

Akira Tsubouchi, Naomi Nakamura, Akira Sugimoto, and Hiroo Inoue\*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593, Japan

Tomohiro Adachi

Faculty of Integrated Arts and Sciences, University of Osaka Prefecture,  
Sakai, Osaka 593, Japan  
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The reaction of 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1**) with the palladium complex  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$  (dba = dibenzylideneacetone) and tetracyanoethylene (TCNE) gave a new palladium complex in which two isopropylthio groups of **1** and the double bond of TCNE were trigonally coordinated to palladium. The X-ray analysis revealed the electron donation from palladium to TCNE, leading to a lengthening of the C=C double bond in TCNE and distortion of TCNE from planarity. The radical cation of **1** and the radical anion of TCNE were detected by ESR spectroscopy in methylene dichloride solution of the complex, although the radical content was estimated from the paramagnetic susceptibility to be less than 1%. The reaction of the complex with aniline gave the same product as that in the reaction of the radical cation of **1** with aniline.

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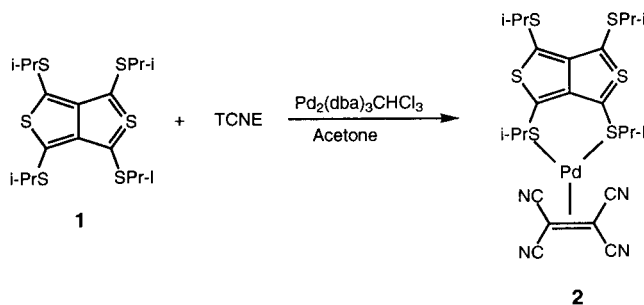
### Introduction.

Thieno[3,4-*c*]thiophenes are 10  $\pi$ -electron heterocycles with a nonclassical structure and have attracted much attention for their chemical and physical properties [1]. In the course of our studies on the reactivity of 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1**) [2], we showed the followings: (1) compound **1** reacts with electrophiles at the 1-position having a large coefficient of the highest occupied molecular orbital (HOMO) [3]; (2) the energy level of the HOMO is estimated by measurement of the photoelectron spectrum to be 6.72 eV and the first and second oxidation potentials by cyclic voltammetry to be +0.19 and +0.54 V vs. SCE in acetonitrile solution respectively, being similar to those of tetrathiafulvalene [4]; (3) therefore, compound **1** is readily oxidized to its radical cation with iodine and to a dication with nitrosonium cation [5]. These results have prompted us to investigate reactions with transition metals. The transition metal complexes of the thieno[3,4-*c*]thiophenes are unknown. We have carried out the reaction of **1** with the palladium complex  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$  (dba = dibenzylideneacetone) in the presence of tetracyanoethylene (TCNE) and now report the new palladium complex coordinated with **1** and TCNE, determined by X-ray analysis, and the reaction of the complex with aniline.

### Results and Discussion.

Thieno[3,4-*c*]thiophene **1** reacted with  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$  in acetone at room temperature in the presence of TCNE to give tetracyanoethylene 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene-palladium (**2**) as a purple

solid in 82% yield based on the palladium atom. A strongly electron-accepting alkene as a ligand was indispensable to the formation of the complex, since, in the absence of TCNE and in the presence of a weak electron-acceptor such as maleic anhydride, compound **1** did not



form the complex with  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ . The complex **2** is fairly stable in the air and can be handled without difficulty. The molar ratio of the ligands to palladium was determined by elemental analysis and fast atom bombardment mass spectroscopy. The ir spectrum of complex **2** exhibited an absorption due to a cyano group at 2218  $\text{cm}^{-1}$ , which was shifted to lower wave number than that (2280 and 2255  $\text{cm}^{-1}$ ) [6] of TCNE, thus indicating an electron donation from palladium to TCNE. The  $^1\text{H}$  nmr spectrum of **2** in deuterochloroform solution showed two doublets at 1.40 and 1.55 ppm, with the same integral value, for the methyl protons of nonequivalent isopropylthio groups which were situated in a different environment. These signals were shifted to lower field than that

(1.29 ppm) [2] of **1** by 0.11 and 0.26 ppm due to the coordination of **1** to the palladium atom. When perdeuterioacetonitrile was used as a solvent, the two sets of doublets became one doublet with a chemical shift of 1.37 ppm. This spectral change would result from the rapid exchange equilibrium between **1** and perdeuterioacetonitrile. The uv spectrum of **2** in methylene dichloride solution showed an absorption maximum (537 nm) at longer wavelength than that of **1** by 25 nm, whereas in acetonitrile solution the spectrum of **2** was almost same as that of **1**, supporting the dissociation of **1** in acetonitrile. The solvent effect in the  $^1\text{H}$  nmr and uv spectra indicates that ligand **1** is weakly coordinated to palladium and can be displaced by another ligand.

