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Cycloplatinated Complexes of Thiosemicarbazones. Synthesis and Crystal Structure of $[Ph_2PC_6H_4CHNNC(S)NHCH_3PtCl]$

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The synthesis and characterization of the platinum heterocyclic carboxaldehyde thiosemicarbazone complexes $[NC_5H_4CRNNC(S)NHR'PtCl]$ (R=H, R'=CH_3(**1**); R=CH_3, R'=CH_3(**2**); R=CH_3, R=H(**3**)) and diphenylphosphinophenyl carboxaldehyde thiosemicarbazone complexes $[Ph_2PC_6H_4CHNNC(S)NHRPtCl]$ (R=CH_3(**5**); R=$^iC_3H_7$ (**6**); R=Ph(**7**)) are described. Compounds **1-3** were prepared by reaction of $Pt(SEt_2)_2Cl_2$ with 2-acetylpyridine-4-alkylthiosemicarbazone in the presence of NEt_3. Compounds **5-7** were prepared using $Pt(SEt_2)_2Cl_2$ in toluene with diphenylphosphinophenyl carboxaldehyde alkylthiosemicarbazone. The compounds have been characterized by microanalysis, NMR (^1H, ^{13}C, ^{31}P) spectroscopy, and single-crystal X-ray diffraction. X-ray single crystal diffraction analysis reveals that compound **5** is a mononuclear platinum compound with P,N,S-coordination mode.

Introduction

Cyclometalated compounds have been extensively studied because of their potential utility in organic synthesis, and a number of their synthethic approaches have been investigated.[1] Recent reports of platinum(II) cyclometalated compounds concern their photochemical and electrochemical properties.[2] Moreover, there is an increasing interest in platinum(II) with either bidentate (C,N; P,N)[3] or terdentate (N, C,N'; C,N,N'; P,C,P'; P,N,C; P,N,P'; S,N,C)[4] ligands. However, platinum(II) complexes of the types [PtX(N,N',S)] or [PtX(P,N,S)] have not been reported. Recently, we have extensively studied the terdentate heterocyclic carboxaldehyde thiosemicarbazone ligands $[NC_5H_4CRNNHC(S)NHR']$ which is a potentially terdentate N,N',S-chelating system.[5] The terdentate heterocyclic carboxaldehyde thiosemicarbazones have been shown to from complexes with various metal ions including Cu(II),[6] Ni(II),[7] Co(II),[8] Fe(II),[9] Hg(I),[10]

Tl(I),[10] and Ga(III),[11]

α-*N*-Heterocyclic carboxaldehyde thiosemicarbazones can exist as *E*(*anti*) or *Z*(*syn*) isomers. The (*E*)-isomer (**1**) is in equilibrium with the tautomeric S-H form (**2**) in the presence of metal ions. Since the general type of reaction, namely evolution of alkane and hydrogen chloride from in-

(1) (2)

teraction of $[PtMe_2(\mu\text{-}SEt_2)_2]/PtCl_2(SEt_2)_2$ with C-H/N-H/S-H bonds, is well established,[12] the α-*N*-heterocyclic carboxaldehyde thiosemicarbazone ligand is valuable in the preparation of cyclometalated complexes of platinum(II).

Motivated by an interest in the effects of α-*N*-heterocyclic and diphenylphosphinophenyl carboxaldehyde thiosemicarbazone geometry, we began a systematic study of the use of the terdentate ligands for organometallic platinum compounds. We have now described the interaction of the *cis*-dichlorobis(diethylsulfide)platinum with N,N',S and P,N, S-terdentate ligands.

Experimental Section

General Methods. All manipulations were performed under a nitrogen atmosphere in an inert-atmosphere glovebox or by standard high-vacuum line techniques. Toluene and THF were distilled from sodium-benzophenone prior to use. Chloroform was distilled from CaH_2. Potassium tetrachloroplatinate was purchased from Sterm Chemicals, Inc.. 4-Methyl-3-thiosemicarbazide and 2-acetylpyridine were purchased from Aldrich. All ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker AM-360 spectrometer. ^1H NMR spectra were referenced against the residual ^1H impurity of the deuterated solvent, and ^{13}C NMR spectra were referenced against the ^{13}C resonance of the solvent. ^{31}P NMR data were referred to 85% H_3PO_4 as an external standard. IR spectra were recored on a Shimazu FT IR-8501 spectrometer. Mass spectra were recorded on a high resolution VG 70-VSEG instrument, and elemental analysis were performed by the Basic Science Center. The ligands $[NC_5H_4CRNNHC(S)NHR']$ (R=H, CH_3; R'=H, CH_3),[19] $Ph_2PC_6H_4CRNNHC(S)NHR'$, and the compound $Ph_2PC_6H_5CHO$[20] were prepared according to the literature methods.

