Nucleophilic addition of bifunctional sulfimidosulfides to platinum(IV)-coordinated nitriles

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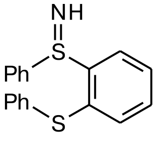
Reactions of the platinum(IV) nitrile complexes $[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph) with 1,2- and 1,4-$PhS(=NH)C_6H_4SPh$ in CH_2Cl_2 afforded addition products of sulfimides and coordinated nitriles, *viz*., the $[PtCl_4\{NH=C(R)N=S(Ph)(C_6H_4SPh)\}_2]$ complexes. The latter were isolated in 75—90% yields and characterized by elemental analysis, positive-ion FAB mass spectrometry, IR spectroscopy, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The temperature dependence of the ^1H NMR spectra of the model $[PtCl_4\{NH=C(R)N=SPh_2\}_2]$ complexes (R = Me, Et) in CD_2Cl_2 studied in a temperature range from +40 to −70 °C demonstrated that *E—Z* isomerization of the ligands is a dynamic process in a range from +40 to −10 °C. The activation free energy of this process was calculated.

Key words: nitriles, sulfimides, platinum(IV) complexes, nucleophilic addition, reactivity of ligands, *E—Z* isomerization.

Nitriles are widely used in organic chemistry for the synthesis of compounds containing C—O, C—N, C—S, or C—C bonds by the addition of O-, N-, S-, or C-nucleophiles, respectively, to the carbon atom of the nitrile group.[1] Generally, for the reactions involving the strong C≡N bond to occur, nitrile must be subjected to additional electrophilic activation, which can be achieved, for example, by coordination of the RCN molecule to a metal ion. In this case, the reactivity of the RCN ligands can be changed to an extent that the inner-sphere nitriles become able to be involved in addition reactions even with weak nucleophiles, for example, with oximes.[2—4] An additional advantage of activation of RCN upon its coordination to a metal ion is that the imine, which is derived from the nitrile as a result of the inner-sphere transformation, can usually be isolated in the free state by a substitution reaction.

Metal-promoted reactions of coordinated nitriles with N-nucleophiles containing the sp^3-hybridized N atom (ammonia,[5] primary and secondary amines[6,7]), which give rise to amidines, have been studied in sufficient detail. By contrast, the reactions with N-nucleophiles containing the sp^2-hybridized N atom are poorly known. A few studies have been devoted to the addition of nitrogen heterocycles,[8—10] benzophenone imine $Ph_2C=NH$,[11,12] and sulfimide $Ph_2S=NH$ [13—15] to inner-sphere nitriles. The present study is a continuation of our research on the reactions of sulfimides with organonitrile complexes of platinum(IV). The aim of the present study was to reveal the type of reactivity of bifunctional sulfimidosulfides **1** and **2** in the reactions with the $[PtCl_4(RCN)_2]$ complexes (R = Me, CH_2Ph, Ph).



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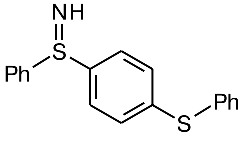

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Another purpose was to elucidate an exchange process responsible for broadening of signals of the heterodiazadiene ligands, which we have observed earlier[15] in the NMR spectra of the $[PtCl_4\{NH=C(R)N=SPh_2\}_2]$ complexes (R = Me, Et) prepared by the reactions of the platinum(IV) nitrile complexes with $Ph_2S=NH$.

Results and Discussion

The reactions of sulfimides **1** and **2** with nitriles in the coordination sphere of platinum(IV) can, in principle, in-

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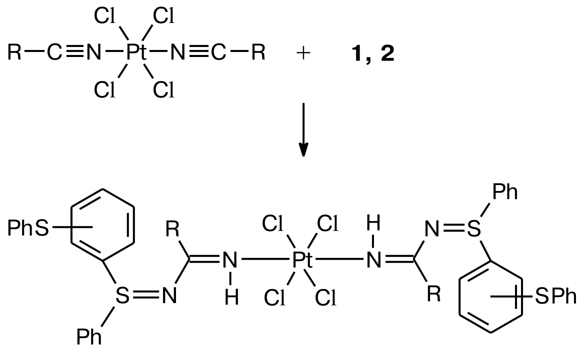
volve several processes: first, the replacement of nitrile with the HN=S [14] or —SPh groups of sulfimidosulfide **1** or **2**;[16] second, the nucleophilic addition of the HN=S group at the nitrile C≡N bond resulting in the closure of the chelate ring H<u>N</u>=C(R)—N=<u>S</u>Ar through the S atom;[13] and third, the nucleophilic addition of sulfimide to the coordinated nitrile to form the monodentate heterodiazadiene ligand H<u>N</u>=C(R)—N=SAr.[15]

