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Biscyclometalated platinum complexes with thiophene ligands

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ABSTRACT

The reaction of $[Pt_2(CH_3)_4(\mu-S(CH_3)_2)_2]$ with four equivalents of ligand $C_4H_3SCH=NCH_2C_6H_5$ gives the platinum (II) complex $[Pt\{(C_4H_2S)CH=NCH_2C_6H_5\}_2]$ with two cyclometalated C-N ligands. $[Pt\{(C_4H_2S)CH=NCH_2C_6H_5\}_2]$ can also be prepared by refluxing the monometalated species $[Pt(C_4H_2SCH=NCH_2C_6H_5)CH_3(S(CH_3)_2)]$, alone in toluene or with the addition of one equivalent of ligand $C_4H_3SCH=NCH_2C_6H_5$. Similar reactions were observed for $[Pt_2(CH_3)_4(\mu-S(CH_3)_2)_2]$ with the ligands $(S)-C_4H_3SCH=NCH_2C_6H_5$ and $C_4H_3SCH=NC_6H_5$, and the corresponding monocyclometalated species. A mechanism of formation is proposed with the support of DFT calculations. The complexes show emission, in solution, at room temperature, with emission bands red-shifted ~ 200 nm, excited state lifetimes of the order of 1 μ s, and modest quantum yields up to 0.012. DFT calculations were used to assist in the assignment of the electronic spectroscopy.

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1. Introduction

C–H activation is an important area of research and the subject of much recent work in several areas of chemistry, including organometallic chemistry, catalytic chemistry, and bioinorganic chemistry [1–12,47]. The activation and selective functionalization of C-H bonds for industrial and synthetic purposes is a rich area of research [13-20]. Over the past several years we have synthesized a number of organometallic, cyclometalated complexes by C-H or C-X bond activation [21-23], as cyclometalated compounds and polypyridyl compounds, due to their interesting and rich photophysical properties, have applications in many areas, including, OLEDs, catalysts, solar energy conversion, molecular switches, molecular devices, and sensors [24-35]. Interest in such compounds stretches into bioinorganic applications as well [36,37]. Furthermore, thiophene-transition metal complexes have been studied for the important reason of understanding the process of hydrodesulfurization [38-41]. Here we describe the synthesis of biscyclometalated, thiophene, platinum compounds that emit at room temperature. Interestingly, the complexes may be synthesized in several straightforward ways by C-H activation/oxidative addition

followed by subsequent reductive elimination of methane with no prior activation of ligands.

2. Results and discussion

2.1. Synthesis

Imine ligands C₄H₃SCH=NCH₂C₆H₅, **3a** and (S)-C₄H₃SCH= NCHCH₃C₆H₅, **5a**, (Chart 1) were prepared from the condensation reactions of the appropriate primary amine and the appropriate aldehyde as previously reported [42,43]. 4a, C₄H₃SCH=NC₆H₅, and **7a**, $C_4H_3SCH = NCH_2C_{10}H_7$, which have not been previously reported, were prepared similarly. When four equivalents of 3a, 4a, and 5a, were allowed to react with the platinum dimer, $[Pt_2(CH_3)_4(\mu -$ S(CH₃)₂)₂ [44], **1**, in refluxing toluene (Scheme 1), the complexes with two cyclometalated ligands, 3c, 4c, and 5c, (Chart 1) were formed. The new complexes were characterized by their NMR, IR, UV/vis, emission spectra, quantum yields, excited state lifetimes, elemental analyses, as well as by high-resolution mass spectrometry (HRMS). The compounds 4b and 4c were characterized by X-ray diffraction, XRD, (see below) and, in the case of 3c, a low quality XRD study was conducted that was only good enough to indicate the connectivity of atoms, which showed a structure to be consistent with our spectroscopic data. In all cases the complexes are square

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Scheme 1. Synthesis of Complexes.

planar with the carbon donors of each chelate ligand trans to the imine nitrogen of the other chelate ligand.

The NMR spectra are very helpful in the characterization of the complexes. In the case of **3c**, the imine proton is observed at 7.98 ppm with Pt satellites of 70 Hz and the methylene protons at 4.70 ppm with Pt satellites of 12 Hz, all characteristic of platinum (II) cyclometalated species. All of our complexes have similar spectra and their peaks are in the same range as similar structures [23]. All bismetalated (mono and bis refer to the number of rings formed by C–H activation with a platinum center) compounds were analyzed using a high-resolution quadrupole time of flight mass spectrometer. In all cases, the observed *m*/*z* of the predominant [M + H]⁺ ion agreed with the exact mass of the predicted molecular formula within 3 ppm. The isotope distribution observed for each compound agrees with the isotope pattern predicted, further confirming that the compounds have the molecular formula reported.