Preparation of $[NC_5H_4CHNNC(S)NHMePtCl]$ (1). A mixture of $NC_5H_4CHNNH\text{-}C(S)NHMe$ (250 mg, 1.28 mol), $Pt(Et_2S)_2Cl_2$ (580 mg, 1.28 mol) and NEt_3 (0.1 mL) in 20 mL of benzene were refluxed for 15 h. The brownish-red precipitate was filtered, washed with acetone (10 mL) and ethanol (10 mL), and dried under vacuum (yield 78%): Mp 158 °C (dec.); ^1H NMR (DMSO-d_6, 300 MHz) δ 8.73 (s, 1H, C*H*), 8.42 (m, 1H, *Ph*), 8.15 (m, 1H, *Ph*), 7.71 (m, 2H, *Ph*), 3.35 (s, 1H, N*H*), 2.50 (d, *J*=6.42 Hz, 3H, N-CH_3); ^{13}C NMR (DMSO-d_6, 25 °C) δ 184.86 (*CS*), 159.46 (*CN*), 147.23, 146.49, 140.68, 126.15, 125.42 (NC_5H_4), 33.02 (CH_3); IR (on KBr pellet; cm $^{-1}$) 3424 (m), 3328 (m), 3184 (w), 2925 (w), 1602 (m), 1501 (m), 1454 (vs), 1350 (w), 1315 (w), 1173 (m), 1114 (w), 1041 (w), 845 (w), 767 (m), 725 (w), 625 (w), 565 (m), 522 (w). Anal. Calcd for $C_8H_9N_4SPtCl$: C, 22.68; H, 4.23. Found: C, 22.17; H, 4.38.

Preparation of $[NC_5H_4CCH_3NNC(S)NHMePtCl]$ (2). A mixture of $NC_5H_4CMeNNHC(S)NHMe$ (300 mg, 1.44 mmol), $Pt(Et_2S)_2Cl_2$ (643 mg, 1.44 mmol), and NEt_3 (0.1 mL) in 20 mL of benzene were heated to 60 °C. The reaction was continued for 10 h at that temperature. The dark orange precipitate was filtered, washed with THF (15 mL) and acetone (15 mL), and dried under vacuum. The orange solid was dissolved in DMSO (5 mL), layered with THF (3 mL) and ether (5 mL) whereupon orange crystals formed in 88% yield : Mp 168 °C; ^1H NMR (DMSO-d_6, 25 °C) δ 8.82, 8.17, 7.82, 7.68 (4H, m, *Py*), 3.38 (s, 1H, N*H*), 3.30 (s, 3H, CCH_3), 3.26 (s, 3H, NCH_3); IR (on KBr pellet; cm $^{-1}$) 3311 (s), 3025 (w), 2945 (w), 1625 (w), 1575 (w), 1522 (s), 1464 (s), 1405 (s), 1335 (w), 1253 (m), 1187 (m), 1064 (w), 842 (w), 768 (m), 682 (w), 571 (m), 462 (w). Anal. Calcd for $C_9H_{11}N_4SPtCl$: C, 24.70: H, 2.53. Found: C, 25.36; H, 2.73.

