp*Ir(η^4-C$_6$H$_4$S$_2$)] (**3**) (43 mg, 0.093 mmol). Anal. Calcd for C$_{52}$H$_{39}$F$_{12}$IrN$_4$O$_6$Pt$_2$S$_4$·CH$_2$Cl$_2$: C, 34.60; H, 2.23; N, 3.05. Found: C, 34.25; H, 2.24; N, 3.13. ^{1}H NMR (400 MHz, CD$_3$NO$_2$): δ 8.87 (d, J = 6.0 Hz, $^3J_{Pt-H}$ = 34.1 Hz, 4H; H$_a$), 8.17 (td, J = 7.8 and 1.2 Hz, 4H; H$_c$), 7.85 (d, J = 8.0 Hz, 4H; H$_d$), 7.71 (s, 4H; H$_e$), 7.42 (td, J = 7.2 and 1.2 Hz, 4H; H$_b$); 6.85 (s, 4H; arene), 1.85 (s, 15H; Cp*).^{13}C NMR{^{1}H} (100.61 MHz, CD$_3$NO$_2$): δ 165.9, 152.3, 141.4, 140.8, 126.1, 125.6, 123.4, 121.7 (q, $^1J_{C-F}$ = 192.8 Hz), 121.1, 119.5, 104.3, 101.2, 92.0, 7.8. ^{19}F NMR (282 MHz, CD$_3$NO$_2$): δ −63,9 (6F; −CF$_3$); −80,7 (6F; OTf). IR (neat ATR Harricks, cm^{-1}): ν(CF$_3$SO$_3$) 1256; 1027.

Synthesis of [(4-CF$_3$-N^C^N)$_2$Pt$_2${Cp*Ir-η^4-(p-C$_6$H$_4$S$_2$)}][SbF$_6$]$_2$ (6b). This compound was prepared following the general procedure described for **6a** but using AgSbF$_6$ instead of AgOTf.

6b was obtained as orange microcrystalline solid (158 mg, 0.082 mmol). Yield: 88% starting with [(CF$_3$-N^C^N)PtCl] (100 mg, 0.186 mmol), AgSbF$_6$ (63 mg, 0.186 mmol), and p-[Cp*Ir(η^4-C$_6$H$_4$S$_2$)] (**3**) (43 mg, 0.093 mmol). Anal. Calcd for C$_{50}$H$_{39}$Sb$_2$F$_{18}$IrN$_4$Pt$_2$S$_2$·1/2(CH$_3$)$_2$CO: C, 31.61; H, 2.14; N, 2.86. Found: C, 31.75; H, 2.04; N, 2.80. ^{1}H NMR (400.13 MHz, CD$_3$NO$_2$): δ 9.00 (d, J = 5.6 Hz, $^3J_{Pt-H}$ = 32.6 Hz, 4H; H$_a$), 8.23 (td, J = 7.2 and 1.2 Hz, 4H; H$_c$), 8.00 (d, J = 8.0 Hz, 4H; H$_d$), 7.87 (s, 4H; H$_e$); 7.48 (td, J = 6.8 and 2.0 Hz, 4H; H$_b$), 6.94 (s, 4H; arene), 1.93 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (75.4 MHz, CD$_3$NO$_2$): δ 165.9, 152.2, 141.3, 140.8, 139.2, 126.3, 126.1, 126.0; 125.5, 123.4, 121.1, 120.8, 92.0, 7.9. ^{19}F NMR (375 MHz, CD$_3$NO$_2$): δ −63.9 (6F; −CF$_3$). IR (neat ATR Harricks, cm^{-1}): ν(SbF$_6$) 651.

Synthesis of [(4-CF$_3$-N^C^N)$_2$Pt$_2${Cp*Ir-η^4-(p-C$_6$H$_4$Se$_2$)}][OTf]$_2$ (7a). This compound was prepared following the general procedure described for **6a** but using the organometallic ligand p-[Cp*Ir(η^4-C$_6$H$_4$Se$_2$)] (**4**).