One interesting point about the synthesis of these compounds is that the compounds can be made by three different methods. The most straightforward is the method mentioned above where four equivalents of ligand are allowed to react with the platinum dimethyl precursor. The second method involves the reaction of the monometalated species, 3b, 4b, or 5b, (Chart 1) with one equivalent of ligand (Scheme 1) in refluxing toluene. The third method, in our opinion the most interesting, is to reflux the monometalated species (Scheme 1) in toluene with no additional ligand. This third method produces the final bismetalated product in small yields, is accompanied by decomposition of some starting monocyclometalated material, and must involve a sacrificial platinum complex in order that the final complex include the second cyclometalated ligand (Scheme 1). It appears that 3c, using the third method, is formed under more mild conditions (as determined by the time of reflux needed to complete the reaction) than 5c, which in turn, is formed under more mild conditions than **7c**, which was never obtained in pure form because of excessive decomposition. 7c was obtained only by the third method, not the other two methods, and only in miniscule amounts. However, 7c was partially characterized by NMR and HRMS, as it was the major product of the impure mixture. 6c (S.I.), a target compound with two cyclometalated (R)-C₄H₃SCH= NCHCH₃C₁₀H₇ ligands [45], was not obtained under any reaction conditions attempted. The monometalated species, 6b, has been reported [45] and forms easily under mild conditions. 7b was formed analogously to 6b. We can speculate that steric hindrance in the transition state may be the relevant variable in the formation of the products involving a sacrificial platinum complex, as we propose a bimetallic intermediate in order to facilitate the transfer of the second ligand to the first metal center (see below and Scheme 2). 3c has the least amount of steric crowding (Chart 1), as it has a small methylene group between the thiophene ring and the dangling phenyl ring off of the imine. 5c has an additional methyl group in between the two rings, while 7c has a dangling naphthyl instead of the phenyl group. 6c would have had both the methyl in the spacer group and a dangling naphthyl, which leads us to speculate that the steric hindrance precludes any reaction to afford product in this case. **4c** has no methylene spacer and only a phenyl group directly attached to the thiophene ring; therefore, it is somewhat structurally different and more rigid than the others and is not included in this direct comparison. Cyclometalated ligands are usually very rigid and somewhat inert. The complexes with two such ligands are much more inert than the complexes with only one C_N ligand, as can be observed from their lack of reactivity in refluxing toluene and they are also relatively unreactive for several days at room temperature in common solvents. The biscyclometalated compounds reported here are formed as a straightforward manner as a direct result of oxidative addition of the appropriate C-H bond followed by a subsequent reductive elimination of methane and are more easily prepared and purified than the previously reported thienvlpyridine complexes. which do not have an imine functionality, were orthometalated at the 3-position of the thiophene ring, and required lithiation of the ligands to activate them in order to obtain the bismetalated products [46]. Therefore our synthesis allows for a direct reaction and eliminates the need of extra halogenation/lithiation steps.

DFT studies at the B3LYP/LANL2DZ level were preformed on all intermediates for a proposed pathway for the formation of **3c** (Scheme 2a and b). The GaussianO3 suite of programs was used to do all calculations. The reaction path has two possible routes, one involving bimetallic intermediates and another that involves single metal intermediates. Scheme 2a and b lists the energies of the intermediates along the reaction coordinate for both the bimetallic route and the route when an additional equivalent of ligand is added to the system, respectively (see Scheme 1 for overall details). All reported structures were optimized to ground states as



Chart 1. : Structure of ligands and complexes. Compound 7c was not obtained in pure form.

confirmed by frequency analysis of each structure. All thermodynamic values appear reasonable given the required experimental reaction conditions. Although transition states have not been located along the entire route for each path, much information can be gained by ground state calculations of suspected intermediates [2,47]. Either mechanism is plausible given the energy of the intermediates and the reaction conditions used to make the bismetalated products.

In the case of the reaction without free ligand, where a sacrificial metal compound is needed, we hypothesize that the intermediate is bimetallic with the sulfur of the thiophene ring being loosely coordinated to the platinum (Fig. 1) [47] thus stabilizing the molecule. The structure **C5** depicted in Fig. 1 is that of an optimized ground state. Furthermore, in order to test whether the

conformations of the bimetallic species were reasonable multiple conformations were energy optimized and each found the same lowest energy structure. That is, the geometry (Fig. 1) is for the minimum in which the sulfur of the thiophene ring is directed toward what would otherwise be a vacant site at platinum. The energy of this conformation is lower than that of any in which the sulfur is pointed away from the metal center. In this case, without additional ligand, we would not expect both ends of the C-N chelate ligand to dissociate from one metal center completely and then subsequently attack the second platinum center. We note that the calculations for loss of dimethylsulfide are favored compared to dissociation of the imine nitrogen, thus favoring an entry into our proposed mechanism for bismetalation. On a separate note, the equilibrium between the starting material (C-N)PtMe(S(CH₃)₂) and



All units are in kcal/mol and are the deltaH or deltaG reaction for the indicated step as gas phase. Gtoluene also includes a pcm solvent model with toluene as solvent.



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Scheme 2. a: Proposed bimetallic, bismetalation mechanism. b: Proposed reaction mechanism with additional ligand added.



Fig. 1. Molecule **C5** (see Scheme 2a) showing close contact between thiophene sulfur and platinum. Close contact distance is calculated as 2.77 A in optimized structure. Starting an energy optimization from other conformations show that the molecule will approach the depicted structure.

 (C_N) PtMe (H_2O) is essentially thermoneutral (Hrxn = 0.9 kcal/mol), very slightly favoring water coordination at platinum. Given the above, adventitious water in the solvent may provide the hydrogen source for the elimination of the ligand from the platinum (C6 through C8). Since the equilibrium seems viable, it is reasonable to consider the reaction of C1 and C2 to make the dinuclear species, which, as stated above, our calculations suggest is stabilized by sulfur from thiophene coordinating at the 'vacant site' of the three coordinate species C2. Finally, refluxing the monometalated species in toluene would certainly give enough thermal energy to drive all reactions as written. An alternative mechanism involving a simple transmetalation is also possible. Several calculations were run to obtain thermodynamic data for a variety of transmetalation reactions (Scheme SI-1) and in all cases the reactions were close to thermoneutral in the gas phase. When solvent correction was added the free energy increased, slightly disfavoring the formation of the initial products, as written in the scheme, for all cases. However, these reactions had platinum metal precipitation associated with them therefore the products listed in the schemes are most likely not the final decomposition products. Hence the fate of the second platinum atom and other ligands is not explicitly known but can only be labeled as "unidentifiable decomposition products". No compound in the crude reaction mixtures other than starting material or product could be definitively assigned.