Preparation of $[NC_5H_4CCH_3NNC(S)NH_2PtCl]$ (3). 3 was prepared according to the same method used for **1**, except that $NC_5H_4CCH_3NNHC(S)NH_2$ was used instead of $NC_5H_4CHNNHC(S)MHMe$. Yield: 76%. Mp 162 °C. ^1H NMR (DMSO-d_6, 25 °C) δ 8.62, 8.17, 7.77, 7.74 (*Py*), 3.30 (s, 2H, NH_2), 2.53 (s, 3H, CCH_3); ^{13}C NMR (DMSO-d_6, 25 °C) δ 183.99 (*CS*), 160.27 (*CN*) 154.71, 146.43, 140.94, 127.03, 125.66 (*Py*), 13.65 (CCH_3); IR (on KBr pellet; cm $^{-1}$) 3424 (m), 3323 (s), 3122 (w), 1602 (s), 1501 (m), 1455 (vs), 1312 (w), 1284 (w), 1173 (m), 1108 (w), 1045 (w), 1002 (w), 767 (m), 718 (w), 672 (w), 642 (w), 605 (m), 584 (w). Anal. Calcd for $C_8H_9N_4SPtCl$: C, 42.37; H, 2.12. Found: C, 41.84, H, 2.32.

Preparation of $[NC_5H_4CMeNNC(S)NH_2PtN_3]$ (4). A mixture of **3** (250 mg. 0.59 mmol) and NaN_3 (60 mg, 0.90 mmol) in DMSO (25 mL) was refluxed for 48 h. The solvent was removed under reduced pressure and washed with H_2O (15 mL) and C2H5OH (15 mL). The orange solid was recrystallized with DMSO (5 mL) and ether (10 mL). yield: 76%. Mp 166 °C (dec.). ^1H NMR (DMSO-d_6, 25 °C) δ 8.42, 8.14, 7.67, 7.70 (NC_5H_4), 3.26 (s, 2H, NH_2), 2.48 (s, 3H, CCH_3); ^{13}C NMR (DMSO-d_6, 25 °C) δ 181.94 (*CS*), 159.28 (*CN*), 154.24, 146.01, 140.62, 127.24, 125.20 (NC_5H_4), 13.48 (CCH_3); IR (on KBr pellet; cm $^{-1}$) 3649 (w), 3382 (m), 3301 (m), 2064 (s), 1636 (m), 1599 (w), 1576 (w), 1501 (m), 1454 (vs), 1441 (sh), 1362 (W), 1321 (w), 1292 (w), 1261 (w), 1175 (m), 1132 (w), 1043 (w), 818 (w), 772 (m), 739 (w), 540 (br), 476 (w), 421 (w). Anal. Calcd for $C_8H_9N_7PtS$: C, 22.33; H, 2.09. Found: C, 21.81; H, 2.28.

Preparation of $[Ph_2PC_6H_4CHNNC(S)NHCH_3PtCl]$ (5). To a solution of $[Ph_2PC_6H_4CHNNHC(S)NHMe]$ (254 mg, 0.67 mmol) in toluene (15 mL) was added $Pt(Et_2S)_2Cl_2$ (300 mg, 0.67 mmol) and NEt_3 (0.1 mL) at room temperature. The solution was stirred at that temperature for 12 h and filtered. Evaporation of the filtrate to dryness and treatment with CH_3CN (10 mL) and Et_2O (10 mL) afforded **5** as an orange solid (yield 74%). mp 167 °C (dec.); ^1H NMR ($CDCl_3$, 25 °C) δ 8.58 (s, 1H, C*H*), 7.69-7.18 (m, 14H, aromatic), 3.21 (s, 1H, N*H*), 1.39 (d, *J*=7.18 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) δ 186.22 (*CS*), 152.32 (*CN*), 138.23, 138.00, 135.48, 135.36, 134.94, 134.09,

133.95, 132.30, 131.66, 131.22, 129.54, 128.72, 128.57, 119.84 (aromatic), 35.58 (CH_3). ^{31}P NMR ($CDCl_3$) δ 9.32 (J_{Pt-P}=4068 Hz). IR (on KBr pellet; cm $^{-1}$) 3348 (w), 3059 (w), 2925 (w), 1559 (m), 1505 (s), 1481 (m), 1436 (s), 1404 (m), 1374 (w), 1312 (m), 1265 (w), 1186 (w), 1170 (w), 1098 (s), 1070 (sh), 1000 (w), 905 (w), 806 (w), 749 (s), 694 (vs), 620 (w), 541 (s), 507 (s), 468 (w). MS: m/z 607 (M^+). Anal. Calcd for $C_{21}H_{19}N_3SPPtCl$: C, 41.56 H, 3.13. Found; C, 40.88; H, 3.36.

