Synthesis and Characterization of and Stereoselective Oxidative Addition of Chlorine or Bromine to [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)]

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The title complex [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)] (1; C$_5$H$_4$NS = pyridine-2-thiolate) can be obtained in high yield by reaction (1:2) of [NBu$_4$]$_2$[Pt(μ-Cl)(C$_6$F$_5$)$_2$]$_2$ with *in situ* generated LiC$_5$H$_4$NS. 1 is suggested to be monomeric. The N end of the chelate pyridine-2-thiolate ligand in 1 can be released by reaction with P(C$_6$H$_5$)$_3$, which gives [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS){P(C$_6$H$_5$)$_3$}] (2). 1 reacts with CCl$_4$ solutions of Cl$_2$ or Br$_2$, yielding [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)X$_2$] (X = Cl (**3a**), Br (**3b**)). In each reaction a single product can be spectroscopically detected, which means that the oxidative addition proceeds stereoselectively. In order to establish the actual geometry of the reaction product, the molecular structure of **3b** was determined by X-ray diffraction. **3b** crystals are monoclinic, space group *C*2/*c*, with a = 2186.0(13) pm, b = 2088.6(4) pm, c = 1703.5(5) pm, β = 99.43(1)°, V = 7672 × 10^6 pm^3, and Z = 8. The structure determination revealed that the anion exists as the enantiomeric couple *OC*-6-42-*A* and *OC*-6-42-*C*. Substitution of one of the halogens attached to Pt by a neutral or anionic ligand can be easily accomplished, and accordingly, the complexes [Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)(CN-*t*-C$_4$H$_9$)X] (X = Cl (**4a**), Br (**4b**)) and [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)BrCl] (**3c**) have been prepared. A single product is obtained in each case, suggesting that the substitution reaction proceeds with stereoretention. The molecular structure of **4b** was also determined by X-ray methods. **4b** crystals are triclinic, space group $P\bar{1}$, with a = 913.1(2) pm, b = 1085.1(2) pm, c = 1363.9(3) pm, α = 89.50(1)°, β = 72.82(2)°, γ = 77.81(2)°, V = 1260 × 10^6 pm^3, and Z = 2. The molecule exists as the enantiomeric couple *OC*-6-54-*A* and *OC*-6-54-*C*, showing that the equatorial halogenide in its parent compound **3b** is more labile than the axial one.

Introduction

The pentafluorophenyl group belongs to that class of organic radicals without hydrogen substituents in β-positions, which has proven to be able to stabilize organometallic complexes of palladium and platinum in high oxidation states.[1,2] It has been pointed out that the presence of chelating agents also plays an important role in stabilizing organometallic M(IV) complexes (M = Pd, Pt). Together with the classical didentate ligands 2,2′-bipyridine, 1,10-phenanthroline, 1,2-ethylenediamine and *N,N,N′,N′*-tetramethylethylenediamine,[3] tridentate[4] and tripod[5] ligands such as [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]$^-$ and [(pz)$_x$H$_{3-x}$ER]$^{n-}$ (pz = pyrazol-1-yl or related radicals; n = 0, ER = CH; n = 1, ER = BH, Bpz) have also been widely used. Herewith, we describe the synthesis and characterization of the complex [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)], in which the pyridine-2-thiolate ligand (C$_5$H$_4$NS$^-$) is acting as a chelate together with its oxidative-addition products. Some substitution reactions essayed on both Pt(II) and Pt(IV) derivatives are described as well.

Experimental Section

General Procedures and Materials. C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 4000–200 cm^{-1}). NMR spectra were recorded on the following Varian spectrometers: XL-200, Unity-300, and Unity-400. Mass spectra were registered on a VG-Autospec spectrometer using the standard Cs ion FAB (acceleration voltage 35 kV). Conductivities were measured on ~5 × 10^{-4} M acetone solutions with a Philips PW 9509 conductometer. [NBu$_4$]$_2$[Pt(μ-Cl)(C$_6$F$_5$)$_2$]$_2$ was synthesized by literature methods.[6] LiC$_5$H$_4$NS was prepared *in situ* by reaction of a THF solution of C$_5$H$_5$NS with an equimolar amount of Li-*n*-Bu at 0 °C.

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$[\mathrm{NBu_4}][\mathrm{Pt(C_6F_5)_2(C_5H_4NS)}]$ (1). To a THF solution (20 mL) of $\mathrm{LiC_5H_4NS}$ (0.93 mmol) at 0 °C was added the substrate $[\mathrm{NBu_4}]_2[\mathrm{Pt}(\mu\text{-Cl})(\mathrm{C_6F_5})_2]_2$ (0.5 g, 0.31 mmol), and the mixture was stirred for 8 h. In the meanwhile, the temperature of the bath was raised to room temperature. Then, the solvent was evaporated under vacuum and the resulting residue was extracted with $\mathrm{CH_2Cl_2}$ (3 × 10 mL). After filtration, the filtrate was concentrated almost to dryness; the addition of *i*-PrOH (10 mL) with stirring caused a yellow solid to precipitate (1: 0.4 g, 73% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 1582, 1426, 1269, 1152, 1139, 1058, 883, 760. ^{1}H NMR ([^{2}H]chloroform):[8] δ 7.39 [d, ^3J(H,H) = 5.1 Hz, ^3J(^{195}Pt,H) ≈ 30 Hz, 1H, 6-H], 7.30 [td, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.8 Hz, 1H, 4-H], 6.62 [t, ^3J(H,H) = 8.1 Hz, 1H, 5-H], 6.59 [d, ^3J(H,H) = 8.1 Hz, 1H, 3-H]. ^{13}C{^{1}H} NMR ([^{2}H]chloroform):[8] δ 182.5 (s, C2), 145.0 (s, C6), 135.5 (s, C5), 128.0 (s, C3), 116.7 (s, C4). ^{19}F NMR ([^{2}H]chloroform): δ −117.6 [m$_c$, ^3J(^{195}Pt,F) = 495 Hz, 2F, *o*-F], −119.9 [m$_c$, ^3J(^{195}Pt,F) = 451 Hz, 2F, *o*-F], −165.3 (m$_c$, 1F, *p*-F), −166.5 (m$_c$, 2F, *m*-F), −166.7 (m$_c$, 1F, *p*-F), −167.7 (m$_c$, 2F, *m*-F). ^{195}Pt{^{1}H} NMR ([^{2}H]acetone): δ −3420 [br quint, ^3J(^{19}F,Pt) ≈ 475 Hz, $w_{1/2}$ = 316 Hz]. FAB-MS: *m/z* 639 ($\mathrm{C_{17}H_4F_{10}NPtS^-}$). Λ_M = 105.4 Ω^{-1} cm^2 mol^{-1}. Anal. Found (calcd) for $\mathrm{C_{33}H_{40}F_{10}N_2PtS}$: C, 45.13 (44.95); H, 4.74 (4.57); N, 2.95 (3.18).