To understand the coordination mode of the ligand in detail, the X-ray crystallographic analysis was performed. A single crystal employed for the analysis was obtained by diffusion of diethyl ether vapor to a solution of **2** in methylene dichloride. An overall structure of the molecule is given in Figure 1, hydrogen atoms being omitted for clarity. Table 1 shows the atomic parameters, and Tables 2 and 3 the bond distances and angles. The thieno[3,4-*c*]thiophene **1** is coordinated to palladium at the sulfur atom of the two isopropylthio groups without a notable difference in bond distances between coordinated and uncoordinated thieno[3,4-*c*]thiophenes. The C=C double bond of TCNE lies in the coordination plane and the palladium atom is situated on the least-square plane

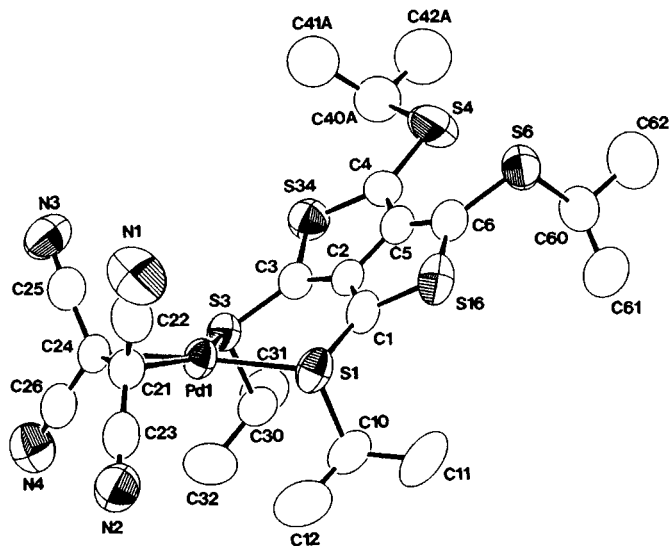


Figure 1. Molecular structure and atomic numbering scheme of complex **2**.

defined by S1, S3, C21, and C24 within the deviation of 0.054 Å from the plane. Although the distances of Pd1-C21 and Pd1-C24 are slightly different from each other,

Table 1  
Positional Parameters with Estimated Standard Deviations  
in Parentheses

Atom	x	y	z	B (Å) [a]
Pd1	0.24415(4)	0.07384(2)	0.10461(1)	4.53(2)
S1	0.1315(1)	0.15883(6)	0.08080(5)	5.17(7)
S3	0.1284(1)	0.05034(5)	0.18045(5)	4.25(6)
S4	0.0494(2)	0.23218(6)	0.33058(6)	7.9(1)
S6	0.0390(1)	0.33354(6)	0.23485(7)	7.0(1)
S16	0.0745(1)	0.26452(5)	0.14041(6)	5.97(8)
S34	0.0958(1)	0.12034(6)	0.27479(5)	5.39(8)
N1	0.5849(6)	0.1332(2)	0.0604(2)	9.8(4)
N2	0.3267(5)	0.0275(2)	-0.0350(2)	8.2(3)
N3	0.5642(5)	0.0178(2)	0.1696(2)	8.0(3)
N4	0.2996(5)	-0.0851(2)	0.0761(2)	8.2(3)
C1	0.0924(4)	0.1920(2)	0.1383(2)	4.6(3)
C2	0.0908(4)	0.1697(2)	0.1879(2)	3.9(3)
C3	0.1030(4)	0.1156(2)	0.2093(2)	4.0(3)
C4	0.0742(4)	0.1925(2)	0.2760(2)	4.8(3)
C5	0.0749(4)	0.2136(2)	0.2260(2)	4.4(3)
C6	0.0640(5)	0.2684(2)	0.2049(2)	5.1(3)
C10	-0.0319(5)	0.1399(2)	0.0519(2)	6.0(3)
C11	-0.1099(5)	0.1933(3)	0.0395(2)	8.6(4)
C12	-0.0020(7)	0.1048(3)	0.0055(3)	11.4(5)
C21	0.4016(5)	0.0566(2)	0.0550(2)	4.7(3)
C22	0.5040(6)	0.0992(3)	0.0571(2)	6.2(4)
C23	0.3606(6)	0.0406(2)	0.0046(2)	5.9(3)
C24	0.3942(5)	0.0146(2)	0.0961(2)	4.4(3)
C25	0.4908(6)	0.0157(2)	0.1369(2)	5.4(3)
C26	0.3430(6)	-0.0412(3)	0.0846(2)	5.7(3)
C30	-0.0421(5)	0.0260(2)	0.1644(2)	5.1(3)
C31	-0.1098(5)	0.0042(2)	0.2122(2)	6.4(3)
C32	-0.0326(6)	-0.0178(3)	0.1228(2)	8.0(4)
C40A	0.071(1)	0.1748(4)	0.3834(4)	6.8(3)*
C40B	0.006(2)	0.1925(9)	0.3745(8)	6.6(5)*
C41A	0.217(1)	0.1574(4)	0.3892(4)	8.3(3)*
C41B	0.139(2)	0.1679(8)	0.4016(7)	6.2(5)*
C42A	0.020(1)	0.2012(5)	0.4304(4)	10.0(3)*
C42B	-0.073(2)	0.2204(8)	0.4168(8)	8.9(6)*
C60	-0.1423(5)	0.3301(2)	0.2469(3)	7.1(4)
C61	-0.2195(5)	0.3370(2)	0.1983(3)	8.2(4)
C62	-0.1751(7)	0.3721(3)	0.2868(3)	11.5(5)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3) \times [a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + ab(\cos \gamma) \times B(1,2) + ac(\cos \beta) \times B(1,3) + bc(\cos \alpha) \times B(2,3)]$ .