In the case where additional ligand has been added or is available, the reaction may certainly proceed as outlined in Scheme 2b, where the imine nitrogen of the second ligand coordinates to the platinum after the dimethylsulfide has dissociated. The reaction would then continue with oxidative addition of the C–H bond of the thiophene followed by reductive elimination of methane, two well-known reactions.

2.2. Structures of complexes 4b and 4c

Suitable crystals of [C₆H₅NC₅H₃SPt(S(CH₃)₂)CH₃], **4b**, were grown by the vial-in-a-vial technique with slow diffusion of pentane into an acetone solution. The crystal structure is composed of discrete molecules separated by van der Waals interactions. No pi-stacking or intermolecular interactions were found. Selected bond lengths and angles are given in Table 1a and a molecular view is shown in Fig. 2a. The compound consists of a square planar platinum (II) center bonded to one cyclometalated 4a ligand, a methyl group, and a dimethylsulfide ligand. Bond lengths and angles are in the expected range for analogous compounds [23,45,46]. Suitable crystals of $[Pt((C_4H_2S)CH=N(C_6H_5))_2]$, 4c, were grown by slow evaporation of acetone. The crystal structure is composed of discrete molecules separated by van der Waals interactions. No pi-stacking or intermolecular interactions were found. However the two dangling phenyl rings have an intramolecular pistacking interaction. Selected bond lengths and angles are given in Table 1b and a molecular view is shown in Fig. 2b. The compound consists of a square planar platinum (II) center bonded to two identical 4a ligands. Each cyclometalated ligand in each structure behaves as a [C,N]-bidentate and a five-membered chelate ring is formed in each case, fused with the thiophene moiety, as fivemembered metallacycle rings are quite common [22]. The imine N donor atom of each ligand is trans to a carbon donor atom; methyl in the case of **4b** and a carbon of the thiophene ring of the second ligand for 4c, which agrees with our NMR data. The five-membered rings are relatively planar. The angles between adjacent atoms in the coordination sphere of platinum lie in the range $78-104^{\circ}$, with the N(1)–Pt–N(2) angle of **4c** being the largest at $103.7(1)^{\circ}$. This is probably due to the crowding caused by the pendant phenyl rings. 4c has no methylene spacer between the metallacycle and the dangling phenyl group, unlike many of our earlier reported structures. However, bond lengths and angles are in the expected range for analogous compounds [23,45,46]. In all cases, the stereochemistry at the C=N is necessarily trans. The metallacycle is approximately planar and coplanar with the thiophene ring.

3. Absorption and emission spectroscopy

The absorption spectra of ligands **3a**, **4a**, and **5a** were recorded and the compounds do not absorb in the visible region. Numerical data for all absorption and emission spectra is given in Table 2.

3a and **5a** have very similar spectra (see S.I.) whereas **4a**'s spectrum has its peaks red-shifted by approximately 30 nm. The ligands show no emission at 300 K when excited at their lowest energy peak. The absorbance spectra of the monocyclometalated complexes **3b**, **4b**, and **5b** are shown in Fig. 3. They show several bands in the UV/vis range with the lowest energy bands at 420 nm for **3b** and **5b**, and 435 nm for **4b**. All three compounds emit in the visible when excited at these wavelengths (Fig. 4). The emission spectra of **3b** and **4b** are very similar. They are broad and have a maximum at approximately 610 nm. **5b**'s spectrum is slightly different with a peak at 650 nm and a shoulder at 575 nm.

Table 1a							
Selected bond	lengths (Å)	and angles	(°) with	estimated	standard	deviations	for
compounds Al	h						

F F F F F F F F F F F F F F F F F F F			
Pt(1)-C(1)	1.9719(18)	Pt(1)–C(14)	2.0447(19)
Pt(1)-N(1)	2.1662(15)	Pt(1)-S(2)	2.3416(5)
S(2)-C(12)	1.797(2)	S(2)-C(13)	1.800(2)
C(1) - Pt(1) - C(14)	93.93(8)	C(1) - Pt(1) - N(1)	78.20(7)
C(14) - Pt(1) - N(1)	170.71(7)	C(1) - Pt(1) - S(2)	171.12(6)
C(14) - Pt(1) - S(2)	92.47(6)	N(1)-Pt(1)-S(2)	94.86(4)
C(1)-S(1)-C(2)	94.21(9)	C(12)-S(2)-C(13)	98.52(11)



Fig. 2. a) Molecular structure of compound 4b, b) Molecular structure of compound 4c.