7a was obtained as a burgundy microcrystalline solid (159 mg, 0.086 mmol). Yield: 91%, starting with [(CF$_3$-N^C^N)PtCl] (100 mg, 0.186 mmol), AgOTf (48 mg, 0.186 mmol), and p-[Cp*Ir(η^4-C$_6$H$_4$Se$_2$)] (**4**) (52 mg, 0.093 mmol). Anal. Calcd for C$_{52}$H$_{39}$F$_{12}$IrN$_4$O$_6$Pt$_2$S$_2$Se$_2$·2CH$_2$Cl$_2$: C, 32.14; H, 2.15; N, 2.78. Found: C, 31.90; H, 2.10; N, 2.74. ^{1}H NMR (300.13 MHz, CD$_3$NO$_2$): δ 9.27 (d, J = 5.2 Hz, $^3J_{Pt-H}$ = 33.8 Hz, 4H; H$_a$); 8.23 (t, J = 7.8 Hz, 4H; H$_c$); 8.03 (d, J = 7.2 Hz, 4H; H$_d$), 7.91 (s, 4H; H$_e$), 7.48 (t, J = 7.0 Hz, 4H; H$_b$), 7.08 (s, 4H; arene), 1.93 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (75.4 MHz, CD$_3$NO$_2$): δ 152.5, 140.3, 140.0, 139.5, 124.7, 121.1, 120.0, 119.8, 118.9, 116.9, 6.4. ^{19}F NMR (375 MHz, CD$_3$NO$_2$): δ −64.0 (6F; −CF$_3$); −80.7 (6F; OTf). IR (neat ATR Harricks, cm^{-1}): ν(CF$_3$SO$_3$) 1251; 1025.

Synthesis of [(4-CF$_3$-N^C^N)$_2$Pt$_2${Cp*Ir-η^4-(p-C$_6$H$_4$Se$_2$)}][SbF$_6$]$_2$ (7b). This compound was prepared following the procedure described for **7a** but using AgSbF$_6$ instead of AgOTf.

7b was obtained as burgundy microcrystalline solid (148 mg, 0.073 mmol). Yield: 78%, starting with [(CF$_3$-N^C^N)PtCl] (100 mg, 0.186 mmol), AgSbF$_6$ (63 mg, 0.186 mmol), and p-[Cp*Ir(η^4-C$_6$H$_4$Se$_2$)] (**4**) (52 mg, 0.093 mmol). Anal. Calcd for C$_{50}$H$_{39}$Sb$_2$F$_{18}$IrN$_4$Pt$_2$Se$_2$·CH$_2$Cl$_2$: C, 29.07; H, 1.94; N, 2.65. Found: C, 29.27; H, 1.96; N, 2.70. ^{1}H NMR (300.13 MHz, CD$_3$NO$_2$): δ 9.12 (d, J = 5.6 Hz, $^3J_{Pt-H}$ = 31.1 Hz, 4H; H$_a$), 8.14 (t, J = 8.0 Hz, 4H; H$_c$), 7.85 (d, J = 8.4 Hz, 4H; H$_d$), 7.72 (s, 4H; H$_e$), 7.35 (t, J = 7.2 Hz, 4H; H$_b$), 6.96 (s, 4H; arene), 1.85

(s, 15H; Cp*). ^{13}C{^{1}H} NMR (75.4 MHz, CD$_3$NO$_2$): δ 164.9, 152.5, 140.4, 139.6, 124.6, 119.9, 119.5, 100.6, 94.9, 6.3. ^{19}F NMR (375 MHz, CD$_3$NO$_2$): δ −64.0 (6F; −CF$_3$). IR (neat ATR Harricks, cm^{-1}): ν(SbF$_6$) 635.

X-ray Crystal Structure Determination. Single crystals were selected, mounted, and transferred into a cold nitrogen gas stream. Intensity data was collected with Bruker Kappa-APEX2 systems using microsource Cu Kα for 4-CF$_3$-N^CH^N or fine-focus sealed tube Mo Kα radiation for [(4-CF$_3$-N^C^N)Pt—Cl, **5**, **6a**]. Unit-cell parameters determination, data collection strategy, integration, and absorption correction were carried out with the Bruker APEX2 suite of programs. The structures were solved with SHELXT-2014[44] [(4-CF$_3$-N^CH^N), (4-CF$_3$-N^C^N)Pt—Cl)] or SIR92[45] (**5**, **6a**) and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[44] using the WinGX suite.[46] The structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 1538568 for ligand (4-CF$_3$-N^CH^N), CCDC 1538569 for complex (4-CF$_3$-N^C^N)Pt—Cl), CCDC 1538570 for **5**, and CCDC 1538571 for **6a** and can be obtained free of charge via www.ccdc.cam.ac.uk.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00680.

Crystallographic data of 4-CF$_3$-N^CH^N, [(4-CF$_3$-N^C^N)PtCl], **5**, and **6a**. ^{1}H and ^{13}C NMR spectra of compounds **5**, **6a**, **6b**, **7a** and **7b** (PDF)

Accession Codes

CCDC 1538568−1538571 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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