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Article

First Example of the Solid-State Thermal Cyclometalation of Ligated Benzophenone Imine Giving Novel Luminescent Platinum(II) Species

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The (benzophenone imine)platinum(II) compounds *trans*-$[PtCl_2(Ph_2C{=}NH)(RR'SO)]$ [R, R′ = Me, Me (**2**); *n*-Pr, *n*-Pr (**3**); $(CH_2)_4$ (**4**); Me, Ph (**5**); Me, *p*-MeC_6H_4 (**6**)] were prepared by the reaction of $Ph_2C{=}NH$ with $K[PtCl_3(RR'SO)]$, obtained in situ from $K_2[PtCl_4]$ and the corresponding sulfoxide, giving **2**–**6** as well as *cis*-$[PtCl_2(Ph_2C{=}NH)_2]$ (**1**) as a minor product. The complexes were characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR and IR spectroscopy, electrospray ionization mass spectrometry, and C, H, and N elemental analysis. The X-ray crystallography of **1** enables confirmation of the cis configuration of the complex, while in **2** and **4**·$^{1}/_{2}CHCl_3$, the imine and sulfoxide ligands are mutually trans. The solid-state structure of **4**·$^{1}/_{2}CHCl_3$ consists of two dimeric Pt moieties representing a rather weak Pt···Pt interaction. The dimeric architecture of **4**·$^{1}/_{2}CHCl_3$ is enhanced by the hydrogen bonding between imine H atoms and O atoms. The orthometalation of **1** and **2**–**6** proceeds both in the solid phase and in a toluene suspension, leading to the formation of $[PtCl\{Ph(C_6H_4)C{=}NH\}(Ph_2C{=}NH)]$ (**7**) and $[PtCl\{Ph(C_6H_4)C{=}NH\}(RR'SO)]$ (**8**–**12**), respectively, isolated in nearly quantitative yields. Complexes **8**–**12** are emissive at room temperature both in solution (λ_{em}^{max} ~535 nm) and in the solid state (λ_{em}^{max} 560–610 nm), with excited-state lifetimes of ca. 300–600 ns, representing a new family of Pt^{II}-based luminescent complexes. Compounds **8** and **10** have been characterized by X-ray analysis, confirming the square-planar coordination geometry of the metal center with the almost planar platinacycles. In **8**, the asymmetric unit contains two independent Pt molecules, while in **10**, it includes four Pt molecules linked by the intermolecular hydrogen-bonding network between the NH group and Cl atoms.

Introduction

In the recent years, there has been an increasing interest in metal-mediated synthesis, properties, and reactivity patterns of ligated imines.[1] Unlike *N-substituted* imines $R'N{=}CR_2$ ($R' = Alk, Ar$; $R = H, Alk, Ar$), which are mostly stable and serve as ligands for many metal complexes,[2] the *unsubstituted* aldimines or ketimines $HN{=}CR_2$ are, with the exception of diarylketimines, very susceptible to hydrolysis and subject to oligo- and polymerization and various redox-type conversions.[3] However, they can be stabilized via coordination to a metal center; in particular, Pt group metals provide enormous stabilization of the potentially unstable imines.[4−9]

Metal imine species are the subject of rapt attention because of the importance of their potential properties, i.e., (i) Pt^{II} complexes containing coordinated acetimine display a tumor cell growth inhibitory potency, similar to that of

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the corresponding Pt^{II} complexes with iminoethers,[10] and in addition the ability to circumvent (either partially or completely) cisplatin resistance;[11] (ii) ytterbium(II) imine complexes exhibit a high catalytic activity in the dehydrogenative silylation of terminal alkynes[12a] and hydrosilylation of imines;[12b] (iii) metal complexes of simple imines are observed/proposed to be intermediates in the metal-mediated imine aziridination,[13] imine/imide/alkylidene metathesis,[14] and amine ↔ nitrile interconversion;[15] (iv) α,α-diimines in their main-group metal complexes may possess different oxidation states, thus acting as an electron sponge or sink toward organic substrates;[16] (v) Pd^{II}- and Ni^{II}-based catalysts containing bulky diimine ligands exhibit extremely high activities in the conversion of ethylene,[17a−c] α-olefins,[17a,b,d] cyclopentene,[17e] and trans-1,2-disubstituted olefins[17f] to high-molecular-weight polymers with unique microstructures as well as in copolymerization of polar monomers with ethylene and α-olefins.[17g,h] Therefore, synthetic approaches to new arylimine metal complexes as well as examination of their reactivity are crucial for the development of that type of compound and to a considerable degree determinative for the progress of metal-mediated arylimine functionalization.

In view of our general interest in imines as ligands[4−9] and ligand reactivity in general,[18] we continued our work in these directions and focused our attention on a rather stable and commercially available imine, i.e., benzophenone imine, $HN{=}CPh_2$, which can be considered as a model for unstable imines in examinations of their reactivity. Although coordination properties of $HN{=}CPh_2$ were extensively studied, e.g., exhaustively in the case of group VIII metals (Fe,[19] Ru,[20]

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Os;[21] Co,[22] Rh,[23] Ir;[23a] Ni,[24] Pd,[25] Pt[9b,26]) and partially for some representatives of group III (Sm[27]), IV (Ti,[28] Zr[28,29]), VI (Cr[30]), and VII (Mn,[31] Re[31,32]) metals, reports on the *reactivity of the metal-bound* $HN{=}CPh_2$ are rather scarce. Thus, several papers devoted to its deprotonation, resulting in the formation of azavinylidene complexes,[21a,b] the addition of tolylacetilyde to the coordinated $HN{=}CPh_2$,[19] and the formation of ligated $\sigma-\eta^1$-$C_6H_4C(Ph){=}NH$ species, were published.[20d] In this context, also a few reports on the orthometalation of the coordinated $HN{=}CPh_2$ species leading to N,C-chelates, performed in most cases in toluene or tetrahydrofuran solutions at elevated temperatures, are available.[20c,21c,h,j,22,23d,26]

Herein, we report on the preparation of (benzophenone imine)(sulfoxide)platinum(II) complexes. The reactivity of the $HN{=}CPh_2$ ligand both in the solid state and in a toluene suspension, leading to the formation of the corresponding orthometalated species exhibiting luminescent properties, was studied. It is worth emphasizing that within the framework of this project we observed for the first time *the solid-state reactivity* of the coordinated benzophenone imine, namely, the formation of a platinacycle via elimination of HCl upon heating of the solid platinum(II) imine complexes.

Results and Discussion

In general, the orthometalation reaction—activation of a C−H bond in the ortho position of an aromatic ring by a transition-metal center—continues to be an important class of reactions[33] owing to the broad application spectrum of the orthometalated species, e.g., in catalysis,[33b,34] organic synthesis,[35] and material science.[36] The activation of C−H bonds by transition-metal compounds is of general interest because of the possibility of functionalizing nonactivated organic molecules.[33a,37] For instance, the Murai reaction,[38] which represents one of the most important processes in organic synthesis, allows the alkylation of aromatic ketones,[39] esters,[40] and imines,[41] as well as the copolymerization of aromatic ketones and α,ω-divinylsilanes.[42] Consequently, stable and structurally characterized compounds containing N,C-metallacycles are of high interest and can be considered as models for the organometallic intermediates in C−C coupling reactions between aromatic imines and olefins.[43]

Orthometalation of Pt^{II} compounds with N-donor ligands giving N,C-platinacycles is rather well documented.[44] However, there are only a few examples of orthoplatinated imino species.[26,45] In addition to mononuclear platinacycles with η^2-coordinated imines,[26,45e,i] some Pt^{II} complexes with C,N,S-[45a] and C,N,N-[45d,g,j] pincer ligands, orthoplatinated heterocycle-derived imino species,[45b] and bridged[45c,h] and tetrameric orthometalated Pt^{II} compounds[45f] obtained as a result of metalation of a Pt^{II}-bound imine were reported.

Thus, we have focused on the study of cyclometalation of $(Ph_2C{=}NH)Pt^{II}$ species and intended (i) to prepare Pt^{II} complexes with both benzophenone imine and various sulfoxides, (ii) to investigate the solid-state and solution reactivities of $(Ph_2C{=}NH)Pt^{II}$ species, (iii) to verify possible routes for cyclometalation of $(Ph_2C{=}NH)Pt^{II}$ complexes, and (iv) to study properties of the cyclomelatated species. The report on our experiments given below follows these lines.