The reactions of the platinum(IV) nitrile complexes with sulfimides **1** and **2** proceed at room temperature in a CH_2Cl_2 solution for 1 h (Scheme 1). Reaction products **3**—**8** were isolated in 75—90% yields and characterized by elemental analysis, positive-ion FAB mass spectrometry, IR spectroscopy, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In addition, small amounts of the platinum(IV) iminol complexes with composition *trans*-$[PtCl_4\{NH=C(OH)R\}_2]$, which have been characterized earlier,[17] were detected by NMR spectroscopy, FAB mass spectrometry, and TLC. Apparently, the formation of the latter complexes is attributable to hydrolysis of the $[PtCl_4(RCN)_2]$ complex by water, which is present as an impurity in the solvents used.

Scheme 1



3—8

	3	**4**	**5**	**6**	**7**	**8**	
R	Me	CH_2Ph	Ph	Me	CH_2Ph	Ph	
Position of the SPh group		2	2	2	4	4	4

The results of elemental analysis for complexes **3**—**8** are indicative of the presence of two monodentate heterodiazadiene ligands formed as a result of the nucleophilic addition of sulfimides to nitriles. The observed fragmentation and the character of isotope distribution in the FAB mass spectra of the complexes are close to those expected for the $[PtCl_4\{NH=C(R)N=S(Ph)(C_6H_4SPh)\}_2]$ compounds.

The IR spectroscopic data also confirm the hypothesis of the nucleophilic addition of sulfimides to the RCN ligands and rule out the possibility of replacement of nitriles involved in platinum(IV) complexes with sulfimides. For example, a comparison of the IR spectra of the compounds synthesized in the present study with the spectra of the starting complexes shows the absence of an absorption band ν(C≡N) at 2350—2300 cm^{-1}, the presence of an intense stretching band ν(C=N) at 1533—1523 cm^{-1}, and the presence of weaker bands ν(N—H) at 3373—3319 cm^{-1}.

In the ^1H NMR spectra recorded at room temperature, all signals of the $[PtCl_4\{NH=C(R)N=S(Ph)(C_6H_4SPh)\}_2]$ complexes are noticeably broadened. Apparently, this is associated with fast dynamic *E*—*Z* isomerization of the heterodiazadiene ligands in solution, which occurs within the NMR time scale (see below). The signal of the imine group (δ 6.15—6.52) is shifted upfield compared to those observed in the spectra of other platinum imine complexes (δ 8—9),[2—4] in which hydrogen bonding was established. The position of the signal at such a high field is indirect evidence that the proton of the C=NH group is not involved in hydrogen bonding in solution.[12,15] The $^{13}C\{^1H\}$ NMR spectra show a signal of the C=NH group at δ 170—174, which corresponds to the characteristic C=N resonances in platinum imine complexes.[2—4,15,17,18]

To prove the occurrence of equilibrium dynamic processes in solutions of complexes **3**—**8** and elucidate their nature, we studied the temperature dependence of the ^1H NMR spectra of the $[PtCl_4\{NH=C(R)N=SPh_2\}_2]$ complexes (R = Me (**9**), Et (**10**)) in solution in a temperature range from +40 to −70 °C. Complexes **9** and **10** were chosen as model compounds because, unlike compounds **3**—**8**, they are devoid of the sulfide group SPh. Hence, an exchange process associated with inversion at the S atom can be excluded from consideration. At room temperature, the signals for the NH protons (δ 7.11—6.11) and the protons of the alkyl group (δ 2.36—1.96 (Me); 3.13 and 1.27 (Et)) in complexes **9** and **10**, like those in compounds **3**—**8**, are substantially broadened.[15] An increase in the temperature to +40 °C is accompanied by narrowing of these signals, whereas a decrease in the temperature below −10 °C leads to the appearance of a triple set of these signals corresponding to three forms of the complexes, which are interconverted under conditions of a slow (within the NMR time scale) equilibrium process (Fig. 1).