$[\mathrm{NBu_4}][\mathrm{Pt(C_6F_5)_2(C_5H_4NS)\{P(C_6H_5)_3\}}]$ (2). To a $\mathrm{CH_2Cl_2}$ solution (20 mL) of 1 (0.1 g, 0.11 mmol) was added $\mathrm{P(C_6H_5)_3}$ (29.7 mg, 0.11 mmol). After 7 h of stirring, the solution was evaporated to dryness. When the resulting residue was treated with *i*-PrOH (15 mL), a yellow solid formed, which was filtered off and dried (2: 0.1 g, 77% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 1570, 1548, 1406, 1124, 1098, 1058, 1051, 885, 758, 745, 703, 696, 533, 514, 492. ^{1}H NMR ([^{2}H]acetone):[8] δ 7.92 [d, ^3J(H,H) = 8.1 Hz, 1H, 3-H], 7.77 [ddd, ^3J(H,H) = 4.9 Hz, ^4J(H,H) = 2.0 Hz, ^5J(H,H) = 0.9 Hz, 1H, 6-H], 7.72–7.65 (m, 6H, $\mathrm{C_6H_5}$), 7.36–7.23 (m, 9H, $\mathrm{C_6H_5}$), 7.08 [ddd, ^3J(H,H) = 7.3 Hz, 1H, 4-H], 6.48 [ddd, ^4J(H,H) = 1.1 Hz, 1H, 5-H]. ^{19}F NMR ([^{2}H]acetone): δ −115.07 [m$_c$, ^3J(^{195}Pt,F) = 370 Hz, 2F, *o*-F], −115.81 [m$_c$, ^3J(^{195}Pt,F) = 405 Hz, 2F, *o*-F], −166.41 (m$_c$, 2F, *m*-F), from −166.6 to −167.2 (m, 3F, *m*- and *p*-F), −167.34 (m$_c$, 1F, *p*-F). ^{31}P{^{1}H} NMR ([^{2}H]acetone): δ 18.72 [pseudosept, ^4J(^{19}F,P) = 18.4 Hz, ^5J(^{19}F,P) = 10.0 Hz, ^1J(^{195}Pt,P) = 2590 Hz]. Λ_M = 90.8 Ω^{-1} cm^2 mol^{-1}. Anal. Found (calcd) for $\mathrm{C_{51}H_{55}F_{10}N_2PPtS}$: C, 53.37 (53.54); H, 4.96 (4.84); N, 2.29 (2.45).

$[\mathrm{NBu_4}][\mathrm{Pt(C_6F_5)_2(C_5H_4NS)Cl_2}]$ (3a). To a solution of 1 (0.2 g, 0.23 mmol) in $\mathrm{CHCl_3}$ (10 mL) was added a slight excess of $\mathrm{Cl_2}$ in $\mathrm{CCl_4}$ (0.25 mmol). After 15 min of stirring, the solution was evaporated to dryness. When the resulting residue was treated with $\mathrm{Et_2O}$ (5 mL), a yellow solid could be obtained, which was identified as **3a** (0.17 g, 79% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 1636, 1590, 1558, 1266, 1157, 1142, 1068, 884, 755, 658, 490, 317 (Pt–Cl), 303, 284 (Pt–Cl). ^{1}H NMR ([^{2}H]chloroform):[8] δ 8.65 [t, ^3J(H,H) = J(^{19}F,H) = 5.6 Hz, ^3J(^{195}Pt,H) = 28 Hz, 1H, 6-H], 7.48 [td, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.5 Hz, 1H, 4-H], 6.95 (dd, 1H, 5-H), 6.65 (d, 1H, 3-H). ^{13}C{^{1}H} NMR ([^{2}H]acetone):[8] δ 178.2 [s, ^2J(^{195}Pt,C) = 67 Hz, C2], 145.5 (d, J(^{19}F,C) = 4.4 Hz, C6), 138.7 (s, C5), 126.5 [s, ^3J(^{195}Pt,C) = 40.6 Hz, C3], 117.8 [s, ^4J(^{195}Pt,C) = 18.7 Hz, C4]. ^{19}F NMR ([^{2}H]chloroform): δ −114.95 [m$_c$, ^3J(^{195}Pt,F) = 154 Hz, 1F, *o*-F), −117.28 [m$_c$, ^3J(^{195}Pt,F) = 174 Hz, 1F, *o*-F], −118.19 [m$_c$, ^3J(^{195}Pt,F) = 112 Hz, 1F, *o*-F], −121.61 [m$_c$, ^3J(^{195}Pt,F) = 92 Hz, 1F, *o*-F], −161.13 (m$_c$, 1F, *p*-F), −162.65 (m$_c$, 1F, *p*-F), −164.61 (m$_c$, 2F, *m*-F), −165.89 (m$_c$, 1F, *m*-F), −166.13 (m$_c$, 1F, *m*-F). FAB-MS: *m/z* 709 ($\mathrm{C_{17}H_4Cl_2F_{10}NPtS^-}$). Λ_M = 102.3 Ω^{-1} cm^2 mol^{-1}. Anal. Found (calcd) for $\mathrm{C_{33}H_{40}Cl_2F_{10}N_2PtS}$: C, 41.76 (41.60); H, 4.12 (4.23); N, 2.80 (2.94).

$[\mathrm{NBu_4}][\mathrm{Pt(C_6F_5)_2(C_5H_4NS)Br_2}]$ (3b). To a solution of 1 (0.2 g, 0.23 mmol) in $\mathrm{CHCl_3}$ (10 mL) at 40–50 °C was added $\mathrm{Br_2}$ in $\mathrm{CCl_4}$ (0.23 mmol), and the mixture was stirred for 30 min. After it was cooled, the suspension was filtered off in order to eliminate a small amount of yellow solid.[9] The filtrate was evaporated to dryness. The resulting residue was subsequently treated with *i*-PrOH (10 mL), and after intensive stirring, a yellow solid separated, which was filtered off, washed with *n*-hexane (3 × 10 mL), and dried (**3b**: 0.2 g, 85% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 1635, 1589, 1558, 1266, 1157, 1142, 1066, 884, 755, 657, 490, 304. ^{1}H NMR ([^{2}H]acetone):[8] δ 8.74 [tdd, ^3J(H,H) = J(^{19}F,H) = 5.7 Hz, ^4J(H,H) = 1.5 Hz, ^5J(H,H) = 1.2 Hz, ^3J(^{195}Pt,H) = 30 Hz, 1H, 6-H], 7.64 [ddd, ^3J(3-H,4-H) = 8.4 Hz, ^3J(4-H,5-H) = 7.5 Hz, 1H, 4-H], 7.12 [ddd, ^4J(H,H) = 1.2 Hz, 1H, 5-H], 6.76 (d, 1H, 3-H). ^{13}C{^{1}H} NMR ([^{2}H]acetone):[8] δ 178.6 [s, ^2J(^{195}Pt,C) = 64 Hz, C2], 147.1 [d, J(^{19}F,C) = 3.3 Hz, C6], 138.1 (s, C5), 126.8 [s, ^3J(^{195}Pt,C) = 40.6 Hz, C3], 117.9 [s, ^4J(^{195}Pt,C) = 19.8 Hz, C4]. ^{19}F NMR ([^{2}H]chloroform): δ −110.89 [m$_c$, ^3J(^{195}Pt,F) = 163 Hz, 1F, *o*-F], −113.20 [m$_c$, ^3J(^{195}Pt,F) = 122 Hz, 1F, *o*-F], −117.09 [m$_c$, ^3J(^{195}Pt,F) = 172 Hz, 1F, *o*-F], −118.56 [m$_c$, ^3J(^{195}Pt,F) = 98 Hz, 1F, *o*-F], −161.13 (m$_c$, 1F, *p*-F), −162.66 (m$_c$, 1F, *p*-F), from −164.3 to −164.7 (m, 2F, *m*-F), −165.89 (m$_c$, 1F, *m*-F), −166.17 (m$_c$, 1F, *m*-F). FAB-MS: *m/z* 797 ($\mathrm{C_{17}H_4Br_2F_{10}NPtS^-}$). Λ_M = 96.0 Ω^{-1} cm^2 mol^{-1}. Anal. Found (calcd) for $\mathrm{C_{33}H_{40}Br_2F_{10}N_2PtS}$: C, 37.91 (38.05); H, 3.63 (3.87); N, 2.59 (2.69).