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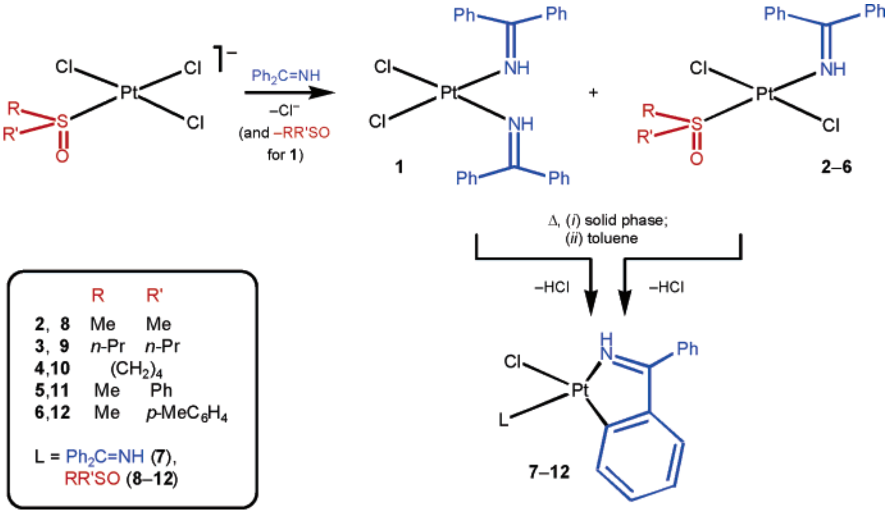
Scheme 1



Synthesis, Characterization, and X-ray Structure Determinations of (Benzophenone imine)platinum(II) Complexes. As starting materials for the preparation of (benzophenone imine)platinum(II) compounds, we addressed the easily accessible complexes K[$PtCl_3$(sulfoxide)][46] [sulfoxide = Me_2SO, *n*-Pr_2SO, $(CH_2)_4SO$, racemic mixture of Me(Ph)-SO, *S*-(−)-*p*-MeC_6H_4(Me)SO] for the following reasons: on the one hand, a significant trans effect of S-coordinated sulfoxides[47] facilitates the substitution and directs the reaction to the formation of the isomerically pure product; on the other hand, as far as Me_2SO is concerned, the coordinated dimethyl sulfoxide ligand with its characteristic spectral pattern[48] serves as an "internal" reference for the integration of ^{1}H NMR spectra.

The reaction between the platinum(II) sulfoxide complexes K[$PtCl_3$(RR′SO)] [R, R′ = Me, Me; *n*-Pr, *n*-Pr; $(CH_2)_4$; Me, Ph; Me, *p*-MeC_6H_4], obtained in situ from $K_2[PtCl_4]$ and the corresponding sulfoxide,[46] and benzophenone imine $Ph_2C{=}NH$ proceeds in aqueous solution at room temperature and leads to the formation of *trans*-[$PtCl_2$($Ph_2C{=}NH$)(RR′SO)] (**2**−**6**; Scheme 1) obtained as pale-yellow precipitates and isolated in 40−60% yields. The diiminoplatinum(II) complex *cis*-[$PtCl_2(Ph_2C{=}NH)_2$] (**1**), prepared earlier by Grøndahl et al. via the reaction of *trans*-[$PtCl_2(CH_3CN)_2$] with $Ph_2C{=}NH$,[26] is formed in all syntheses as a minor product and isolated in 6−8% yields.

Complexes **1**−**6** were characterized by C, H, and N microanalysis, ^{1}H, $^{13}C\{^1H\}$, and ^{195}Pt NMR and IR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and also X-ray crystallography (for **1**, **2**, and **4**). All compounds gave satisfactory C, H, and N elemental analyses. ESI-MS spectra displayed the fragments $[M + Na]^+$ and $[M + K]^+$ having isotopic patterns that were in accordance with calculated ones. The IR spectra of **1**−**6** showed strong-to-medium ν(C=N) [1597−1607 cm^{-1}] and medium ν(NH) [3195−3294 cm^{-1}] stretching vibrations. In addition, **2**−**6** displayed very strong ν(S=O) [1113−1134 cm^{-1}] bands shifted vs ν(S=O) of the free sulfoxides due to S coordination.[49]

The structures of **1**, *trans*-[$PtCl_2$($Ph_2C{=}NH$)(Me_2SO)] (**2**), and *trans*-[$PtCl_2$($Ph_2C{=}NH$){$(CH_2)_4SO$}] (**4**) were determined by X-ray single-crystal diffraction (Table 1 and Figures 1−3). The coordination geometries of the three complexes are slightly distorted square-planar.

In all three structures, the Pt atoms are located at a crystallographic inversion center. The Pt−Cl bond distances are in the range from 2.297 to 2.308 Å, and these distances agree well with those in the previously characterized plati-

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, **4**·$^1/_2$CHCl$_3$, **8**, and **10**

	1	**2**	**4**	**4B**	**8**	**8B**	**10A**	**10B**	**10C**	**10D**
Pt1−Cl1	2.298(2)	2.2969(9)	2.306(4)	2.302(4)	2.392(2)	2.395(2)	2.3925(11)	2.3864(11)	2.3808(11)	2.3971(12)
Pt1−Cl2	2.291(2)	2.3034(9)	2.307(4)	2.308(4)						
Pt1−N1	2.001(7)	2.021(3)	2.017(13)	2.024(13)	2.019(6)	2.022(6)	2.019(4)	2.016(4)	2.013(4)	2.021(4)
Pt1−N2	2.034(6)									
Pt1−S1		2.2131(9)	2.210(4)	2.215(4)	2.215(2)	2.216(2)	2.2063(13)	2.2054(12)	2.2215(12)	2.2132(13)
Pt1−C13					2.006(9)	1.978(9)	2.016(4)	2.010(4)	2.005(4)	2.001(5)
Pt2−Cl3			2.302(4)	2.305(4)						
Pt2−Cl4			2.298(4)	2.299(4)						
Pt2−N2			2.037(13)	2.029(12)						
Pt2−S2			2.222(4)	2.208(4)						
S1−O1		1.467(3)	1.469(11)	1.457(11)	1.476(5)	1.480(5)	1.479(4)	1.474(3)	1.473(3)	1.472(4)
S2−O2			1.464(11)	1.447(11)						
N1−C1	1.274(10)	1.289(4)	1.26(2)	1.27(2)	1.280(10)	1.282(10)				
N2−C18			1.30(2)	1.26(2)						
N2−C14	1.259(10)									
Cl1−Pt1−Cl2	92.83(8)	175.81(3)	176.94(15)	175.75(14)						
N1−Pt1−N2	94.1(3)									
N1−Pt1−S1		175.66(9)	175.2(4)	176.0(4)	179.7(2)	178.9(2)	175.40(11)	175.73(12)	178.30(12)	174.38(12)
C13−Pt1−N1					79.7(3)	79.7(3)	79.7(2)	79.4(2)	80.5(18)	79.2(2)
Pt1−N1−C1	130.5(6)	131.8(2)	129.0(10)	131.8(11)						
Pt2−N2−C18			129.0(11)	131.0(11)						
Pt1−N2−C14	137.2(6)									
Cl3−Pt2−Cl4			175.81(15)	176.18(15)						
N2−Pt2−S2			178.3(4)	177.2(4)						

num(II) chloride compounds.[50] In **1**, the two imino ligands are mutually cis, which is the thermodynamically stable form for the complexes having two strong π-acceptor ligands insofar as (d−d) π bonding is known to be more effective in the cis configuration.[51] In **2** and **4**, the imine and sulfoxide ligands are mutually trans, which is the result of a significant trans effect of sulfoxides compared to chloride ligands facilitating the formation of kinetically controlled trans isomers. In the coordinated imine, the values of the C═N bond length [1.261−1.300 Å] are similar within 3σ and correspond to the previously reported distances of the C═N double bond in the metal-bound $Ph_2C{=}NH$ [1.285−1.310 Å].[20d,f,32] In complexes **2** and **4**, the Pt−S bond distances are in the range from 2.210 to 2.222 Å, which is in good agreement with the mean values of the Pt−S bond [2.216 Å] for S-coordinated sulfoxides.[52] The solid-state structure of **4** consists of two dimeric Pt moieties with the Pt···Pt distances at 3.271 and 3.314 Å, which are less than a double van der Waals radius for Pt [$1.72 \times 2 = 3.44$ Å]. This case represents a rather weak interaction taking into account that the Pt···Pt contacts in numerous examples of dimeric Pt^{II} complexes are in the range 2.7−3.4 Å; no Pt···Pt contacts of less than 5 Å were observed for the other complexes studied in this work by X-ray crystallography.[53] The dimeric architecture of **4** is enhanced by the hydrogen bonding between imine H atoms and O atoms. The N1···O2 and N1B···O2B distances are 2.995(17) and 2.952(16) Å for the first and second Pt$_2$ moieties, respectively. These bond lengths fall into the range of typical N···O distances when NH···O hydrogen bonding takes place.[54] The angles N1···H1···O2 and N1B···H1B···O2B are 158.0 and 160.4°, respectively.

Cyclometalation of the Ligated Benzophenone Imine. For both **1** and **2**−**6**, a thermally induced solid-state cyclometalation was observed. A thermal analysis was performed for all synthesized compounds, and the mass loss on the first step of thermal conversion, corresponding to the loss of 1 equiv of HCl, was observed when they were heated to 150−200 °C, with the heating rate being 5 °C min^{-1} (see Figures S1−S6 in the Supporting Information). In a preparative experiment, the yellow powders of **1**−**6** were heated in an open test tube at a specific temperature (see the Experimental Section) overnight, giving a bright-orange product. The evolution of HCl was detected by a pH indicator, and weight monitoring proved the loss of 1 equiv of HCl. The measurement of the NMR spectra enabled the establishment that a solid-state conversion of **1**−**6** into orthometalated products $[PtCl\{Ph(C_6H_4)C{=}NH\}(Ph_2C{=}NH)]$ (**7**) and $[PtCl\{Ph(C_6H_4)C{=}NH\}(RR'SO)]$ (**8**−**12**) (Scheme 1) took place. The yield of **8** was almost quantitative, while compounds **1** and **3**−**6** partially decomposed on heating and were recrystallized to obtain analytically pure samples.