To establish the structures of the complexes and make the assignment of the signals, we used the data from the NOESY-EXSY spectrum recorded under these conditions (−40 °C). This spectrum has positive exchange cross-peaks along with cross-peaks with negative polarity between the signals for the NH protons and the protons of the alkyl group for one of the isomers (*Z* configuration). Taking into account the absence of this cross-peak between the analogous signals for the second isomer, it can be stated with assurance that *E*—*Z* isomerization is a dynamic process in a temperature range from +40 to −10 °C (Scheme 2). The ratio between the *E* and *Z* isomers was determined by the integration of the signals for the pro-

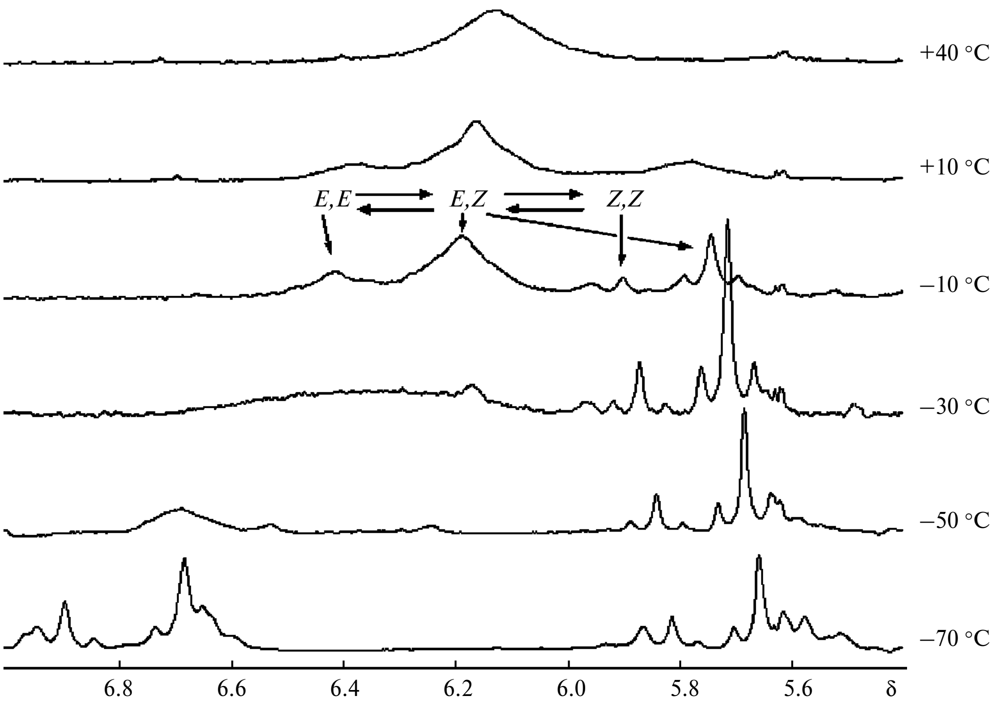
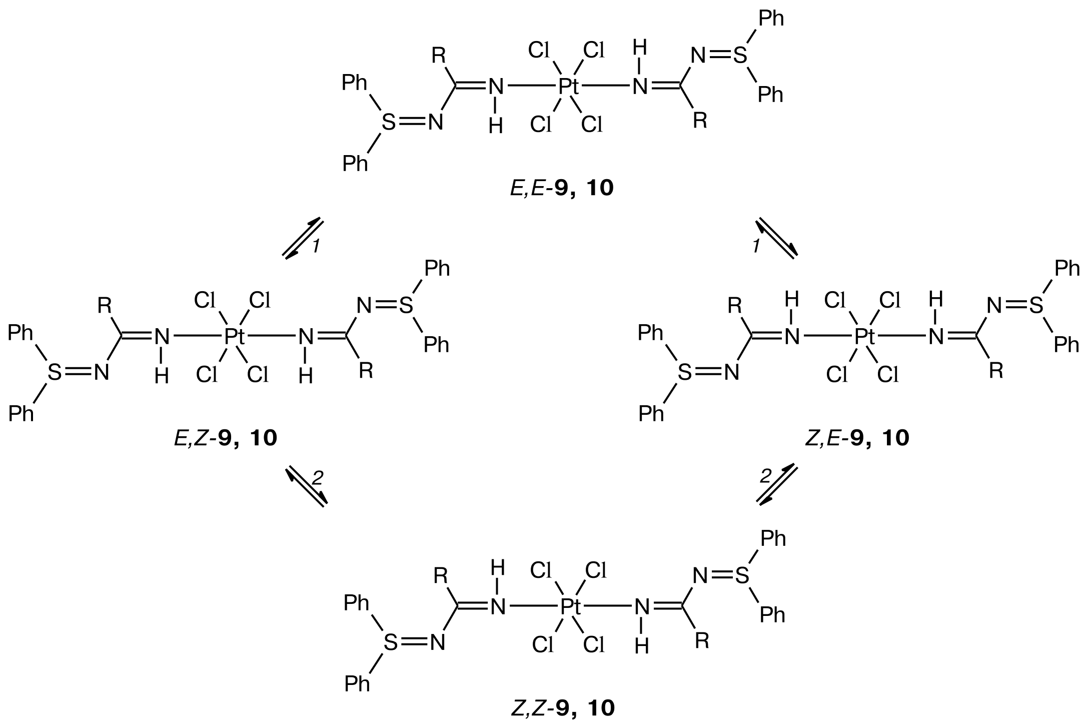