$[\mathrm{NBu_4}][\mathrm{Pt(C_6F_5)_2(C_5H_4NS)BrCl}]$ (3c). An excess of AgCl (83 mg, 0.58 mmol) was added to a solution of **3b** (0.3 g, 0.29 mmol) in $\mathrm{(CH_3)_2CO}$ (10 mL). After 4 days of stirring in the dark, the suspension was filtered off in order to eliminate silver halide. The filtrate was subsequently concentrated to dryness under vacuum. When the resulting residue was treated with $\mathrm{Et_2O}$ (10 mL), a yellow solid separated, which was filtered off, washed with *n*-hexane (3 × 10 mL), and dried (**3c**: 0.23 g, 80% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 1636, 1590, 1558, 1266, 1157, 1142, 1067, 883, 754, 658, 490, 317 (Pt–Cl), 291. ^{1}H NMR ([^{2}H]chloroform):[8] δ 8.67 [t, ^3J(H,H) = J(^{19}F,H) = 6.5 Hz, ^3J(^{195}Pt,H) = 28 Hz, 1H, 6-H], 7.48 [td, ^3J(H,H) = 83 Hz, ^4J(H,H) = 1.5 Hz, 1H, 4-H], 6.95 (t, 1H, 5-H), 6.64 (d, 1H, 3-H). ^{13}C{^{1}H} NMR ([^{2}H]acetone):[8] δ 178.2 [s, ^2J(^{195}Pt,C) = 67 Hz, C2], 145.8 [d, J(^{19}F,C) = 4.4 Hz, C6], 138.6 (s, C5), 126.5 [s, ^3J(^{195}Pt,C) = 41.2 Hz, C3], 117.7 [s, ^4J(^{195}Pt,C) = 19.8 Hz, C4]. ^{19}F NMR ([^{2}H]chloroform): δ −112.03 [m$_c$, ^3J(^{195}Pt,F) = 162 Hz, 1F, *o*-F], −117.85 [m$_c$, ^3J(^{195}Pt,F) = 127, 157 Hz, 2F, *o*-F], −122.36 [m$_c$, ^3J(^{195}Pt,F) = 88 Hz, 1F, *o*-F], −160.98 (m$_c$, 1F, *p*-F), −162.54 (m$_c$, 1F, *p*-F), −164.50 (m$_c$, 2F, *m*-F), −165.90 (m$_c$, 1F, *m*-F), −166.14 (m$_c$, 1F, *m*-F). FAB-MS: *m/z* 753 ($\mathrm{C_{17}H_4BrClF_{10}NPtS^-}$). Λ_M = 101.3 Ω^{-1} cm^2 mol^{-1}. Anal. Found (calcd) for $\mathrm{C_{33}H_{40}BrClF_{10}N_2PtS}$: C, 39.70 (39.75); H, 3.93 (4.04); N, 2.47 (2.81).

$[\mathrm{Pt(C_6F_5)_2(C_5H_4NS)(CN\text{-}\mathit{t}\text{-}C_4H_9)Cl}]$ (4a). This compound was prepared as described for **4b**, by starting from **3a** (0.2 g, 0.21 mmol), CN-*t*-$\mathrm{C_4H_9}$ (23 μL, 0.21 mmol), and $\mathrm{AgClO_4}$ (43.5 mg, 0.21 mmol). The reaction mixture needed 6 h of stirring in this case. **4a** was finally obtained as a yellow solid (80 mg, 50% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 2267 (C≡N), 1640, 1592, 1557, 1277, 1194, 1144, 1131, 1072, 880, 844, 760, 659, 533, 493, 424, 315 (Pt–Cl), 301. ^{1}H NMR ([^{2}H]chloroform): δ 8.21 [d, ^3J(H,H) = 5.4 Hz, ^3J(^{195}Pt,H) = 28 Hz, 1H, 6-H], 7.56 [td, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 0.8 Hz, 1H, 4-H], 7.04 (pseudo t, 1H, 5-H), 6.79 (d, 1H, 3-H), 1.66 (s, 9H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR ([^{2}H]chloroform): δ 178.8 [s, ^2J(^{195}Pt,C) = 66.7 Hz, C2], 145.4 (s, C6), 137.5 (s, C5), 128.1 [s, ^3J(^{195}Pt,C) = 35.9 Hz, C3], 118.7 [s, ^4J(^{195}Pt,C) = 19.2 Hz, C4], 61.3 (s, C≡N*C*), 29.6 (s, $\mathrm{CH_3}$). ^{19}F NMR ([^{2}H]chloroform): δ −115.79 [m$_c$, ^3J(^{195}Pt,F) = 145 Hz, 1F, *o*-F], −117.1 (br, 1F, *o*-F), −120.66 [m$_c$, ^3J(^{195}Pt,F) = 158 Hz, 1F, *o*-F], −122.05 (br, 1F, *o*-F), −157.23 (m$_c$, 1F, *p*-F), −158.09 (m$_c$, 1F, *p*-F), −160.9 (br, 1F, *m*-F), −161.85 (m$_c$, 1F, *m*-F), −162.85 (br, 1F, *m*-F), −163.90 (m$_c$, 1F, *m*-F). FAB-MS: *m/z* 722 ($\mathrm{C_{22}H_{13}F_{10}N_2PtS^+}$). Anal. Found (calcd) for $\mathrm{C_{22}H_{13}ClF_{10}N_2PtS}$: C, 35.66 (34.86); H, 1.9 (1.73); N, 3.81 (3.70).

$[\mathrm{Pt(C_6F_5)_2(C_5H_4NS)(CN\text{-}\mathit{t}\text{-}C_4H_9)Br}]$ (4b). To a $\mathrm{CH_2Cl_2}$ (10 mL) solution containing **3b** (0.2 g, 0.19 mmol) and CN-*t*-$\mathrm{C_4H_9}$ (25 μL, 0.23 mmol) was added $\mathrm{AgClO_4}$ (39.9 mg, 0.19 mmol). After

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(7) Relevant absorptions involving the pentafluorophenyl groups are to be found in Table IV.

(8) The ionic complexes always present signals corresponding to the $\mathrm{NBu_4^+}$ cation, which irrespective of the anion appear at about the following chemical shifts: ^{1}H NMR δ ~3.1 (m$_c$, 8H, α-$\mathrm{CH_2}$), 1.5 (m$_c$, 8H, β-$\mathrm{CH_2}$), 1.3 (m$_c$, 8H, γ-$\mathrm{CH_2}$), 0.9 [t, ^3J(H,H) = 7.2 Hz, 12H, $\mathrm{CH_3}$]; ^{13}C{^{1}H} NMR δ ~58.6 (br, C1), 23.7 (s, C2), 19.4 (s, C3), 13.3 (s, C4). There exists, however, some solvent dependence.

(9) The nature of this compound, which can be obtained in higher yields in other oxidation processes, is currently under study.

2 h of stirring in the dark, the suspension was filtered and the filtrate was evaporated to dryness. The resulting residue was treated with Et_2O (20 mL), giving rise to a suspension of a white solid (NBu_4ClO_4) in a yellow solution, which were separated by filtration. The filtrate was concentrated to dryness, and the residue obtained was treated with *n*-hexane (20 mL). After intensive stirring a yellow solid formed, which was filtered off and dried (**4b**: 0.11 g, 71% yield). IR (Nujol):[7] $\tilde{\nu}$ (cm^{-1}) 2267 (C≡N), 1640, 1592, 1556, 1277, 1191, 1144, 1131, 1073, 879, 845, 759, 659, 533, 491. ^{1}H NMR ([^{2}H]chloroform): δ 8.21 [d, ^3J(H,H) = 5.4 Hz, ^3J(^{195}Pt,H) = 28 Hz, 1H, 6-H], 7.55 [td, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.5 Hz, 1H, 4-H], 7.02 [ddd, ^4J(H,H) = 1.1 Hz, 1H, 5-H], 6.76 (d, 1H, 3-H), 1.67 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ([^{2}H]chloroform): δ 178.8 [s, ^2J(^{195}Pt,C) = 66 Hz, C2], 145.6 (s, C6), 137.4 (s, C5), 128.1 [s, ^3J(^{195}Pt,C) = 36 Hz, C3], 118.6 [s, ^4J(^{195}Pt,C) = 20 Hz, C4], 61.2 (s, C≡N*C*), 29.6 (s, CH_3). ^{19}F NMR ([^{2}H]chloroform): δ −113.75 [m$_c$, ^3J(^{195}Pt,F) = 154 Hz, 1F, *o*-F], −117.9 (br, 1F, *o*-F), −120.38 [m$_c$, ^3J(^{195}Pt,F) = 157 Hz, 1F, *o*-F], −122.4 (br, 1F, *o*-F), −157.36 (m$_c$, 1F, *p*-F), −158.31 (m$_c$, 1F, *p*-F), −160.9 (br, 1F, *m*-F), −162.11 (m$_c$, 1F, *m*-F), −163.0 (br, 1F, *m*-F), −163.97 (m$_c$, 1F, *m*-F). FAB-MS: *m/z* 801 ($C_{22}H_{13}BrF_{10}N_2PtS^+$). Anal. Found (calcd) for $C_{22}H_{13}BrF_{10}N_2PtS$: C, 33.17 (32.93); H, 1.56 (1.63); N, 3.58 (3.49).