Along with the solid-state cyclometalation of **1**−**6**, an analogous process was observed on heating of the compounds in a toluene suspension. The complexes **1** and **2**−**6** were refluxed in toluene for 12−16 h, resulting in the elimination of 1 equiv of HCl and the formation of a five-membered platinacycle. The cyclometalated products **7**−**12** (Scheme 1) were isolated in nearly quantitative yields. For **1**, a change of the relative position of the N atoms proved to take place as a result of the cyclometalation process. It is worth noticing that **7** was obtained earlier but in rather low yield.[26]

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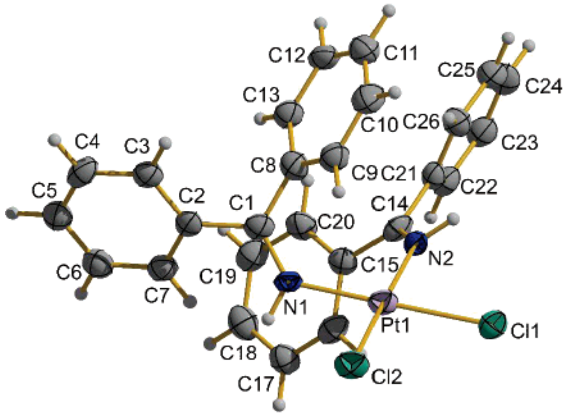

Figure 1. View of complex **1** with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability.

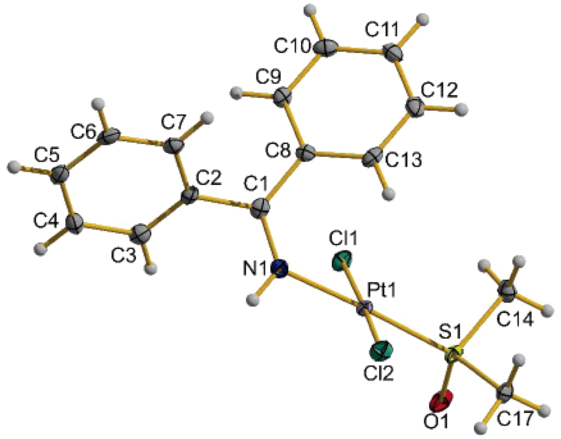

Figure 2. View of complex **2** with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability.

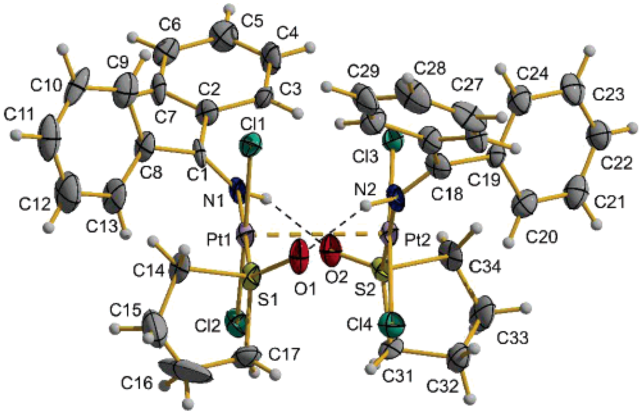

Figure 3. View of complex $\mathbf{4}\cdot{}^1/_2CHCl_3$ with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The second Pt_2 moiety has been omitted for clarity. Intermolecular contacts and hydrogen bonding: Pt1···Pt2 3.2871(9) Å, Pt1B···Pt2B 3.3140(9) Å, N1−H1 0.88 Å, H1···O2 2.16 Å, N1···O2 2.995(17) Å, N1−H1···O2 158.0°, N2−H2 0.88 Å, H2···O1 2.15 Å, N2···O1 2.991(16) Å, N2−H2···O1 159.0°, N1B−H1B 0.88 Å, H1B···O2B 2.11 Å, N1B···O2B 2.952(16) Å, N1B−H1B···O2B 160.4°, N2B−H2B 0.88 Å, H2B···O1B 2.14 Å, N2B···O1B 2.994(16) Å, N2B−H2B···O1B 164.6°.

One should mention that, although numerous examples of cyclometalation in solution were comprehensively covered in the literature,[55] reactions in the solid phase were studied in much less detail. To our knowledge, only a few examples of solid-state cyclometalation were reported, i.e., the cycloplatination of dimethyl(1-naphthyl)phosphine and dimethyl(1-naphthyl)arsine,[56] O-metalation of (2-alkoxyphenyl)phosphines by Pt^{II},[57] cyclometalation of triphenylphosphine by Ir^{III},[58] O- and C-metalation of (dimethoxyphenyl)phosphines by Pt^{II} and Pd^{II},[59] cycloplatination of *o*-diphenylphosphinebenzaldehyde,[60a] cyclopalladation of benzylamines,[60b] cyclometalation of tris(1-pyrazolyl)methane by a Pt^{II} center,[61] and 1-methyl-2,4′-bipyridinium by Pt^{II} and Pd^{II} centers.[62] Hence, the solid-state conversion of the ligated $Ph_2C{=}NH$ species at the Pt^{II} center represents the first example in the chemistry of imines.

A significant research effort has been focused on cyclometalated compounds because of the ability of some of them to display interesting photophysical properties.[63] In this regard, the cyclometalated Pt^{II} complexes[64] are among the

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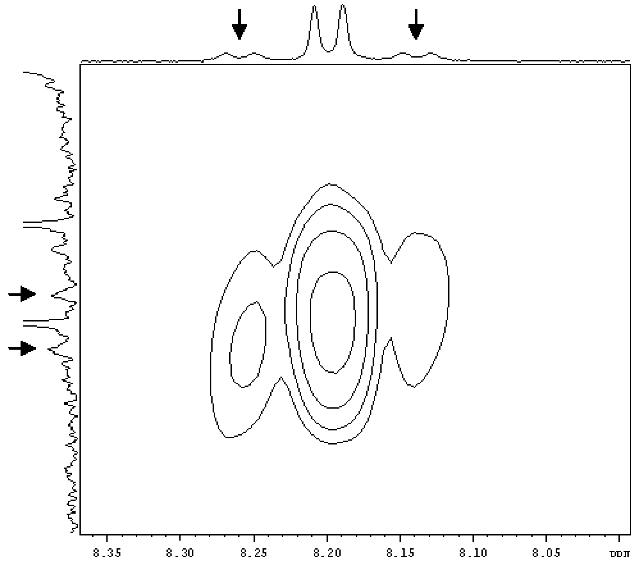

Figure 4. $^{1}H-^{13}C$ COSY NMR spectrum of **8** in CD_3OD, showing the C2−H2 correlation signal in the aromatic region. Pt satellites in the directly measured one-dimensional ^{1}H and ^{13}C NMR spectra are marked with arrows.

most advantageous owing to such useful features as high efficiency and long lifetimes of the emissive states and potential applications in many fields, e.g., chemosensors[65] and light-emitting diodes (LEDs).[64g,66] In most cases, the luminescence property is associated with cyclometalated Pt^{II} compounds containing various heterocyclic ligands, e.g., pyridine[64b,66b,67] and dipyridine,[65b,c,67h,68] generally with different aromatic substituents, as well as 7,8-benzoquinoline,[64c,67d,69] and aryldiamine[64e,f] ligands. Surprisingly, nearly no attention was drawn so far to the luminescent cycloplatinated imino species.[64a,i] In the present work, we observed that the cyclometalated compounds (**7**−**12**) obtained exhibit bright-yellow-to-orange luminescence at room temperature in solution, in the solid state, and on being spread onto thin-layer chromatography (TLC) SiO_2 plates. Therefore, we conducted a study of their solution and solid-state photophysical properties, and the results are given below in this paper.

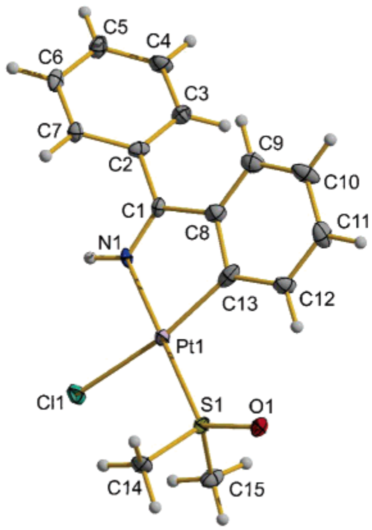

Figure 5. View of complex **8** with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The second Pt molecule in the asymmetric unit has been omitted for clarity.

Characterization and X-ray Structure Determinations of the Cyclometalated Pt^{II} Complexes. The cyclometalated complexes **8**−**12** gave satisfactory elemental analyses and the expected molecular ion/fragmentation patterns in ESI-MS spectra (the presence of the $[M - Cl]^{+}$ and $[M + Na]^{+}$ peaks was recognized). Complexes **8**−**12** were characterized by IR spectroscopy: the characteristic $\nu(S{=}O)$ [1116−1126 cm^{-1}], $\nu(C{=}N)$ [1569−1587 cm^{-1}], and $\nu(NH)$ [3200−3340 cm^{-1}] bands were observed. The most significant difference of the stretching vibrations between the starting (imine)(sulfoxide)platinum(II) complexes (**2**−**6**) and the corresponding cyclometalated products (**8**−**12**) was observed for the C═N double bond: the respective absorption band showed a red shift of up to 30 cm^{-1} in the IR spectrum. In ^{1}H NMR spectra of **8**−**12**, protons H2 displayed satellites deriving from the coupling of the protons with the ^{195}Pt nuclei; typical $^{3}J_{Pt,H}$ coupling constants between 47.0 and 49.2 Hz could be detected. Coupling of the C2 atoms in complexes **8**−**12** to ^{195}Pt were also determined in both directly measured ^{13}C NMR and two-dimensional $^{1}H-^{13}C$ COSY NMR spectra ($^{2}J_{Pt,C} = 52.5-61.2$ Hz; Figure 4). The presence of the satellites undoubtedly proves the elimination of HCl as a consequence of the cyclometalation process. As expected, a significant difference in δ_{Pt} was observed between the starting (imine)(sulfoxide)platinum(II) complexes **2**−**6** (between −1292.3 and −1339.0 ppm) and the corresponding cyclo-

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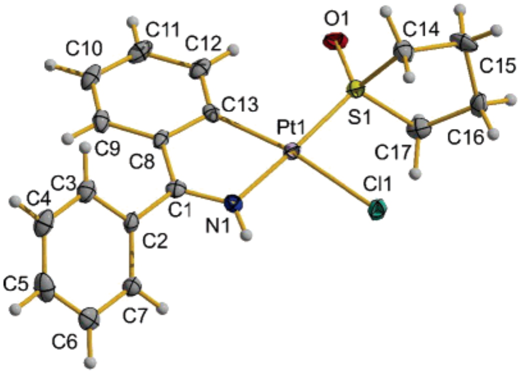

Figure 6. View of complex **10** with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The other three Pt molecules in the asymmetric unit have been omitted for clarity (see Figure 7).

metalated products **8**−**12** (between −2240.3 and −2281.7 ppm) because of the change in the ligand sphere (Cl vs C).

