Inorg. Chem. **2003**, *42*, 301–311

Platinum(IV)-Mediated Nitrile–Sulfimide Coupling: A Route to Heterodiazadienes

Anastassiya V. Makarycheva-Mikhailova,[†] Nadezhda A. Bokach,[†] Vadim Yu. Kukushkin,*[,†] Paul F. Kelly,*[,‡] Liam M. Gilby,[‡] Maxim L. Kuznetsov,[§] Kathryn E. Holmes[‡], Matti Haukka,[||] Jonathan Parr,[‡] Julia M. Stonehouse,[‡] Mark R. J. Elsegood,[‡] and Armando J. L. Pombeiro*[,§]

Department of Chemistry, St. Petersburg State University, 198504 Stary Petergof, Russian Federation, Department of Chemistry, Loughborough University, Loughborough LE11 3TU, U.K., Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101, Joensuu, Finland, and Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

Received August 20, 2002

Pt(IV)-mediated addition of the sulfimide $Ph_2S{=}NH$ and the mixed sulfide/sulfimides *o*- and *p*-{PhS(=NH)}(PhS)-C_6H_4 by the S=NH group to the metal-bound nitriles in the platinum(IV) complexes $[PtCl_4(RCN)_2]$ proceeds smoothly at room temperature in CH_2Cl_2 and results in the formation of the heterodiazadiene compounds $[PtCl_4\{NH{=}C(R)N{=}SR'Ph\}_2]$ (R′ = Ph, R = Me, Et, CH_2Ph, Ph; R′ = *o*- and *p*-$(PhS)C_6H_4$; R = Et). While *trans*-$[PtCl_4(RCN)_2]$ (R = Et, CH_2Ph, Ph) reacting with $Ph_2S{=}NH$ leads exclusively to *trans*-$[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$, *cis/trans*-$[PtCl_4(MeCN)_2]$ leads to cis/trans mixtures of $[PtCl_4\{NH{=}C(Me)N{=}SPh_2\}_2]$ and the latter have been separated by column chromatography. Theoretical calculations at both HF//HF and MP2//HF levels for the cis and trans isomers of $[PtCl_4\{NH{=}C(Me)N{=}SMe_2\}_2]$ indicate a higher stability for the latter. Compounds *trans*-$[PtCl_4\{E\text{-}NH{=}C(R)N{=}SPh_2\}_2]$ (R = Me, Et) and *cis*-$[PtCl_4\{E\text{-}NH{=}C(Me)N{=}SPh_2\}\{Z\text{-}NH{=}C(Me)N{=}SPh_2\}]$ have been characterized by X-ray crystallography. The complexes $[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ undergo hydrolysis when treated with HCl in nondried CH_2Cl_2 to achieve the amidines $[PtCl_4\{NH{=}C(NH_2)R\}_2]$ (the compound with R = Et has been structurally characterized) and Ph_2SO. The heterodiazadiene ligands, formed upon Pt(IV)-mediated RCN/sulfimide coupling, can be liberated from their platinum(IV) complexes $[PtCl_4\{NH{=}C(R)N{=}SR'Ph\}_2]$ by reaction with $Ph_2PCH_2CH_2PPh_2$ (dppe) giving free NH=C(R)=SR′Ph and the dppe oxides, which constitutes a novel route for such rare types of heterodiazadienes whose number has also been extended. The hybrid sulfide/sulfimide species *o*- and *p*-{PhS(=NH)}(PhS)C_6H_4 also react with the Pt(II) nitrile complex $[PtCl_2(MeCN)_2]$ but the coupling—in contrast to the Pt(IV) species—gives the chelates $[PtCl_2\{NH{=}C(Me)N{=}S(Ph)C_6H_4SPh\}]$. The X-ray crystal structure of $[PtCl_2\{NH{=}C(Me)N{=}S(Ph)C_6H_4SPh\text{-}o\}]$ reveals the bond parameters within the metallacycle and shows an unusual close interaction of the sulfide sulfur atom with the platinum.

Introduction

Addition to metal-activated RC≡N species is one of the frontier areas of current research on organonitriles, and this topic has been the subject of comprehensive reviews[1] including a recent survey by two of us.[2] In general, the interest in conversions of nitriles at metal centers stems from the possibilities (i) to use nitriles as versatile synthons for the preparation of new compounds, often unreachable in pure organic synthesis, via C−O, C−N, C−C, C−P, and C−S

* To whom correspondence should be addressed. E-mail: kukushkin@VK2100.spb.edu (V.Yu.K.); P.F.Kelly@lboro.ac.uk (P.F.K.); pombeiro@ist.utl.pt (A.J.L.P.).

[†] St. Petersburg State University.

[‡] Loughborough University.

[§] Instituto Superior Técnico.

[||] University of Joensuu.

(1) (a) Eglin, J. L. *Comments Inorg. Chem.* **2002**, *23*, 23. (b) Murahashi, S.-I.; Takaya, H. *Acc. Chem. Res.* **2000**, *33*, 225. (c) da Rocha, Z. N.; Chiericato, G., Jr.; Tfouni, E. *Adv. Chem. Ser.* **1997**, *253*, 297. (d) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299. (e) Murahashi, S.-I.; Naota, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1805. (f) Murahashi, S.-I.; Naota, T. *Chemtracts: Org. Chem.* **1994**, *7*, 281. (g) Corain, B.; Basato, M.; Veronese, A. C. *J. Mol. Catal.* **1993**, *81*, 133.

(2) (a) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771. (b) Pombeiro, A. J. L.; Kukushkin, V. Yu. In *Comprehensive Coordination Chemistry*, 2nd ed.; Elsevier: New York, 2003; Vol. 1, in press.

10.1021/ic025960w CCC: $25.00
Published on Web 12/28/2002

bond making, (ii) to provide environmentally friendly metal-catalyzed hydrolytic transformation of RCN species to amides, e.g., of industrial and pharmacological significance, and (iii) to synthesize, via nucleophilic addition, diverse imino complexes, e.g., exhibiting unusual antitumor properties. The analysis of experimental material collected to date[2] shows that the largest fraction of research is devoted to the creation of the C−N bond by the addition of ammonia, primary and secondary amines, hydrazines, and hydroxylamines as well as by coupling of some nitrogen heterocycles with ligated RCN species. New reactions leading to the C−N bond that have emerged in the past months (and were not covered in the review[2]) include the Ni(II)-templated formation of imidoylamidines,[3] molybdenum-[4a] and platinum-mediated[4b] amine−nitrile coupling, and the formation of amidines from conversions of alkyl nitriles at a Pt(II) center;[5] the latter is relevant to the formation of amidines at a Co(II) center observed previously by us.[6]

Despite the large number of examples of the metal-mediated RCN−*amine* integration, only a few works deal with nitrile−*imine* (or *heteroimine*) coupling. Thus, one part of the current team has pioneered the addition of the sulfimide Ph_2S═NH to (nitrile)Pt^{II} complexes,[7,8] while the other part of the team observed the addition of Ph_2C═NH to (nitrile)Pt^{IV} complexes.[9] Such reactions generate chelated[7,8] or monodentate[8,9] diazadiene species of the type HN═C(R)N═EPh_2 (E = S, C). We have now endeavored to extend our investigations by combining the experience of both groups to assess the reactivity of sulfimides toward the organonitrile platinum(IV) complexes $[PtCl_4(RCN)_2]$. Our interest in these processes was at least 3-fold: (i) to verify the effect of the oxidation state of the Pt center on the addition of Ph_2S═NH to coordinated nitriles; (ii) to liberate HN═C(R)N═SPh_2 species and to develop a route for preparation of this little explored type of heterodiazadiene; (iii) to assess the effect of derivatization upon the reactivity of the sulfimide (toward both Pt(II) and Pt(IV)) by observing the analogous reactions of mixed sulfide/sulfimides. The presence of the thioether unit in the latter species provides an extra potential coordinating atom for the new ligands formed in such reactions. Previous work[7] has demonstrated that the addition reaction with nitriles tends to activate the sulfimide sulfur atom toward metal coordination; thus successful reactions involving the mixed ligands would provide routes to ligands that would be potentially tridentate in nature.

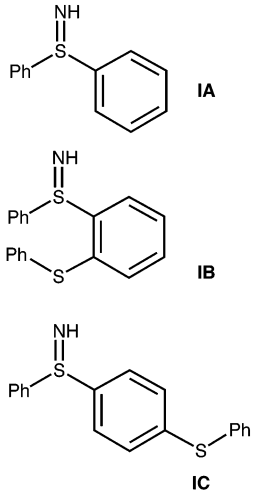


Figure 1.

We report herein on the facile and selective Pt(IV)-mediated addition of sulfimides and mixed sulfide/sulfimides by the S═NH group to metal-bound nitriles to produce ligated heterodiazadienes which can be liberated by the reaction with 1,2-bis(diphenylphosphino)ethane (dppe) and isolated as solids.

Experimental Section

Instrumentation and Materials.

Instrumentation has been previously described.[9] Sulfimides **IA**[10] (see Figure 1) and **IB**[11] were synthesized in accord with the published methods, while **IC** was prepared in an analogous manner to **IB** using *p*-$(PhS)_2C_6H_4$ as the starting sulfide. Solvents were obtained from commercial sources and used as received. Ph_3P═$CHCO_2Me$ was purchased from Lancaster. In the nitrile compounds $[PtCl_4(RCN)_2]$ (R = Me, Et, CH_2Ph, Ph), the first complex was prepared by chlorination of a mixture of the *cis*- and *trans*-$[PtCl_2(MeCN)_2]$ isomers (ca. 5:1 for R = Me[12]) giving a mixture of *cis/trans*-$[PtCl_4(MeCN)_2]$ with almost the same isomeric ratio. *trans*-$[PtCl_4(RCN)_2]$ (R = Et, CH_2Ph) were obtained by chlorination of the pure *trans*-$[PtCl_2(RCN)_2]$ isomers,[13,14] while the latter complex, i.e. *trans*-$[PtCl_4(PhCN)_2]$, was obtained by heating of *cis/trans*-$[PtCl_2(MeCN)_2]$ in neat PhCN; isolation of *trans*-$[PtCl_2(PhCN)_2]$[15] was followed by its oxidation with Cl_2 in accord with the published procedure.

Synthetic Work.