X-ray Structure Determinations. Single crystals suitable for X-ray structure determinations of compounds **3b** and **4b** were grown by room-temperature slow diffusion of *n*-hexane layers (15 mL) on $CHCl_3$ solutions (3 mL) of the corresponding product (40 mg each). Preliminary examination and data collection were carried out with Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. Final cell constants were obtained by least-squares refinements of 25 automatically centered high-order reflections (34.9° < 2θ < 40.2° and 40.0° < 2θ < 43.8°, respectively). Data were collected by the ω-scan mode. Orientation control reflections were monitored every 200 reflections, and the intensities of three reflections were checked every 3600 s. Changes in intensities were not observed. All data were corrected for Lp and for absorption effects on the basis of a ψ scan (**3b**) or numerical data (**4b**). Detailed crystal data and intensity collection parameters together with details of the refinements are summarized in Table I. Both structures were solved by Patterson synthesis and subsequent difference Fourier maps. Full-matrix least-squares refinements were carried out by minimizing $\sum w(|F_o| - |F_c|)^2$. Final positional parameters are given in Tables II and III. Hydrogen atoms were included at their calculated positions (d_{C-H} 95 pm; $B_H = 1.3B_C$) but were not refined. The analysis was based on scattering factors for neutral atoms.[10a] Anomalous dispersion is considered.[10b] The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features. All calculations were performed on a MicroVAX 3100 computer with the STRUX-*IV* system,[11] including the programs SDP,[12] SHELX-76,[13] ORTEP-II,[14] and SCHAKAL.[15]

Table I. Summary of Crystal Data and Details of Intensity Collection and Refinement for [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)Br$_2$] (3b) and [Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)(CN-*t*-C$_4$H$_9$)Br] (4b)

	3b	4b
	Crystal data	
formula	$C_{33}H_{40}Br_2F_{10}N_2PtS$	$C_{22}H_{13}BrF_{10}N_2PtS$
fw	1041.6	802.4
cryst syst	monoclinic	triclinic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
cryst size, mm		0.23 × 0.31 × 0.32
cryst color and habit	orange prism	yellow block
a, pm	2186.0(13)	913.1(2)
b, pm	2088.6(4)	1085.1(2)
c, pm	1703.5(5)	1363.9(3)
α, deg	90	89.50(1)
β, deg	99.43(1)	72.82(2)
γ, deg	90	77.81(2)
V, 10^6 pm^3	7672	1260
Z	8	2
density (calcd), g cm^{-3}	1.804	2.115
μ(Mo Kα), cm^{-1}	58.8	73.6
transmissn factors (min/max)	0.776/1.000	0.155/0.294
F_{000}	4048	756
	Data Collection	
temp, K	293	223
monochromator	highly oriented graphite cryst	
scan time, s	variable; max 60	variable; max 60
scan width, det	1.10 + 0.30 tan θ	0.80 + 0.35 tan θ
2θ range, deg/octants	2.0–40.0/±*h*,−*k*,−*l*	2.0–50.0/*h*,*k*,±*l*
Bkgd	±25% additional scan at each end of scan	
no. of rflns collected	3641	4601
no. of indep rflns	3005	4227
R(merge)	0.025	0.012 (F_0)
no. of obsd rflns (NO)	3005 ($I > 0$)	4227 ($I > 0$)
	Solution and Refinement	
syst used	STRUX *IV*	
soln	heavy-atom methods	
refinement method	full-matrix least squares	
weighting scheme	$1/\sigma^2(F_0)$	$1/\sigma^2(F_0)$
params refined	217	335
R/R_w indices (all data)[a]	0.069/0.046	0.025/0.023
GOF,[b] *p*	3.905, 0.00	2.528, 0.00
data-to-param ratio	13.8:1	12.6:1
largest difference peak, e Å^{-3}	1.49	1.33 (near Pt)
largest difference hole, e Å^{-3}	−1.22	−0.98 (near Pt)
largest shift/err	<0.001	<0.001

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [b] GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Results

(a) Synthesis and Characterization of [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)] (1).

The dinuclear complex $[NBu_4]_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ reacts with LiC_5H_4NS in a 1:2 molar ratio according to Scheme I, giving rise to **1** as a yellow, air-stable solid in 73% yield. The IR spectrum of **1** shows the presence of two absorptions corresponding to the X-sensitive modes of vibration of the C_6F_5 group,[16] suggesting that a *cis* geometry is maintained.[17] This spectroscopic feature is common to all the complexes described in this paper (Table IV), and we will not refer to it from now on. The ^{1}H NMR signal corresponding to 6-H (δ 7.39) shows two broad shoulders, which can be assigned to not completely resolved platinum satellites (^3J(^{195}Pt,H) ≈ 30 Hz), thus suggesting that coordination takes place through the N atom. Since the molar conductivity of **1** in acetone falls in the range described for 1:1 electrolytes,[18] it seems sensible to conclude that, in this complex, the $C_5H_4NS^-$ ligand is acting as a chelate.[19] Accordingly, the ^{19}F NMR spectrum of **1** shows resonances due to two chemically nonequivalent C_6F_5 groups.

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Table II. Final Fractional Atomic Coordinates and Equivalent Temperature Factors for [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)Br$_2$] (3b)[a]

