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Metal Complexes of Functionalized Sulfur-Containing Ligands, VII[1]

Synthesis of Platinum(II) Alkane- and Arenethiosulfinato Complexes – Crystal Structure Analysis of *N*-[(Benzylsulfinyl)thio]phthalimide

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The oxidative addition of *N*-[(alkyl- and arylsulfinyl)thio]-phthalimides **3a–d** to $Pt(PPh_3)_2(C_2H_4)$ gives the platinum(II) thiosulfinato complexes *cis*-$Pt[(S-S(O)-R)(Nphth)(PPh_3)_2]$ **4a–d**; the structure of *N*-[(benzylsulfinyl)thio]phthalimide (**3c**) has been characterized by *X*-ray crystallography.

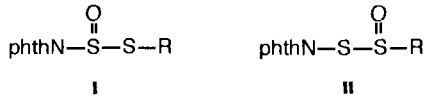
The synthesis and investigation of thiosulfinic *S*-esters R–S(O)–S–R′ (thiosulfinates) have received much attention in recent years. The impetus stems from the observation that some of these compounds cause inhibition of the enzymes cyclooxygenase and 5-lipoxygenase[2]. However, the corresponding free thiosulfinic acids R–S(O)–SH could yet not be isolated. Some relatively stable salts of thiosulfinic acids containing bulky substituent groups have been synthesized by Mikołajczyk et al.[3]. Shaver et al.[4] and we[5,6] have recently prepared for the first time stable thiosulfinato complexes of ruthenium(II) by the reaction of *N*-(alkyl- and arylsulfinyl)phthalimides phthN–S(O)–R (phthN = phthalimido) with $C_5H_5Ru(L)(PPh_3)(SH)$ (L = CO, PPh_3).

In this paper we report on the synthesis, characterization, and X-ray analysis of *N*-[(sulfinyl)thio]phthalimides phthN–S–S(O)–R and their oxidative addition to $Pt(PPh_3)_2(C_2H_4)$ resulting in novel platinum(II) thiosulfinato complexes.

Results and Discussion

A benzene solution of *N,N′*-thiobis(phthalimide) (**1**) has been treated with thiols to give the phthalimido disulfides **2a–d**[7] which have been oxidized by *m*-chloroperbenzoic acid (*m*CPBA) according to the procedure published by Harpp[8]. Two regioisomers of **3** are formed as a result of oxidation either at the sulfur atom bound to the nitrogen atom (regioisomer **I**) or at the sulfur atom bound to alkyl or aryl groups (regioisomer **II**). Originally, formation of **I** has been proposed[8]. IR spectra (see Experimental) are not diagnostic; in fast-atom bombardment mass spectra (FAB MS) two fragments are observed which could arise from regioisomer **I** $[phthN-S(O)]^+$ (*m/z* = 194) and regioisomer **II** $[phthN-SH+H]^+$ (*m/z* = 180). ^1H- and ^{13}C-NMR spectra (see Experimental) do not discriminate between the structures **I** and **II**, but they exclude a mixture of **I** and **II**.

An X-ray structural analysis[9] of **3c** proves the formation of regioisomer **II** (Figure 1). The sulfur-sulfur bond lengths [molecule A: 214.0(2), molecule B: 215.2(2) pm] of **3c** are slightly longer than



those in tol–S(O)–S–tol (tol = *p*-$CH_3C_6H_4$) [210.8(2)/212.4(3) pm][10] and in Ph–S–S(O)–S–Ph [212.4/214.1(2) pm][10], respectively, but significantly longer than the sulfur-sulfur bond in acyclic disulfides[11]. The sulfur-oxygen bond lengths [molecule A: 147.7(5), molecule B: 148.7(6) pm] are similar to those in thiosulfinates[10], sulfoxides[12], and thiosulfinato complexes[4–6]. The dihedral angles C(1)–S(1)–S(2)–N(1) and C(16)–S(3)–S(4)–N(2) (158.3°/145.6°) are comparable to those found in tol–S(O)–S–tol[10] and $(\eta^5-C_5H_5)Ru(PPh_3)_2[S-S(O)-CH_2Ph]$[5,6].