Preparation of [$Ph_2PC_6H_4CHNNC(S)NHC_3H_7PtCl$] (6). **6** was prepared according to the same method used for **5** except that $Ph_2PC_6H_4CHNNHC(S)NHA'C_3H_7$ was used instead of $Ph_2PC_6H_4CHNNHC(S)NHMe$. Yield: 82%. mp 253 °C (dec.). ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.52 (s, 1H, C*H*), 7.68-7.27 (m, 14H, aromatic), 5.03 (br, 1H, N*H*), 4.04 (sept, *J*=6.32 Hz, 1H, C*H*), 1.23 (d, *J*=6.32 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) δ 185.33 (*C*S), 149.43 (*C*N), 138.24, 138.00, 135.48, 135.36, 134.94, 134.09, 133.95, 132.30, 131.66, 131.32, 129.54, 128.72, 128.57, 119.84 (aromatic), 48.39 (CCH_3), 23.06 (CCH_3), ^{31}P NMR ($CDCl_3$) δ 9.88 (J_{Pt-P}=4088 Hz). IR (on KBr pellet; cm $^{-1}$) 3349 (s), 3033 (w), 2959 (w), 1579 (w), 1558 (w), 1500 (vs), 1471 (s), 1437 (m), 1379 (w), 1321 (w), 1279 (w), 1261 (w), 1208 (w), 1151 (m), 1105 (w), 1034 (m), 1000 (w), 959 (w), 924 (w), 839 (w), 795 (w), 764 (m), 741 (m), 696 (s), 629 (w), 541 (s), 508 (m). Anal. Calcd for $C_{23}H_{23}N_3PSPtCl$: C, 43.49; H, 3.62. Found: C, 42.92; H, 3.82.

Preparation of [$Ph_2PC_6H_4CHNNC(S)NHPhPtCl$] (7). **6** was prepared according to the same method used **5** except that $Ph_2PC_6H_4CHNNHC(S)NHPh$ was used instead of $Ph_2PC_6H_4CHNNHC(S)NHMe$. Yield: 76%. mp 254 °C (dec.). ^{1}H ($CDCl_3$, 25 °C) δ 8.76 (s, 1H, C*H*), 7.67-7.27 (m, 14H, aromatic), 5.31 (s, 1H, N*H*); ^{13}C NMR ($CDCl_3$, 25 °C) δ 182.78 (*C*S), 151.28 (*C*N), 134.11, 133.74, 133.22, 132, 87, 132.44, 132.02, 131.44, 131.28, 128.83, 128.66, 128.40, 127.96 127.42, 123.48, 122.96, 120.24, 119.88 (aromatic). IR (on KBr pellet; cm $^{-1}$) 3428 (m), 3051 (w), 1595 (w), 1580 (w), 1561 (w), 1539 (m), 1509 (vs), 1497 (s), 1436 (s), 1383 (w), 1321 (m), 1255 (m), 1184 (w), 1141 (w), 1098 (m), 1081 (e), 1039 (m), 931 (w), 909 (w), 891 (w), 805 (w), 769 (w), 741 (w), 710 (w), 691 (s), 540 (s), 506 (s), 474 (m). Anal. Calcd for $C_{26}H_{21}N_3PSPtCl$: C, 46.67; H, 3.14. Found: C, 46.12; H, 3.38.

Preparation of [$Ph_2PC_6H_4CHNNC(S)NHCH_3PtN_3$] (8). To a stirred THF (20 mL) solution of **5** (100 mg, 0.165 mmol) was added NaN_3 (18 mg, 0.275 mmol). The solution was refluxed for 48 h. The solvent was removed and washed with H_2O (15 mL) and EtOH (10 mL). The resulting orange solid was recrystallized with CH_2Cl_2 and hexane (10 mL). Yield: 72%. mp 131 °C (dec.). ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.62 (s, 1H, C*H*), 7.92-7.04 (m, 14H, aromatic), 3.42 (s, 1H, N*H*), 1.59 (d, *J*=8.61 Hz, 3H, CH_3). IR (on KBr pellet; cm $^{-1}$), 3425 (br). 3050 (s), 2948 (w), 2045 (vs), 1559 (m), 1505 (w), 1480 (w), 1435 (m), 1405 (w), 1318 (m), 1261 (w), 1185 (w), 1100 (s), 1073 (m), 1035 (w), 1000 (w), 805 (w), 750 (m), 699 (s), 555 (s), 508 (m), Anal. Calcd for $C_{21}H_{19}N_6PSPt$: C, 39.94; H, 3.10. Found: C, 39.26; H, 3.36.