Addition of Sulfimides to $[PtCl_4(RCN)_2]$ Complexes. Ph_2S═NH·H_2O (**IA**) (0.1 mmol) is added to a suspension of $[PtCl_4(RCN)_2]$ (R = Me, Et, CH_2Ph, Ph) (0.05 mmol) in CH_2Cl_2 (2 mL). The reaction mixture becomes orange-yellow in 1−2 min, whereupon the solvent is evaporated to dryness and the orange residue is

(3) Kryatov, S. V.; Nazarenko, A. Y.; Smith, M. B.; Rybak-Akimova, E. V. *Chem. Commun*. **2001**, 1174.
(4) (a) Du., S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans*. **2002**, 1553. (b) Belluco, U.; Benetollo, F.; Bertani, R.; Bombieri, G.; Michelin, R. A.; Mozzon, M.; Tonon, O.; Pombeiro, A. J. L.; Guedes da Silva, F. C. *Inorg. Chim. Acta* **2002**, *334*, 437.
(5) Longato, B.; Bandoli, G.; Mucci, A.; Schenetti, L. *Eur. J. Inorg. Chem*. **2001**, 3021.
(6) Kopylovich, M. N.; Kukushkin, V. Yu.; Guedes da Silva, M. F. C.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1569.
(7) Kelly, P. F.; Slawin, A. M. Z. *Chem. Commun*. **1999**, 1081.
(8) Kelly, P. F.; Slawin, A. M. Z. *Eur. J. Inorg. Chem*. **2001**, 263.
(9) Garnovskii, D. A.; Kukushkin, V. Yu.; Haukka, M.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2001**, 560.
(10) Kelly, P. F.; Man, S.-M.; Slawin, A. M. Z.; Waring, K. W. *Polyhedron* **1999**, *18*, 3173.
(11) Elsegood, M. R. J.; Holmes, K. E.; Kelly, P. F.; Parr, J.; Stonehouse, J. M. *New J. Chem*. **2002**, *26*, 202.
(12) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Chem. Soc., Dalton Trans*. **1990**, 199.
(13) (a) Svensson, P.; Lövqvist, K.; Kukushkin, V. Yu.; Oskarsson, Å. *Acta Chem. Scand*. **1995**, *49*, 72. (b) Kukushkin, V. Yu.; Oskarsson, Å.; Elding, L. I. *Inorg. Synth.* **1997**, *31*, 279.
(14) Kukushkin, V. Yu.; Tkachuk, V. M.; Vorobiov-Desiatovsky, N. V. *Inorg. Synth.* **1998**, *32*, 144.
(15) (a) Uchiyama, T.; Nakamura, Y.; Miwa, T.; Kawaguchi, S.; Okeya, S. *Chem. Lett*. **1980**, 337. (b) Uchiyama, T.; Toshiyasu, Y.; Nakamura, Y.; Miwa, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181.

washed by Et_2O (two 3-mL portions) and dried in air at 20−25 °C. Yield: 75−90%. Reaction with **IB** or **IC** is performed similarly.

Complexes **1** and **2** were prepared from the mixture of the *cis*- and *trans*-$[PtCl_2(MeCN)_2]$ isomers and **IA**, and after the reaction, **1** and **2** were separated by column chromatography on silica gel (Chemapol Silicagel L 40/100; eluent is $CHCl_3$). The ratio between *trans*-**1** and *cis*-**2** approximately corresponds to the ratio between the trans and cis isomers in the starting mixture of *trans*- and *cis*-$[PtCl_4(MeCN)_2]$.

***trans*-[PtCl$_4${NH=C(Me)N=SPh$_2$}$_2$] (1).** Anal. Calcd for $C_{28}H_{28}N_4Cl_4PtS_2$: C, 40.93; H, 3.44; N, 6.82; S, 7.81. Found: C, 40.50; H, 3.35; N, 6.12; S, 7.75. FAB$^+$-MS, *m*/*z*: 843 $[M + Na]^+$, 823 $[M + H]^+$, 785 $[M - Cl]^+$, 715 $[M - 3Cl]^+$. Mp: 137 °C (dec). TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.46$ (eluent $Et_2O-CH_2Cl_2$, 1:20). IR spectrum in KBr, selected bands, cm^{-1}: 3326 m ν(N−H), 3052 w and 2920 w ν(C−H), 1539 s ν(C=N), 1437 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: 7.67 and 7.52 (m, Ph, 10*H*), 6.53 (s, br, NH, 1*H*), 2.75 (s, br, Me, 3*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 176.37 (C=N), 135.96 (C_{ipso}), 132.61 (*p*-Ph), 130.12 and 127.34 (*m*-Ph and *o*-Ph), 21.85 (Me). $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 110.0 (640 Hz). Crystals for X-ray study were obtained by slow evaporation of a $CDCl_3$ solution.

***cis*-[PtCl$_4${NH=C(Me)N=SPh$_2$}$_2$] (2).** Anal. Calcd for $C_{28}H_{28}N_4Cl_4PtS_2 \cdot H_2O$: C, 40.06; H, 3.60; N, 6.67; S, 7.64. Found: C, 40.35; H, 3.33; N, 6.10; S, 7.65. FAB$^+$-MS, *m*/*z*: 843 $[M + Na]^+$, 823 $[M + H]^+$, 785 $[M - Cl]^+$, 715 $[M - 3Cl]^+$. Mp: 151 °C (dec). TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.34$ (eluent $Et_2O-CH_2Cl_2$, 1:5). IR spectrum in KBr, selected bands, cm^{-1}: 3425 s-m ν(O−H), 3331 m ν(N−H), 3055 w and 2923 w ν(C−H), 1534 s ν(C=N), 1440 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: two sets of signals from *E* and *Z* isomers of the ligand, 7.9−7.3 (m, 10*H* both, Ph), 7.11 and 6.11 (two s, br, 2*H* both, NH), 2.36 and 1.96 (two s, br, 3*H* both, Me). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 176.37 (C=N), 135.96 and 136.41 (C_{ipso}), 132.61 (*p*-Ph), 130.12 and 130.36, 127.34 and 127.79 (*m*-Ph and *o*-Ph), 21.85 and 24.14 (Me). $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 187.9 (740 Hz). Slow evaporation of a $CH_2Cl_2-Et_2O$ solution of **2** gave crystals (used for X-ray study) of the bis-solvate *cis*-$[PtCl_4\{NH=C(Me)N=SPh_2\}_2]\cdot 2CH_2Cl_2$. Anal. Calcd for $C_{28}H_{28}N_4Cl_4PtS_2 \cdot 2CH_2Cl_2$: C, 36.34; H, 3.25; N, 5.65; S, 6.47. Found: C, 36.02; H, 3.39; N, 5.72; S, 6.35. Note that only one solvent molecule appears in the X-ray structure due to disorder of the second molecule.

***trans*-[PtCl$_4${NH=C(Et)N=SPh$_2$}$_2$]·2H$_2$O (3).** The complex was prepared from *trans*-$[PtCl_4(EtCN)_2]$ and **IA**. Anal. Calcd for $C_{30}H_{36}N_4Cl_4O_2PtS_2$: C, 40.68; H, 4.10; N, 6.33; S, 7.24. Found: C, 41.07; H, 3.25; N, 6.28; S, 7.21. FAB$^+$-MS, *m*/*z*: 743 [M − 3Cl]. Mp: 185 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.70$ (eluent $Et_2O-CH_2Cl_2$, 1:20). IR spectrum in KBr, selected bands, cm^{-1}: 3431 s-m ν(O−H), 3321 m-w ν(N−H), 3054 w and 2971 w ν(C−H), 1522 s ν(C=N), 1440 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: 7.73 and 7.50 (m, br, 10*H*, Ph), 6.24 (s, br, 1*H*, NH), 3.13 (s, br, 2*H*, CH_2 from Et), 1.27 (t, br, 3*H*, CH_3 from Et). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 179.99 (C=N), 135.72 (C_{ipso}), 132.47(*p*-Ph), 130.01 and 127.28 (*m*-Ph and *o*-Ph), 30.04 (CH_2 from Et), 12.95 (CH_3 from Et). $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 134.7 (400 Hz). Crystals for X-ray study were obtained directly from the reaction mixture by slow, partial evaporation of the solvent. The X-ray structure determination does not allow one to locate the water of crystallization.

***trans*-[PtCl$_4${NH=C(CH$_2$Ph)N=SPh$_2$}$_2$]·2H$_2$O (4).** The complex was prepared from *trans*-$[PtCl_4(PhCH_2CN)_2]$ and **IA**. Anal. Calcd for $C_{40}H_{40}N_4Cl_4O_2PtS_2$: C, 47.58; H, 3.99; N, 5.55; S, 6.35. Found: C, 47.14; H, 3.57; N, 5.32; S, 6.70. FAB$^+$-MS, *m*/*z*: 973 $[M - H]^+$, 901 $[M - H - 2Cl]^+$, 867 $[M - 3Cl]^+$, 830 $[M - 4Cl - H]^+$. Mp: 138 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.59$ (eluent $Et_2O-CH_2Cl_2$, 1:40). IR spectrum in KBr, selected bands, cm^{-1}: 3437 s-m ν(O−H), 3325 m-w ν(N−H), 3055 w and 2923 w ν(C−H), 1524 s ν(C=N), 1440 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: 7.3 and 7.1 (m, 15*H*, CH_2*Ph* and =SPh_2), 6.80 (s, br, 1*H*, NH), 4.63 (s, br, 2*H*, CH_2Ph). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 176.93 (C=N), 134.19 (C_{ipso}), 132.15 (*p*-Ph), 129.72 and 127.00 (*m*- and *o*-Ph), 130.08, 128.08 and 127.90 (*o*-, *m*- and *p*-CH_2Ph), *C*H_2Ph not detected. $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 94.2 (370 Hz).

***trans*-[PtCl$_4${NH=C(Ph)N=SPh$_2$}$_2$] (5).** The complex was prepared from *trans*-$[PtCl_4(PhCN)_2]$ and **IA**. Anal. Calcd for $C_{38}H_{32}N_4Cl_4PtS_2$: C, 48.26; H, 3.41; N, 5.92; S, 6.78. Found: C, 48.02; H, 3.50; N, 5.45; S, 6.21. FAB$^+$-MS, *m*/*z*: 839 $[M - 3Cl]^+$, 802 $[M - 4Cl - H]^+$. Mp: 163 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.54$ (eluent $Et_2O-CH_2Cl_2$, 1:40). IR spectrum in KBr, selected bands, cm^{-1}: 3377 m-w ν(N−H), 3053 w and 2923 w ν(C−H), 1524 s ν(C=N), 1443 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: 8.0, 7.8 and 7.4 (m, 15*H*, Ph), 6.11 (s, br, 1*H*, NH). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 133.12 (*p*-PhS), 132.05 (*p*-Ph), 130.32 and 128.68 (*o*- and *m*-Ph), 129.85 and 127.44 (*o*- and *m*-PhS), C_{ipso} and C=N not detected. $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 92.0 (780 Hz).

***trans*-[PtCl$_4${NH=C(Et)N=S(Ph)(*o*-C$_6$H$_4$SPh)}$_2$] (6).** The complex was prepared from *trans*-$[PtCl_4(EtCN)_2]$ and **IB**. Anal. Calcd for $C_{42}H_{40}N_4Cl_4PtS_4$: C, 47.32; H, 3.78; N, 5.26; S, 12.03. Found: C, 47.75; H, 3.72; N, 5.18; S, 12.21. FAB$^+$-MS, *m*/*z*: 994 $[M - 2Cl]^+$, 958 $[M - 3Cl - H]^+$. Mp: 197 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.61$ (eluent $Et_2O-CH_2Cl_2$, 1:40). IR spectrum in KBr, selected bands, cm^{-1}: 3323 m-w ν(N−H), 3055 w and 2930 w ν(C−H), 1516 s ν(C=N), 1440 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: two isomers in ca. 2:3 ratio, 8.1−7.2 (*m*, Ph, both isomers), 6.36 (s, br, NH, major), 5.95 (s, br, NH, minor), 3.12 (s, br, CH_2 from Et, major), 2.56 (s, br, CH_2 from Et, minor), 1.21 (t, br, CH_3 from Et), 1.18 (s, br, CH_3 from Et, minor). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 134.1, 132.8, 132.2, 131.0, 129.8, 129.7, 128.1, and 127.9 (*o*-, *m*- and *p*-Ph, C_6H_4), 29.05 (CH_2 from Et), 12.85 (CH_3 from Et). $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: two isomers in ca. 2:3 ratio, 140.7 (major, 320 Hz) and 102.0 (minor, 360 Hz).