Absorption spectra of 3c, 4c, and 5c are shown in Fig. 5. 3c and 5c each have a pronounced peak at around 420 nm, and 4c has a well-defined peak at 435 nm. These peaks have extinction coefficients that are several times greater than the corresponding peaks

Table 1h Selected bond lengths (Å) and angles (°) with estimated standard deviations for annda Aa

compounds 4c.			
Pt(1)-Cl(1)	1.969(3)	Pt(1)-C(12)	1.974(3)
Pt(1)-N(1)	2.134(2)	Pt(1) - N(2)	2.141(2)
S(1) - C(1)	1.712(3)	S(2)-C(12)	1.713(3)
C(1) - Pt(1) - C(12)	99.1(2)	C(1) - Pt(1) - N(1)	78.6(1)
C(12) - Pt(1) - N(1)	177.6(1)	C(1) - Pt(1) - N(2)	171.8(1)
C(12) - Pt(1) - N(2)	78.7(1)	N(1) - Pt(1) - N(2)	103.7(1)
C(1)-S(1)-C(2)	93.9(2)	C(12)-S(2)-C(13)	94.4(2)

in monocyclometalated compounds. This increase indicates that the biscyclometalated complexes are not just two discrete ligands bound to one metal center and indicates that these peaks are probably not intraligand bands. Since the ligands themselves do not absorb in the visible and the extinction coefficients for these biscvclometalated complexes in the 400-440 nm range are on the order of 10^3 (M⁻¹ cm⁻¹), we tentatively assign the absorbance peaks as charge transfer bands. These bands have traditionally been assigned [46,48-50] as MLCT, but more recent reports [29,33], in conjunction with computational studies (see below), would have us assign these transitions as mixed metal-ligand to ligand charge transfer (MM-LLCT). In addition, these biscyclometalated complexes have a much less intense absorbance peak at lower energy, with 4c's being the most pronounced at 530 nm. This peak at lower energy is assigned to the direct excitation to the triplet state similar to the biscyclometalated complexes recently reported [33]. TDDFT calculations predict such a peak to occur at 543 nm. The bismetalated complexes are clearly different than the monometalated cases, probably due to the presence of two strongly donating, rigid, relatively inert, chelate ligands [31]. The complexes showed emission at room temperature when excited at the appropriate wavelength 420 or 435 nm. 3c and 5c have essentially identical emission spectra, while 4c's spectrum has its peak at slightly higher wavelength (Fig. 6). All three emission spectra tail off with a slight shoulder on the lower energy side. **4c** has slightly different spectra then its analogs probably due to the lack of a methylene spacer between the phenyl ring and the metallacycle. This missing spacer may allow for better conjugation and cause the peak to shift to lower energy.

All six metal complexes have their emission peaks red-shifted between 190 and 245 nm, characteristic of phosphorescence emission expected from a triplet state typical for heavy metal complexes with strong spin-orbit coupling [30,51]. All three biscyclometalated complexes and 5b have larger red-shifts than the two monometalated species 4b and 3b. 4c has the greatest shift at 245 nm, which can be attributed to the structure and the rigidity of the ligands. **5b** has a discernible shoulder on the higher energy side of its peak while **3b** and **4b** have peaks that are very broad. All bismetalated species have narrower bands with some slight asymmetry. The lifetimes of the excited states for all six compounds were determined and all were found to be in the 700-1300 ns range, which is consistent with the above assignment. In addition, there is a very short-lived state (approx. 60 ns) for all of the monometalated species but none of the bismetalated complexes. This may be due to fluorescence from the excited singlet state or an intraligand band. Quantum yields for all species are modest [32c], with the monometalated species being the lowest (Table 2). Both sets of the emission spectra and the absorbance spectra of all six compounds had similar shape and relative ratio of band intensities as a function of concentration.

DFT calculations were performed to help explain the electronic spectra of the complexes. These calculations show that the predicted bands for the lowest energy transition can be explained by charge transfer from HOMO to LUMO, which are mixed metal/ ligand-based and ligand-based respectively, whereby electron density is moved from the platinum and coordinated thiophene to the N=C-C=C ring attached to the metal (see S.I. for orbital diagrams). This type of charge transfer is consistent among each of the compounds 3c, 4c and 5c. All three compounds have remarkably similar orbital compositions for the HOMO – 1, HOMO, LUMO, and LUMO + 1 (Table 3). Similarly for compounds **3b** and **4b**, the excitation from HOMO to LUMO moves electron density from a mixed metal-ligand HOMO to a ligand LUMO where electron density is primarily transferred from the Pt-thiophene moiety to the N=C-C=C ring. With **5b** the energy of the HOMO and

Table 2		
UV/vis and	emission	data.

Compley	Absorption $\frac{1}{2}$ /pm ($\frac{1}{2}$ /M ⁻¹ cm ⁻¹)	Emission) /nm	Red shift) /nm	Quantum vield %	Lifetime ns ^a
complex	Absolption Amax/IIII (2/W CIII)	Linission Amax/IIII	Red Shire Amax/IIII	Quantum yielu //	
3a	252 (15,900), 296 (1980)				
4a	270 (16,000), 335 (3910)				
5a	250 (15,900), 296 (3090)				
3b	257 (17,800), 335 (2950), 381 (2070), 420 (718)	613	193	0.47	61(1)
					1360(10)
4b	265 (19,000), 342 (5490), 391 (2780), 435 (1960)	623	188	0.11	178(2)
					758(14)
5h	258 (20 100) 336 (3100) 377 (2430) 420 (1040)	647	227	0.59	60(5)
56	230 (20,100), 330 (3100), 377 (2130), 120 (1010)	017	227	0.55	877(3)
30	260 (23 000) 295 (10 400) 360 (4390) 420 (8820)	650	230	10	1324(2)
J.	200 (23,000), 233 (10,400), 300 (4330), 420 (8820)	630	230	1.2	1324(2)
40	264 (308,000), 290 (17,600), 320 (11,700), 365 (6540), 435 (7890),	680	245	0.25	705(1)
	530 (1510)				
5c	260 (28,600), 290 (14,600), 360 (5570), 420 (10,500)	650	230	1.2	839(2)

^a Error associated with lifetime value is given in parentheses.