they are ordinary ones which have been found in transition metal-olefin complexes [7]. The coordinated TCNE is nonplanar and each cyano group is bent away from the metal atom; the dihedral angle between two planes, one plane containing N1, C22, C21, C23, and N2 and the other plane containing N3, C25, C24, C26, and N4, is 129.8°. The C=C double-bond distance (1.460 Å) of the coordinated TCNE becomes longer than that of the uncoordinated one [8] by 0.116 Å. This change in the bond distance may be explained by donation of an electron from the palladium atom to TCNE.

The ESR spectrum of this complex in methylene dichloride solution at room temperature exhibited two sets of

partially overlapped signals with a hyperfine structure attributable to the radical cation of **1** and the radical anion

of TCNE (Figure 2). The  $g$  value and hyperfine coupling constant were found from the spectrum to be 2.0046 and

Table 2

Bond Distances (Å) with Estimated Standard Deviations in Parentheses

Bond	Distance	Bond	Distance
Pd1 - S1	2.370(1)	Pd1 - S3	2.359(1)
Pd1 - C21	2.077(5)	Pd1 - C24	2.054(5)
S1 - C1	1.735(5)	S1 - C10	1.851(5)
S3 - C3	1.725(5)	S3 - C30	1.842(5)
S4 - C4	1.722(5)	S4 - C40A	1.94(1)
S4 - C40B	1.54(2)	S6 - C6	1.734(5)
S6 - C60	1.837(5)	S16 - C1	1.711(5)
S16 - C6	1.692(5)	S34 - C3	1.716(5)
S34 - C4	1.705(5)	N1 - C22	1.136(7)
N2 - C23	1.130(6)	N3 - C25	1.126(6)
N4 - C26	1.139(6)	C1 - C2	1.398(6)
C2 - C3	1.392(6)	C2 - C5	1.440(6)
C4 - C5	1.398(6)	C5 - C6	1.400(6)
C10 - C11	1.509(7)	C10 - C12	1.495(7)
C21 - C22	1.429(7)	C21 - C23	1.430(7)
C21 - C24	1.460(6)	C24 - C25	1.439(7)
C24 - C26	1.435(7)	C30 - C31	1.508(6)
C30 - C32	1.501(7)	C40A - C41A	1.52(1)
C40A - C42A	1.47(1)	C40B - C41B	1.61(3)
C40B - C42B	1.50(2)	C60 - C61	1.493(7)
C60 - C62	1.472(8)		