***trans*-[PtCl$_4${NH=C(Et)N=S(Ph)(*p*-C$_6$H$_4$SPh)}$_2$]·3H$_2$O (7).** The complex was prepared from *trans*-$[PtCl_4(EtCN)_2]$ and **IC**. Anal. Calcd for $C_{42}H_{46}N_4Cl_4O_3PtS_4$: C, 45.04; H, 4.14; N, 5.00; S, 11.45. Found: C, 44.73; H, 3.66; N, 5.11; S, 11.34. FAB$^+$-MS, *m*/*z*: 1067 $[M + H]^+$, 1030 $[M + H - Cl]^+$, 994 $[M - 2Cl]^+$, 959 $[M - 3Cl]^+$, 923 $[M - 4Cl - H]^+$. Mp: 118 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.70$ (eluent $Et_2O-CH_2Cl_2$, 1:80). IR spectrum in KBr, selected bands, cm^{-1}: 3435 s-m ν(O−H), 3321 w ν(N−H), 3052 w and 2968 w ν(C−H), 1523 s ν(C=N), 1439 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: 7.5−7.2 (m, 14*H*, Ph), 6.18 (s, br, 1*H*, NH), 3.11 (s, br, 2*H*, CH_2 from Et), 1.25 (t, br, 3*H*, CH_3 from Et). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 179.65 (C=N), 134.23, 132.46, 131.36, 131.04, 130.05, 129.79, 129.15, 128.35, 127.90, and 127.17 (*o*-, *m*- and *p*-Ph, C_6H_4), 28.88 (CH_2 from Et), 12.67 (CH_3 from Et). $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 133 (567 Hz).

Addition of IB to the Nitrile in [PtCl$_2$(MeCN)$_2$]. A solution of $[PtCl_2(MeCN)_2]$ (0.109 g, 0.313 mmol) in MeCN (10 mL) is treated dropwise, with stirring, with a solution of **IB** (0.097 g, 0.313 mmol) in an equal volume of the same solvent. After being stirred at 50 °C for 4 h, the mixture is reduced to dryness in vacuo and quickly washed with ice cold CH_2Cl_2 (10 mL). The resulting solid

is then dissolved in CH_2Cl_2 (20 mL) at ambient temperature through vigorous stirring and gentle heating and then crystallized by slow diffusion of Et_2O vapor into this solution. A further small crop of crystals is obtained by Et_2O vapor diffusion into the initial CH_2Cl_2 washings; these can be separated from the other material present in this solution, which precipitates as an amorphous powder. Combined yield of crystalline material: 98 mg (51%).

[$PtCl_2${*N*H=C(Me)N=S(Ph)C_6H_4SPh-*o*}] (8). Anal. Calcd for $C_{20}H_{18}N_2Cl_2PtS_2$: C, 39.0; H, 2.9; N, 4.5. Found: C, 38.7; H, 2.8; N, 4.3. FAB^+-MS, *m*/*z*: 616 $[M]^+$, 581 $[M - Cl]^+$. Mp: 215 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.29$ (eluent hexane−Et_2O, 1:8). IR spectrum in KBr, selected bands, cm^{-1}: 3343 m ν(N−H), 1523 m ν(C=N), 801 m ν(S=N). ^1H NMR spectrum in $CDCl_3$, δ: 8.24 (2*H*, dd, Ph C−H), 7.75−7.26 (12*H*, m, Ph C−H), 2.28 (3*H*, s, br, CH_3). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 182.3 (N−C=N), 133.4, 133.2, 133.0, 132.7, 132.0, 131.8, 131.4, 131.2, 129.7, 128.9, 128.8, 128.6, 128.1, 127.7, 127.5, 126.9, and 125.7 (Ph C−H), 18.1 (CH_3). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −3087 (346 Hz).

Addition of IC to the Nitrile in [$PtCl_2$(MeCN)$_2$]. A solution of [$PtCl_2$(MeCN)$_2$] (0.107 g, 0.307 mmol) in MeCN (10 mL) is treated dropwise, with stirring, with a solution of **IC** (0.095 g, 0.307 mmol) in an equal volume of the same solvent. After being stirred at 50 °C for 4 h, the mixture is reduced to dryness in vacuo, dissolved in CH_2Cl_2 (20 mL), and loaded onto a silica column. Elution with hexane−Et_2O (1:8) allows isolation of a yellow band ($R_f = 0.2$) containing the product. Yield: 46 mg (24%) after column chromatography.

[$PtCl_2${*N*H=C(Me)N=S(Ph)C_6H_4SPh-*p*}] (9). Anal. Calcd for $C_{20}H_{18}N_2Cl_2PtS_2$: C, 39.0; H, 2.9; N, 4.5. Found: C, 38.8; H, 3.5; N, 3.7. FAB^+-MS, *m*/*z*: 581 $[M - Cl]^+$. Mp: 120 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.20$ (eluent hexane−Et_2O, 1:8). IR spectrum in KBr, selected bands, cm^{-1}: 3290 m ν(N−H), 1528 m ν(C=N), 805 m ν(S=N). ^1H NMR spectrum in $CDCl_3$, δ: 8.02 (2*H*, d, Ph C−H), 7.83 (2*H*, d, Ph C−H), 7.55−7.37 (8*H*, m, Ph C−H), 7.13 (2*H*, d, Ph C−H), 2.32 (3*H*, s, CH_3). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 182.6 (N−C=N), 134.3, 134.1, 133.2, 132.2, 130.4, 130.1, 129.6, 129.1, 129.0, 128.9, 128.6, 128.3, 127.4, 127.0, 126.4, 126.1, and 122.4 (Ph C−H), 18.0 (CH_3). ^{195}Pt NMR spectrum in $CDCl_3$, δ: −3167 (318 Hz).

HCl-Promoted Hydrolysis of [$PtCl_4${NH=C(R)N=SPh_2}$_2$] (R = Me, Et, CH_2Ph, Ph). Dry HCl is passed through a solution of [$PtCl_4${NH=C(R)N=SPh_2}$_2$] (0.02 mmol) in dichloromethane (2 mL) placed in an open beaker at 20−25 °C for 10−15 min, whereupon the beaker is kept in a desiccator with a small amount of concentrated aqueous HCl on the bottom. The precipitate formed is filtered off, washed with three 3-mL portions of CH_2Cl_2, and dried in air at room temperature. In the case of R = Me the precipitate (yield is 40%) is released from the reaction mixture after 2.5 h and the filtrate contains a number of yet unidentified species. In the other cases the precipitates (crystals in the case of R = Et) formed after ca. 2 h (yields are 60−70%). All thus prepared complexes exhibit poor solubility in the most common organic solvents, and we were unable to measure their $^{13}C\{^1H\}$ and ^{195}Pt NMR spectra even at high accumulation time.

The filtrate is evaporated at room temperature to give an oily residue. IR, FAB-MS, EI-MS, and TLC analyses of the latter showed the presence of Ph_2S=O and chloro- and dichlorodiphenyl sulfides in the mixture.

***trans*-[$PtCl_4${NH=C(Me)N=SPh_2}$_2$]·$(HCl)_2$·$2H_2O$ (10).** This complex was obtained by starting from **1**. Anal. Calcd for $C_{28}H_{34}N_4Cl_6O_2PtS_2$: C, 36.15; H, 3.66; N, 6.02. Found: C, 35.96; H, 3.83; N, 6.14. FAB^+-MS, *m*/*z*: 919 $[M - Cl + Na]^+$, 860 $[M - 2Cl]^+$, 825 $[M - 3Cl]^+$, 788 $[M - 4Cl - H]^+$. Mp: 133 (dec) °C. IR spectrum in KBr, selected bands, cm^{-1}: 3458 s-m ν(O−H), 3330 m ν(N−H), 3059 w and 2928 w ν(C−H), 1666 and 1539 s ν(C=N), 1438 m ν(C=C Ar). The solubility of this compound in $CDCl_3$ or acetone-d_6 is insufficient to measure even the ^1H NMR spectrum.

***cis*-[$PtCl_4${NH=C(NH_2)Me}$_2$] (11).** This complex was obtained by starting from **2**. Anal. Calcd for $C_4H_{12}N_4Cl_4Pt$: C, 10.60; H, 2.67; N, 12.37. Found: C, 10.89; H, 2.74; N, 12.19. FAB^+-MS, *m*/*z*: 382 $[M - 2Cl]^+$, 312 $[M - 4Cl]^+$. Mp: 185 (dec) °C. IR spectrum in KBr, selected bands, cm^{-1}: 3341 m ν(N−H), 3220 w and 3187 w ν(C−H), 1666 s ν(C=N), 1437 m ν(C=C Ar). ^1H NMR spectrum in acetone-d_6, δ: 8.12, 7.75, 7.52 (s, br, 1*H* each, NH and NH_2), 2.37 (s, 3*H*).

***trans*-[$PtCl_4${NH=C(NH_2)Et}$_2$] (12).** This complex was obtained by starting from **3**. Anal. Calcd for $C_6H_{16}N_4Cl_4Pt$: C, 14.98; H, 3.35; N, 11.65. Found: C, 14.38; H, 3.35; N, 11.67. FAB^+-MS, *m*/*z*: 410 $[M - 2Cl]^+$, 338 $[M - 4Cl - H]^+$. Mp: 137 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3357 and 3321 w ν(N−H), 2989 w and 2938 w ν(C−H), 1655 s ν(C=N). ^1H NMR spectrum in DMSO-d_6, δ: 8.45, 7.57, 7.17 (s, br, 1*H* each, NH and NH_2), 1.64 (t, 3*H*, CH_3 from Et), CH_2 from Et was not detected due to overlap with the solvent signal. Crystals for the X-ray study were obtained directly from the reaction mixture.

[$PtCl_4${NH=C(NH_2)CH_2Ph}$_2$] (13). This complex was obtained by starting from **4**. Anal. Calcd for $C_{16}H_{20}N_4Cl_4Pt$: C, 31.75; H, 3.33; N, 9.26. Found: C, 31.54; H, 3.48; N, 9.13. FAB^+-MS, *m*/*z*: 628 $[M + Na]^+$, 534 $[M - 2Cl]^+$. Mp: 192 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3455 s-m ν(O−H), 3333 and 3341 w ν(N−H), 2925 w ν(C−H), 1657 s ν(C=N), 1408 m ν(C=C Ar). ^1H NMR spectrum in DMSO-d_6, δ: 8.02, 6.99, 6.89 (s, br, 1*H* each, NH and NH_2), 7.39−7.24 (m, 5*H*, Ph), 3.84 (s, br, 2*H*, CH_2-Ph).

[$PtCl_4${NH=C(NH_2)Ph}$_2$] (14). This complex was obtained by starting from **5**. Anal. Calcd for $C_{14}H_{16}N_4Cl_4Pt·0.5H_2O$: C, 28.68; H, 2.92; N, 9.56. Found: C, 28.64; H, 2.92; N, 9.27. FAB^+-MS, *m*/*z*: 506 $[M - 2Cl]^+$, 434 $[M - 4Cl - H]^+$. Mp: 214 °C (dec). IR spectrum in KBr, selected bands, cm^{-1}: 3445 s-m ν(O−H), 3348 and 3387 w ν(N−H), 1647 s ν(C=N), 1434 m ν(C=C Ar). ^1H NMR spectrum in DMSO-d_6, δ: 8.70, 7.34 (s, br, 1*H* each, NH_2), 6.54 (s + d, br, $^2J_{PtH}$ 23.4 Hz, 1*H*, =N*H*−Pt), 7.65−7.55 (m, 5*H*, Ph).