The crystal structures of two cyclometalated products, i.e., **8** and **10**, were determined by X-ray diffraction (Table 1 and Figures 5 and 6). In both structures, the Pt atoms are located at a crystallographic inversion center and display a slightly distorted square-planar coordination. The Pt−Cl bond distances are in the range from 2.381 to 2.397 Å, which is significantly longer compared to those of the corresponding noncyclometalated complexes [2.297−2.308 Å]. The difference in the Pt−Cl bond lengths trans to Cl and trans to C is due to the well-known strong ground-state trans influence of C-bonded ligands.[70] However, these distances agree well with those in the previously characterized Pt^{II} compounds containing a Cl ligand in the trans position to the platinated C atom.[71] In **8** and **10**, the coordinated sulfoxide and the platinated C13 center are mutually cis, which is preferable because both centers possess a significant trans influence. The five-membered platinacycles deviate slightly from the plane, with a maximum deviation of 0.149 Å. In **8**, the asymmetric unit contains two independent Pt molecules, while in **10**, it includes four Pt molecules linked by the intermolecular hydrogen-bonding network between the NH group and Cl atoms (Figure 7). The distances H1···Cl1B, H1B···Cl1, H1C···Cl1D, and H1D···Cl1C are 2.49, 2.55, 2.54, and 2.38 Å, respectively, which fall into the range of the typical NH···Cl distances when this type of hydrogen bonding takes place.[72]

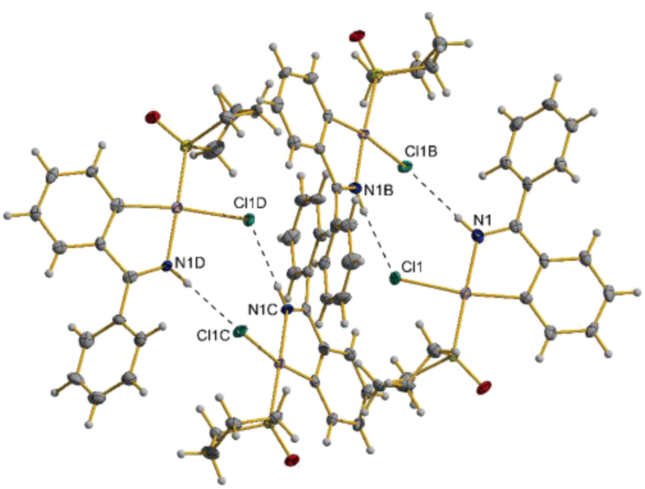

Figure 7. Hydrogen-bonding network in structure **10**: N1−H1 0.88 Å, H1···Cl1B 2.49 Å, N1···Cl1B 3.366(4) Å, N1−H1···Cl1B 176.0°, N1B−H1B 0.88 Å, H1B···Cl1 2.55 Å, N1B···Cl1 3.426(4) Å, N1B−H1B···Cl1 172.9°, N1C−H1C 0.88 Å, H1C···Cl1D 2.54 Å, N1C···Cl1D 3.416(4) Å, N1C−H1C···Cl1D 175.7°, N1D−H1D 0.88 Å, H1D···Cl1C 2.38 Å, N1D···Cl1C 3.262(4) Å, N1D−H1D···Cl1C 175.4°.

Luminescence Studies. Luminescent square-planar Pt^{II} complexes have attracted a great deal of interest because of their useful photochemical properties, i.e., high efficiency and long lifetimes of the emissive states and potential applications in many fields, such as chemosensors,[73] photocatalysts,[74] LEDs,[75] and photocatalytic devices.[76] The most advantageous d^8 Pt^{II} luminescent systems are based on $[PtX_2(diimine)]$ (X = halide, cyanide, thiolate, alkyl, aryl,

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Table 2. Photophysical Properties of the Pt Complexes at Room Temperature

Solution Data			
sample	ϵ (dm^3 mol^{-1} cm^{-1}) (λ_{ab} = 400 nm)	λ_{em} (nm)^a	ϕ_{em} (%)^b
8	3400	535, 565	0.0071
9	1600	535, 565	0.019
10	3100	535, 565	0.0056
11	3900	500−750	0.0042
12	1400	535, 565	0.0045

Solid-State Data		
sample	λ_{em} (nm)^a	τ (ns)^c
8	542, 571, 624	455
9	575, 655	575
10	525, 559, 610	615
11	600, 655	323
12	608, 655	507

[a] λ_{ex} = 400 nm. [b] Determined using $[Ru(bpy)_3]^{2+}$ as the standard, ϕ = 0.062 (ref 83). [c] Excited state (λ_{ex} = 400 nm) lifetimes (±50 ns) reported with λ_{em} = 575 nm.

or acetylide),[77] terpyridine[78] complexes, or phosphorescent platinum(II) porphryins.[79] A separate group of Pt^{II}-based luminescent compounds is comprised of complexes with N,C,N-[67a,75a,80] or S,C,S-[80a,81] pincer ligands and some other cyclometalated Pt^{II} compounds.[64a,82]

The UV−vis absorption and emission data of complexes **8**−**12** are summarized in Table 2 (*Attention! For ref 83, see footnote b in Table 2*). All of the complexes show an absorption band at 400 nm (Figure 8) with extinction coefficients (ϵ) on the order of 10^3 dm^3 mol^{-1} cm^{-1}. These characteristic metal complex absorptions are only reported for $\lambda > 350$ nm. Below 350 nm, high-intensity intraligand absorptions predominate in the spectra. The broad but well-defined absorption band at 400 nm may be attributed to a triplet metal-to-ligand charge-transfer (^{3}MLCT) transition corresponding to $d\pi(Pt) \rightarrow \pi^*(C^\frown N)$, based on similarities in the energy and intensity of MLCT transitions of related platinum(II) terpyridyl and cyclometalated diimine complexes.[76a,78,84] In Figure 9, all of the Pt^{II} complexes except **11** show an emission with λ_{em}^{max} of 535 nm, along with another less intense emission at 565 nm. Complex **11** has a broad emission ranging from 500 to 650 nm. The solution quantum yields of the complexes are rather low, with values smaller than 0.0071, the exception being **9**, the quantum yield of which (0.019) is nearly 3 times that of the other compounds.

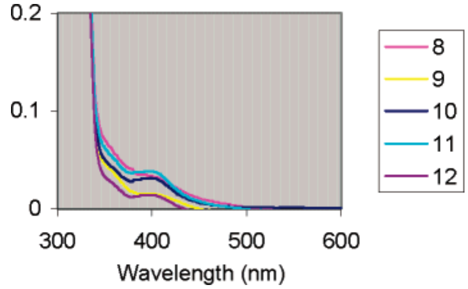

Figure 8. Absorption spectra of a 1.0 × 10^{-5} M solution in acetone at room temperature.

Figure 10 shows normalized solid-state emission spectra for the complexes that exhibit differences with respect to the structure and intensity of the emission bands but have similar emission energies. The solid-state emission data listed in Table 2 show compounds **8** and **10** having λ_{em}^{max} at 571 and 559 nm, respectively. These two complexes also exhibit some structure on the emission bands with high- and low-energy shoulders at 542 and 624 nm and at 525 and 610 nm, respectively. Complex **9** shows a λ_{em}^{max} at 575 nm with a shoulder at 655 nm. Complexes **11** and **12** exhibit a red shift in the value of λ_{em}^{max} in going from solution to the solid state. It is possible that, in the more rigid solid state, the phenyl rings of the sulfoxide substituent in **11** and **12** have an effect on their solid-state packing arrangement. For compounds **8**−**12**, the excited-state emission lifetimes at 575 nm are in the range of 320−615 ns (Table 2), consistent with the spin-forbiddenness associated with metal complex phosphorescence.[64c,74b] There is no observed correlation of λ_{em} and τ.

Figure 11 shows the solution emission spectra of **12** at three different concentrations. It is found that the emission intensity increases with increasing concentration but the λ_{em}^{max} energies do not change, consistent with the absence of intermolecular Pt···Pt aggregation.[82c,85] Though the solid-state quantum yields for the compounds were not obtained, they are indeed very brightly emissive when irradiated with 400 nm light, raising the possibility that these systems may be useful for sensor or display applications, upon proper derivatization.