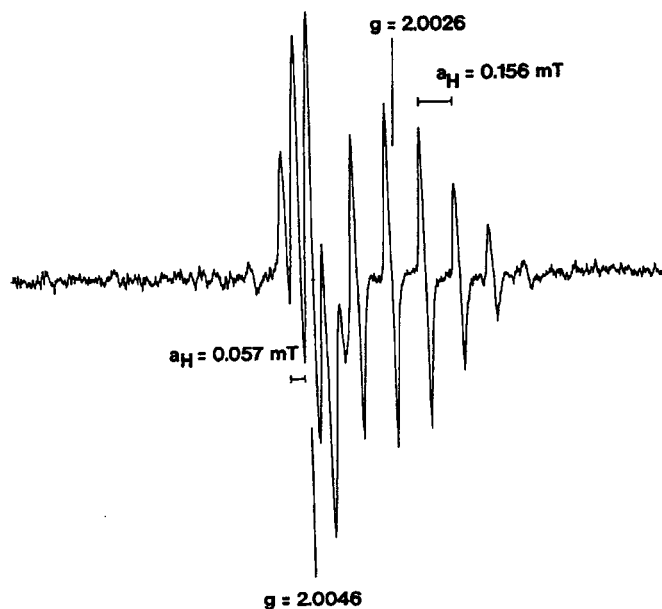


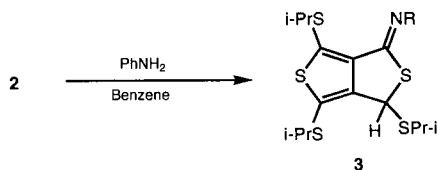
Figure 2. ESR spectrum of complex **2** in methylene dichloride solution at room temperature.

Table 3

Bond Angles (°) with Estimated Standard Deviations in Parentheses

Bond	Angle	Bond	Angle
S1 - Pd1 - S3	100.64(4)	S1 - Pd1 - C21	111.0(1)
S3 - Pd1 - C24	106.9(1)	C21 - Pd1 - C24	41.4(2)
Pd1 - S1 - C1	104.8(2)	Pd1 - S1 - C10	108.9(2)
C1 - S1 - C10	105.3(2)	Pd1 - S3 - C3	103.4(2)
Pd1 - S3 - C30	109.5(2)	S3 - C3 - C30	103.8(2)
C4 - S4 - C40A	101.5(4)	C4 - S4 - C40B	109.4(8)
C6 - S6 - C60	100.4(2)	C1 - S16 - C6	95.3(2)
C3 - S34 - C4	95.0(2)	S1 - C1 - S16	119.8(3)
S1 - C1 - C2	129.7(4)	S16 - C1 - C2	109.8(4)
C1 - C2 - C3	135.4(5)	C1 - C2 - C5	112.1(4)
C3 - C2 - C5	112.5(4)	S3 - C3 - S34	120.0(3)
S3 - C3 - C2	130.1(4)	S34 - C3 - C2	109.8(3)
S4 - C4 - S34	124.7(3)	S4 - C4 - C5	125.8(4)
S34 - C4 - C5	109.5(4)	C2 - C5 - C4	113.2(4)
C2 - C5 - C6	113.1(5)	C4 - C5 - C6	133.7(5)
S6 - C6 - S16	120.4(3)	S6 - C6 - C5	129.9(4)
S16 - C6 - C5	109.7(4)	S1 - C10 - C11	110.0(4)
S1 - C10 - C12	106.7(4)	C11 - C10 - C12	112.7(5)
Pd1 - C21 - C22	112.4(4)	Pd1 - C21 - C23	114.2(4)
Pd1 - C21 - C24	68.4(3)	C22 - C21 - C23	115.1(5)
C22 - C21 - C24	118.6(5)	C23 - C21 - C24	119.1(5)
N1 - C22 - C21	177.8(8)	N2 - C23 - C21	179.0(7)
Pd1 - C24 - C21	70.2(3)	Pd1 - C24 - C25	113.3(4)
Pd1 - C24 - C26	112.3(4)	C21 - C24 - C25	120.0(5)
C21 - C24 - C26	118.6(5)	C25 - C24 - C26	114.3(5)
N3 - C25 - C24	178.0(6)	N4 - C26 - C24	178.3(7)
S3 - C30 - C31	109.3(4)	S3 - C30 - C32	108.5(4)
C31 - C30 - C32	113.3(5)	S4 - C40A - C41A	111.4(7)
S4 - C40A - C42A	105.4(8)	C41A - C40A - C42A	111(1)
S4 - C40B - C41B	108(1)	S4 - C40B - C42B	116(2)
C41B - C40B - C42B	105(1)	S6 - C60 - C61	111.0(4)
S6 - C60 - C62	108.1(4)	C61 - C60 - C62	114.6(5)

0.057 mT for  $1^{\bullet+}$  and 2.0026 and 0.156 mT for TCNE $\bullet$  respectively being identical with those reported previously [5,9]. On the other hand, no signal was observed in the ESR spectrum of a mixture of **1** and TCNE in acetonitrile solution. The magnetic susceptibility of the complex **2** was measured at room temperature by a SQUID magnetometer to estimate the amount of the radical species. The value of the paramagnetic susceptibility was *ca.*  $2 \times 10^{-5}$  emu mol $^{-1}$  indicative of the radical content of less than 1% [10].