Reduction of *trans*-[$PtCl_4${NH=C(R)N=SPh_2}$_2$] (R = Me, Et). The ylide Ph_3P=$CHCO_2Me$ (0.07 mmol) is added to a solution of *trans*-[$PtCl_4${NH=C(R)N=SPh_2}$_2$] (**1** or **3**) (0.05 mmol) in CH_2Cl_2 (2 mL). The reaction mixture is left to stand at 45 °C for 24−36 h. The product is separated by column chromatography on SiO_2 (Merck silica gel, grade 60, 70−230 mesh, eluent CH_2Cl_2−Et_2O, 10:1).

[$PtCl_2${*N*H=C(Me)N=SPh_2}] (15). This product was obtained by the reduction of **1**. Anal. Calcd for $C_{14}H_{14}N_2Cl_2PtS$: C, 33.08; H, 2.78; N, 5.51; S, 6.31. Found: C, 33.52; H, 2.89; N, 5.34; S, 6.05. FAB^+-MS, *m*/*z*: 471 $[M - Cl]^+$. Mp: 222 °C (dec). TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.58$ (eluent Et_2O−CH_2Cl_2, 1:8). IR spectrum in KBr, selected bands, cm^{-1}: 3304 m ν(N−H), 3061 w and 2924 w ν(C−H), 1530 s ν(C=N), 1446 m ν(C=C Ar). ^1H NMR spectrum in $CDCl_3$, δ: 8.09 and 7.60 (m, 10*H*, Ph), 6.51 (s + d, J_{PtH} 55.0 Hz, br, 1*H*, NH), 2.40 (s, 3*H*, Me). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 135.34 (C_{ipso}), 134.21 (*p*-Ph), 130.07 and 128.14 (*o*- and *m*-Ph), 19.08 (Me). $^{195}Pt\{^1H\}$ NMR spectrum in $CDCl_3$, δ: −3167 (530 Hz).

[$PtCl_2${*N*H=C(Et)N=SPh_2}] (16). This product was obtained by the reduction of **2**. Anal. Calcd for $C_{15}H_{16}N_2Cl_2PtS$: C, 34.49; H, 3.09; N, 5.36; S, 6.14. Found: C, 35.87; H, 3.17; N, 5.10; S,

5.73. FAB$^+$-MS, *m*/*z*: 545 $[M + Na]^+$, 522 $[M]^+$, 487 $[M - Cl]^+$. The complex has no characteristic melting point, and on heating it gradually decomposes above 220 °C. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.57$ (eluent $Et_2O-CH_2Cl_2$, 1:20). IR spectrum in KBr, selected bands, cm^{-1}: 3293 m-w ν(N−H), 3051 w and 2926 w ν(C−H), 1523 s ν(C═N), 1446 s ν(C═C Ar). ^{1}H NMR spectrum in $CDCl_3$, δ: 8.09 and 7.60 (m, 10*H*, Ph), 6.49 (s, br, 1*H*, NH), 2.67 (quart, 7.6 Hz, 2*H*, CH_2 from Et), 1.29 (t, 7.6 Hz, 3*H*, CH_3 from Et). ^{13}C{^{1}H} NMR spectrum in $CDCl_3$, δ: 187.88 (C═N), 135.86 (C_{ipso}), 134.09 (*p*-Ph), 130.05 and 128.09 (*o*- and *m*-Ph), 26.67 (CH_2 from Et), 11.80 (CH_3 from Et). ^{195}Pt{^{1}H} NMR spectrum in $CDCl_3$, δ: −3167.9 (485 Hz).

Liberation of the Heterodiazadiene from the Platinum(IV) Complexes. ^{31}P{^{1}H} NMR monitoring of the reaction between $[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ and dppe in $CDCl_3$ shows signals from the following phosphorus-containing species: $[Pt(dppe)_2]Cl_2$ (45.7, J_{Pt-P} 2360.5 Hz; lit.[16]), $Ph_2P(=O)(CH_2)_2PPh_2$ (31.2, d, J_{P-P} 48.5 Hz for $Ph_2P(=O)(CH_2)_2PPh_2$ and −13.5, d, J_{P-P} 48.5 Hz for $Ph_2P(=O)(CH_2)_2PPh_2$; lit.[17−19]), $Ph_2P(=O)(CH_2)_2P(=O)Ph_2$ (31.2 s; lit.[20]) and $Ph_2P(CH_2)_2PPh_2$ (−14.1 s).

In a preparative experiment, dppe (0.12 mmol) is added to a solution of the complex (0.05 mmol) in $CHCl_3$ (2 mL) at 20−25 °C, whereupon the color turns from orange to colorless for 2 min and a colorless precipitate is released. The solvent is decanted and evaporated until half of the initial volume and Et_2O (1 mL) is added, whereupon the mixture is left to stand at ca. −5 °C for 2−3 min. The precipitate of $[Pt(dppe)_2]Cl_2$ is separated by filtration, and the filtrate is evaporated until dryness. The solids are washed with Et_2O (1 mL) and dried in a vacuum.

NH═C(Me)N═SPh$_2$ (17). FAB$^+$-MS, *m*/*z*: 243 $[M + H]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3382 s ν(O−H), 3006 w and 2903 w ν(C−H), 1623 m ν(C═N in L·HCl), 1528 m ν(C═N in free L, see lit.[21]), 1437 m ν(C═C Ar). ^{1}H NMR spectrum in $CDCl_3$, δ: 9.61 and 9.45 (two s, br, 2*H*, NH), 7.9−7.2 (m, 10*H*, Ph), 1.99 (s, 3*H*, C*H*$_3$).

NH═C(Et)N═SPh$_2$ (18). FAB$^+$-MS, *m*/*z*: 257 $[M + H]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3422 s ν(O−H), 3054 w and 2926 w ν(C−H), 1648 m ν(C═N in L·HCl), 1549 m ν(C═N in free L, see lit.[21]), 1440 m ν(C═C Ar). ^{1}H NMR spectrum in $CDCl_3$, δ: 9.55 and 9.40 (two s, br, 2*H*, NH), 7.9−7.2 (m, 10*H*, Ph), 2.69 (quart, 7.5 Hz, 2*H*, CH_2 from Et), 1.25 (t, 7.5 Hz, 3*H*, CH_3 from Et).

NH═C(Et)N═SPh(*o*-C$_6$H$_4$SPh) (19). FAB$^+$-MS, *m*/*z*: 364 $[M]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3086 w and 2926 w ν(C−H), 1527 s ν(C═N in free L, see lit.[21]). ^{1}H NMR spectrum in $CDCl_3$, δ: 8.15 (d), 7.87 (d), 7.16 (m), 7.01 (m) (C_6H_4, 4*H*), 7.7−7.28 (m, 10*H*, 2Ph), 2.67 (quart, 7.5 Hz, 2*H*, CH_2 from Et), 1.21 (t, 7.5 Hz, 3*H*, CH_3 from Et).

NH═C(Et)N═SPh(*p*-C$_6$H$_4$SPh) (20). FAB$^+$-MS, *m*/*z*: 365 $[M + H]^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3053 w and 2926 w ν(C−H), 1527 s ν(C═N in free L, see lit.[21]). ^{1}H NMR spectrum in $CDCl_3$, δ: 9.59 and 9.40 (two s, br, 2*H*, NH), 7.8, 7.4 and 7.2 (m, 14*H*, Ph), 2.67 (quart, 7.5 Hz, 2*H*, CH_2 from Et), 1.25 (t, 7.5 Hz, 3*H*, CH_3 from Et).

X-ray Structure Determinations.

Data were collected at 150 K with a Bruker SMART 1000 CCD diffractometer and Mo Kα radiation (λ = 0.710 73 Å) using ω-rotation and narrow frames (compounds **3**, **8**, and **21**) or with a Nonius KappaCCD diffractometer (**1**, **2**, and **12**). Data were corrected for absorption semiempirically from equivalent reflections. Structure **12** was solved by the Patterson method. All other structures were solved by direct methods and refined by full-matrix least-squares methods on F^2. NH hydrogens in **2**, **3**, **8**, and **21** were located from the difference map, and their coordinates were freely refined. NH and NH_2 hydrogens in **1** and **12** were also located from the difference Fourier map but were constrained to ride on their parent atom. All other hydrogens were placed in geometrical positions using a riding model. Programs used were Bruker SMART,[22] SAINT,[22] SHELXTL,[23] DENZO-SCALEPACK,[24] SHELXS-97,[25] SHELXL97,[26] WINGX,[27] and local programs. In the case of **21** (this complex was prepared by the literature route[8] and crystallized by slow diffusion of Et_2O into an acetonitrile solution), the data were collected using crystals harvested immediately after growing to the requisite size, thereby obviating an unavoidable decomposition which occurs in the solid state, even under inert atmosphere. Crystallographic data are summarized in Table 1, and selected bond lengths and angles, in Figures 2, 3, and 5−7.

Computational Details

The full geometry optimization of all structures has been carried out in Cartesian coordinates using the quasi-Newton−Raphson gradient method and the restricted Hartree−Fock approximation with the help of the GAMESS[28] program package. Symmetry operations were not applied. The single-point calculations at the MP2[29] level on the basis of the equilibrium Hartree−Fock geometries also have been performed to take into account the electron correlation effects. A quasi-relativistic Stuttgart pseudopotential described 60 core electrons, and the appropriate contracted basis set (8s7p6d)/[6s5p3d] for the platinum atom[30] were used. The standard basis set of Gauss functions 6-31G[31,32] was selected for all other atoms, and d-type of polarization functions with exponent 0.75 and 0.65[32,33] were added for the Cl and S atoms, respectively.

(16) Anderson, G. K.; Davies, J. A.; Schoeck, D. J. *Inorg. Chim. Acta* **1983**, *76*, L251.
(17) Mason, M. R.; Verkade, J. G. *Organometallics* **1990**, *9*, 864.
(18) Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 2212.
(19) Brock, S. L.; Mayer J. M. *Inorg. Chem.* **1991**, *30*, 2138.
(20) Calcagno, P.; Kariuki, B. M.; Kitchin, S. J.; Robinson, J. M. A.; Philp, D.; Harris, K. D. M. *Chem.—Eur. J.* **2000**, *6*, 2338.
(21) Yoshida, H.; Ogata, T.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3302.
(22) *SMART and SAINT software for CCD diffractometers*; Bruker AXS Inc.: Madison, WI, 1994.
(23) Sheldrick, G. M. *SHELXTL user manual*, version 5; Bruker AXS Inc.: Madison, WI, 1994.
(24) Otwinowski, Z.; Minor, W. DENZO-SCALEPACK "Processing of X-ray Diffraction Data Collected in Oscillation Mode". In *Methods in Enzymology*, *Volume 276*, *Macromolecular Crystallography*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Part A, pp 307−326.
(25) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.
(26) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(27) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.
(28) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(29) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum. Chem.* **1975**, *9*, 229.
(30) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
(31) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(32) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
(33) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