Final Remarks

In the current work, we succeeded in synthesizing a new family of orthometalated Pt^{II} complexes of the general formula $[PtCl\{Ph(C_6H_4)C{=}NH\}(RR'SO)]$ [R, R′ = Me, Me; *n*-Pr, *n*-Pr; $(CH_2)_4$; Me, Ph; Me, *p*-MeC_6H_4] (**8**−**12**). It was shown that the cyclometalation of *trans*-$[PtCl_2(Ph_2C{=}NH)(RR'SO)]$ (**2**−**6**) proceeds both in the solid phase and in a toluene suspension, leading to the formation of N,C-chelates in high isolated yields. Thermogravimetric analysis (TGA) proved to be a perfectly suitable method for the observation of the processes taking place on heating of the solid sample

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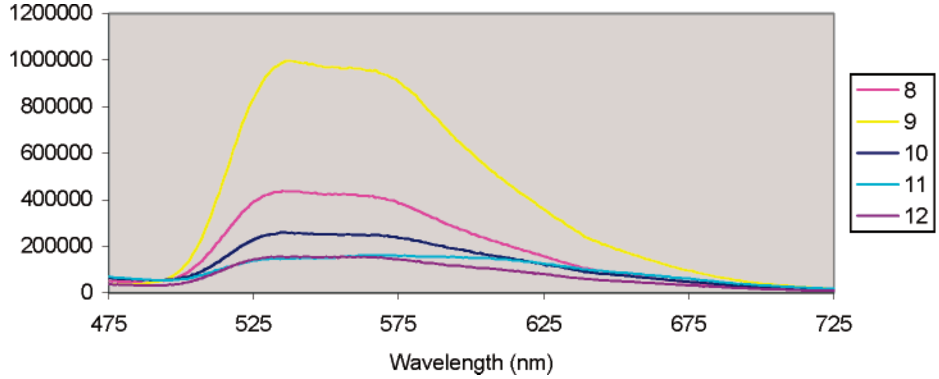

Figure 9. Emission spectra of a 1.0 × 10^{-5} M solution in acetone at room temperature.

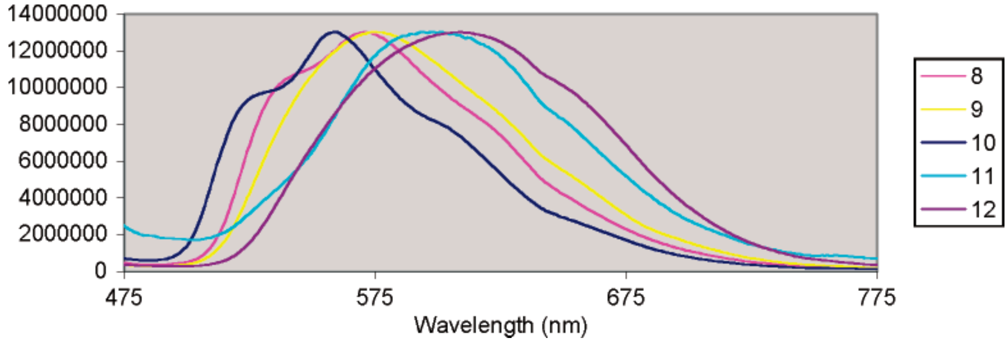

Figure 10. Normalized solid-state emission spectra at room temperature.

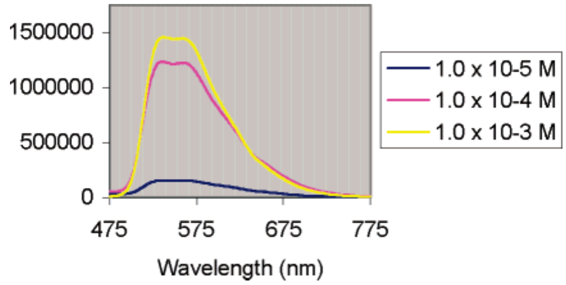

Figure 11. Emission spectra of **12** in acetone at different concentrations at room temperature (λ_{ex} = 400 nm).

at elevated temperatures. It is important that the orthometalated complexes obtained exhibit luminescent properties at room temperature both in solution and in the solid state and also on being spread onto TLC SiO_2 plates. The broad application spectrum of luminescent Pt^{II} complexes stimulates our interest in the further elaboration of the current topic, and studies on the cyclometalated benzophenone imine complexes and on their emission properties are underway in our group.

Experimental Section

General Procedures. Solvents were obtained from commercial sources and used as received. *n*-Propyl sulfoxide was purchased from Acros, while the remaining sulfoxides and benzophenone imine were obtained from Aldrich. The complexes $K[PtCl_3(RR'SO)]$ (R, R′ = Me, Me; *n*-Pr, *n*-Pr; $(CH_2)_4$; Me, Ph; Me, *p*-MeC_6H_4) were prepared in situ according to published methods.[46] For TLC, Merck UV 254 SiO_2 plates were used. Fluka silica gel 60 (220−440 mesh) was used for column chromatography. C, H, and N elemental analyses were carried out by the elemental analyses laboratory of the University of Vienna using a Perkin-Elmer 2400 CHN elemental analyzer. Melting points were determined with a Büchi B-540 melting point apparatus and are uncorrected. TGA/DTA studies were performed with a Mettler Toledo TGA850 instrument (temperature range from 20 to 1000 °C with a heating rate of 5 °C min^{-1}, an air flow of 3 L h^{-1}, and a sample mass of 5−10 mg in an aluminum crucible; the buoyancy correction for TGA was done by measuring a blank). ESI-MS spectra were obtained with a Bruker Esquire 3000 instrument. IR spectra (4000−400 cm^{-1}) were recorded with a Perkin-Elmer Fourier transform (FTIR) instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectra were measured with a Bruker Avance DPX 400 spectrometer at 400.13 MHz (^1H), 100.63 MHz (^{13}C), and 85.99 MHz (^{195}Pt), correspondingly, at ambient temperature. ^{195}Pt chemical shifts are given relative to $K_2[PtCl_4]$, and the half-height line width is given in parentheses.

Reaction of $Ph_2C{=}NH$ with $K[PtCl_3(RR'SO)]$ Obtained in Situ. In a typical experiment, a solution of RR′SO (0.25 mmol) in water (1 mL) was added dropwise to a solution of $K_2[PtCl_4]$ (100 mg, 0.24 mmol) in water (3 mL) at 20−25 °C. The mixture was stirred for 4−5 h at room temperature until the color of the solution turned from reddish-orange to yellow. When Me(Ph)SO and *p*-MeC_6H_4(Me)SO were employed, small amounts of the known pale-yellow *cis*-$[PtCl_2\{Me(Ph)SO\}_2]$[46c,86] and *cis*-$[PtCl_2\{p\text{-}MeC_6H_4(Me)SO\}_2]$[87] complexes were obtained and removed by filtration (yields are 10 and 4%, respectively).

A solution of $Ph_2C{=}NH$ (44 mg, 0.24 mmol) in $CHCl_3$ (1 mL) was added to the yellow filtrate obtained as described above. A pale-yellow amorphous precipitate appeared immediately, whereupon the reaction mixture was stirred overnight at room temperature and the precipitate was separated by filtration. The yellow solid was dried at 20−25 °C and washed with two 2-mL portions of

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Table 3. Crystallographic Data for **1**, **2**, **4**·$^1/_2$CHCl$_3$, **8**, and **10**

	1	**2**	**4**	**8**	**10**
empirical formula	$C_{26}H_{22}Cl_2N_2Pt$	$C_{15}H_{17}Cl_2NOPtS$	$C_{35}H_{39}Cl_7N_2O_2Pt_2S_2$	$C_{15}H_{16}ClNOPtS$	$C_{17}H_{18}ClNOPtS$
fw	628.45	525.35	1222.13	488.89	514.92
temp (K)	120(2)	100(2)	120(2)	120(2)	120(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1$
a (Å)	9.510(2)	5.5695(5)	19.869(2)	10.0666(3)	10.38390(10)
b (Å)	9.680(2)	16.5381(13)	18.081(3)	10.5808(3)	24.3071(4)
c (Å)	14.006(3)	17.9682(15)	23.197(2)	14.7570(3)	13.4799(2)
α (deg)	70.557(18)	90	90	107.833(2)	90
β (deg)	83.699(18)	98.032(7)	99.181(11)	95.223(2)	99.749(9)
γ (deg)	67.909(12)	90	90	92.2130(10)	90
V (Å^3)	1126.3(4)	1638.8(2)	8226.8(19)	1486.40(7)	3353.23(8)
Z	2	4	8	4	8
ρ_{calc} (Mg/m^3)	1.853	2.129	1.973	2.185	2.040
μ(Mo Kα) (mm^{-1})	6.483	9.012	7.385	9.754	8.653
reflns collected	6792	22642	57627	23370	54166
unique reflns	3194	3601	14385	5236	15058
R1^a ($I \geq 2\sigma$)	0.0351	0.0201	0.0631	0.0320	0.0231
wR2^b ($I \geq 2\sigma$)	0.0806	0.0411	0.1462	0.0719	0.0474

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

diethyl ether. The analytically pure products **1**[26] and **2**−**6** were separated by column chromatography, correspondingly, in the first and second fractions [eluent: 1:8 (v/v) Me$_2$CO/CHCl$_3$]. The products were dried at room temperature. Yield of **1**: 6−8%, based on Pt. Yield of **2**−**6**: 40−60%, based on Pt.