HOMO-1 is reversed compared to **3b** and **4b**. This could be explained due to the variation of the R group adjusting the energies of the frontier orbitals. Given this reversal, it is interesting that the emission spectrum of **5b** is somewhat different than that of **3b** and **4b**, in that it has a larger red-shift and a well-defined shoulder at higher energy. The composition of the orbitals and their energies are shown in Table 3.

The predicted wavelengths of transitions based on these frontier orbitals match reasonably well with the UV/vis data for the biscyclometalated complexes and aided our assignment of the absorption spectra as mixed metal–ligand charge transfer to ligand [33]. In addition, the relative changes between HOMO/LUMO within both the monometalated analogs and the bismetalated analogs match the experimental values very well. For example, **3b** and **5b** have very similar absorption maxima, while the maximum of **4b** is ~20 nm higher in wavelength.

4. Concluding remarks

Bismetalated platinum complexes were synthesized by several different methods, including the reaction of a monometalated precursor with a second sacrificial molecule. The complexes are luminescent at ambient temperature, have lifetimes of around 1 μ s, and exhibit shifts in the emission spectra of ~200 nm. This data is characteristic of cyclometalated platinum complexes and consistent with our electronic assignments. The compounds **5b**, **5c**, and **3c** have intense emission peaks at around 650 nm, while **4c** has its emission peak at around 690 nm and tails off up to 800 nm. Platinum complexes with MLCT-type bands and an emission tail in the



UV/Vis Spectra of 3b, 4b and, 5b in DCM

Fig. 3. UV/vis spectra for 3b, 4b, and 5b.

NIR may possibly be of interest as red-emitting photosensitizers with potential applications in biological systems as new ruthenium/bipyridine/bicyclic—guanidine complexes have been reported with such an interest in mind. These ruthenium complexes emit at longer wavelengths (around 740 nm), but have shorter excited state lifetimes and lower quantum yields [52]. We are currently testing our compounds in catalytic systems.

5. Experimental

5.1. General

¹H and ¹³C NMR spectra were recorded using a Varian 400 MHz (¹H, 400 MHz; ¹³C, 100 MHz) spectrometer, and referenced to Si(CH₃)₄ (¹H, ¹³C). δ values are given in ppm and *J* values in Hz. IR spectra were recorded on a Thermo-Nicolet FT-IR Spectrophotometer with a diamond ATR. UV–vis spectra were recorded using an Agilent 8453 spectrophotometer.

5.2. Photophysical measurements

Steady-state emission spectra were recorded using a PTI QM-3 instrument with an R928 PMT detector, which is sensitive up to 850 nm. The solutions were de-gassed before spectra were taken and the concentrations for the spectra in Figs. 4 and 6 were in the range 10^{-5} — 10^{-4} M. Emission spectra were recorded using excitation wavelengths of 420 nm for **3b**, **5b**, **3c**, and **5c**; and 435 nm for **3c** and **4c**. Luminescence quantum yields were determined using [Ru(bipy)₃]Cl₂ (in aqueous solution) as a standard following known



Fig. 4. Emission spectra for **3b**, **4b**, and **5b** (excitation wavelength 420, 435, and 420 nm, respectively; concentration (6.78, 6.64, 7.36) \times 10⁻⁵ M, respectively).



Fig. 5. UV/vis spectra for 3c, 4c, and 5c.

procedures; uncertainties are estimated at 20% or better [32]. In these experiments, concentrations of the metal species (in dichloromethane) ranged from 10^{-5} to 10^{-4} M for **3b**; 10^{-6} to 10^{-5} M for **3c**, **4c**, **5c**, and **5b**; and 10^{-5} to 10^{-3} M for **4b**. Temperatures were in the range of 25–26 °C. The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting following excitation at 405 nm with a pulsed-diode laser in methylene chloride. All samples were de-gassed and had concentrations adjusted so that the absorbance at 405 nm was between 0.1 and 0.3 A.U. immediately prior to excitation and measurement.

5.3. Mass spectrometry

The compounds were re-suspended in CHCl₃ and were analyzed in the positive mode using an Agilent 6520 electrospray ionization quadrupole time-of-flight mass spectrometer. Using an Agilent 1100 HPLC system, 10 mL of sample was injected using CHCl₃ as the mobile phase and a flow rate of 0.4 mL/min. No column was used. Samples were ionized by electrospray ionization in the positive mode. Mass spectra were obtained scanning from 100 to 2000 at 1 spectra per second with the following instrument parameters: fragmentor voltage, 175 V; drying gas temperature, 325 °C; drying gas flow, 11 L/min; nebulizer pressure, 45 psig; capillary voltage, 4000 V. Data were collected with the instrument set to 3200 m/zrange under high resolution conditions at 4 GHz data acquisition rate. Data were collected in profile mode. The instrument was calibrated using Agilent ESI-L low concentration tuning mix and under



Fig. 6. Emission spectra for 3c, 4c, and 5c (excitation wavelength 420, 435, and 420 nm, respectively; concentration (1.17, 1.16, 11.0) \times 10⁻⁵ M, respectively).