Preparation of [$Ph_2PC_6H_4CHNNC(S)NHCH_3PtNCS$] (9). **9** was prepared according to the same method used for **8** except that NaNCS was used instead of NaN_3. Yield: 68%. mp 162 °C (dec.). ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.52 (s, 1H, CH), 7.87-7.09 (m, 14H, aromatic), 3.36 (s, 1H, N*H*), 1.52 (d, *J*=8.48 Hz, CH_3). IR (on KBr pellet; cm $^{-1}$) 3375 (br), 3050 (w), 2953 (w), 2100 (s), 1559 (m), 1509 (s), 1471 (m), 1435 (m), 1406 (m), 1375 (w), 1319 (m), 1261 (w), 1908 (s), 905 (w), 804 (w), 749 (m), 691 (s), 619 (w), 541 (m), 509 (m), 491 (w), 459 (w). MS: m/z 630 (M^+) Anal. Calcd for $C_{22}H_{19}N_4PS_2Pt$: C, 41.96; H, 3.02. Found: C, 41.28; H, 3.24.

X-ray Analysis of [$Ph_2PC_6H_4CHNNC(S)NHCH_3PtCl$]. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo K_α (λ= 0.71073 Å) at ambient temperature. The data were corrected for Lorentz and polarization effects, and empirically for absorption. The structures were solved by the Patterson method (SHELXS-86) and were refined by full-matrix least-squares techniques (SHELXS-93). The absolute configuration of the diphenylphosphinophenyl carboxaldehyde thiosemicarbazone ligand was determined on the basis of the Flack absolute structure parameters and matched with the chemical need. For **5**, non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added at calculated position. Crystal parameters and procedural information corresponding to data collection and structure are given in Table 1.

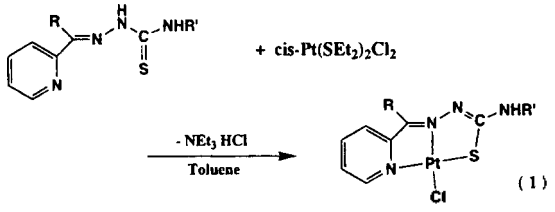
Results and Discussion

Synthesis and Characterization of [$NC_5H_4CRNNC(S)NHR'PtX$] (R=H, CH_3; R'=H, CH_3; X=Cl, N_3). The reaction of 2-acetylpyridine-4-alkylthiosemicarbazones with *cis*-dichlorobis(diethylsulfide)platinum in the presence of NEt_3 affords the corresponding cyclometallated platinum complexes, in which one hydrogen atom has been lost from the *aza* hydrogen atom *via* the hydrogen chloride el-

Table 1. Crystallographic Data for the Structural study of Compound 5

empirical formula	$C_{21}H_{19}ClPN_3SPt$
formula weight	606.9
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	14.695(6)
b, Å	16.683(7)
c, Å	19.297(9)
β	102.83(6)°
V, Å^3	4613(4)
D_c, gcm^{-3}	1.736
F(000)	4
μ (Mo-Kα), mm^{-1}	6.371
no. of indep. reflcns	4903
params refined	4886
goodness of fit	1.046
R_1[a]	0.065
wR_2	0.086

[a] $R_1=\Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2=\{\Sigma[w(Fo^2-Fc^2)]/\Sigma[wFo^2]\}^{1/2}$

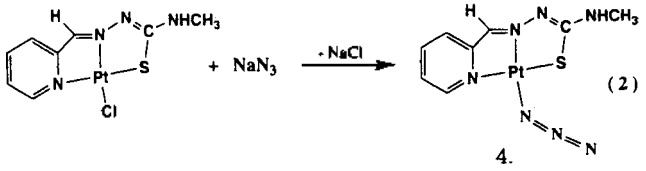


1. R = H, R' = CH_3
2. R = CH_3, R' = CH_3
3. R = CH_3, R' = H

imination reaction (eq. 1).