1. Anal. Calcd for $C_{26}H_{22}N_2Cl_2Pt$: C, 49.69; H, 3.53; N, 4.46. Found: C, 49.52; H, 3.76; N, 4.36. ESI-MS$^+$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 433 [M − HCl − Ph$_2$C=NH + Na]$^+$, 556 [M − HCl − Cl]$^+$, 651 [M + Na]$^+$, 667 [M + K]$^+$. ESI-MS$^-$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 409 [M − HCl − Ph$_2$C=NH − H]$^-$, 446 [M − HCl − Ph$_2$C=NH + Cl]$^-$, 627 [M − H]$^-$, 663 [M + Cl]$^-$. Mp: 212−213 °C. TGA curve, mass loss: 6.4% (−HCl, 200 °C, calcd 5.8%), 18% (310 °C), 37% (410 °C). TLC (20:1 (v/v) CHCl$_3$/Me$_2$CO): $R_f = 0.56$. IR (KBr, cm^{-1}): ν 3199 (m, NH), 1591 and 1565 (s, C=N). ^{1}H NMR (acetone-d_6): δ 8.89 (s, br, 2H, N*H*), 8.27 (d, 4H, H_{ar}(o), $^3J_{H,H} = 7.0$ Hz), 7.80 (t, 2H, H_{ar}(p), $^3J_{H,H} = 7.5$ Hz), 7.63 (t, 4H, H_{ar}(m), $^3J_{H,H} = 7.8$ Hz), 7.47 (t, 2H, H_{ar}(p), $^3J_{H,H} = 7.3$ Hz), 7.25 (t, 4H, H_{ar}(m), $^3J_{H,H} = 7.8$ Hz), 6.59 (d, 4H, H_{ar}(o), $^3J_{H,H} = 7.5$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 179.08 (*C*=NH), 137.73 (C_{ar}), 136.74 (C_{ar}), 132.94 (C_{ar}), 132.69 (C_{ar}), 130.83 (C_{ar}), 129.06 (C_{ar}), 128.99 (C_{ar}), 128.59 (C_{ar}). ^{195}Pt NMR (acetone-d_6): δ −240.5 ($J = 660$ Hz). Crystals for X-ray study were obtained by slow evaporation of a chloroform/acetone solution.

2. Anal. Calcd for $C_{15}H_{17}NCl_2OPtS$: C, 34.29; H, 3.26; N, 2.66. Found: C, 34.31; H, 3.41; N, 2.40. ESI-MS$^+$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 490 [M − Cl]$^+$, 548 [M + Na]$^+$, 564 [M + K]$^+$, 671 [M + Ph$_2$C=NH − Cl]$^+$, 706 [M + Ph$_2$C=NH + H]$^+$. ESI-MS$^-$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 411 [M − Me$_2$SO − Cl]$^-$. Mp: 172 °C. TGA curve, mass loss: 7.5% (−HCl, 160 °C, calcd 7.0%), 21% (310 °C), 42% (450 °C). TLC (8:1 (v/v) CHCl$_3$/Me$_2$CO): $R_f = 0.56$. IR (KBr, cm^{-1}): ν 3294 (m, NH), 1599 (m, C=N), 1134 (s, S=O), 702 (s, C−S). ^{1}H NMR (acetone-d_6): δ 10.46 (s, br, 1H, N*H*), 8.15 (d, 2H, $^3J_{H,H} = 7.0$ Hz), 7.69 (m, 2*H*) and 7.59 (m, 6H) (two Ph), 3.29 (s + d, 6H, C*H*$_3$, $^3J_{Pt,H} = 16.6$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 183.79 (*C*=NH), 137.83 (C_{ar}), 137.13 (C_{ar}), 133.48 (C_{ar}), 132.83 (C_{ar}), 131.48 (C_{ar}), 129.85 (C_{ar}), 129.34 (C_{ar}), 128.28 (C_{ar}), 44.04 (*C*H$_3$). ^{195}Pt NMR (acetone-d_6): δ −1339.0 ($J = 550$ Hz). Crystals for X-ray study were obtained by slow evaporation of a toluene/dichloromethane solution.

3. Anal. Calcd for $C_{19}H_{25}NCl_2OPtS$: C, 39.25; H, 4.33; N, 2.41. Found: C, 39.20; H, 4.33; N, 2.42. ESI-MS$^+$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 604 [M + Na]$^+$, 620 [M + K]$^+$, 727 [M + Ph$_2$C=NH − Cl]$^+$. Mp: 134−135 °C. TGA curve, mass loss: 6.2% (−HCl, 150 °C, calcd 6.3%), 26% (220 °C), 35% (370 °C). TLC (8:1 (v/v) CHCl$_3$/Me$_2$CO): $R_f = 0.61$. IR (KBr, cm^{-1}): ν 3195 (m, NH), 1601 (m, C=N), 1113 (s, S=O), 702 (m, C−S). ^{1}H NMR (CDCl$_3$): δ 8.90 (s, br, 1H, N*H*), 8.12 (d, 2H, $^3J_{H,H} = 7.0$ Hz) and 7.58 (m, 8H) (two Ph), 3.53 (td, 2H, 2SCH*H*, $^2J_{H,H} = 12.6$ Hz, $^3J_{H,H} = 5.0$ Hz), 3.08 (td, 2H, 2SCH*H*, $^2J_{H,H} = 11.0$ Hz, $^3J_{H,H} = 5.0$ Hz), 2.24 (m, 2H, C*H*$_2$), 2.13 (m, 2H, C*H*$_2$), 1.18 (t, 6H, 2C*H*$_3$, $^3J_{H,H} = 7.5$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 184.27 (*C*=NH), 133.60 (C_{ar}), 132.68 (C_{ar}), 131.47 (C_{ar}), 129.54 (C_{ar}), 129.46 (C_{ar}), 128.29 (C_{ar}), 56.34 (S*C*H$_2$), 16.95 (*C*H$_2$), 13.29 (*C*H$_3$). ^{195}Pt NMR (CDCl$_3$): δ −1329.1 ($J = 550$ Hz).

4. Anal. Calcd for $C_{17}H_{19}NCl_2OPtS$: C, 37.03; H, 3.47; N, 2.54. Found: C, 37.05; H, 3.47; N, 2.54. ESI-MS$^+$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 516 [M − Cl]$^+$, 574 [M + Na]$^+$, 590 [M + K]$^+$, 697 [M + Ph$_2$C=NH − Cl]$^+$. Mp: 168−169 °C. TGA curve, mass loss: 6.2% (−HCl, 200 °C, calcd 6.6%), 16% (260 °C), 37% (350 °C). TLC (8:1 (v/v) CHCl$_3$/Me$_2$CO): $R_f = 0.49$. IR (KBr, cm^{-1}): ν 3227 (m, NH), 1607 (m, C=N), 1129 (s, S=O), 701 (s, C−S). ^{1}H NMR (CDCl$_3$): δ 9.48 (s, br, 1H, N*H*), 8.16 (d, 2H, $^3J_{H,H} = 7.0$ Hz) and 7.56 (m, 8H) (two Ph), 3.96 (m, 2H, SC*H*$_2$), 3.50 (m, 2H, SC*H*$_2$), 2.33 (m, 2H, C*H*$_2$), 2.14 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 183.65 (*C*=NH), 137.84 (C_{ar}), 137.16 (C_{ar}), 133.40 (C_{ar}), 132.78 (C_{ar}), 131.49 (C_{ar}), 129.86 (C_{ar}), 129.31 (C_{ar}), 128.26 (C_{ar}), 56.82 (S*C*H$_2$), 25.19 (*C*H$_2$). ^{195}Pt NMR (CDCl$_3$): δ −1292.3 ($J = 470$ Hz). Crystals for X-ray study were obtained by slow evaporation of a chloroform/acetone solution.

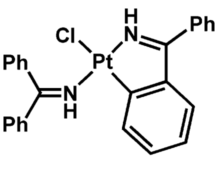
5. Anal. Calcd for $C_{20}H_{19}NCl_2OPtS$: C, 40.89; H, 3.26; N, 2.38. Found: C, 40.91; H, 3.41; N, 2.25. ESI-MS$^+$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 610 [M + Na]$^+$, 626 [M + K]$^+$, 734 [M + Ph$_2$C=NH − Cl]$^+$. ESI-MS$^-$ (1:10 (v/v) CHCl$_3$/MeOH): *m/z* 441 [M − Ph$_2$C=NH + Cl]$^-$. Mp: 162−163 °C. TGA curve, mass loss: 6.9% (−HCl, 180 °C, calcd 6.4%), 14% (260 °C), 43% (370 °C). TLC (20:1 (v/v) CHCl$_3$/Me$_2$CO): $R_f = 0.43$. IR (KBr, cm^{-1}): ν 3225 (m, NH), 1599 (s, C=N), 1133 (s, S=O). ^{1}H NMR (acetone-d_6): δ 10.62 (s, br, 1H, N*H*), 8.10 (d, 2H, $^3J_{H,H} = 7.0$ Hz), 7.92 (m, 2H) and 7.60 (m, 11H) (three Ph), 3.32 (s + d, 3H, C*H*$_3$, $^3J_{Pt,H} = 12.2$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 182.79 (*C*=NH), 143.18 (C_{ar}), 137.65 (C_{ar}), 137.59 (C_{ar}), 133.27 (C_{ar}), 132.85 (C_{ar}), 132.09 (C_{ar}), 131.29 (C_{ar}), 130.13 (C_{ar}), 129.52 (C_{ar}), 129.16 (C_{ar}), 128.25 (C_{ar}), 125.92 (C_{ar}), 45.23 (CH_3). ^{195}Pt NMR ($CDCl_3$): δ −1334.1 (J = 520 Hz).