Table 3				
Orbital	composition of HOMO	and	LUMC)

	•				
	HOMO - 1	НОМО	LUMO	LUMO + 1	
Pt contribution to orbital (%D character)					
3b	89(72)	36(36)	7(4)	1(~0)	
4b	88(72)	37(37)	8(5)	13(3)	
5b	34(34)	78(41)	1(1)	0(0)	
3c	23(23)	37(37)	4(1)	8(8)	
4c	22(22)	33(33)	7(7)	7(7)	
5c	25(25)	37(37)	5(1)	8(8)	
Energies in eV					
3b	-5.6053	-5.2097	-1.3023	-0.7818	
4b	-5.7111	-5.3424	-1.6776	-0.7372	
5b	-5.6500	-5.1993	-1.3113	-0.5426	
3c	-5.6195	-5.2453	-1.9399	-0.8694	
4c	-5.7969	-5.3887	-2.3206	-1.4526	
5c	-5.6083	-5.2467	-1.9225	-0.9301	

normal operating conditions the resolution of the instrument was \sim 15,000 and the mass accuracy of the instrument was between 1 and 5 ppm; therefore, measured masses are given to three decimal places. Data acquisition and analysis was performed using Agilent MassHunter Workstation Acquisition Software and Agilent Mass-Hunter Workstation Qualitative Analysis Software (Agilent Technologies, Santa Clara, CA), respectively. Exact masses and isotope distributions were calculated using CS ChemBioDrawUltra.

5.4. X-ray diffraction

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo K α ($\lambda = 0.71073$ Å)) at 125 K. Crystals were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.14) [53]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. See Chart 1 for drawings and labels. Table 4 lists crystal data.

Table 4

Summary of crystal data and intensity collection and structure refinement parameters for complexes **4c** and **4b**.

	Compound 4c	Compound 4b
Empirical	Formula C22H16N2PtS2	C ₁₄ H ₁₇ NPtS ₂
Molecular weight	567.58	458.50
Crystal color, habit	Plate, red	
Crystal size (mm)	$0.20 \times 0.20 \times 0.02$	0.20 \times 0.20 \times
		0.10 mm
Temperature (K)	125(2)	125(2)
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2/n
Unit cell dimensions		
a (Å)	16.492(2)	8.0682(3)
b (Å)	10.2704(14)	17.7063(6)
<i>c</i> (Å)	22.112(3)	10.7177(4)
α (0)	90	90
β(0)	94.743(2)	107.05
γ (o)	90	90
V (Å ³), Z	3732.4(9), 8	1463.82(9), 4
$D_{\text{calc}} (\text{mg m}^{-3})$	2.020	2.080
Absorption coeff. (μ , mm ⁻¹)	7.752	9.852
Φ range collected (°)	1.85-31.88	2.30-30.53
Completeness to Φ max (%)	99.6	99.8
Reflns collected/unique (R(int))	16,061/5934 (0.0367)	23,547/4471
		(0.0229)
Data/restraints/parameters	5934/0/244	4471/0/166
R1, wR2 $(I > 2sI)$	0.0239, 0.0537	0.0138, 0.0319
R1, wR2 (all data)	0.0322, 0.0568	0.0156, 0.0325
Goodness of fit on F ²	1.007	1.026
Largest diff peak/hole (e/Å ³)	1.446, -1.064	1.216, -0.665

5.5. Computational work

The Gaussian03 suite of programs was used to do calculations [54a]. DFT studies at the BL3LYP/LANL2DZ [54b] level were preformed on all intermediates of a proposed pathway for the formation of **3c** (Scheme 2). Solvation was modeled with the selfconsistent reaction field (SCRF) calculations using the PCM-UA0 solvation model [55,56] and was carried out for the gas-phase optimized structures. The solvation model otherwise used the default parameters for the solvents chosen. Free energies are taken at 298.15 K and 1 atm. All reported structures optimized to ground states as confirmed by frequency analysis of each structure. Furthermore, in order to test whether the conformations of the bimetallic species were reasonable multiple conformations were energy optimized and each found the same lowest energy structure.

5.6. Synthesis

 $[Pt_2(CH_3)4(\mu-S(CH_3)_2)_2]$, **1**, ligand $[(C_4H_3S)CH=NCH_2(C_6H_5)]$, **3a**, compound $[PtCH_3(S(CH_3)_2){(C_4H_2S)CH=NCH_2(C_6H_5)}]$, **3b**, ligand $[(S)-(C_4H_3S)CH=NCH_2CH_3(C_6H_5)]$, **5a**, compound $[PtCH_3(S(CH_3)_2){(S)-(C_4H_2S)CH=NCH_2CH_3(C_6H_5)}]$, **5b**, ligand $[(R)-(C_4H_3S)CH=NCH_2CH_3(C_{10}H_7)]$, **6a**, compound $[PtCH_3(S(CH_3)_2){(R)-(C_4H_2S)CH=NCH_2CH_3(C_{10}H_7)}]$, **6b**, were prepared as reported [42,44,45].