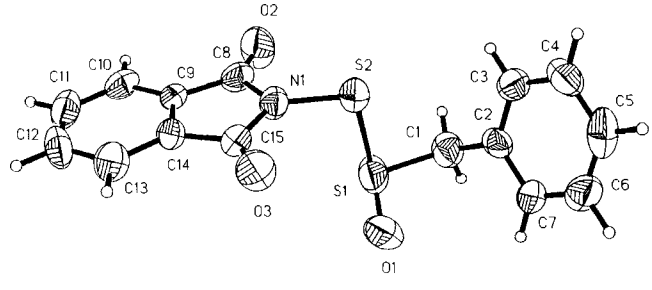


Figure 1. Molecular structure of **3c** in the crystal. Selected bond distances [pm] and angles [°]: S(1)–S(2) 214.0(2), S(3)–S(4) 215.2(2), S(1)–O(1) 147.7(5), S(3)–O(4) 148.7(6), S(2)–N(1) 170.4(5), S(4)–N(2) 170.0(5); S(2)–S(1)–O(1) 109.8(2), S(4)–S(3)–O(4) 110.4(2), S(1)–S(2)–N(1) 96.9(2), S(3)–S(4)–N(2) 97.1(2), S(2)–S(1)–C(1) 95.9(2) S(4)–S(3)–C(16) 96.2(2)

The oxidative addition of the *N*-[(sulfinyl)thio]phthalimides **3a–d** to $Pt(PPh_3)_2(C_2H_4)$ in toluene yields the platinum(II) thiosulfinato complexes **4a–d**; the formation of the cationic species $[Pt(PPh_3)_2(Nphth)SH]^+$ (*m/z* = 897) and $[Pt(PPh_3)_2(Nphth)H]^+$

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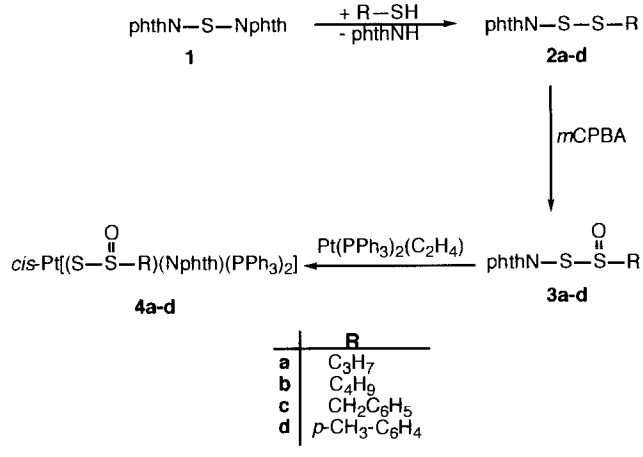
(*m/z* = 865) in the FAB MS[12] is an important evidence for the cleavage of the sulfur-nitrogen instead of the sulfur-sulfur linkage. The ν(S=O) absorption band occurs in a range similar to that of the compounds $(C_5H_5)Ru(L)(PPh_3)[S-S(O)-R]$ (L = CO, PPh_3) [ν(S=O) 1020–1030 cm^{-1}][4–6]. The ^{31}P-NMR spectra (see Experimental) exhibit an AB spin system; this non-equivalence of the phosphorus atoms in **4a–d** proves the *cis* geometry of these complexes.



The formation of complexes **4a–d** is a very important evidence that the oxidation of the phthalimido disulfides **2a–d** yields exclusively the regioisomer **II**.

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Experimental

The experiments yielding **4a–d** were performed under dry, oxygen-free nitrogen in distilled solvents. – IR (KBr): Nicolet ZDX 5. – ^1H NMR (internal standard TMS), ^{13}C NMR (internal standard TMS), ^{31}P NMR (external standard 85% aqueous H_3PO_4): (a): Jeol FX 90, (b): Jeol GSX 270, (c): Jeol EX 400. – FAB MS: VG-ZAB-VSEQ spectrometer[13].