6. Anal. Calcd for $C_{21}H_{21}NCl_2OPtS$: C, 41.94; H, 3.52; N,2.33. Found: C, 41.90; H, 3.45; N, 2.38. ESI-MS$^+$ (1:10 (v/v) $CHCl_3$/MeOH): *m/z* 602 [M + H]$^+$, 624 [M + Na]$^+$, 640 [M + K]$^+$. Mp: 164−165 °C. TGA curve, mass loss: 6.3% (−HCl, 190 °C, calcd 6.1%), 6.2% (270 °C), 6.6% (340 °C), 45% (410 °C). TLC (8:1 (v/v) $CHCl_3/Me_2CO$): $R_f = 0.70$. IR (KBr, cm^{-1}): ν 3198 (m, NH), 1597 (s, C=N), 1131 (s, S=O), 699 (s, C−S). ^{1}H NMR ($CDCl_3$): δ 9.83 (s, br, 1H, NH), 8.10 (d, 2H, H1 and H4, $^3J_{H,H}$ = 7.0 Hz), 7.90 (d, 2H, H2 and H3, $^3J_{H,H}$ = 8.1 Hz), 7.66 (m, 1H, H_{ar}), 7.62 (m, 2H, 2H_{ar}), 7.53 (m, 3H, 3H_{ar}), 7.44 (m, 2H, 2H_{ar}), 7.38 (m, 2H, 2H_{ar}), 3.46 (s, 3H, SCH_3), 2.50 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.84 (C=NH), 143.65 (C_{ar}(q)), 140.06 (C_{ar}(q)), 137.67 (C_{ar}(q)), 137.61 (C_{ar}(q)), 133.26 (C_{ar}), 132.15 (C_{ar}), 131.34 (C_{ar}), 130.13 (C_{ar}), 130.09 (C_{ar}, $^3J_{Pt,C}$ = 87.5 Hz), 129.16 (C_{ar}), 128.25 (C_{ar}), 125.89 (C_{ar}), 45.42 (SCH$_3$), 21.94 (CH$_3$). ^{195}Pt NMR ($CDCl_3$): δ −1318.0 (J = 450 Hz).

Cyclometalation of the Complexed Benzophenone Imine in the Solid State and on Heating in Toluene. The yellow powders of **1** or **2**−**6** (0.04 mmol) were heated in an open test tube at 180 °C (**1**), 140 °C (**2**), 140 °C (**3**), 180 °C (**4**), 160 °C (**5**), or 170 °C (**6**) overnight, giving a bright-orange product; elimination of HCl was detected by a pH indicator, and weight monitoring proved the loss of 1 equiv of HCl. The yield of **8** was almost quantitative. When **1** and **3**−**6** were heated, along with cyclometalated complexes **7** and **9**−**12**, the resulting orange solids contained some impurities deriving from decomposition products, as could be detected by ^{1}H NMR spectroscopy.

In a typical experiment, suspensions of **1** or **2**−**6** (0.1 mmol) in toluene (10 mL) were refluxed for 12−16 h, whereupon the solvent was removed at 40 °C under reduced pressure. The bright-orange-yellow powders of **7** or **8**−**12** were dried in vacuo at room temperature. Yields were almost quantitative.

7. IR (KBr (selected bands), cm^{-1}): ν(C=N) 1594 m [lit.[26] IR 1597 m cm^{-1}], ν(C=N) 1578 m [lit.[26] IR 1577 m cm^{-1}]. ^{1}H NMR ($CDCl_3$): δ 9.99 (s, br, 1H, NH) [lit.[26] δ 10.13], 8.91 (s, br, 1H, NH) [lit.[26] δ 8.87], 8.31 (d, 2H, H_{ar}, $^3J_{H,H}$ = 7.3 Hz) [lit.[26] δ 8.28 (d)], 7.66 (m, 1H, H_{ar}), 7.55 (m, 10H, H_{ar}), 7.42 (t, 2H, H_{ar}, $^3J_{H,H}$ = 7.7 Hz) [lit.[26] δ 7.35−7.7 (m)], 7.12 (dd, 1H, H_{ar}, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.6 Hz), 6.97 (m, 2H, H_{ar}), 6.85 (d, 1H, H_{ar}, $^3J_{H,H}$ = 7.6 Hz) [lit.[26] δ 6.8−7.1 (m)]. In addition, ESI-MS$^+$ analysis was carried out. ESI-MS$^+$ (MeOH): *m/z* 556 [M − Cl]$^+$, 732 [M + Ph_2C=NH − Cl]$^+$.



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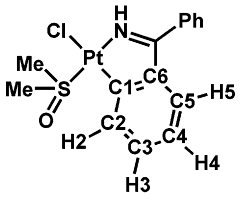
8. Anal. Calcd for $C_{15}H_{16}NClOPtS$: C, 36.85; H, 3.29; N, 2.86. Found: C, 37.08; H, 3.28; N, 2.86. ESI-MS$^+$ (MeOH): *m/z* 453 [M − Cl]$^+$, 511 [M + Na]$^+$. Mp: 185−186 °C. TLC (1:10 (v/v) $Me_2CO/CHCl_3$): $R_f = 0.54$. IR (KBr, cm^{-1}): ν 3340 (m, NH), 1569 (m, C=N), 1126 (s, S=O). ^{1}H NMR (CD_3OD): δ 10.50 (s, br, 1H, NH), 8.20 (d + q, 1H, H2, $^3J_{H,H}$ = 7.5 Hz, $^3J_{Pt,H}$ = 48.7 Hz), 7.63 (m, 5H, Ph), 7.24 (m, 1H, H3), 7.13 (m, 2H, H4 and H5), 3.55 (s + d, 6H, CH_3, $^3J_{Pt,H}$ = 22.1 Hz). ^{13}C{^{1}H} NMR (CD_3OD): δ 188.41 (C=N), 145.17 (C1), 134.13 (C2, $^2J_{Pt,C}$ = 54.4 Hz), 133.13 (C3, $^3J_{Pt,C}$ = 50.5 Hz), 131.55 (C_{ar}), 131.49 (C5), 128.99 (C_{ar}), 128.30 (C_{ar}), 124.28 (C4), 45.05 (CH$_3$, $^2J_{Pt,C}$ = 55.4 Hz). ^{195}Pt NMR (CD_3OD): δ −2261.7 (J = 710 Hz). Crystals for X-ray study were obtained by slow evaporation of an acetone solution.



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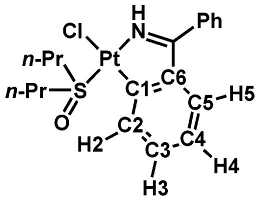
9. Anal. Calcd for $C_{19}H_{24}NClOPtS$: C, 41.87; H, 4.44; N, 2.57. Found: C, 41.93; H, 4.40; N, 2.55. ESI-MS$^+$ (MeOH): *m/z* 509 [M − Cl]$^+$, 568 [M + Na]$^+$. Mp: 190−192 °C. TLC ($CHCl_3$): $R_f = 0.44$. IR (KBr, cm^{-1}): ν 3206 (w, NH), 1580 (m, C=N), 1116 (s, S=O). ^{1}H NMR (CD_3OD): δ 10.43 (s, br, 1H, NH), 8.23 (d + q, 1H, H2, $^3J_{H,H}$ = 7.5 Hz, $^3J_{Pt,H}$ = 47.2 Hz), 7.63 (m, 5H, Ph), 7.22 (m, 1H, H3), 7.12 (m, 2H, H4 and H5), 3.78 (m, 2H, SCH_2), 3.40 (m, 2H, SCH_2), 2.17 (m, 2H, CH$_3$CH_2), 2.09 (m, 2H, CH$_3$CH_2), 1.19 (m, 6H, CH_3). ^{13}C{^{1}H} NMR (CD_3OD): δ 177.06 (C=N), 144.69 (C1), 135.89 (C6), 134.35 (C2, $^2J_{Pt,C}$ = 52.5 Hz), 132.95 (C3, $^3J_{Pt,C}$ = 51.5 Hz), 132.57 (C_{ar}(q)), 131.49 (C_{ar}), 131.39 (C5), 128.99 (C_{ar}), 128.30 (C_{ar}), 124.18 (C4), 57.81 (SCH$_2$, $^2J_{Pt,C}$ = 38.9 Hz), 17.32 (CH$_2$, $^3J_{Pt,C}$ = 22.4 Hz), 12.23 (CH$_3$). ^{195}Pt NMR (CD_3OD): δ −2281.7 (J = 570 Hz).