atom	*x*	*y*	*z*	B_{eq} (Å^2)[b]
Pt	0.30577(3)	0.30673(3)	0.24619(3)	4.01(1)
Br1	0.26991(10)	0.27100(10)	0.37066(10)	7.56(6)
Br2	0.25208(9)	0.41139(9)	0.26121(9)	6.03(5)
S	0.3141(2)	0.3355(2)	0.1143(2)	5.1(1)
F12	0.4366(4)	0.2705(4)	0.1915(4)	6.0(2)*
F13	0.4836(4)	0.1622(5)	0.1503(5)	7.5(3)*
F14	0.4200(5)	0.0514(5)	0.1551(5)	8.9(3)*
F15	0.3074(5)	0.0532(5)	0.2020(5)	8.1(3)*
F16	0.2586(4)	0.1602(4)	0.2437(5)	6.5(2)*
F22	0.3869(5)	0.4332(5)	0.2328(5)	8.9(3)*
F23	0.4835(6)	0.4835(7)	0.3198(7)	14.2(4)*
F24	0.5454(8)	0.4167(8)	0.4414(8)	17.3(5)*
F25	0.5025(6)	0.2914(8)	0.4754(7)	15.2(5)*
F26	0.4067(4)	0.2437(5)	0.3884(5)	7.7(3)*
N1	0.2259(5)	0.2839(6)	0.1671(6)	4.5(3)*
N2	0.2696(6)	0.0504(6)	0.4712(7)	5.5(3)*
C2	0.2415(6)	0.3035(7)	0.0975(7)	3.9(3)*
C3	0.1953(7)	0.3030(8)	0.0285(8)	5.2(4)*
C4	0.1398(8)	0.2782(9)	0.0358(9)	6.9(5)*
C5	0.1239(8)	0.2579(8)	0.1048(9)	6.2(4)*
C6	0.1708(7)	0.2602(8)	0.1738(8)	5.6(4)*
C11	0.3446(6)	0.2243(7)	0.2216(7)	3.8(3)*
C12	0.4028(6)	0.2182(7)	0.1977(7)	4.1(4)*
C13	0.4274(7)	0.1615(7)	0.1752(8)	4.9(4)*
C14	0.3945(8)	0.1084(8)	0.1777(9)	5.9(4)*
C15	0.3401(7)	0.1084(8)	0.2001(8)	5.6(4)*
C16	0.3178(7)	0.1650(7)	0.2250(7)	4.4(4)*
C21	0.3883(7)	0.3366(8)	0.3108(8)	5.4(4)*
C22	0.4101(7)	0.3980(8)	0.2940(8)	5.9(4)*
C23	0.4722(9)	0.4280(10)	0.3504(10)	8.9(6)*
C24	0.4870(10)	0.3792(11)	0.3952(11)	10.8(7)*
C25	0.4887(11)	0.3308(12)	0.4258(13)	12.8(8)*
C26	0.4235(7)	0.2992(8)	0.3735(9)	6.4(4)*
C211	0.3096(9)	0.0728(10)	0.5473(11)	9.6(6)*
C212	0.3517(9)	0.1268(9)	0.5353(10)	8.4(5)*
C213	0.3897(11)	0.1427(12)	0.6172(12)	12.6(8)*
C214	0.4320(14)	0.1931(15)	0.6159(15)	17.7(10)*
C221	0.2441(10)	−0.0145(9)	0.4910(10)	8.6(5)*
C222	0.1923(8)	−0.0096(8)	0.5426(9)	6.8(5)*
C223	0.1762(10)	−0.0725(10)	0.5716(11)	9.5(6)*
C224	0.1278(10)	−0.0698(11)	0.6225(1)	10.4(6)*
C231	0.2257(9)	0.0977(9)	0.4404(10)	8.3(5)*
C232	0.1748(10)	0.0784(10)	0.3776(11)	9.7(6)*
C233	0.1209(14)	0.1263(15)	0.3527(16)	18.1(11)*
C234	0.0767(21)	0.1213(23)	0.3792(23)	31.2(20)*
C241	0.3103(9)	0.0326(10)	0.4061(10)	9.0(6)*
C242	0.3600(9)	−0.0104(10)	0.4251(11)	9.0(6)*
C243	0.4046(12)	−0.0089(11)	0.3645(13)	12.8(8)*
C244	0.4453(15)	−0.0527(15)	0.3780(16)	19.2(12)*

[a] Estimated standard deviations are given in parentheses. The starred values denote atoms refined isotropically. [b] Equivalent isotropic B_{eq} defined as $B_{eq} = {}^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)]$.

(b) Reactions of 1 with CO, SC$_4$H$_8$, or P(C$_6$H$_5$)$_3$. A dichloromethane solution of 1 does not react with CO under normal conditions, as evidenced by IR spectroscopy. After prolonged treatment, only unaltered starting material can be recovered. Similar attempts to coordinate SC$_4$H$_8$ to substrate 1 also failed. On the other hand, 1 reacts with P(C$_6$H$_5$)$_3$, giving rise to [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS){P(C$_6$H$_5$)$_3$}] (2) in high yield as an air-stable, yellow solid, according to Scheme I. The signal assigned to 6-H in its ^{1}H NMR spectrum (δ 7.77) shows no evidence of ^{195}Pt satellites, which can be considered as an indication of S vs N coordination of the C$_5$H$_4$NS$^-$ anion according to the soft character of both the donor atom and the metal center.[20]

Table III. Final Fractional Atomic Coordinates and Equivalent Temperature Factors for [Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)(CN-*t*-C$_4$H$_9$)Br] (4b)[a]

atom	*x*	*y*	*z*	B_{eq} (Å^2)[b]
Pt	0.51728(2)	0.26521(2)	0.18917(1)	1.901(3)
Br	0.68173(5)	0.30742(5)	0.01306(3)	3.31(1)
S	0.4746(1)	0.0789(1)	0.12224(8)	3.14(2)
F11	0.8094(3)	0.0261(3)	0.1100(2)	4.22(7)
F12	1.0515(3)	−0.0681(3)	0.1769(2)	4.75(7)
F13	1.0944(3)	0.0447(3)	0.3396(2)	5.23(7)
F14	0.8835(3)	0.2563(3)	0.4356(2)	5.09(7)
F15	0.6383(3)	0.3516(2)	0.3737(2)	3.36(6)
F21	0.5221(3)	0.0151(2)	0.3251(2)	3.02(6)
F22	0.3393(3)	−0.0262(2)	0.5060(2)	3.92(6)
F23	0.1103(3)	0.1634(3)	0.6223(2)	5.02(8)
F24	0.0612(4)	0.3940(3)	0.5472(2)	5.44(8)
F25	0.2305(3)	0.4381(2)	0.3595(2)	4.13(7)
N1	0.5134(4)	0.5448(3)	0.2419(2)	2.73(8)
N2	0.3184(4)	0.3030(3)	0.1400(2)	2.56(8)
C1	0.5193(4)	0.4409(4)	0.2267(3)	2.28(9)
C2	0.5052(5)	0.6782(4)	0.2673(3)	3.1(1)
C3	0.5475(7)	0.6809(5)	0.3649(4)	6.6(1)
C4	0.3382(7)	0.7488(5)	0.2802(5)	6.2(2)
C5	0.6186(8)	0.7231(5)	0.1756(5)	7.4(2)
C11	0.8239(5)	0.0892(4)	0.1895(3)	2.7(1)
C12	0.9496(5)	0.0379(4)	0.2236(3)	3.1(1)
C13	0.9713(5)	0.0948(4)	0.3061(3)	3.3(1)
C14	0.8663(5)	0.2000(4)	0.3534(3)	3.1(1)
C15	0.7393(4)	0.2487(4)	0.3193(3)	2.42(9)
C16	0.7129(4)	0.1974(4)	0.2339(3)	2.08(8)
C21	0.4064(4)	0.1127(4)	0.3747(3)	2.20(8)
C22	0.3141(5)	0.0900(4)	0.4704(3)	2.63(9)
C23	0.1993(5)	0.1838(4)	0.5279(3)	3.2(1)
C24	0.1738(5)	0.3005(4)	0.4899(3)	3.2(1)
C25	0.2643(5)	0.3205(4)	0.3928(3)	2.7(1)
C26	0.3837(4)	0.2290(4)	0.3317(3)	2.13(9)
C31	0.3167(5)	0.1871(4)	0.1062(3)	3.2(1)
C32	0.1993(5)	0.1693(5)	0.0641(3)	4.3(1)
C33	0.0860(5)	0.2735(6)	0.0612(4)	5.2(1)
C34	0.0885(6)	0.3919(6)	0.0952(4)	5.2(1)
C35	0.2101(5)	0.4037(5)	0.1344(4)	4.1(1)

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic B_{eq} defined as $B_{eq} = {}^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + bc(\cos\alpha)\beta(2,3) + ac(\cos\beta)\beta(1,3) + ab(\cos\gamma)\beta(1,2)]$.

(c) Oxidative Addition of X$_2$ (X = Cl, Br) to 1. Treatment of chloroform solutions of 1 at either room temperature (X = Cl) or 40 °C (X = Br) with the stoichiometrically required amount of X$_2$ in CCl$_4$ solution affords [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)X$_2$] (X = Cl (**3a**), Br (**3b**)), according to Scheme I. Both complexes can be isolated as air-stable, yellow solids in high yields and behave as 1:1 electrolytes in acetone solution. Their IR spectra show a noticeable shift of both the ν(C—C) and the ν(C—F) modes of vibration toward higher frequencies (Table IV), in accord with an increase in the oxidation state of the metal center.[1] The ^{1}H NMR spectra of **3a** and **3b** show only one type of C$_5$H$_4$NS$^-$ ligand, which means that a single diastereomer is present. Since the analysis of all available spectroscopic data did not allow us to distinguish between isomers *OC*-6-42 and *OC*-6-43, the structure of **3b** was determined by X-ray diffraction methods.[21]

The stereo geometry of the anionic platinum complex **3b** is illustrated in Figure 1. Relevant bond parameters are listed in Table V. The anion shows octahedral geometry around the platinum atom. As shown in Figure

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[19] The crystal structure of [NBu$_4$][Ni(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)] has been determined by X-ray diffraction methods: López, G.; Sánchez, G.; García, G.; García, J.; Martínez, A.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1992**, *435*, 193.