Compound $[Pt{(C_4H_2S)CH=NCH_2(C_6H_5)}_2]$, **3c**, was prepared by the three methods. Method 1: 3c was obtained by refluxing ligand 3a (70.1 mg, 0.348 mmol) with $[Pt_2(CH_3)_4(\mu-S(CH_3)_2)_2]$ (50.0 mg, 0.0871 mmol) in a 4:1 ratio in anhydrous toluene (20 mL) for 30 min. The resulting brown powder was washed and triturated in cold diethyl ether. Yield: 57.7 mg (55.6%). Method 2: 3c was obtained by refluxing ligand 3a (8.9 mg, 0.044 mmol) with compound 3b (20.0 mg, 0.0423 mmol) in anhydrous toluene (20 mL) in a 1:1 ratio for 2 h. The resulting brown powder was washed and triturated in cold diethyl ether. Yield: 11.8 mg (46.8%). *Method* 3: **3c** was obtained by refluxing compound **3b** (15.3 mg, 0.0324 mmol) in anhydrous toluene (35 mL) for 1 h. Yield: 7.1 mg (74%). [Pt{(C₄H₂S)CH=NCH₂(C₆H₅)}₂], **3c**. ¹H NMR (400 MHz, CDCl₃): $\delta = 4.70$ [s, ³](Pt-H^b) = 12, 2H, H^b]; {7.13-7.38, aromatics}; 7.98 [s, ${}^{3}J(Pt-H^{a}) = 70$, 1H, H^a]. ${}^{13}C$ NMR (100 MHz, CDCl₃): $\delta = 62.10$ [C^b]; {126.72; 127.41; 128.95; 156.96 [s, C^f], aromatics}; {126.56 [s, J(Pt-C) = 57]; 124.86 [s, J(Pt-C) = 48]; 138.23 $[s, C^{h}]; 147.23 [s, C^{g}], thiophene \}; 171.13 [s, {}^{3}J(Pt-C^{a}) = 66, C^{a}]. ESI-MS$ (*m*/*z*): Found: *m*/*z* 595.0771, Calculated for [Pt{(C₄H₂S)CH= NCH₂(C_6H_5)₂]: m/z 595.0767. Elemental Analysis Calc. for C_{25.5}H₂₅N₂O_{1.5}PtS₂ (**3c** · 0.5(CH₃)₂CO · H₂O): C, 47.65; H, 3.92; N, 4.36. Found: C = 47.80; H = 3.49; N = 4.38.

Ligand [(C₄H₃S)CH=N(C₆H₅)], **4a**, was obtained by stirring a 1:1 ratio of 3-thiophene carboxaldehyde (602 mg, 5.37 mmol) and aniline (500. mg, 5.37 mmol) in methylene chloride (17 mL) for 90 min. This was dried over MgSO₄ and filtered, yielding a brown oil. Yield: 813 mg (80.9%). [(C₄H₃S)CH=N(C₆H₅)], **4a**. ¹H NMR (400 MHz, CDCl₃): $\delta = \{7.26-7.80, \text{ aromatics}\}; 8.48 [s, 1H, H^a]. ESI-MS ($ *m*/*z*): Found:*m*/*z*188.0530, Calcd for [(C₄H₃S)CH=N(C₆H₅)],*m*/*z*188.0528.

Compound [PtCH₃(S(CH₃)₂){(C₄H₂S)CH=N(C₆H₅)]], **4b**, was obtained by combining [Pt₂Me₄(μ -SMe₂)₂] (76.4 mg, 0.133 mmol) dissolved in acetone (25 mL) with ligand **4a** (49.9 mg, 0.266 mmol) in a 1:2 ratio. The solution was stirred for 90 min at room temperature. The resulting orange solid was washed in cold diethyl ether. Yield: 47.0 mg (38.5%). This contained two isomers in an approximate 5:1 ratio. The isomer in least abundance was washed away with cold ether to afford a pure product. [PtCH₃(S(CH₃)₂) {(C₄H₂S)CH=N(C₆H₅)]], **4b**. ¹H NMR (400 MHz, CDCl₃): δ = 1.23 [s, ²J(Pt-H^c) = 81, 3H, H^c]; 2.13 [s, ³J(Pt-H^d) = 30, 6H, H^d]; {7.17-7.42, aromatics}; 8.36 [s, ³J(Pt-H^a) = 48, 1H, H^a]. Elemental Analysis Calc.

for $C_{15,5}H_{21}NOPtS_2$ (**4b** $\cdot 0.5(CH_3)_2CO \cdot 0.5H_2O$): C, 37.49; H, 4.26; N, 2.82. Found: C = 37.52; H = 3.60; N = 3.14.

Compound $[Pt{(C_4H_2S)CH=N(C_6H_5)}_2]$, **4c**, was prepared by three methods:

Method 1: **4c** was obtained by refluxing a solution of [Pt₂(CH₃)₄(µ-S(CH₃)₂)₂] (77.3 mg, 0.134 mmol) with ligand 4a (101 mg, 0.540 mmol) in a 1:4 ratio in anhydrous toluene (21 mL) for 4 h. Removing the solvent resulted in a dark red powder which was washed and triturated with cold diethyl ether. Yield: 66.8 mg (43.7%). Method 2: 4c was obtained by stirring a solution of 4b (11.8 mg, 0.0257 mmol) with ligand 4a (4.7 mg, 0.025 mmol) in a 1:1 ratio in anhydrous toluene (21 mL) for 4 h. Removing the solvent resulted in a dark red powder, which was washed and triturated with cold diethyl ether. Yield: 2.9 mg (20.%). Method 3: 4c was obtained by refluxing **4b** (14.8 mg, 0.0322 mmol) in 10 mL of anhydrous toluene for 1.5 h. Removing the solvent resulted in a dark red powder. Yield: 2.2 mg (25%). $[Pt{(C_4H_2S)CH=N(C_6H_5)}_2],$ **4c.** ¹H NMR (400 MHz, CDCl₃): $\delta = \{6.82 - 7.29, \text{ aromatics}\}; 8.16 [s,]$ ${}^{3}J(Pt-H^{a}) = 67, 1H, H^{a}]$. ${}^{13}C$ NMR (100 MHz, CDCl₃): $\delta = \{121.77;$ 126.13; 128.53; 158.30, aromatics}; {125.50 [s, J(Pt-C) = 49]; 126.93 [s, J(Pt-C) = 58]; 148.49 [s, J(Pt-C) = 33]; 149.37, thiophene}; 169.57 [²](Pt-C) = 62, Me^a]. ESI-MS (m/z): Found: m/z[567.0441], Calcd for $[Pt{(C_4H_2S)CH=N(C_6H_5)}_2]: m/z$ [567.0455]. Elemental Analysis Calc. for C₂₂H₁₈N₂OPtS₂ (4c·H₂O): C, 45.12; H, 3.10; N, 4.78. Found: C, 45.39; H, 2.98; N, 4.57.