Preparation of the N-[(Alkyl- and Arylsulfinyl)thio]phthalimides **3a–d**: A solution of 60% *m*CPBA (6 mmol) in 30 ml of dichloromethane was added dropwise and with stirring during 30 min to an ice-cold solution of the phthalimido disulfides[7] **2a–d** (6 mmol) in 20 ml of dichloromethane. Stirring and cooling were continued for 45 min, after which time the solvent was evaporated at 0°C in vacuo. The resulting white solid was triturated five times with 10 ml of ice-cold ether (**3c,d**) or −50°C cold ether (**3a,b**), respectively. Recrystallization of the residue from dichloromethane/ether at 0–4°C gave colourless crystals, which were dried in vacuo. Compounds **3a,b** had to be stored at −20°C.

N-[(Propylsulfinyl)thio]phthalimide (**3a**): 1.52 g (6.0 mmol) of **2a**, 1.72 g (6.0 mmol) of 60% *m*CPBA; yield 0.52 g (32%), m.p. 118–121°C. – IR: $\tilde{\nu}$ = 1096 cm^{-1} (m) (S=O). – ^1H NMR (c, $CDCl_3$): δ = 1.14 (t, *J* = 7.6 Hz, 3H, CH_3), 1.97 (dsext, *J* = 7.6/12.0/8.0 Hz, 2H, CH_2CH_3), 3.24 (dt, *J* = 14.1/8.0 Hz, 2H, SCH_2). – ^{13}C NMR (c, $CDCl_3$): δ = 13.13 (s, CH_3), 16.97 (s, CH_2CH_3), 56.58 (s, SCH_2). – MS, *m/z* (%): 270 (100) $[M+H]^+$. – $C_{11}H_{11}NO_3S_2$ (269.1): calcd. C 49.05, H 4.09, N 5.20; found C 48.68, H 3.92, N 5.42.

N-[(Butylsulfinyl)thio]phthalimide (**3b**): 1.60 g (6.0 mmol) of **2b**, 1.72 g (6.0 mmol) of 60% *m*CPBA; yield 0.88 g (52%), m.p. 74–77°C. – IR: $\tilde{\nu}$ = 1083 cm^{-1} (m) (S=O). – ^1H NMR (c, $CDCl_3$): δ = 1.00 (t, *J* = 7.3 Hz, 3H, CH_3), 1.54 (m, 2H, CH_2CH_3), 1.91 (m, 2H, CH_2CH_2), 3.28 (t, *J* = 7.8 Hz, 2H, SCH_2). – ^{13}C NMR (c, $CDCl_3$): δ = 13.43 (s, CH_3), 21.71 (s, CH_2CH_3), 25.04 (s, CH_2CH_2), 54.52 (s, SCH_2). – $C_{12}H_{13}NO_3S_2$ (283.1): calcd. C 50.86, H 4.59, N 4.94; found C 50.60, H 4.56, N 4.99.

N-[(Benzylsulfinyl)thio]phthalimide (**3c**): 1.90 g (6.0 mmol) of **2c**, 1.72 g (6.0 mmol) of 60% *m*CPBA; yield 1.28 g (67%), m.p. 145–146°C. – IR: $\tilde{\nu}$ = 1089 cm^{-1} (s) (S=O). – ^1H NMR (b, $CDCl_3$): δ = 4.47/4.51 (AB system, *J* = 16 Hz, 2H, CH_2). – ^{13}C NMR (b, $CDCl_3$): δ = 62.47 (s, CH_2). – $C_{15}H_{11}NO_3S_2$ (317.2): calcd. C 56.75, H 3.47, N 4.41; found C 56.50, H 3.57, N 4.39.

N-[(p-Tolylsulfinyl)thio]phthalimide (**3d**): 1.90 g (6.0 mmol) of **2c**, 1.72 g (6.0 mmol) of 60% *m*CPBA; yield 1.58 g (87%), m.p. 121–123°C. – IR: $\tilde{\nu}$ = 1106 cm^{-1} (m) (S=O). – ^1H NMR (a, $CDCl_3$): δ = 2.45 (s, 3H, CH_3). – MS, *m/z* (%): 318 (88) $[M+H]^+$. – $C_{15}H_{11}NO_3S_2$ (317.2): calcd. C 56.75, H 3.47, N 4.41; found C 56.00, H 3.47, N 4.89.