The resulting orange compounds **1-3** were isolated as air-stable crystalline solids in a high yield. These compounds are virtually insoluble in common organic solvents but soluble in DMSO. The complexes **1-3** have been charaterized by ^1H, ^{13}C NMR, IR, and elemental analyses. The ^1H NMR spectrum of **1** shows two peaks at 8.73 and 3.35 ppm due to the hydrogen atom of C-H and N-H, respectively. The chemical shifts of these resonances are consistent with prior observations of thiosemicarbazone complexes. The carbons attached to the imine groups appears at 184.86 and 159.46 ppm in the ^{13}C NMR spectrum. The resonance of 184.86 ppm is assigned to the carbon atom bonded to S atom. The value is within the range observed for other metal complexes. The infrared spectrum of **1** indicates the mode of the ligand coordination to platinum moiety. The peak at 1062 cm^{-1} is assigned to the ring deformation mode. Positive shift of the mode compared to that of ligand indicates the mode of the ligand coordination to platinum moiety. The stretching mode of ν (CS) at 767 cm^{-1} significantly decreased. This could involve an azine ⟷ imine hydrazone tautomerism(I-II).

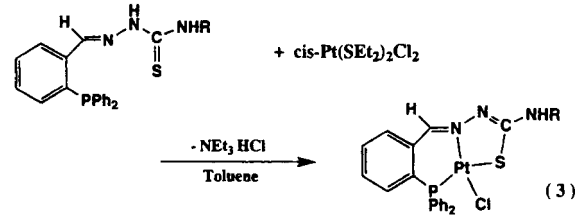
Addition of sodium azide to dimethyl sulfate solution of [$NC_5H_4CHNNC(S)NHMePtCl$] (**1**) leads to salt elimination and the formation of Pt-N_3 (eq. 2). IR data and micro-



4.

analytical data are both in agreement with the formulation of **4**. The infrared spectrum of **4** clearly indicates the presence of the Pt-N_3 bond The intensive peak at 2064 cm^{-1} is assigned to the N_3 stretching mode, which is expected to exhibit a bond with stretching frequency in the region 2300-2000 cm^{-1}.[13]

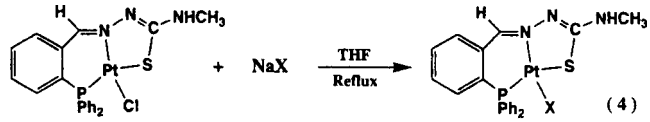
Synthesis and Characterization of [$Ph_2PC_6H_4CHNNC(S)NHRPtX$] (R=$CH_3$, $^iC_3H_7$, C_6H_5; X=Cl, N_3, NCS). The diphenylphosphinophenyl carboxaldehyde thiosemicarbazone complexes of platinum were synthesized by relatively straight- forward means in toluene as reaction solvent (eq. 3). The complexes **5-7** are orange crystalline solids at room temperature which are soluble in benzene, toluene, and THF. The complexes **5-7** were identified by ^1H, ^{13}C, ^{31}P NMR, IR, mass spectra and elemental analyses.



5. R = CH_3 6. R = $^iC_3H_7$ 7. R = C_6H_5

The initial indication of a mononuclear formulation for **5** stemmed from the observation of a parent ion in the mass spectrum at m/z 607, followed by a series of fragmentations attributable to the loss of Cl. The ^{31}P NMR spectrum of **5** shows one peak at 9.32 ppm with large Pt-P coupling constant of 4068 Hz The value is very close to that of the compound [$(Ph_2PC_6H_4CHNCH_2CH_2NC_5H_4)Pt(CH_3)$]Cl reported by Vrieze *et al.*[14] Even though the proposed formulation was futher supported by ^1H, ^{13}C, NMR, IR spectrum, the bonding mode in **5** is still not clear. Therefore, conformation of the structure of **5** was provided by X-ray crystallography.

The addition of sodium azide or sodium thiocyanate to **5** allows the isolation of the Pt-N_3 or Pt-NCS complex on high yield (eq. 4). ^1H NMR and microanalytical data are both in agreement with the formulation of **8** and **9**. The in-



8. X = N_3 9. X = NCS

tensive peak at 2100 cm^{-1} of **9** is assigned to the NCS stretching mode. Compound **9** was futher characterized by mass spectroscopy. A signal at m/z 630 is present which is clearly due to **9**.