Fig. 1. Temperature dependence of the ^{1}H NMR spectra of compound **10** in the region of the signal for the NH proton.

Scheme 2



R = Me (**9**), Et (**10**)

Configuration	Content (%)	
	9	**10**
E,E	77	51
E,Z	22	45
Z,Z	1	4

Table 1. Activation free energies ($\Delta G^{\neq}$) for the equilibria *1* and *2* in solutions of complexes **9** and **10** (see Scheme 2)

Equilibrium	Configuration	$\Delta G^{\neq}$/kcal mol^{-1}			
		I*		II**	
		9	**10**	**9**	**10**
1	*E,E*	15.2	15.1	15.5	15.1
1	*E,Z*	16.2	15.1	16.6	15.1
2	*E,Z*	15.2	15.0	15.5	14.9
2	*Z,Z*	17.2	16.5	17.5	16.4

* The calculations were based on the integration of the signals for the NH protons in the ^{1}H NMR spectra.

** The calculations were based on the integration of the signals for the Alk protons in the ^{1}H NMR spectra.

tons of NH and the alkyl group at −10 °C (see Scheme 2). The activation free energy was also calculated from these data.[19] The calculated values are in a range of 15—17 kcal mol^{-1} (Table 1).

A further decrease in the temperature (from −10 to −70 °C) causes analogous changes in the ^{1}H NMR spectra. This fact is indicative of the second exchange process. The latter is, apparently, associated with inversion at the S atom or hindered rotation of the —N=SPh$_2$ group about a single bond.

We believe that broadening of the signals in the ^{1}H NMR spectra of complexes **3—8** recorded at room temperature,[15] like that observed in the spectra of model compounds **9** and **10**, is attributable to *E—Z* isomerization of the heterodiazadiene ligands.

Separate experiments demonstrated that sulfimides **1** and **2** do not react with free nitriles even on heating (10 h, 50 °C). This observation indicates that the reagents add to inner-sphere nitriles.

To summarize, we established that bifunctional sulfimidosulfides are selectively involved in the metal-promoted nucleophilic addition to nitrile ligands in platinum(IV) complexes to form new *N*-monodentate ligands. This reaction can be used as a simple procedure for the synthesis of heterodiazadienes NH=C(R^1)N=SR^{2}R^3, which are difficult to prepare according to conventional procedures without the involvement of metal complexes.[20,21]

Experimental

The melting points were determined in a capillary. The TLC analysis was carried out on Silufol UV254 plates. The positive-ion FAB mass spectra were obtained on a Trio 2000 instrument using bombardment of a nitrobenzyl alcohol matrix with Xe atoms (8 keV; ~$1.28 \cdot 10^{15}$ J). The IR spectra were measured in KBr pellets on a BIO-RAD FTS 3000MX instrument in a range of 4000—400 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian UNITY 300 spectrometer at ~20 °C. The variable-temperature ^{1}H NMR experiment was carried out in a temperature range from +40 to −70 °C in CD$_2$Cl$_2$. The NOESY experiment was performed at −40 and −70 °C (τ_{mix} = 0.5 s).

Functionalized sulfimides **1** and **2** were prepared according to known procedures.[22] The platinum(IV) complexes were synthesized according to a procedure described earlier:[2] the [PtCl$_4$(MeCN)$_2$] complex was prepared by chlorination of a mixture of the *cis* and *trans* isomers of [PtCl$_2$(MeCN)$_2$] giving rise to a mixture of *cis—trans*-[PtCl$_4$(MeCN)$_2$] in a ratio of 1 : 5; the pure *trans* isomers of [PtCl$_4$(RCN)$_2$] (R = CH$_2$Ph, Ph) were prepared by heating [PtCl$_2$(MeCN)$_2$] in the corresponding nitrile followed by chlorination.