[20] Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265.

[21] The quality of the X-ray refinement is affected by high thermal motion or disorder of the γ- and δ-carbon atoms in the tetra-*n*-butylammonium cation. Lowering the temperature results in twinning of the crystal.

Scheme I

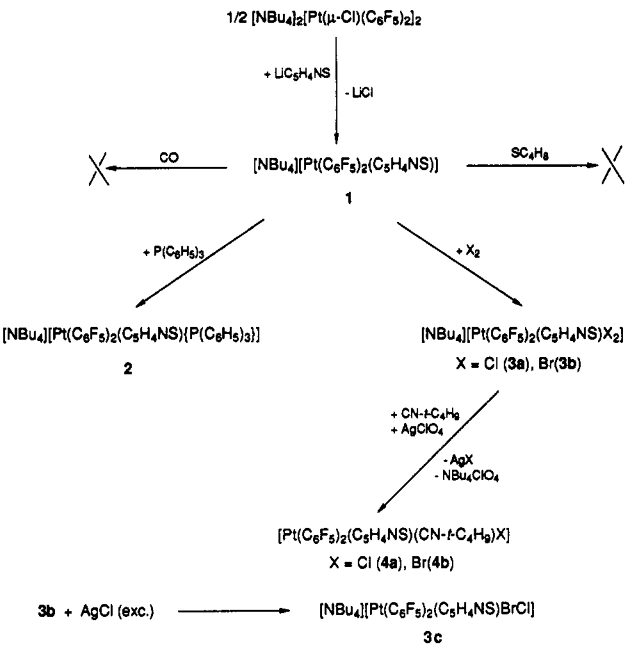

Table IV. IR Data (cm^{-1}) Relevant to the Pentafluorophenyl Groups[a]

complex	X-sensitive[b]	ν(C–C)	ν(C–F)
1	803, 793	1500	956
2	791, 777	1495	951
3a	801, 793	1505	969
3b	799, 790	1505	965
3c	800, 791	1506	968
4a	802, 795	1514	970
4b	801, 794	1515	971

[a] All the remaining absorptions appear listed for each complex in the Experimental Section. [b] See ref 16.

1a, the equatorial plane defined by the atoms Br1, N1, S, and C21 and the $C_5H_4NS^-$ ring are nearly coplanar (interplanar angle 4.7°). The Pt atom is 5 pm out of the equatorial plane on the side of the C_6F_5 ligand. Although the bromo ligands are not expected to be electronically equivalent due to their different *trans* ligands, only very slight differences in the Pt–Br distances can be observed (Pt–Br1 = 249.3(1) pm; Pt–Br2 = 251.4(1) pm). The difference between the Pt–C(phenyl) distances is also negligible. As shown from the space-filling model in Figure 1b, the rigidity of the C_6F_5 groups toward the rotation around Pt–C is strictly evident. The F16···C6 interatomic distance (295.3 pm) is slightly shorter than the sum of the van der Waals radii (310 pm), the F16···H16 distance (272.5 pm) being, in turn, longer than the corresponding radii (240 pm).[22] Recently, Perutz and co-workers[23] have prepared and characterized the complexes $[Ir(\eta^5\text{-}C_5R_5)(\eta^2\text{-}C_6F_6)(C_2H_4)]$ (R = H, CH_3). The distance between the ethene carbon atoms and the F substituents attached to the η^2-coordinated double bond of the C_6F_6 ring in the solid state (C···F = 287(2) pm) together with the $^{19}F,^{1}H$ and $^{19}F,^{13}C$ couplings between them observed in solution by NMR spectroscopy have been considered by these authors as enough evidence of the existence of very close C–H···F contacts.

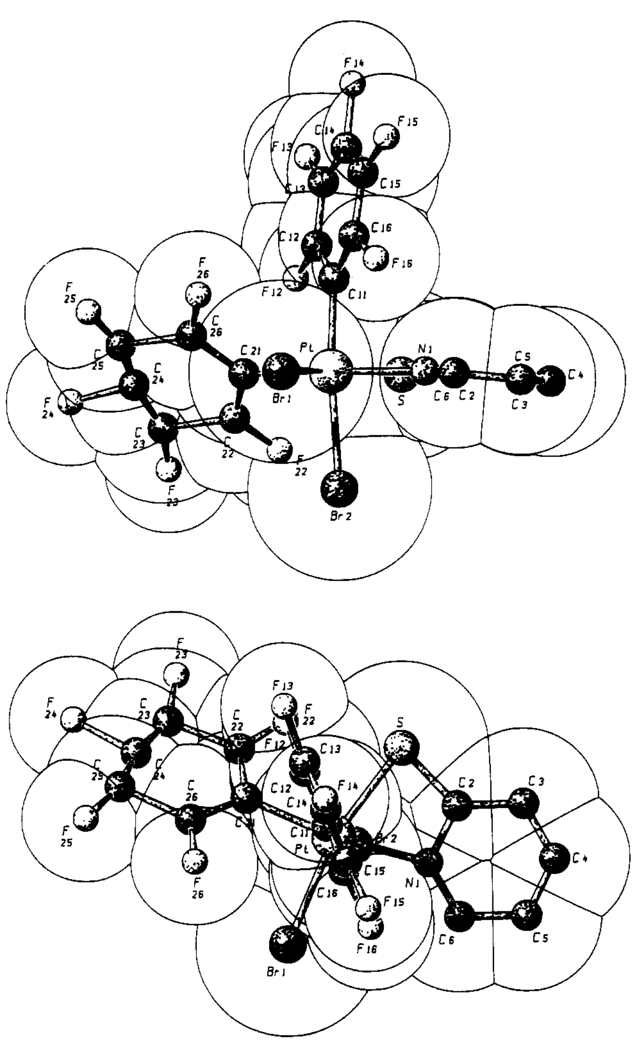

Figure 1. Space-filling model corresponding to the anion of **3b**: (a, top) side view; (b, bottom) top view.

Table V. Selected Interatomic Distances (pm) and Angles (deg) for $[NBu_4][Pt(C_6F_5)_2(C_5H_4NS)Br_2]$ (3b) and for $[Pt(C_6F_5)_2(C_5H_4NS)(CN\text{-}t\text{-}C_4H_9)Br]$ (4b)

3b		4b	
Pt–Br1	249.3(1)	Pt–C1	198.4(3)
Pt–Br2	251.4(1)	Pt–Br	252.5(<1)
Pt–S	236.1(2)	Pt–S	237.6(1)
Pt–N1	207.9(6)	Pt–N2	207.8(2)
Pt–C11	199.4(8)	Pt–C26	205.1(3)
Pt–C21	205.1(8)	Pt–C16	204.5(3)
Br1–Pt–Br2	87.51(3)	C1–Pt–Br	84.80(7)
Br1–Pt–S	165.85(7)	C1–Pt–S	166.39(7)
Br1–Pt–N1	97.77(18)	C1–Pt–N2	98.52(10)
Br1–Pt–C11	97.15(21)	C1–Pt–C26	95.83(10)
Br1–Pt–C21	90.34(23)	C1–Pt–C16	90.87(10)
Br2–Pt–S	89.16(6)	Br–Pt–S	90.83(2)
Br2–Pt–N1	84.79(17)	Br–Pt–N2	89.92(6)
Br2–Pt–C11	173.71(19)	Br–Pt–C26	179.38(7)
Br2–Pt–C21	93.71(25)	Br–Pt–C16	91.78(7)
S–Pt–N1	68.22(18)	S–Pt–N2	68.52(7)
S–Pt–C11	85.30(21)	S–Pt–C26	88.55(7)
S–Pt–C21	103.61(24)	S–Pt–C16	102.16(7)
N1–Pt–C11	90.39(27)	N2–Pt–C26	89.95(9)
N1–Pt–C21	171.67(30)	N2–Pt–C16	170.56(10)
C11–Pt–C21	90.49(33)	C26–Pt–C16	88.25(10)