Table 1. Summary of Crystal Data and Structure Determination for Compounds **1**−**3**, **8**, **12**, and **21**

param	**1**	**2**·CH_2Cl_2	**3**	**8**	**12**	**21**
formula	$C_{28}H_{28}Cl_4N_4PtS_2$	$C_{29}H_{30}Cl_6N_4PtS_2$	$C_{30}H_{32}Cl_4N_4PtS_2$	$C_{20}H_{18}Cl_2N_2PtS_2$	$C_6H_{16}Cl_4N_4Pt$	$C_{52}H_{50}F_{12}N_6P_2PtS_4$
M	821.55	906.48	849.61	616.47	481.12	1372.25
cryst dimens	0.35 × 0.25 × 0.25	0.25 × 0.10 × 0.10	0.59 × 0.27 × 0.17	0.13 × 0.12 × 0.06	0.25 × 0.10 × 0.10	0.90 × 0.50 × 0.20
cryst morphology and color	block, yellow	needle, yellow	needle, orange	block, yellow	needle, orange	block, yellow
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	10.9079(2)	12.5674(4)	10.9307(4)	9.4631(5)	6.2593(2)	10.2602(9)
b/Å	13.1920(2)	18.1314(7)	12.7847(5)	17.7135(9)	11.8609(4)	10.9478(9)
c/Å	10.9699(2)	16.0115(6)	11.8655(5)	12.4772(7)	9.2909(3)	14.2229(12)
α/deg	90	90	90	90	90	106.369(2)
β/deg	94.9210(9)	107.3600(10)	93.362(2)	100.347(2)	94.656(2)	100.965(2)
γ/deg	90	90	90	90	90	110.358(2)
V/Å^3	1572.72(5)	3482.3(2)	1655.30(11)	2057.47(19)	687.49(4)	1361.3(2)
Z	2	4	2	4	2	1
μ/mm^{-1}	4.959	4.636	4.714	7.291	10.959	2.873
θ range/deg	3.75−26.00	2.61−25.00	1.87−29.03	2.02−25.00	3.69−26.02	2.13−28.70
measd reflcns	18 919	20 411	14 404	14 800	8024	11 296
indpdt reflcns	3091	6121	4022	2973	1363	6144
Rint	0.0381	0.0639	0.0148	0.0340	0.0530	0.0300
R [$F^2 > 2\sigma(F^2)$][a]	0.0182	0.0465	0.0138	0.0242	0.0251	0.0333
wR2 (all data)[b]	0.0444	0.1027	0.0339	0.0505	0.0667	0.0848
largest diff map features/e Å^{-3}	0.497, −0.709	2.998, −1.103	0.753, −0.591	1.056, −0.631	1.168, − 1.338	2.995, −2.326

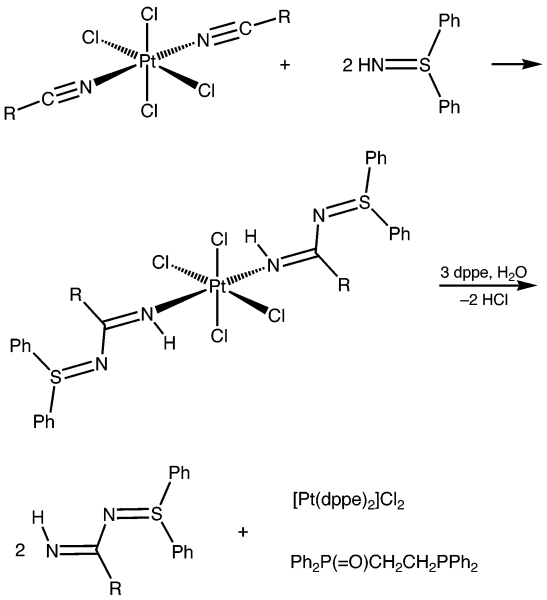
[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Results and Discussion

The sulfimides are a family of organo-sulfur−nitrogen ylides of formula $R_2S{=}NR'$.[34] Until recently the inorganic—or, more specifically, the coordination chemistry—of sulfimides, in general, and of $Ph_2S{=}NH$ **IA**, Figure 1 (the most frequently studied sulfimide), in particular, had been the subject of few studies. Building on data from a few early works,[35] one of us has found that $Ph_2S{=}NH$ acts as an effective N-donor ligand to a range of metals.[36] Significantly, the products of such reactions often exhibit important features such as unexpected isomerism,[37] unique unit cell formulation,[38] or strong hydrogen bond interactions between the sulfimide ligands and anions;[39] the latter effect has recently been utilized in the formation of extended metal arrays.[40] The feature of the coordination chemistry of $Ph_2S{=}NH$ which is most pertinent to this work stems from the observation of the platinum(II)-mediated nucleophilic addition of a sulfimide to a nitrile.[7] In this work, we have taken this a stage further by not only attempting to liberate the nitrile addition products of **IA** but also by investigating the reactivity of *o*-{PhS(=NH)}(PhS)C_6H_4 (**IB**) and *p*-{PhS(=NH)}(PhS)C_6H_4 (**IC**) (Figure 1) toward both Pt(II) and Pt(IV) centers.

Coupling between Platinum(IV)-Bound Nitriles and $Ph_2S{=}NH$. Reaction of **IA** with a range of Pt(IV) nitrile complexes of formula $[PtCl_4(RCN)_2]$ at room temperature in CH_2Cl_2 results in the formation of $[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ (**1**−**5**) in ca. 75−90% yields. While *trans*-$[PtCl_4(RCN)_2]$ (R = Et, CH_2Ph, Ph) leads exclusively to *trans*-$[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ (Scheme 1), *cis/trans*-$[PtCl_4(MeCN)_2]$ leads to cis/trans mixtures of the products **1** and **2**, which can be separated by column chromatography on silica gel. As noted previously for Pt(II) work,[7] such couplings do not occur in the absence of the metal center—the sulfimide is inert toward nitriles even at elevated temperatures.

Scheme 1



In addition to microanalysis and FAB mass spectrometry, the resulting complexes have been characterized by infrared and NMR spectroscopy. IR spectra show that the C≡N stretching vibrations associated with the starting materials are replaced by strong ν(C=N) bands at lower frequencies (1522−1539 cm^{-1}). This range corresponds well to the

(34) Oae, S.; Furukawa, N. *Sulfilimines and Related Derivatives*; American Chemical Society: Washington, DC, 1983.
(35) (a) Cramer, R. E.; Ariyaratne, K. A. N. S.; Gilje, J. W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1856. (b) Toriuchi, M.; Matsubayashi, G.; Koezuka, H.; Tanaka, T. *Inorg. Chim. Acta* **1976**, *17*, 253.
(36) E.g., see: Kelly, P. F.; Macklin, A. C.; Slawin, A. M. Z.; Waring, K. W. *Polyhedron* **2000**, *19*, 2077 and references therein.
(37) Kelly, P. F.; Slawin, A. M. Z.; Waring, K. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2853.
(38) Kelly, P. F.; Slawin, A. M. Z.; Waring, K. W.; Wilson, S. *Inorg. Chim. Acta* **2001**, *312*, 201.
(39) Kelly, P. F.; Slawin, A. M. Z.; Waring, K. W. *Inorg. Chem. Commun.* **1998**, *1*, 249.
(40) Holmes, K. E.; Kelly, P. F.; Elsegood, M. R. J. *Cryst. Eng. Commun.* **2002**, *4*, 172.

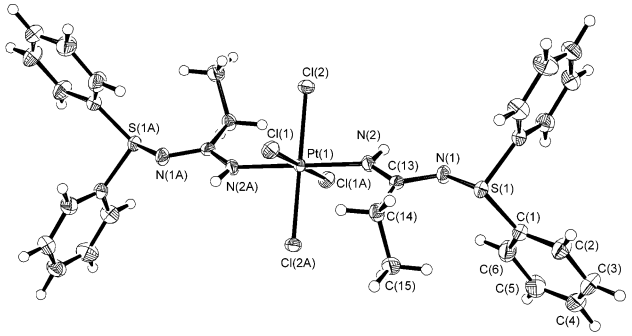


Figure 2. ORTEP view of complex **3** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The same numbering scheme was applied also to structure **1**. Selected bond lengths (Å) and angles (deg) (corresponding values for structure **1** are shown in brackets): Pt(1)−N(2) 2.0276(14) [2.022(2)], Pt(1)−Cl(1) 2.3279(4) [2.3236(6)], Pt(1)−Cl(2) 2.3196(4) [2.3205(6)], N(2)−C(13) 1.309(2) [1.302(3)], C(13)−C(14) 1.500(2), [1.502(4)], C(13)−N(1) 1.355(2) [1.354(3)], N(1)−S(1) 1.6362(15) [1.639(2)], S(1)−C(1) 1.792(2) [1.796(3)], S(1)−C(7) 1.778(2) [1.771(3)]; N(2)−Pt(1)−Cl(1) 95.09(4) [86.30(6)], N(2)−Pt(1)−Cl(2) 86.14(4) [86.07(6)], C(13)−N(2)−Pt(1) 137.06(12) [137.0(2)], N(2)−C(13)−C(14) 120.97(15) [121.7(2)], C(13)−N(1)−S(1) 115.60(12) [115.0(2)], C(7)−S(1)−C(1) 102.30(8) [102.88(12)].

ν(C═N) values (1530−1540 cm^{-1}) for the previously reported Pt(II) complexes in which the ligand is either chelated or monodentate.[7,8] In addition, N−H stretching vibrations are seen in the region 3321−3377 cm^{-1}.

The most significant feature of the $^{13}C\{^1H\}$ NMR spectra of the new complexes is the signal from the carbon of the *C*═N bond (range 176−180 ppm). The signals in the ^{195}Pt NMR spectra of the trans complexes occur in the range of 92−135 ppm, while the only isolated cis isomer, i.e. *cis*-$[PtCl_4\{NH{=}C(Me)N{=}SPh_2\}_2]$ (**2**), displays the peak at 188 ppm. The relative position of ^{195}Pt NMR peaks for the geometrical isomers is consistent with that for other cis/trans-isomeric pairs of Pt(IV) complexes.[41−43]

Compounds *trans*-$[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ [R = Me (**1**) and Et (**3**)] have been structurally characterized by X-ray crystallography, which confirms a Pt(IV) structure with the two new heterodiazadiene ligands in *E*-configuration trans to each other (Figure 2). Calculations investigating the relative dispositions of the ligands are presented below.

Comparison of the bond lengths and angles within the heterodiazadiene ligand with those in other systems is complicated by the fact that the only fully (X-ray crystallographically) characterized complexes contain such ligands in the chelating mode. The only example of a complex containing a N-bound monodentate ligand came in the form of $[Pt(NH{=}SPh_2)_2\{NH{=}C(Me)N{=}SPh_2\}_2][PF_6]_2$, which we[8] reported but for which we were unable to obtain X-ray crystallographic data of sufficient quality to ascertain anything more than the connectivity of the molecule. To provide some context for the structures of *trans*-$[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ (**1**−**5**) we have now revisited this problem and have successfully solved the structure of $[Pt(NH{=}SPh_2)_2\{NH{=}C(Me)N{=}SPh_2\}_2][PF_6]_2$ (**21**).

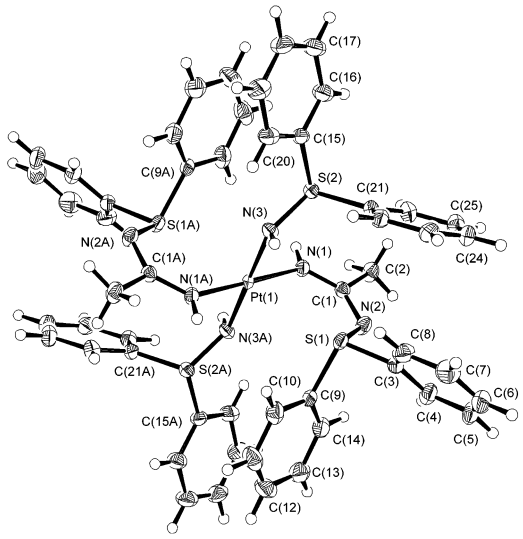


Figure 3. ORTEP view of complex **21** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.023(3), Pt(1)−N(3) 2.034(3), N(2)−C(1) 1.341(4), S(2)−N(3) 1.618(3), S(2)−C(15) 1.793(3), S(2)−C(21) 1.795(3), N(1)−C(1) 1.306(4), C(1)−C(2) 1.526(4), S(1)−N(2) 1.661(3), S(1)−C(3) 1.796(3), S(1)−C(9) 1.800(3); S(2)−N(3)−Pt(1) 121.07(15), C(1)−N(1)−Pt(1) 131.6(2), N(3)−S(2)−C(15) 106.41(15), N(3)−S(2)−C(21) 110.60(15), N(1)−C(1)−N(2) 129.7(3), N(1)−C(1)−C(2) 116.7(3), C(1)−N(2)−S(1) 117.2(2), C(3)−S(1)−C(9) 98.44(15).