Addition of sulfimides 1 and 2 to the platinum(IV) acetonitrile complex (general procedure). Sulfimide **1** or **2** (0.100 mmol) was added with stirring to a suspension of [PtCl$_4$(MeCN)$_2$] (0.05 mmol) in CH$_2$Cl$_2$ (2 mL) at ~20 °C. The reaction mixture turned bright-yellow during 1—2 min. After 30 min, the solution was concentrated to dryness. The orange oily residue was washed with Et$_2$O (5 mL) and crystallized from Et$_2$O (5 mL) at ~20 °C. The precipitate that formed was filtered off on a Hirsh funnel and dried in air at 20—25 °C. The yield was 75—90%.

Addition of sulfimides 1 and 2 to the platinum(IV) benzo- and benzylonitrile complexes (general procedure). Sulfimide **1** or **2** (0.100 mmol) was added with stirring to a suspension of [PtCl$_4$(RCN)$_2$] (R = CH$_2$Ph, Ph) (0.05 mmol) in CH$_2$Cl$_2$ (2 mL) at ~20 °C. The reaction mixture turned bright-yellow during 1—2 min, after which a precipitate formed. The latter was filtered off on a Hirsh funnel, washed with Et$_2$O (3×5 mL), and dried in air at 20—25 °C. The yield was 75—90%. Complexes **4**, **5**, **7**, and **8** are poorly soluble in most organic solvents. The ^{13}C{^{1}H} NMR spectra were not recorded because of a very long signal accumulation time.

Tetrachloro[bis(*N*-{phenyl[2-(phenylsulfanyl)phenyl]-λ^4-sulfanylidene}ethanimide-κ*N*-amide)]platinum(IV), [PtCl$_4${NH=C(Me)N=S(Ph)(*o*-C$_6$H$_4$SPh)}$_2$] (3). M.p. 172 °C, R_f 0.53 (Me$_2$CO—CHCl$_3$, 1 : 6, as the eluent). Found (%): C, 46.43; H, 3.51; N, 5.15. C$_{40}$H$_{36}$Cl$_4$N$_4$PtS$_4$. Calculated (%): C, 46.29; H, 3.50; N, 5.40. MS, *m/z*: 930 [M – 2 Cl]$^+$. IR, ν/cm^{-1}: 3319 (ν(N—H)); 3049, 2922 (ν(C—H)); 1533 (ν(C=N)); 1439 (ν(C=C arom.)). ^{1}H NMR (CDCl$_3$), δ: 7.5—7.2 (m, 14 H, H arom.); 6.18 (br.s, 1 H, NH); 2.67 (br.s, 3 H, Me). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 170.77 (C=N); 139.57, 133.14, 132.64, 130.03, 129.85, 129.66, 129.66, 127.63, 127.56 (Ph and C arom.); 24.77 (Me).

Tetrachloro[bis(*N*-{phenyl[2-(phenylsulfanyl)phenyl]-λ^4-sulfanylidene}-2-phenylethanimide-κ*N*-amide)]platinum(IV), [PtCl$_4${NH=C(CH$_2$Ph)N=S(Ph)(*o*-C$_6$H$_4$SPh)}$_2$] (4). M.p. 150 °C, R_f 0.74 (Me$_2$CO—CHCl$_3$, 1 : 5, as the eluent). Found (%): C, 51.35; H, 3.85; N, 4.41. C$_{52}$H$_{44}$Cl$_4$N$_4$PtS$_4$. Calculated (%): C, 52.48; H, 3.73; N, 4.71. MS, *m/z*: 1118 [M – 2 Cl]$^+$, 1083 [M – 3 Cl]$^+$. IR, ν/cm^{-1}: 3321 (ν(N—H)); 3054, 2922 (ν(C—H)); 1523 (ν(C=N)); 1442 (ν(C=C arom.)). ^{1}H NMR (CDCl$_3$), δ: 8.0—7.0 (br.m, H arom.); 6.15 (br.s, 1 H, NH); 4.81, 4.40, 4.03 (br.s, 2 H, C$\underline{\text{H}}_2$Ph).