A magnetic F16···C6–H interaction has also been found to be present in **3a** and **3b**. Selective ^1H decoupling at the frequency characteristic of 6-H (**3b**: δ 8.74) makes the *o*-F signal at −117.09 ppm lose one of its coupling constants. The reverse experiment further confirms that both nuclei are coupled. Similarly, the fact that the signals assigned

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to C6 in the ^{13}C NMR spectra of **3a** and **3b** appear as doublets is actually due to a ^{19}F,^{13}C coupling, as revealed by double-irradiation experiments performed on a sample of **3b**. Considering the large number of bonds connecting any of the *o*-F atoms with 6-H (n = 6) or C6 (n = 5), the extra splittings observed in the NMR signals of these nuclei could reasonably be due to "through-space" couplings. This would imply that the anions of **3a** and **3b** would have a remarkably rigid structure even in solution at room temperature. When the temperature is raised, however, this magnetic interaction seems to weaken until it completely disappears, as evidenced by high-temperature ^{1}H NMR measurements (**3a**, [^{2}H]dimethyl sulfoxide). The 6-H signal gradually broadens and at 100 °C becomes a normal doublet with no sign of ^{19}F,^{1}H coupling. This experimental observation is consistent with a "through-space" ^{19}F,^{1}H coupling, which would vanish by rotation of the corresponding C$_6$F$_5$ group.

(d) Substitution Reactions on 3a and 3b. **3b** reacts with an excess of AgCl, giving rise to [NBu$_4$][Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)BrCl] (**3c**) in good yield (80%), according to Scheme I. On the other hand, **3a** and **3b** react with the stoichiometric amount of CN-*t*-C$_4$H$_9$ in the presence of AgClO$_4$ to give [Pt(C$_6$F$_5$)$_2$(C$_5$H$_4$NS)(CN-*t*-C$_4$H$_9$)X] (X = Cl, (**4a**), Br (**4b**)), which can be isolated as yellow, air-stable solids in high yields (Scheme I).

The stereo geometry of the neutral platinum complex **4b**, as determined by single-crystal X-ray experiments, is illustrated in Figure 2. Relevant bond parameters are listed in Table V. The molecule shows octahedral geometry around the platinum atom, very similar to that found in **3b**. As shown in Figure 2a, the equatorial plane defined by the atoms C1, N2, S, and C16 and the C$_5$H$_4$NS$^-$ ring are coplanar (interplanar angle 1.3°) within the esd's. The Pt atom fits these planes. As observed in **3b**, the Pt–C(phenyl) distances are comparable to normal Pt–C(sp^2) single bonds[24] (sum of the covalent radii 207 pm).

In contrast, the Pt–C1 bond is shortened and the value of 198.4 pm can be explained in terms of a partial double bond.[25] Bond distances Pt–C below 200 pm are normally observed in Pt–carbene compounds. All other Pt–ligand distances are normal.[26] Similar to **3b**, the C$_6$F$_5$ groups are rigid toward the rotation around the Pt–C(phenyl) bond (Figure 2b). The F25···C35 interatomic distance (316.0 pm) is in this case slightly longer than the sum of the van der Waals radii, and the F35···H351 distance is 283.5 pm (cf. X-ray structure of **3b**). These differences in the solid-state structures of complexes **3b** and **4b** could be related to the more mobile character of the apical C$_6$F$_5$ group observed in solution for the latter compound (see below).

The ^{19}F NMR spectrum of **3c** is similar to those discussed for complexes **3a** and **3b** and is in accord with the existence of two chemically nonequivalent C$_6$F$_5$ groups whose rotation about the Pt–C bond is constrained. An analogous situation is also observed for complexes **4** at low temperature (–60 °C). However, raising the temperature causes the coalescence of two pairs of resonances, each corresponding to *o*- and *m*-F, respectively, while all other signals remain unaltered. Additionally, the triplet observed in the ^{1}H NMR spectrum of **4a** at –60 °C assignable to 6-H (δ 8.21) changes into a doublet at room temperature. These facts are also consistent with the above-mentioned behavior of **3a** both at room temperature and at 100 °C. The noticeable lowering in the activation barrier for the rotation of the axial C$_6$F$_5$ group as one goes from **3a** to **4a** could be related to the smaller size of the C≡N end of the CN-*t*-C$_4$H$_9$ ligand compared with that of bromine (van der Waals radii: C, 170 pm; Br, 200 pm).[22] However, electronic factors relying on the existence of some degree of double-bond character in M–C$_6$F$_5$ bonds which could be affected by the total charge of the complex as well as by the different donating abilities of the CN-*t*-C$_4$H$_9$ and Br ligands cannot be excluded either.[27]

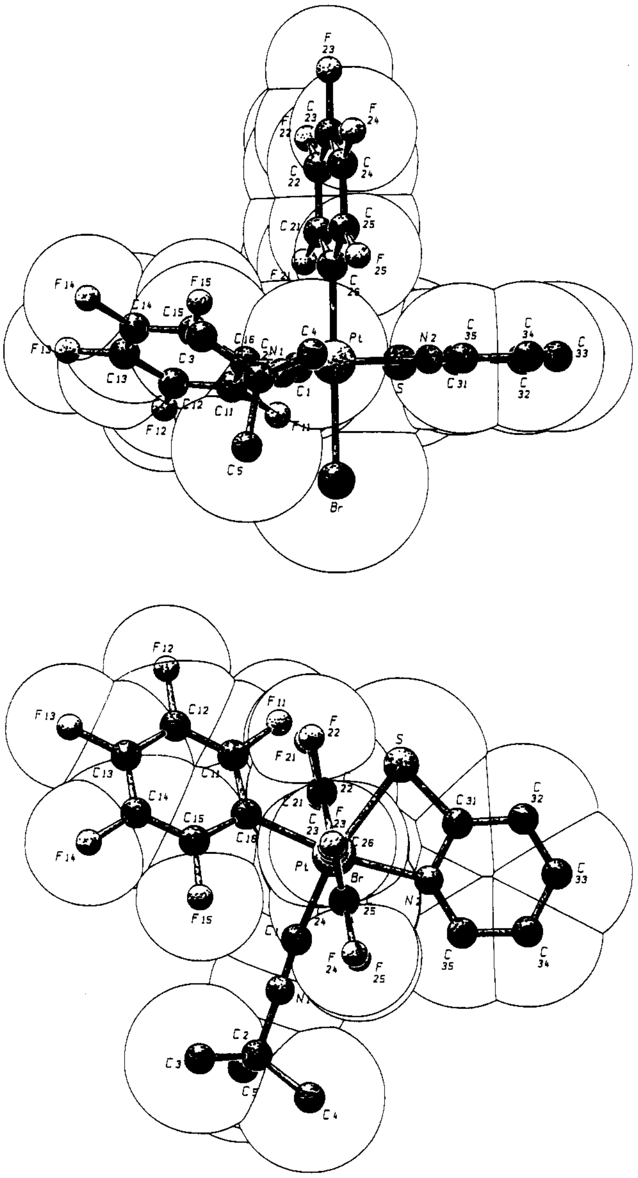

Figure 2. Space-filling model of **4b**: (a, top) side view; (b, bottom) top view.