Compound $[Pt{(S)-(C_4H_2S)CH=NCHCH_3(C_6H_5)}_2]$, **5c**, was prepared by three methods.

Method 1: 5c was obtained by reacting $[Pt_2(CH_3)_4(\mu-S(CH_3)_2)_2]$ (50.0 mg, 0.0871 mmol) with ligand **5a** (75.4 mg, 0.350 mmol) in a 1:4 ratio in anhydrous toluene (18 mL). The solution was allowed to reflux for 11 h before being washed and triturated in cold diethyl either, resulting in a brown powder. Yield: 40.8 mg (37.6%). Method 2: 5c was obtained by reacting compound 5b (20.5 mg, 0.0421 mmol) with ligand 5a (8.9 mg, 0.041 mmol) in toluene (10 mL) in a 1:1 ratio. The solution was allowed to reflux for 2 h before being washed and triturated in cold diethyl either, resulting in a brown powder. Yield: 3.6 mg (14%). Method 3: 5c was obtained by refluxing compound 5b (26.1 mg, 0.0536 mmol) in anhydrous toluene (20 mL). The solution was allowed to reflux for 1 h. Yield: 2.9 mg(17%). [Pt{(C₄H₂S)CH=NCHCH₃(C₆H₅)}₂], **5c**. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.64 [d, {}^{4}J(Pt-H^{e}) = 7, 3H, H^{e}]; 5.19 [d,]$ ${}^{3}J(Pt-H^{b}) = 7, 1H, H^{b}]; \{6.99-7.52, aromatics\}; 7.96 [s, {}^{3}J(Pt-H^{a}) = 70,$ 1H, H^a]. ¹³C NMR (100 MHz, CDCl₃): $\delta = 21.32$ [C^e]; 62.76 [s, C^b]; {124.95 [s, *J*(Pt-C) = 48]; 126.46; 141.06; 148.12, thiophene}; {127.64; 127.85; 128.95; 155.59, aromatics}; 167.37 [C^a]. ESI-MS (*m*/*z*): Found: *m*/*z* 623.1092, Calculated for [Pt{(C₄H₂S)CH=NCHCH₃(C₆H₅)}₂]: *m*/*z* 623.1080. Elemental Analysis Calc. for C₂₆H₂₇N₂O_{1.5}PtS₂ (**5c** · 1.5H₂O): C, 47.99; H, 4.18; N, 4.30. Found: C, 47.82; H, 3.70; N, 3.95.

Ligand [(C_4H_3S)CH=NCH₂($C_{10}H_7$)], **7a**, was obtained by reacting 1-naphthalene methylamine (228 mg, 1.45 mmol) with 3-thiophene carboxaldehyde (169 mg, 1.51 mmol) in ethanol (20 mL) and refluxing for 3 h. Yield: 48.7 mg (13.3%). [(C_4H_3S)CH=NCH₂($C_{10}H_7$)], **7a**. ¹H NMR (400 MHz, CDCl₃): δ = 5.26 [s, 2H, H^b]; 8.40 [s, 1H, H^a]. ESI-MS (*m*/*z*): Found: *m*/*z* [252.0828], Calculated for [(C_4H_3S)CH=NCH₂($C_{10}H_7$)]: *m*/*z* [252.0841].

Compound [PtCH₃(S(CH₃)₂){(C_4H_2S)CH=NCH₂($C_{10}H_7$)}], **7b**, was obtained by reacting [Pt₂(CH₃)₄(μ -S(CH₃)₂)₂] (75.0 mg, 0.131 mmol) with ligand **7a** (65.0 mg, 0.259 mmol) in acetone (20 mL) and stirring the solution at room temperature for 16 h. It was then washed and triturated in cold diethyl ether, resulting in an orange powder. Yield: 58.3 mg (43.1%). [PtCH₃(S(CH₃)₂){(C₄H₂S) CH=NCH₂(C₁₀H₇)}], **7b**. ¹H NMR (400 MHz, CDCl₃): δ = 1.18 [s, 3H, H^c]; 2.06 [s, ³*J*(Pt-H) = 16, 6H, H^d]; 5.47 [s, ³*J*(Pt-H) = 10, 2H, H^b]; 8.34 [s, ³*J*(Pt-H) = 52, 1H, H^a].

Compound $[Pt{(C_4H_2S)CH=NCH_2(C_{10}H_7)}_2]$, **7c**, was obtained by refluxing compound **7b** (21.2 mg, 0.0406 mmol) in anhydrous toluene (20 mL) for 3 h. It was then washed and triturated in cold diethyl ether, resulting in an impure black powder. However NMR and mass spec were obtained with impurities present. [Pt{(C₄H₂S) CH=NCH₂(C₁₀H₇)]₂], **7c**. ¹H NMR (400 MHz, CDCl₃): δ = 5.02 [s, 2H, H^b]; 7.94 [s, 1H, H^a]. ESI-MS (*m*/*z*): Found: *m*/*z* 695.1082, Calculated for [Pt{(C₄H₂S)CH=NCH₂(C₁₀H₇)]₂]: *m*/*z* 695.1080.

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Appendix A. Supplementary information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.10.027.

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