The resulting structure (Figure 3) confirms the presence of both $HN{=}SPh_2$ and $NH{=}C(Me)N{=}SPh_2$ ligands bound to the platinum. The bond distances within the latter ligand are effectively identical to those within the *E*-$NH{=}C(R)N{=}SPh_2$ ligands in *trans*-$[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ [R = Me (**1**), Et (**3**)] and also within both *E*- and *Z*- $NH{=}C(Me)N{=}SPh_2$ in *cis*-$[PtCl_4(E\text{-}NH{=}C(Me)N{=}SPh_2)(Z\text{-}NH{=}C(Me)N{=}SPh_2)]$ (**2**) (Figure 4) indicating that neither the oxidation state of the platinum nor configuration of the ligand appears to have a great impact upon bond lengths within the addition ligand. An interesting feature of the structure comes with the close approach of the sulfur atoms to axial positions relative to the platinum. The Pt−S distance is 3.0996(8) Å, which represents a significant long-range intramolecular interaction; a further example of such an interaction within one of our complexes is discussed below.

Relative Stability of *cis*- and *trans*-(Sulfimide)platinum-(IV) Complexes. Neither isomer of $[PtCl_4\{NH{=}C(Me)N{=}SPh_2\}_2]$ appears to convert to the other upon heating, either in CH_2Cl_2 at 40 °C for 2 days or in the solid phase (heated until the melting point). Both decompose in boiling $MeNO_2$, again with no evidence for isomerization.

The question of isomer stability in platinum complexes is a significant one, given the pharmaceutical importance of many of the compounds. This is because the biological interactions—such as antitumor activity—which provide the basis for their use as drugs are often isomer dependent. Thus while conventional platinum drugs are based on the cis isomers, some instances of higher activity have been noted for trans imine complexes.[44,45] Such observations have fueled

(41) Kukushkin, V. Yu.; Pakhomova, T. B.; Bokach, N. A.; Wagner,G.; Kuznetsov, M. L.; Galanski, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2000**, *39*, 216.
(42) Luzyanin, K. V.; Haukka, M.; Bokach, N. A.; Kuznetsov, M. L.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2002**, 1882.
(43) Kukushkin, V. Yu.; Belsky, V. K.; Aleksandrova, E. A.; Konovalov, V. E.; Kirakosyan, G. A. *Inorg. Chem.* **1992**, *31*, 3836.

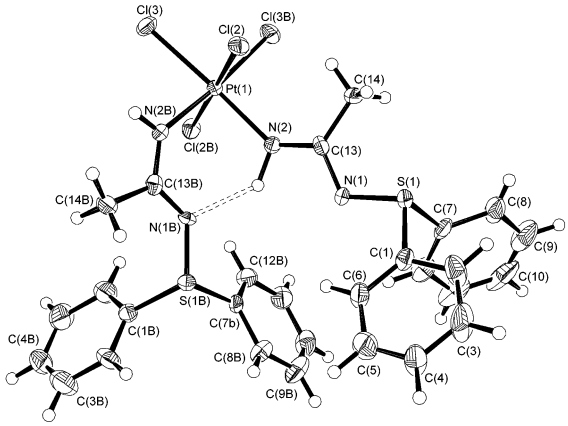


Figure 4. ORTEP view of complex **2** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(2) 2.044(7), N(2)−C(13) 1.285(10), C(14)−C(13) 1.490(11), C(13)−C(14) 1.490(11), N(1)−S(1) 1.636(7), S(1)−C(1) 1.781(9), S(1)−C(7) 1.805(9), Pt(1)−N(2B) 2.030(7), N(2B)−C(13B) 1.303(10), C(13B)−C(14B) 1.515(11), C(13B)−N(1B) 1.345(10), N(1B)−S(1B) 1.647(7), S(1B)−C(1B) 1.794(9), S(1B)−C(7B) 1.770(8); N(2B)−Pt(1)−N(2) 91.2(3), Cl(2B)−Pt(1)−Cl(3) 89.98(8), Cl(2B)−Pt(1)−Cl(2) 177.15(8), Cl(2B)−Pt(1)−Cl(3B) 89.88(8), C(13)−N(2)−Pt(1) 135.0(6), N(2)−C(13)−N(1) 115.2(7), N(2)−C(13)−C(14) 122.7(8), C(13)−N(1)−S(1) 115.9(6), C(1)−S(1)−C(7) 95.9(4), C(13B)−N(2B)−Pt(1) 133.1(6), N(2B)−C(13B)−N(1B) 119.8(8), N(2B)−C(13B)−C(14B) 117.1(7), C(13B)−N(1B)−S(1B) 117.1(6), C(7B)−S(1B)−C(1B) 101.9(4); N(2)···N(1B) 2.828(9). Crystal solvent (CH_2Cl_2) was omitted for clarity.

the search for new drugs on the basis of unconventional arrangements, such as Pt(IV) complexes with the ligands in trans geometry. Understanding the relative stabilities of isomers is crucial to this quest, but in cases such as the cis/trans isomers of $[PtCl_4\{NH{=}C(Me)N{=}SPh_2\}_2]$, the observed lack of interconversion means little can be deduced. To address this issue we have undertaken a computational study of both isomers.

The full geometry optimization of the trans and cis isomers of $[PtCl_4\{N(H){=}C(Me)N{=}SMe_2\}_2]$ (*trans*-**II** and *cis*-**II**) have been performed at the Hartree−Fock level, and the single point calculations at the MP2//HF approach have also been carried out. The starting geometries of both isomers corresponded to the experimental X-ray structures of *EE-trans*-$[PtCl_4\{N(H){=}C(Et)N{=}SPh_2\}_2]$ and *EZ-cis*-$[PtCl_4\{N(H){=}C(Me)N{=}SPh_2\}_2]$ from this work. For *cis*-**II**, the structures of possible conformations of the *EE* isomer also have been calculated starting from geometries with different mutual arrangements of the two $N(H){=}C(Me)N{=}SMe_2$ ligands.

The coordination polyhedra of the Pt atom are octahedral for all trans and cis species located. The conformations of the equilibrium structures of *trans*-**II** and *EZ-cis*-**II** correspond to the experimental ones, i.e., *trans*-$[PtCl_4\{N(H){=}C(Et)N{=}SPh_2\}_2]$ and *EZ-cis*-$[PtCl_4\{N(H){=}C(Me)N{=}SPh_2\}_2]$ (Figure 5). All atoms of the *E*-N(H)=C(C)N=S fragments lie in the same plane that passes between the chlorine atoms. The *Z*-N(H)=C(C)N=S fragment in *EZ-cis*-**II** is not completely planar; the mean deviation from the plane is 0.098 Å. The main calculated bond lengths in *trans*-**II** and *EZ-cis*-**II** are in a good agreement with the X-ray data with the maximum deviation of 0.052 Å for the Pt−Cl bonds (Table S38; see Supporting Information). The differences for other calculated and experimentally found bond lengths do not exceed 0.029 Å. The structure of *EZ-cis*-**II** is stabilized by intramolecular H-bond NH···N with parameters N···N, N−H, and N···H of 2.88, 1.00, and 2.05 Å, respectively, and the NHN angle of 139.7° that is consistent with experimental data. For *EE-cis*-**II**, five minima, associated with the structures (*EE-cis*-**IIa**−**e**) having different mutual positions of the imine moieties (Figure 5), were located on the potential energy surface. The bond lengths all of these structures are very close to each other as well as to those of *trans*-**II** and *EZ-cis*-**II**.

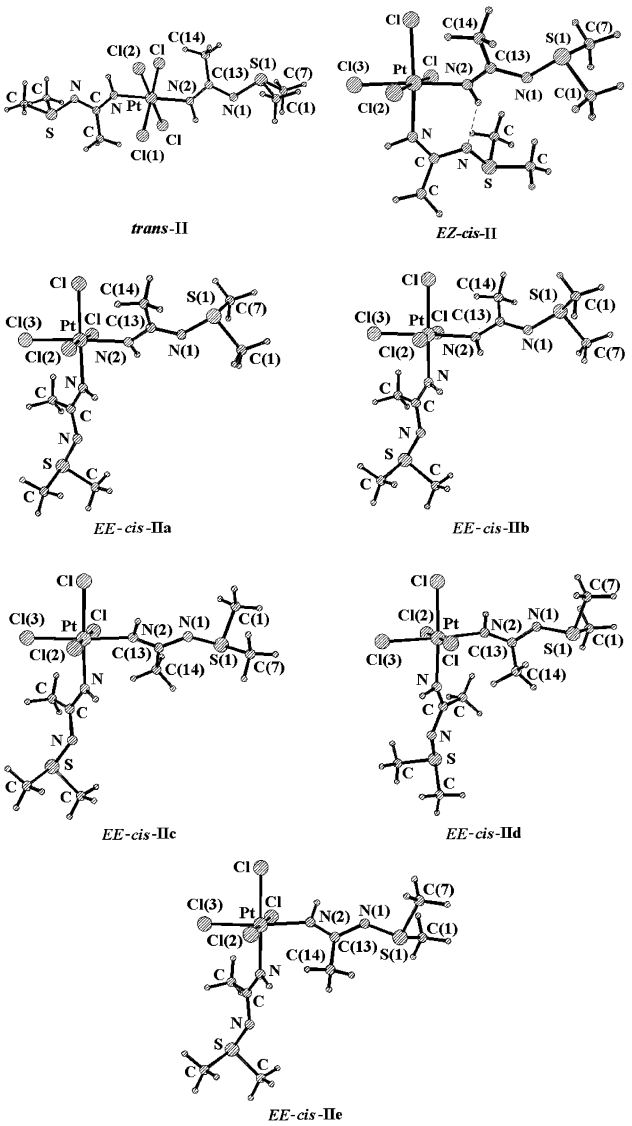


Figure 5. Calculated equilibrium structures of the complexes *trans*- and *cis*-$[PtCl_4\{N(H){=}C(Me)N{=}SMe_2\}_2]$.

The calculations at both HF//HF and MP2//HF levels show that the trans isomer is more stable than each conformation of *EE-cis*-**II** as well as of *EZ-cis*-**II** (even despite the intramolecular H-bond for the latter structure) by 5.35−10.88 kcal/mol (HF//HF) and 4.67−8.80 kcal/mol (MP2//HF),

(44) (a) Natile, G.; Coluccia, M. *Coord. Chem. Rev.* **2001**, *216*−*217*, 383. (b) Liu, Y.; Pacifico, C.; Natile, G.; Sletten, E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1226.
(45) Wong, E.; Giandomenico, C. M. *Chem. Rev.* **1999**, *99*, 2451.