Crystal Data, Data Collection, Solution, and Refinement for **3c**[9]: Colourless plates from a chloroform/hexane solution at room temp. after 3 d. Formula $C_{15}H_{11}NO_3S_2$, molecular mass 317.4, crystal size 0.44× 0.06× 0.20 mm, space group $P2_1/a$ (No. 14); *Z* = 8, *a* = 941.6(2), *b* = 1918.3(4), *c* = 1635.1(3) pm, β = 97.28(1)°, *V* = 2929.5 · 10^6 pm^3, $d_{calcd.}$ = 1.439 g/cm^3, radiation: graphite-monochromated Mo-K_α (λ = 0.71073 Å), temperature 295 K, 2Θ range: 5–45°, scan speed: variable, 1.50–14.65°/min, scan mode: ω, reflections collected: 4312, independent reflections: 3798, observed reflections 2602 with $|F| > 2\sigma_{|F|}$, R_{int} = 0.0044, index ranges: $0 \le h \le 10$, $0 \le k \le 20$, $-17 \le l \le 17$, absorption correction: face-indexed numerical, min./max. transmission: 0.9213/0.9798; programme system used: SHELXTL-PLUS, solution of the phase problem: direct methods, weighting scheme: $w^{-1} = \sigma^2_{|F|}$, hydrogen atoms: placed in calculated positions, U_{iso}, nonhydrogen atoms refined anisotropically (382 parameters), final residuals (observed data): *R* = 0.0829, R_w = 0.0475, R_g = 0.0196, extrema of the final difference Fourier synthesis: +0.42/−0.37 e · 10^{-6} pm^{-3}.

Preparation of the Platinum(II) Complexes **4a–d**: The *N*-[(sulfinyl)thio]phthalimides **3a–d** (0.20 mmol) were added to a solution of $Pt(PPh_3)_2(C_2H_4)$[14] (0.20 mmol) in 10 ml of toluene. After having been stirred for 1–2 d this solution changed its colour from orange to yellow. Then 40 ml of hexane was added giving the products **4a,b** as bright yellow microcrystalline powders; complexes **4c,d** precipitated directly from the toluene solution. Centrifuging and washing this precipitate twice with ether and drying it in vacuo gave the pure products **4a–d** in 28–35% yield.

cis-(Ph3P)2Pt[S–S(O)–(CH2)2CH3](Nphth) (**4a**): 54 mg (0.20 mmol) of **3a**, 149 mg (0.20 mmol) of $Pt(PPh_3)_2(C_2H_4)$; yield 55 mg (28%), m.p. 172–175°C. – IR: $\tilde{\nu}$ = 1060 cm^{-1} (m) (S=O). – ^1H NMR (b, $CDCl_3$): δ = 0.59 (t, *J* = 7.4 Hz, 3H, CH_3), 1.29 (m, 2H, CH_2CH_3), 2.51 (m, 1H, SCH_aH_b), 2.63 (m, 1H, SCH_aH_b). – ^{13}C NMR (c, $CDCl_3$): δ = 11.94 (s, CH_3), 16.46 (s, CH_2CH_3), 62.11 [d, $^4J(^{31}P^{13}C)$ = 5.5 Hz, SCH_2]. – ^{31}P NMR (b, $CDCl_3$): δ = 21.2/9.6 [AB system, $^2J(^{31}P^{31}P)$ = 19.0, $^1J(^{195}Pt^{31}P)$ = 3083/3234 Hz]. – MS, *m/z* (%): 989 (1) $[M+H]^+$, 897 (6), 865 (12). – $C_{47}H_{41}NO_3P_2PtS_2$ (988.6): calcd. C 57.07, H 4.15, N 1.42; found C 56.50, H 3.57, N 1.27.