Description of the Molecular Structure of [$Ph_2PC_6H_4CHNNC(S)NHCH_3PtCl$] (5). Crystals of **5** suitable for an X-ray diffraction study were grown from CH_3CN/Et_2O at −15 °C, and the structure of **5** was determined from data collected at 25 °C. A summary of data collection and crystallographic parameters are given in Table 1. Atomic positional parameters are given in Table 2, while selected bond lengths and angles are given in Table 3. An ORTEP diagram of the solid state structure giving the atom-numbering scheme used in the tables is shown in Figure 1. The molecule contains both $PtSCN_2$ five-membered ring and $PtNC_3P$ six-membered ring. The chelate distorts the complex slightly away from an ideal square-plannar geometry by pinching back the one phosphine away from the chlorine group. This results in a P(1)-Pt(1)-S(1) bond angle at 177.8 (2)°. As the N(1)-Pt(1)-Cl(1) bond angle is 174.4 (4)° and the sum of bond angles surrounding the Pt atom is 360. 0°, the coordination environment about Pt(I) may be described as a square-planar structure of the three donor atoms of PNS and the chloro ligand around the platinum atom.

The bond angles between Pt and two neighboring donor atoms are between 95.8 (4)° and 84.9(4)°. Values close to

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotopic Displacement Parameters ($A^2 \times 10^3$) for 5

	x	y	z	U(eq)*
Pt(1)	1668(1)	644(1)	1642(1)	34(1)
S(1)	1795(4)	-453(3)	2377(3)	48(1)
Cl(1)	2026(3)	1470(3)	2622(3)	51(1)
P(1)	1494(3)	1725(3)	936(2)	33(1)
N(1)	1411(9)	-171(9)	843(8)	41(4)
N(2)	1404(11)	-976(10)	1021(8)	43(4)
N(3)	1584(11)	-1933(10)	1895(10)	56(5)
C(1)	1611(11)	-1142(11)	1702(11)	39(5)
C(2)	1522(16)	-2585(13)	1379(14)	74(7)
C(3)	1233(14)	-43(13)	155(10)	51(5)
C(4)	1190(12)	685(12)	-228(10)	41(4)
C(5)	1025(14)	544(13)	-970(11)	54(5)
C(6)	972(16)	1184(14)	-1459(12)	61(6)
C(7)	1098(15)	1939(14)	-1213(12)	60(6)
C(8)	1244(15)	2097(15)	-500(13)	67(7)
C(9)	1281(13)	1478(14)	-2(11)	53(6)
C(10)	485(12)	2304(10)	1014(10)	39(4)
C(11)	497(14)	2839(12)	1552(10)	51(5)
C(12)	-319(14)	3212(14)	1645(12)	62(6)
C(13)	-1136(13)	3059(13)	1160(11)	53(5)
C(14)	-1161(13)	2546(13)	603(11)	55(6)
C(15)	-367(130	2165(12)	526(11)	49(5)
C(16)	2481(12)	2401(12)	1078(10)	44(5)
C(17)	2395(15)	3213(12)	929(12)	58(6)
C(18)	3198(24)	3679(18)	979(15)	95(9)
C(19)	4046(23)	3307(22)	1200(16)	97(10)
C(20)	4147(17)	2555(21)	1361(13)	79(8)
C(21)	3369(14)	2051(16)	1425(11)	67(7)

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Length (Å) and Angles (deg) for Compound 5