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10. Anal. Calcd for $C_{17}H_{18}NClOPtS$: C, 39.65; H, 3.52; N, 2.72. Found: C, 39.82; H, 3.65; N, 2.85. ESI-MS$^+$ (MeOH): *m/z* 538 [M + Na]$^+$, 554 [M + K]$^+$, 590 [M + HCl + K]$^+$. Mp: 173−174 °C. TLC (1:10 (v/v) $Me_2CO/CHCl_3$): $R_f = 0.60$. IR (KBr, cm^{-1}): ν 3212 (m, NH), 1587 (m, C=N), 1125 (s, S=O). ^{1}H NMR (CD_3OD): δ 10.57 (s, br, NH), 8.17 (d + q, 1H, H2, $^3J_{H,H}$ = 7.5 Hz,

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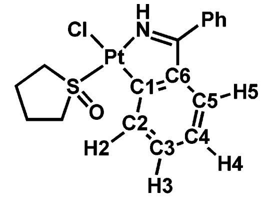
$^{3}J_{\mathrm{Pt,H}} = 49.2$ Hz), 7.62 (m, 5H, *Ph*), 7.23 (m, 1H, *H*3), 7.14 (m, 2H, *H*4 and *H*5), 4.15 (m, 2H, C*H*$_2$), 3.46 (m, 2H, C*H*$_2$), 2.47 (m, 2H, C*H*$_2$), 2.31 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (CD$_3$OD): δ 185.66 (*C*=N), 145.26 (*C*1), 135.74 (*C*6), 134.51 (*C*2, $^{2}J_{\mathrm{Pt,C}} = 61.2$ Hz), 133.89 (C_{ar}(q)), 133.17 (*C*3, $^{3}J_{\mathrm{Pt,C}} = 55.4$ Hz), 131.58 (C_{ar}), 131.54 (*C*5), 128.99 (C_{ar}), 128.34 (C_{ar}), 124.28 (*C*4), 59.54 (2S*C*H$_2$, $^{2}J_{\mathrm{Pt,C}}$ = 59.3 Hz), 25.95 (2*C*H$_2$, $^{3}J_{\mathrm{Pt,C}} = 28.2$ Hz). ^{195}Pt NMR (CD$_3$OD): δ −2240.3 (J = 730 Hz). Crystals for X-ray study were obtained by slow evaporation of an acetone solution.



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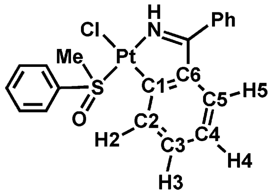
11. Anal. Calcd for C$_{20}$H$_{18}$NClOPtS: C, 43.59; H, 3.29; N, 2.54. Found: C, 43.44; H, 3.25; N, 2.50. ESI-MS$^+$ (acetone): *m*/*z* 515 [M − Cl]$^+$, 574 [M + Na]$^+$, 590 [M + K]$^+$. Mp: 178−180 °C. TLC (1:20 (v/v) Me$_2$CO/CHCl$_3$): R_f = 0.43. IR (KBr, cm^{-1}): ν 3202 (m, NH), 1581 (s, C=N), 1122 (s, S=O). ^{1}H NMR (acetone-d_6): δ 10.17 (s, br, 1H, N*H*), 8.24 (d, 2H, 2H_{ar}, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz), 8.05 (d + q, 1H, *H*2, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, $^{3}J_{\mathrm{Pt,H}} = 47.8$ Hz), 7.67 (m, 8H, 8H_{ar}), 7.16 (m, 1H, *H*3), 7.09 (m, 2H, *H*4 and *H*5), 3.68 (s + d, 3H, C*H*$_3$, $^{3}J_{\mathrm{Pt,H}} = 18.4$ Hz). ^{13}C{^{1}H} NMR (acetone-d_6): δ 188.41 (*C*=N), 167.70 (*C*1), 146.86 (C_{ar}(q)), 145.08 (C_{ar}(q)), 134.92 (*C*2, $^{2}J_{\mathrm{Pt,C}} = 53.5$ Hz), 133.58 (*C*3, $^{3}J_{\mathrm{Pt,C}}$ = 52.5 Hz), 132.80 (C_{ar}), 131.81 (C_{ar}), 131.67 (*C*5, $^{3}J_{\mathrm{Pt,C}} = 48.6$ Hz), 129.69 (C_{ar}), 129.16 (C_{ar}), 128.76 (C_{ar}), 125.97 (C_{ar}), 124.23 (*C*4), 47.17 (*C*H$_3$, $^{2}J_{\mathrm{Pt,C}} = 42.8$ Hz). ^{195}Pt NMR (acetone-d_6): δ −2266.1 (J = 600 Hz).



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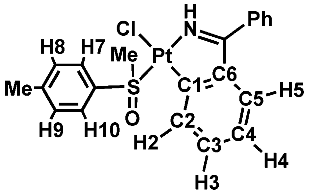
12. Anal. Calcd for C$_{21}$H$_{20}$NClOPtS: C, 44.64; H, 3.57; N, 2.48. Found: C, 44.75; H, 3.65; N, 2.35. ESI-MS$^+$ (MeOH): *m*/*z* 529 [M − Cl]$^+$, 588 [M + Na]$^+$. Mp: 169−170 °C. TLC (1:20 (v/v) Me$_2$CO/CHCl$_3$): R_f = 0.66. IR (KBr, cm^{-1}): ν 3200 (w, NH), 1583 (m, C=N), 1123 (s, S=O). ^{1}H NMR (acetone-d_6): δ 10.14 (s, br, 1H, N*H*), 8.11 (d, 2H, *H*7 and *H*10, $^{3}J_{\mathrm{H,H}} = 8.3$ Hz), 8.05 (d + q, 1H, *H*2, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, $^{3}J_{\mathrm{Pt,H}} = 47.0$ Hz), 7.66 (m, 5H, *Ph*), 7.49 (d, 2H, *H*8 and *H*9, $^{3}J_{\mathrm{H,H}} = 8.1$ Hz), 7.16 (m, 1H, *H*3), 7.09 (m, 2H, *H*4 and *H*5), 3.65 (s + d, 3H, SC*H*$_3$, $^{3}J_{\mathrm{Pt,H}}$ = 18.4 Hz), 2.45 (s, 3*H*, CH$_3$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 191.61 (*C*=N), 146.91 (C_{ar}(q)), 145.68 (C_{ar}(q)), 143.57 (C_{ar}(q)), 142.09 (C_{ar}(q)), 134.93 (*C*2, $^{2}J_{\mathrm{Pt,C}} = 53.5$ Hz), 133.93 (C_{ar}(q)), 133.56 (*C*3, $^{3}J_{\mathrm{Pt,C}} = 51.5$ Hz), 131.80 (C_{ar}), 131.64 (*C*5, $^{3}J_{\mathrm{Pt,C}} = 48.6$ Hz), 130.19 (*C*7 and *C*10), 129.17 (C_{ar}), 128.76 (C_{ar}), 125.98 (*C*8 and *C*9), 124.18 (*C*4), 47.33 (S*C*H$_3$, $^{2}J_{\mathrm{Pt,C}} = 43.7$ Hz), 20.82 (*C*H$_3$). ^{195}Pt NMR (acetone-d_6): δ −2264.9 (J = 620 Hz).



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X-ray Crystallography. The crystals were immersed in perfluoropolyether, mounted in cryoloops, and measured at 100 or 120 K temperature. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The Denzo-Scalepack program or EvalCCD packages[88,89] were used for cell refinements and data reductions. The structures were solved by direct methods or by the heavy-atom method using the *SHELXS-97* or *SIR2002* or the *DIFDIF-99* programs, respectively, with the WinGX graphical user interface.[90−92] An empirical absorption correction based on equivalent reflections was applied to all data (with *XPREP* in *SHELXTL* or with *SADABS*).[93,94] The maximum/minimum transmission factors were 0.3458/0.6932, 0.1842/0.6367, 0.0972/0.2271, 0.3095/0.4600, and 0.2530/0.5747 respectively for **1**, **2**, **4**·$^{1}/_{2}$CHCl$_3$, **8**, and **10**. Structural refinements were carried out with *SHELXL-97*.[95] The imine H atoms in **2** were located from the difference Fourier map but constrained to ride on its parent atom [$U_{\mathrm{iso}} = 1.5U_{\mathrm{eq}}$ (parent atom)]. Other H atoms were positioned geometrically and allowed to ride on their parent atoms, with N−H = 0.88 Å and $U_{\mathrm{iso}} = 1.2U_{\mathrm{eq}}$ (parent atom) and C−H = 0.95−0.99 Å and $U_{\mathrm{iso}} = 1.2{-}1.5U_{\mathrm{eq}}$ (parent atom). The asymmetric unit of **4**·$^{1}/_{2}$CHCl$_3$ contained two dimeric Pt units (four Pt) and one CHCl$_3$ solvent molecule. Structure **8** contained two and structure **10** four Pt moieties in the asymmetric unit. In structure **10**, two C atoms (C15D and C16D) were disordered over two positions with occupancies of 0.51 and 0.49. The selected bond lengths and angles are summarized in Table 1 and crystallographic data in Table 3.

Luminescence Studies. Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200−1100 nm). Luminescence spectra were obtained using a Spex Fluoromax-P fluorimeter corrected for the spectral sensitivity of the photomultiplier tube and the spectral output of the lamp with monochromators positioned for a 2 nm bandpass. Excited-state lifetimes were measured using a Lambda Physik nanosecond laser photolysis system. A Lextra 50 XeCl excimer laser was used to pump 3002 dye laser containing diphenylstilbene, which provided 7 ns, 1 mJ pulses at 400 nm. A monochromator and a fast photomultiplier tube were used to monitor sample emission at 575 nm. For kinetic analysis, the signal from the photomultiplier tube was directed into a Tektronix TDS 620 digitizing oscilloscope and then to a computer for averaging, fitting, and storage. The metal complex concentration of solution samples was 1.0 × 10^{-5} M, and each sample was degassed by at least three freeze−pump−thaw cycles. Solid-state emission and lifetime samples were prepared as a mixture of the Pt complexes (4.10 × 10^{-5} mol) in a matrix of finely ground KBr (3.24 × 10^{-3} mol). All data were recorded at room temperature.

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Note Added after ASAP Publication. This article was released ASAP on April 24, 2007. Additional changes were made to Table 1, and the correct version was posted on May 1, 2007.

Supporting Information Available: TGA curves of complexes **1**−**6** as well as crystallographic information files (CIF) of compounds **1**, **2**, **4**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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