cis-(Ph3P)2Pt[S–S(O)–(CH2)3CH3](Nphth) (**4b**): 57 mg (0.20 mmol) of **3b**, 149 mg (0.2 mmol) of $Pt(PPh_3)_2(C_2H_4)$; yield

52 mg (26%), m.p. 193–194°C. – IR: $\tilde{\nu}$ = 1040 cm^{-1} (m) (S=O). – ^1H NMR (b, $CDCl_3$): δ = 0.66 (t, J = 7.3 Hz, 3H, CH_3), 1.07 (m, 2H, CH_2CH_3), 1.31 (m, 2H, CH_2CH_2), 2.60 (m, 1H, SCH_aH_b), 2.72 (m, 1H, SCH_aH_b). – ^{13}C NMR (c, $CDCl_3$): δ = 13.61 (s, CH_3), 21.67 (s, CH_2CH_3), 26.00 (s, CH_2CH_2), 61.08 [d, $^4J(^{31}P^{13}C)$ = 6.3 Hz, SCH_2]. – ^{31}P NMR (b, $CDCl_3$): δ = 21.2/9.6 [AB system, $^2J(^{31}P^{31}P)$ = 19.0, $^1J(^{195}Pt^{31}P)$ = 3081/3235 Hz]. – MS, *m/z* (%): 1004 (5) $[M+H]^+$, 897 (27), 865 (68). – $C_{48}H_{43}NO_3P_2PtS_2$ (1002.6): calcd. C 57.47, H 4.29, N 1.40; found C 56.25, H 4.22, N 1.35.

cis-(Ph$_3$P)Pt[S–S(O)–CH$_2$Ph](Nphth) (**4c**): 63 mg (0.20 mmol) of **3c**, 149 mg (0.2 mmol) of $Pt(PPh_3)_2(C_2H_4)$; yield 54 mg (26%), m.p. 213–216°C. – IR: $\tilde{\nu}$ = 1052 cm^{-1} (m) (S=O). – ^1H NMR (b, $CDCl_3$): δ = 3.89 (AB system, J = 15 Hz, 2H, CH_2). – ^{13}C NMR (c, $CDCl_3$): δ = 68.04 [d, $^4J(^{31}P^{13}C)$ = 6.1 Hz, SCH_2]. – ^{31}P NMR (b, $CDCl_3$): δ = 21.1/9.2 [AB system, $^2J(^{31}P^{31}P)$ = 18.0, $^1J(^{195}Pt^{31}P)$ = 3104/3226 Hz]. – MS, *m/z* (%): 1038 (2) $[M+H]^+$, 897 (39), 865 (83). – $C_{51}H_{41}NO_3P_2PtS_2$ (1036.7): calcd. C 59.06, H 3.96, N 1.35; found C 58.00, H 4.20, N 1.58.

cis-(Ph$_3$P)$_2$Pt[S–S(O)–C$_6$H$_4$-p-CH$_3$](Nphth) (**4d**): 63 mg (0.20 mmol) of **3d**, 149 mg (0.2 mmol) of $Pt(PPh_3)_2(C_2H_4)$: yield 66 mg (32%), m.p. 180–184°C. – IR: $\tilde{\nu}$ = 1053 cm^{-1} (m) (S=O). – ^1H NMR (b, $CDCl_3$): δ = 3.89 (AB system, J = 15 Hz, 2H, CH_2). – ^{13}C NMR (a, $CDCl_3$): δ = 21.2 (s, CH_3). – ^{31}P NMR (b, $CDCl_3$): δ = 21.1/9.8 [AB system, $^2J(^{31}P^{31}P)$ = 18.0, $^1J(^{195}Pt^{31}P)$ = 3050/3220 Hz]. – MS, *m/z* (%): 1038 (7) $[M+H]^+$, 897 (58), 865 (63). – $C_{51}H_{41}NO_3P_2PtS_2$ (1036.7): calcd. C 59.06, H 3.96, N 1.35; found C 59.38, H 4.39, N 1.27.

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[286/93]