Table 2. Calculated Total Energies, E_{tot} (Hartree), and Relative Energies, E_{rel} (kcal/mol), of the Complexes *trans*/*cis*-[$PtCl_4${N(H)=C(Me)N=SMe_2}$_2$]

	HF//HF		MP2//HF	
	E_{tot}	E_{rel}	E_{tot}	E_{rel}
trans-II	−3283.477 243	0.0	−3285.622 819	0.0
EZ-cis-II	−3283.466 076	7.01	−3285.613 874	5.61
EE-cis-IIa	−3283.468 716	5.35	−3285.615 377	4.67
EE-cis-IIb	−3283.465 490	7.38	−3285.612 487	6.48
EE-cis-IIc	−3283.465 165	7.58	−3285.613 578	5.80
EE-cis-IId	−3283.461 873	9.64	−3285.611 620	7.03
EE-cis-IIe	−3283.459 897	10.88	−3285.608 788	8.80

Table 2. Among the cis isomers the most stable one is *EE-cis*-**IIa** with the torsion angles NPtNH of ca. 52°. In previous works,[41,42] the higher stability of trans imino complexes of platinum compared to their cis isomers was determined theoretically by us, with a similar energy difference between the isomeric forms (5.32−13.32 kcal/mol for [$PtCl_4${NH=C(H)ON=CH_2}$_2$][41] and [$PtCl_4${N(H)=C(OH)Me}$_2$][42]). The higher stability of *trans*-(imino)platinum(IV) species agrees with the direction of the cis-to-trans isomerization observed for a large number of other platinum(IV) complexes.[46] We anticipate that the absence of the isomerization for *cis*- and *trans*-[$PtCl_4${NH=C(Me)N=SPh_2}$_2$] can be connected with a rather high kinetic activation barrier when the decomposition occurs faster than the isomerization.

Coupling between Platinum-Bound Nitriles and Isomers of {PhS(=NH)}(PhS)C_6H_4. The hybrid sulfide/sulfimide species *o*-{PhS(=NH)}(PhS)C_6H_4 (**IB**) and *p*-{PhS(=NH)}(PhS)C_6H_4 (**IC**) (Figure 1) react with both Pt(II) and Pt(IV) nitrile complexes in an fashion analogous to that for **IA** (see Experimental Section and ref 7). In the case of Pt(II), the most readily crystallized product from such reactions comes in the form of [$PtCl_2${*N*H=C(Me)N=*S*(Ph)C_6H_4SPh-*o*}] (**8**), which is generated by reaction of the sulfimide with [$PtCl_2$(MeCN)$_2$] and isolated in ca. 50% yield while the mother liquor contains a mixture of yet unidentified species.

The X-ray crystal structure of the latter product (Figure 6) reveals bond parameters within the metallacycle (see below) little different from those in previously reported [PtCl(NH=SPh_2){*N*H=C(Me)N=*S*Ph_2}]Cl.[7] As Figure 6 shows, the thioether unit of the ligand orientates itself in such a way as to leave the phenyl end unit as far away from the rest of the atoms of the molecule as possible. While steric considerations no doubt provide one driving force for the adoption this orientation, another interesting feature of the structure is the close interaction of the thioether sulfur atom with the platinum. As Figure 6 shows, this atom approaches the axial position of the platinum, resulting in a Pt−S distance of 3.446 Å. This distance is slightly longer than that observed in [Pt(*N*H=SPh_2)$_2${*N*H=C(Me)N=SPh_2}$_2$][PF_6]$_2$ (**21**); both values compare well with those observed in a number of recent examples of complexes exhibiting axial Pt−S interactions. For example, such interactions (in this case slightly shorter, at 3.3 Å or less) result in dimer formation within [ClCr(4-mpyt)$_4$Pt] (mpyt = 4-methylpyridine-2-thiolate).[47] The Cl(1)−Pt−S(1) angle (100.3°) also provides an indication of the presence of a significant Pt−S interaction.

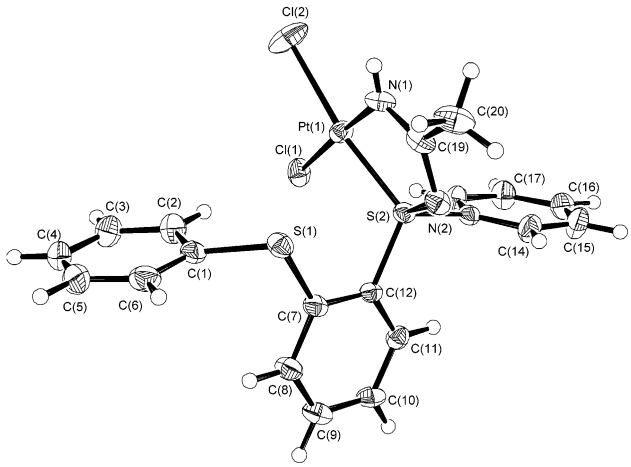


Figure 6. ORTEP view of complex **8** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 1.993(4), Pt(1)−S(2) 2.1748(12), Pt(1)−Cl(2) 2.2794(13), Pt(1)−Cl(1) 2.3267(13), S(1)−C(7) 1.771(5), S(1)−C(1) 1.783(5), C(19)−N(1) 1.297(6), C(19)−C(20) 1.510(7), N(2)−C(19) 1.347(6), S(2)−N(2) 1.632(4), S(2)−C(13) 1.788(5), S(2)−C(12) 1.788(5), Cl(2)−Pt(1)-Cl(1) 91.87(5), C(7)−S(1)-C(1) 101.4(2); N(2)−S(2)−Pt(1) 107.12(15), C(13)−S(2)−Pt(1) 111.96(16), C(12)−S(2)−Pt(1) 119.21(15), N(1)−C(19)−N(2) 123.2(4).

Acid-Catalyzed Hydrolysis of [$PtCl_4${NH=C(R)N=SPh_2}$_2$]. Solution NMR studies reveal that all the complexes of formula [$PtCl_4${NH=C(R)N=SPh_2}$_2$] (**1**−**5**) are stable toward [Bu_4N]OH (10 equiv); acidification with CF_3CO_2H, however, results in some irreversible changes. Thus in each case, apart from *trans*-[$PtCl_4${NH=C(Me)N=SPh_2}$_2$] (**1**), treatment with HCl in (undried) CH_2Cl_2 releases a crystalline material which proves to be an amidine−platinum(IV) complex of formula [$PtCl_4${NH=C(NH_2)R}$_2$] (**11**−**14**). Analysis of the reaction mixtures by TLC and mass spectrometry reveals that diphenyl sulfoxide also forms, indicating that the reactions correspond to the acid-catalyzed hydrolysis shown in Scheme 2 (monochloro- and dichlorodiphenyl sulfides, formed as secondary products on deoxygenation of Ph_2SO with HCl,[48] can also be detected in the reaction mixture). In one case, i.e. the reaction between *trans*-[$PtCl_4${NH=C(Me)N=SPh_2}$_2$] (**1**) and HCl, the product released as the solid was different from the amidine complexes. On the basis of elemental analyses and FAB and IR spectroscopy, it is tentatively formulated as the protonation product *trans*-[$PtCl_4${NH=C(Me)N=SPh_2}$_2$]·$(HCl)_2$·$2H_2O$ (**10**). However, its poor solubility in both water and in the most common organic solvents precluded NMR study and further structural characterization.

The X-ray structural study of *trans*-[$PtCl_4${NH=C(NH_2)Et}$_2$] (**12**) (Figure 7) showed that the two amidines are in trans position to each other and these species are in *Z*-configuration. The latter implies that the configuration of the imino species changes from *E* to *Z* upon the hydrolysis.

(46) Kukushkin, V. Yu. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1988**, *33*, 1085.

(47) Kitano, K.; Tanaka, R.; Kimura, T.; Tsuda, T.; Shimizu, S.; Tagaki, H.; Nishioka, T.; Shiomi, D.; Ichimura, A.; Kinoshita, I.; Isobe, K.; Shun'ichiro, O. *J. Chem. Soc., Dalton Trans.* **2000**, 995.

(48) Kukushkin, V. Yu. *Coord. Chem. Rev.* **1995**, *139*, 375.

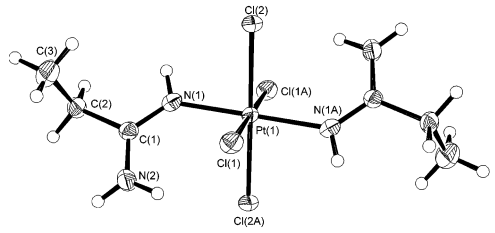
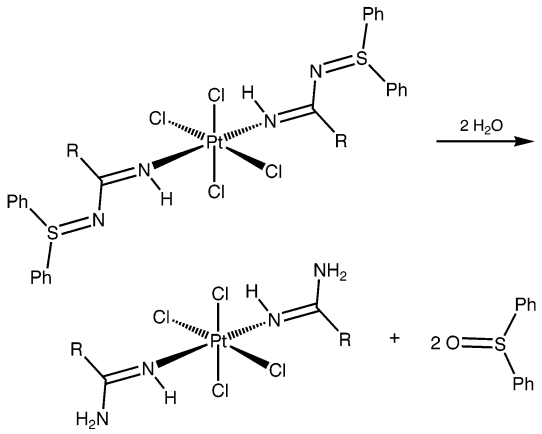


Figure 7. ORTEP view of complex **12** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Pt(1)−Cl(1) 2.3196(13), Pt(1)−Cl(2) 2.3232(13), Pt(1)−N(1) 2.033(4), C(1)−N(1) 1.305(7), C(1)−N(2) 1.315(7), C(1)−C(2) 1.515(7), C(2)−C(3) 1.508(9); Pt(1)−N(1)−C(1) 133.3(4), N(1)−C(1)−N(2) 124.2(5), N(1)−C(1)−C(2) 119.3(5), N(2)−C(1)−C(2) 116.5(5), C(3)−C(2)−C(1) 111.9(5).

Scheme 2



All bond lengths and angles are normal for coordinated amidines[49−51] and for chloroplatinum(IV) complexes.[41,42,52−54]

Interestingly, despite the fact that the X-ray crystallographic determination of the structure of amidine platinum(II) complexes proved an important landmark in developing the metalla-Pinner reaction,[2] until now no platinum(IV) analogues have been fully characterized; the structure reported here is the first one of that kind.

Liberation of the Ligated Heterodiazadienes. Despite the wealth of chemistry associated with sulfimides in general, the chemistry of heterodiazadienes of the type $R^1N{=}C(R^2)N{=}SR^3_2$ (R^1 = H, alkyl, aryl) has so far been little explored, although reactions of $R^1N{=}C(R^2)N{=}SR^3_2$ (R^1 = alkyl, aryl) with CS_2,[55] nitrile oxides,[56] enamines,[57] and diphenylcyclopropenone (to give 4-pyrimidones)[58] have been noted, as have photolysis/thermolysis reactions (which generate heterocycles).[59] One reason for this lack of chemistry is undoubtedly that fact that few synthetic methods for preparation of such compounds have been reported and so only a limited number of heterodiazadienes of this type have ever been prepared. In addition, most of examples prepared so far contain alkyl or aryl groups in the R^1 position; to the best of our knowledge there is only one documented example of compounds bearing R^1 = H, i.e. $HN{=}C(Ph)N{=}SMe_2$,[60] which has been synthesized via chlorination of $HN{=}C(Ph)NH_2$ with NaClO to give $ClN{=}C(Ph)NH_2$, followed by reaction of the latter with Me_2S to achieve $[HN{=}C(Ph)N{-}{}^{+}SMe_2]Cl^{-}$. The sulfonium salt is converted to $HN{=}C(Ph)N{=}SMe_2$ by the reaction with NaOH.[60]

We found that the ligands formed upon Pt(IV)-mediated RCN/sulfimide coupling can be liberated from the platinum(IV) complexes by reaction with $Ph_2PCH_2CH_2PPh_2$ (dppe) (Scheme 1). The role of dppe is dual, i.e. it reduces the Pt(IV) center [reduction of (imine)platinum(IV) species by PPh_3 is known[61]] and substitutes the ligated heterodiazadienes (**17**−**20**). The latter were characterized in solution by ^1H and $^{13}C\{^1H\}$ NMR methods, while the dppe oxides were unambiguously identified by running the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures and comparing the observed chemical shifts with those known from the literature (see Experimental Section). The liberated ligands were isolated as solids after addition of Et_2O to the reaction mixture and additionally characterized by FAB-MS and IR spectroscopy.