Discussion

Complex **1** has been synthesized in high yield by simple metathetical methods. The stability of the chelating

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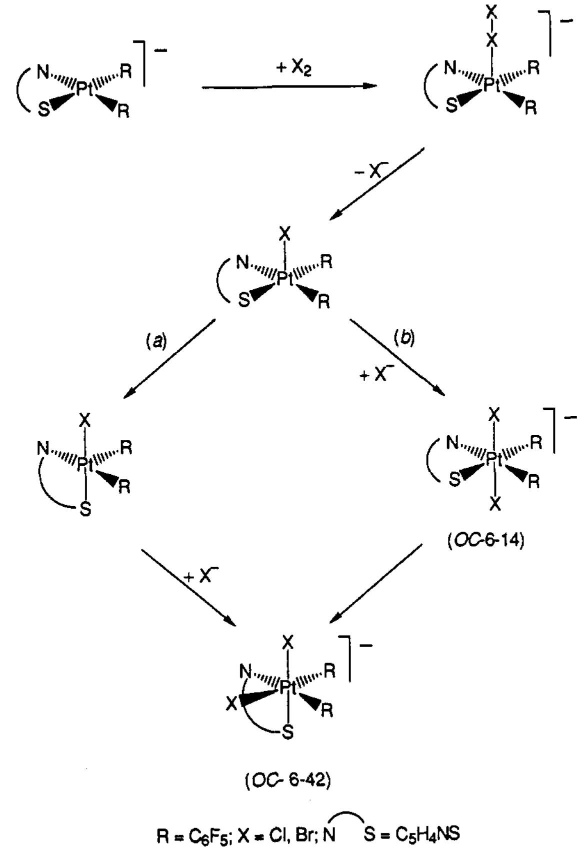
Scheme II



function $C_5H_4NS^-$ on the "*cis*-$Pt(C_6F_5)_2$" fragment has been tested by performing reactions of **1** with various monodentate ligands. The results suggest a moderate strength of the chelate $C_5H_4NS^-$ ligand. The behavior of **1** with Cl_2 and Br_2 was subsequently investigated. Remarkably, these oxidative-addition reactions take place stereoselectively.

The most widely accepted mechanism in oxidative-addition reactions of halogens on square-planar platinum(II) complexes (Scheme II, path b) is that originally formulated by Skinner and Jones[28a] in 1969 as the logical extension of earlier proposals to explain halide-assisted reductive-elimination processes on platinum(IV) substrates.[29] The first step involves a linear adduct between the metal complex and the halogen molecule formed by donation of electron density *from* the metal *to* the X_2 molecule.[28] The anionic nature of the Pt center in **1** should reasonably enhance its donor ability,[30] thus favoring the start of the process.

The subsequent steps in the general scheme for oxidative addition of halogens to platinum(II) substrates (Scheme II, path b) assumes the release of an X^- ion, yielding a five-coordinate platinum(IV) intermediate, whose vacant coordination site can be occupied by either a (donor) solvent molecule or another X^- ion. The whole process should therefore result in a *trans* addition of the halogen. In our case, however, instead of isomer *OC*-6-14 the pair of *OC*-6-42 enantiomers was solely obtained. This result means either that the halogen molecule adds at once in a concerted fashion at *cis* positions or that isomerization must follow some of the proposed steps for the S_N2 mechanism. We tried to find some experimental evidence which could help us to distinguish between these possible reaction pathways. We focused on bromination reactions because they are well-behaved and considered to proceed more smoothly and slowly than chlorinations.

We can start by assuming that the oxidative addition of halogen to **1** takes place in a concerted fashion. Under this assumption, bromination of **1** in the presence of chloride anions should exclusively give[31] products derived from simple halide substitution on already formed **3b**. The nature of the expected substitution products can easily be determined by means of a blank experiment. Consequently, we reacted **3b** with $NEt_3Bz^+Cl^-$ in a 1:1 molar ratio ([^{2}H]chloroform, 50 °C, 30 min) and found (^{19}F NMR) the appearance of a single new product, **3c**, whose integrated abundance relative to the remaining unreacted **3b** was 1.8:1. Pure **3c** could conveniently be obtained and isolated as depicted in Scheme I, and it could be characterized as one of the isomers having the stoichiometry $[NBu_4][Pt(C_6F_5)_2(C_5H_4NS)BrCl]$. Noticeably, halide substitution on **3b** seems to proceed specifically at a certain position.[32] The same behavior can be observed in related substitution reactions using the neutral CN-*t*-C_4H_9 as the incoming ligand. With either **3a** or **3b** as starting material, the corresponding neutral complex **4a** or **4b** can respectively be obtained (Scheme I). The X-ray structure of **4b** (Figure 2) reveals that substitution has taken place at the equatorial bromide of the parent complex, which can be considered as evidence that the halogen *trans* to sulfur is substantially more labile than the one *trans* to the C_6F_5 group. By comparison, it can reasonably be inferred that the geometry of **3c** is most probably that corresponding to the pair of *OC*-6-53 enantiomers.

Once the effect of chloride substitution on **3b** was experimentally determined, we performed the bromination of **1** in the presence of $NEt_3Bz^+Cl^-$ (1:1) under the above-described conditions. The ^{19}F NMR spectrum of the reaction mixture was found to contain signals corresponding not only to **3c** and **3b** but also to **3a** in the integrated ratios 3.5:2:1. The presence of **3a** as a reaction product, yet in a small amount, is very significant because it allows us to exclude the possibility of a concerted mechanism. We are therefore left with the classical S_N2 reaction pathway, including an additional isomerization step to explain the *cis* arrangement of the halogen atoms in the final product. Aiming to detect whether isomer *OC*-6-14 is actually the first product formed, which undergoes

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(31) Formation of the polyhalide anion Br_2Cl^- cannot be excluded. This aggregate, however, would not be expected to oxidatively add to **1**, since its very formation would imply the deactivation of the oxidant. Further complications due to formation of the unstable interhalogen molecule BrCl also seem improbable, as polyhalide anions are prone to dissociate by setting free the smallest (and also the most electronegative) halide, *i.e.*: $Br_2Cl^- \rightleftarrows Br_2 + Cl^-$. The existence of this equilibrium would not essentially affect the interpretation of the results under discussion. Downs, A. J.; Adams, C. J. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, U.K., 1973; Vol. 2, Chapter 26, pp 1534–1556. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, U.K., 1984; pp 964–983.

(32) The reaction of **3a** with NBu_4Br performed under similar conditions, as suggested by one of the reviewers is in turn far from specific. Substitution takes place at either or both chloride positions, yielding a complex mixture containing small amounts of **3a**, **3b**, and **3c** together with the major product, which can be reasonably assigned to the isomer $[(OC\text{-}6\text{-}35)\text{-}Pt(C_6F_5)_2(C_5H_4NS)BrCl]^-$ (**3c′**). This is but a tentative assignment, since **3c′** could not be isolated and independently characterized.

further isomerization, we performed the bromination of 1 at −78 °C in a typical nonaqueous coordinating solvent ($[^2H]$tetrahydrofuran) and in the presence of $NBu_4^+Br^-$ (1:1). Still at this temperature, however, isomer *OC*-6-42 was the only product detectable by ^{19}F NMR spectroscopy, meaning that the isomerization process requires an extremely low activation energy. This would suggest that isomerization could occur at the five-coordinate Pt(IV) intermediate (Scheme II, path a) rather than at the coordinatively saturated species *OC*-6-14, which would in any event require prior ligand dissociation (Scheme II, path b). Moreover, the isomerization process seems clearly not to be driven by steric reasons, since the bulkiest ligands, *i.e.* the C_6F_5 groups, maintain their mutually *cis* position both in isomer *OC*-6-14 and in isomers *OC*-6-42. A plausible way to rationalize the experimental results just discussed is provided by the reaction sequence depicted in Scheme II, path a.

Conclusion

From our study on oxidation reactions of $[NBu_4][Pt(C_6F_5)_2(C_5H_4NS)]$ with chlorine or bromine it can be concluded that the oxidative addition of halogens to 1 does not take place in a concerted fashion in spite of the *cis* arrangement of the halide substituents in the final product. Considering the selectivity of the process, an S_N2 mechanism including an isomerization step seems more likely to be operative.

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Supplementary Material Available: Tables of positional parameters for the hydrogen atoms, anisotropic temperature parameters, and bond distances and angles and ORTEP drawings for compounds **3b** and **4b** (26 pages). Ordering information is given on any current masthead page.

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