Pt(1)-N(1)	2.03(2)	Pt(1)-P(1)	2.239(5)
Pt(1)-S(1)	2.298(5)	Pt(1)-Cl(1)	2.304(5)
S(1)-C(1)	1.71(2)	P(1)-C(10)	1.80(2)
P(1)-C(16)	1.81(2)	P(1)-C(9)	1.82(2)
N(1)-C(3)	1.31(2)	N(1)-N(2)	1.39(2)
N(2)-C(1)	1.31(2)	N(3)-C(1)	1.37(2)
N(3)-C(2)	1.46(3)	C(3)-C(4)	1.41(3)
C(4)-C(9)	1.39(3)	C(4)-C(5)	1.42(3)
C(5)-C(6)	1.42(3)	C(6)-C(7)	1.34(3)
N(1)-Pt(1)-P(1)	95.8(4)	N(1)-Pt(1)-S(1)	84.9(4)
P(1)-Pt(1)-S(1)	177.8(2)	N(1)-Pt(1)-Cl(1)	174.4(4)
P(1)-Pt(1)-Cl(1)	89.5(2)	S(1)-Pt(1)-Cl(1)	89.8(2)
C(1)-S(1)-Pt(1)	95.0(7)	C(10)-P(1)-C(16)	107.4(9)
C(10)-P(1)-C(9)	104.0(9)	C(16)-P(1)-C(9)	104.3(9)
C(10)-P(1)-Pt(1)	111.5(6)	C(16)-P(1)-Pt(1)	115.5(7)
C(9)-P(1)-Pt(1)	113.2(8)	C(3)-N(1)-N(2)	114(2)
C(3)-N(1)-Pt(1)	128.4(14)	N(2)-N(1)-Pt(1)	118.1(11)
C(1)-N(2)-N(1)	116(2)	C(1)-N(3)-C(2)	122(2)
N(2)-C(1)-N(3)	117(2)	N(2)-C(1)-S(1)	126(2)
N(3)-C(1)-S(1)	117(2)	N(1)-C(3)-C(4)	130(2)

the ideal 90° must be attributed to the flexibility of the ligand even when it acts as a terdentate ligand. The pyridyl

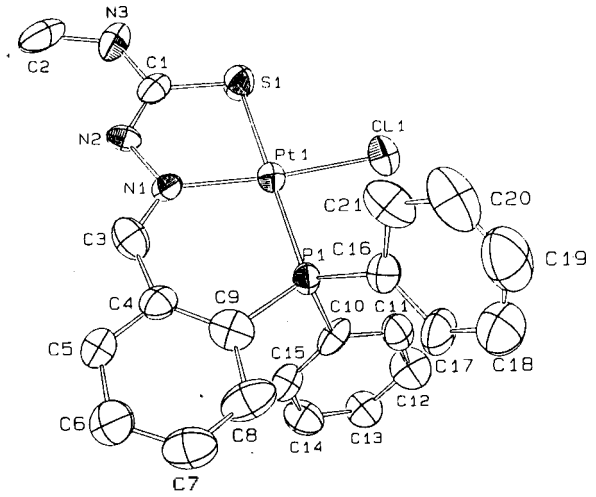


Figure 1. Molecular Structure of $ClPt[Ph_2PC_6H_4CHNNC(S)NHCH_3]$ (5). The thermal ellipsoids are drawn at the 30% probability level.

Pt(1)-N(1) distance (2.03(2) Å) is comparable to that observed for $[PtMe(C_6HF_3CHNR)(PPh_3)]$ (2.156(8) Å),[15] $[PtCl(CH_3SC_6H_4NNC_6H_3CH_3)]$ (1.946(8) Å),[16] and $[Pt(MeCN)(NC_5H_4NC_5H_3C_6H_4)]PF_6$ (2.045 Å).[17] The Pt(1)-P(1) bond distance (2.239(5) Å) falls well within the range commonly for four-coordinate palladium and platinum complexes.[18] The Pt(1)-S(1) distance (2.298(5) Å) is slightly shorter than that observed for $[PtCl_3(CH_3SC_6H_4N_2C_6H_3CH_3)]$ (2.439(2) Å),[16] indicating that the negatively charged sulfato anion is a strong donor to the platinum center than the neutral sulfur atom. The imine N(2)-C(1) bond distance (1.31(2) Å) is shorter than that of single bond distance of C-N. The bond short distance demonstrates the involvement of 1,3-proton shiht.

Concluding Remarks. The synthesis and characterization of cyclometalated heterocyclic carbox- aldehyde thiosemicarbazone complexes of platinum, having the coordination sphere (N,N,S)Cl or Pt(P,N,S) are described. The X-ray structure of **5** have been determined. The observation of a short distance of N(2)-C(1) is also consistent with the tautomeric S-H form(II). Complexes **1-3** and **5-7** are probably formed by a platinum-promoted attack of the imino nitrogen pyridyl nitrogen, followed by elimination of HCl from the tautomeric S-H form. This synthetic approach may be useful in preparing a variety of new organometallic complexes.

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Supplementary Material Available. Tables of fractional coordinates and isotopic temperature factors, additional bond lengths and angles, and anisotropic temperature factors for **5** (14 pages). Supplementary materials are available from one of the authors (J. Ko) upon request.

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