Previously our group[9,52] and Michelin et al.[1d] observed that the liberation of ligated imines is efficient when (imine)platinum(II) complexes are treated with bidentate diphosphines in CH_2Cl_2 to give quantitative yield of the imine in solution and the solid $[Pt(diphosphine)_2]Cl_2$. The phosphorus ylide $Ph_3P{=}CHCO_2Me$ has previously proved to be a mild and selective reducing agent for the conversion of Pt(IV) complexes to appropriate Pt(II) compounds in *nonaqueous* solvents.[62] Unfortunately, attempts to reduce $[Pt^{IV}Cl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ to $[Pt^{II}Cl_2\{NH{=}C(R)N{=}SPh_2\}_2]$ using the latter ylide proved unsuccessful. In the cases of $[PtCl_4\{NH{=}C(R)N{=}SPh_2\}_2]$ [R = Me (**1**), Et (**3**)], only the previously described chelate $[PtCl_2\{\mathit{N}H{=}C(Me)N{=}\mathit{S}Ph_2\}]$[8] (**15**) and the similar complex $[PtCl_2\{\mathit{N}H{=}C(Et)N{=}\mathit{S}Ph_2\}]$ (**16**)—both obtained upon reduction, elimination of one of the sulfimide

(49) (a) Michelin, R. A.; Bertani, R.; Mozzon, M.; Sassi, A.; Benetollo, F.; Bombieri, G. *Inorg. Chem. Commun*. **2001**, *4*, 275. (b) Bertani, R.; Catanese, D.; Michelin, R. A.; Mozzon, M.; Bandoli, G.; Dolmella, A. *Inorg. Chem. Commun*. **2000**, *3*, 16. (c) Michelin, R. A.; Mozzon, M.; Bertani, R.; Benetollo, F.; Bombieri, G.; Angelici, R. J. *Inorg. Chim. Acta* **1994**, *222*, 327.
(50) Fairlie, D. P.; Jackson, W. G.; Skelton, B. W.; Wen, H.; White, A. H.; Wickramasinghe, W. A. *Inorg. Chem*. **1997**, *36*, 1020, 1997.
(51) Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Am. Chem. Soc*. **1986**, *108*, 1180.
(52) (a) Wagner, G.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *J. Am. Chem. Soc*. **2000**, *122*, 3106. (b) Wagner, G.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem*. **2001**, *40*, 264.
(53) Kukushkin, V. Yu.; Pakhomova, T. B.; Kukushkin, Yu. N.; Herrmann, R.; Wagner, G.; Pombeiro, A. J. L. *Inorg. Chem*. **1998**, *37*, 6511.
(54) Kuznetsov, M. L.; Bokach, N. A.; Kukushkin, V. Yu.; Pakkanen, T.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans*. **2000**, 4683.
(55) Yoshida, H.; Ogata, T.; Inokawa, S. *Bull. Chem. Soc. Jpn*. **1977**, *50*, 3302.
(56) (a) Gilchrist, T. L.; Harris, C. J.; Hawkins, D. G.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2166. (b) Gilchrist, T. L.; Harris, C. J.; Moody, C. J.; Rees, C. W. *Chem. Commun*. **1974**, 486.
(57) (a) Rossi, E.; Stradi, R.; Visentin, P. *Tetrahedron* **1990**, *46*, 3581. (b) Rossi, E.; Stradi, R. *Synthesis* **1989**, 214.
(58) (a) Gilchrist, T. L.; Harris, C. J.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1969. (b) Gilchrist, T. L.; Harris, C. J.; Rees, C. W. *Chem. Commun*. **1974**, 487.
(59) (a) Rees, C. W. *Pure Appl. Chem*. **1979**, *51*, 1243. (b) Gilchrist, T. L.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1964.
(60) (a) Fuchigami, T.; Odo, K. *Bull. Chem. Soc. Jpn*. **1977**, *50*, 1793. (b) Fuchigami, T.; Odo, K. *Chem. Lett*. **1974**, 247.
(61) Gonzalez, A. M.; Cini, R.; Intini, F. P.; Pacifico, C.; Natile, G. *Inorg. Chem*. **2002**, *41*, 470.
(62) Wagner, G.; Pakhomova, T. B.; Bokach, N. A.; Fraústo da Silva, J. J. R.; Vicente, J.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem*. **2001**, *40*, 1683.

derived ligands and ring-closure—were separated by column chromatography from other products, while in all of the other cases broad mixtures of yet unidentified compounds were obtained. Although we could so far liberate the sulfimide derived heteroazadienes only when starting from the platinum(IV) complexes, it is believed that preparation of the novel sulfimides by the metal-mediated RCN/sulfimide coupling followed by their liberation opens up a facile route to this class of compounds and could initiate their further exploration and utilization.

Final Remarks

From the work reported herein it is clear that the coordination mode of the heterodiazadiene species formed during the Pt-mediated RCN/HN═SPh_2 coupling depends on the oxidation state of the metal. In the case of reaction at Pt(IV) centers, the coupling brings about the formation of complexes bearing the heterodiazadiene bound monodentately via the imino nitrogen. While this monodentate coordination mode is actually desirable, in that it is a key to the ease of liberation of the new heterodiazadienes, we have yet to find a way to convert such complexes to bidentate examples without concomitant reduction to Pt(II). In the case of Pt(II) complexes there appears to be a clear tendency toward the bidentate coordination mode. Thus earlier reports[7,8] by one of us of the latter within $[PtCl(NH{=}SPh_2)\{\mathit{N}H{=}C(Me)N{=}\mathit{S}Ph_2\}]Cl$ and $[PtCl_2\{\mathit{N}H{=}C(Me)N{=}\mathit{S}Ph_2\}]_2\cdot[PPh_4]Cl$ are augmented by the observation of a bidentate coordination mode for derivatives of the bifunctional sulfimides used in the current study. However, we need to respect the *caveat* that conversion from bidentate to monodentate via substitution at the Pt−S bond is possible, as the structure of $[Pt(\mathit{N}H{=}SPh_2)_2\{\mathit{N}H{=}C(Me)N{=}SPh_2\}_2][PF_6]_2$ (**21**) confirms.

A similar oxidation state dependence of coordination patterns has been observed for the NH═C(R′)ON═CR_2 species formed in the metal-mediated nitrile−oxime coupling. Indeed, the N,N-chelates are formed at Pt(II) centers,[63] while exclusively monodentate coordination of the imino species has been found at Pt(IV) centers.[41,53,54] In addition, the monodentate coordination at a Pt(IV) center—when all conditions for the formation of the stable 5-membered rings are favorable—was found for the iminoacylated hydroxamic acids,[64] hydroxylamines,[65] and dione monoximes.[66] We anticipate that the stability of Pt(IV) complex with *two* monodentate imino ligands is higher than that with the chelated ligand containing only *one* imino group. The above-mentioned facts, combined with data on the enormously high hydrolytic stability of imino species at high oxidation state metal centers, i.e. Pt(IV),[41,53,54,64−66] Re(IV),[67] Rh(III),[68] and Au(III),[69] point out to the need of further investigations, including possibly theoretical studies, of the nature of the M−N═C linkage for the imino complexes.

The ability to isolate the free heterodiazadiene from these reactions provides us with the opportunity to prepare new classes of polydentate ligands. Even when the heterodiazadienes generated in the coupling reactions are bound in the monodentate fashion through the nitrogen, the sulfimide sulfur atom has a tendency toward fulfilling a coordination role, as the axial Pt−S interaction within $[Pt(\mathit{N}H{=}SPh_2)_2\{\mathit{N}H{=}C(Me)N{=}SPh_2\}_2][PF_6]_2$ (**21**) reveals. It would seem that the coupling reaction greatly increases the metal affinity of these sulfur atoms (bearing in mind that no S-bound complexes of simple sulfimides are known). Likewise, the axial interaction of the sulfur atom of the C_6H_4SPh group observed in $[PtCl_2\{\mathit{N}H{=}C(Me)N{=}\mathit{S}(Ph)C_6H_4SPh\text{-}\mathit{o}\}]$ (**8**) indicates that atoms within the functional groups bound to the sulfimidic sulfur atom can also play a coordination role. Given that one can envisage the preparation of sulfimides of the general type HN═$S(C_6H_4X)(Ph)$, wherein X is a coordinating group, it follows that the Pt(IV)-mediated coupling/liberation reactions could provide routes to new tridentate ligand systems.

Acknowledgment. A.V.M.-M. is indebted to the Governor of St. Petersburg for a fellowship (Grant M01-2.5D-446). N.A.B. thanks INTAS for the grant YSF 2002-93. A.V.M.-M., N.A.B., and V.Y.K. express gratitude to the International Science Foundation (Soros Foundation) for the fellowships, while V.Yu.K. additionally thanks the Royal Society of Chemistry for a Grant for International Authors. M.L.K. and V.Yu.K. are very much obliged to the PRAXIS XXI and POCTI programs (Portugal) for the Grants BPD16369/98//BPD/5558/2001 and BCC16428/ 98, correspondingly. A.J.L.P. and V.Yu.K. are grateful to the FCT (Foundation for Science and Technology) (Portugal) and the PRAXIS XXI and POCTI programs for financial support of these studies. P.F.K. is grateful to the EPSRC for studentship (K.E.H. and J.M.S.) and PDRA (L.M.G., Grant GR/N28221) support and to Johnson Matthey for loans of precious metals.

Supporting Information Available: Tables S1−S37, listing crystallographic data, atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for all structures, torsion angles for **1**, **2**, **12**, and **21**, and hydrogen bonds for **2**, **12**, and **21**, X-ray crystallographic files in CIF format, and Table S38 with selected calculated bond lengths of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025960W

(63) Ferreira, C. M. P.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu.; Michelin, R. A. *Inorg. Chem.* **2001**, *40*, 1134.
(64) Luzyanin, K. V.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Garnovskii, D. A.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 2981.
(65) Wagner, G.; Pombeiro, A. J. L.; Kukushkin, Yu. N.; Pakhomova, T. B.; Ryabov, A. D.; Kukushkin, V. Yu. *Inorg. Chim. Acta* **1999**, *292*, 272.
(66) Makarycheva-Mikhailova, A. V.; Haukka, M.; Bokach, N. A.; Garnovskii, D. A.; Galanski, M.; Keppler, B. K.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *New J. Chem.* **2002**, 1085.
(67) Wagner, G.; Pombeiro, A. J. L.; Bokach, N. A.; Kukushkin, V. Yu. *J. Chem. Soc., Dalton Trans.* **1999**, 4083.
(68) (a) Kukushkin, V. Yu.; Ilichev, I. V.; Wagner, G.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1999**, 3047. (b) Kukushkin, V. Yu.; Ilichev, I. V.; Zhdanova, M. A.; Wagner, G.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans*. **2000**, 1567.
(69) (a) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D.; Guerrero, R.; Jones, P. G. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1203. (b) Vicente, J.; Chicote, M. T.; Guerrero, R.; Saura-Llamas, I. M.; Jones, P. G.; Ramírez de Arellano, M. C. *Chem.—Eur. J*. **2001**, *7*, 638.