Tetrachloro[bis(*N*-{phenyl[2-(phenylsulfanyl)phenyl]-λ^4-sulfanylidene}carboximide-κ*N*-amidobenzene)]platinum(IV), [PtCl$_4${NH=C(Ph)N=S(Ph)(*o*-C$_6$H$_4$SPh)}$_2$] (5). M.p. 164 °C (decomp.), R_f 0.72 (Me$_2$CO—CHCl$_3$, 1 : 5, as the eluent). Found (%): C, 51.36; H, 3.55; N, 4.82. C$_{50}$H$_{40}$Cl$_4$N$_4$PtS$_4$. Calculated (%): C, 51.68; H, 3.47; N, 4.82. MS, *m/z*: 1031 [M – 3 Cl]$^+$, 996 [M – 4 Cl]$^+$. IR, ν/cm^{-1}: 3326 (ν(N—H));

3052, 2924 (ν(C—H)); 1529 (ν(C=N)); 1444 (ν(C=C arom.)). ^{1}H NMR (CDCl$_3$), δ: 8.06—6.97 (br.m, H arom.); 6.15 (br.s, 1 H, NH).

Tetrachloro[bis(*N*-{phenyl[4-(phenylsulfanyl)phenyl]-λ^4-sulfanylidene}ethanimide-κ*N*-amide)]platinum(IV), [PtCl$_4${NH=C(Me)N=S(Ph)(*p*-C$_6$H$_4$SPh)}$_2$] (6). M.p. 166 °C, R_f 0.54 (Me$_2$CO—CHCl$_3$, 1 : 6, as the eluent). Found (%): C, 46.51; H, 3.72; N, 5.24. C$_{40}$H$_{36}$Cl$_4$N$_4$PtS$_4$. Calculated (%): C, 46.29; H, 3.50; N, 5.40. MS, *m/z*: 1060 [M + Na – H]$^+$, 1038 [M]$^+$. IR, ν/cm^{-1}: 3323 (ν(N—H)); 3052, 2923 (ν(C—H)); 1528 (ν(C=N)); 1439 (ν(C=C arom.)). ^{1}H NMR (CDCl$_3$), δ: 7.7—7.2 (br.m, 14 H, H arom.); 6.52 (br.s, 1 H, NH); 2.76 (br.s, 3 H, Me). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 174.69 (C=N); 134.55, 131.13, 130.27, 129.95, 129.29, 128.28, 127.91, 127.18 (Ph and C arom.); 24.77 (Me).

Tetrachloro[bis(*N*-{phenyl[4-(phenylsulfanyl)phenyl]-λ^4-sulfanylidene}-2-phenylethanimide-κ*N*-amide)]platinum(IV), [PtCl$_4${NH=C(CH$_2$Ph)N=S(Ph)(*p*-C$_6$H$_4$SPh)}$_2$] (7). M.p. 151 °C, R_f 0.51 (Me$_2$CO—CHCl$_3$, 1 : 6, as the eluent). Found (%): C, 51.46; H, 3.95; N, 4.56. C$_{52}$H$_{44}$Cl$_4$N$_4$PtS$_4$. Calculated (%): C, 52.48; H, 3.73; N, 4.71. MS, *m/z*: 1082 [M – 3 Cl – H]$^+$, 1048 [M – 4 Cl]$^+$. IR, ν/cm^{-1}: 3319 (ν(N—H)); 3052, 2926 (ν(C—H)); 1525 (ν(C=N)); 1439 (ν(C=C arom.)). ^{1}H NMR (CDCl$_3$), δ: 7.9—7.0 (br.m, H arom.); 6.32 (br.s, 1 H, NH); 4.40, 4.23 (br.s, 2 H, C$\underline{\mathrm{H}}_2$Ph).

Tetrachloro[bis(*N*-{phenyl[4-(phenylsulfanyl)phenyl]-λ^4-sulfanylidene}carboximide-κ*N*-amidobenzene)]platinum(IV), [PtCl$_4${NH=C(Ph)N=S(Ph)(*p*-C$_6$H$_4$SPh)}$_2$] (8). M.p. 152 °C (decomp.), R_f 0.58 (Me$_2$CO—CHCl$_3$, 1 : 6, as the eluent). Found (%): C, 51.70; H, 3.51; N, 4.83. C$_{50}$H$_{40}$Cl$_4$N$_4$PtS$_4$. Calculated (%): C, 51.68; H, 3.47; N, 4.82. MS, *m/z*: 1054 [M – 3 Cl + Na]$^+$, 1018 [M – 4 Cl – H + Na]$^+$. IR, ν/cm^{-1}: 3373 (ν(N—H)); 3052, 2929 (ν(C—H)); 1516 (ν(C=N)); 1440 (ν(C=C arom.)). ^{1}H NMR (CDCl$_3$), δ: 8.1—7.0 (br.m, Ph); 6.17 (br.s, 1 H, NH).

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