Complex **2** reacted with aniline in benzene at room temperature for 4 hours to give compound **3** in 100% yield. In contrast to complex **2**, the free ligand **1** failed to react with aniline, but **1** was quantitatively recovered. Compound **3** was identical with the product obtained previously by reaction of the radical cation  $1^{\bullet+}$ , generated by oxidation with iodine, with aniline. As previously proposed for the reaction of the radical cation  $1^{\bullet+}$  with aniline [5], the reaction would proceed through the addition of the aniline at the 1-position of the coordinated **1** or the radical cation  $1^{\bullet+}$ , followed by the elimination of the isopropylthiol. When **2** was allowed to react with *t*-butylthiol, compound **1** was obtained in 67% yield by ligand exchange without formation of the adduct of *t*-butylthiol. The ligand exchange was also observed by  $^1\text{H}$  nmr spectroscopy in the reaction of complex **2** with excess triphenylphosphine; the  $^1\text{H}$  nmr spectrum of **2** in deuteriochloroform quantitatively changed to that of **1** by addition of triphenylphosphine. This fact indicates that the thiol and phosphine nucleophiles attack the palladium atom rather than ligand **1**.

In conclusion, compound **1** acts as a bidentate ligand in reaction with  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$  in the presence of TCNE to give the palladium complex coordinated with TCNE and the two isopropylthio groups of **1**. This complex exhibits reactivity similar to the radical cation  $1^{\bullet+}$  in the reaction with aniline to give the thieno[3,4-*c*]thiophen-3(*1H*)-imine derivative.

## EXPERIMENTAL

Melting points were determined on a Yanaco MP-S3 melting point apparatus and are uncorrected. The ir spectra were obtained on a Hitachi 215 spectrophotometer. The uv spectra were recorded on a Shimadzu UV-160 spectrophotometer. The nmr spectra were recorded on a JEOL JNM-270 FT NMR spec-

trometer with tetramethylsilane as an internal standard. Fast atom bombardment (FAB) mass spectrum was obtained on a Finnigan MAT TSQ 70 with *m*-nitrobenzyl alcohol as a matrix and a parallel run of cesium rubidium iodide for a reference. Elemental analyses were performed on a Yanagimoto MT3 CHN coder. 1,3,4,6-Tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1**) was synthesized by the method described previously [2]. Tris(benzylidenacetone) dipalladium(0) solvate (chloroform) was prepared from palladium dichloride and dibenzylideneacetone according to the literature [11]. Tetracyanoethylene, *t*-butylthiol, and triphenylphosphine were purchased from commercial sources and used without further purification. Acetone, methylene dichloride, acetonitrile, and aniline were dried and distilled by usual method.

Tetracyanoethylene 1,3,4,6-Tetrakis(isopropylthio)thieno-[3,4-*c*]thiophene- Palladium(0) (**2**).

A mixture of **1** (42 mg, 0.095 mmole), TCNE (6.4 mg, 0.049 mmole), and  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$  (20 mg, 0.019 mmole) in degassed acetone (5 ml) was stirred for 1 hour at room temperature. After reducing the solvent to one tenth of the initial volume under vacuum, diethyl ether was added to the solution. Precipitating solids were collected by filtration to give the palladium complex **2** as a purple solid (21 mg, 82% based on the palladium atom), mp 123-125° dec; ir (potassium bromide):  $\nu$  2960, 2218 (C=N), 1506, 1458, 1368, 1278, 1230, 1151, 1048, 993, 700, 550  $\text{cm}^{-1}$ ; uv (methylene dichloride):  $\lambda$  max nm (log  $\epsilon$ ) 238 (4.45), 306 (4.41), 537 (4.41);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.40 (d,  $J = 6.7$  Hz, 12H,  $\text{SCH}(\text{CH}_3)_2$ ), 1.55 (d,  $J = 6.7$  Hz, 12H,  $\text{SCH}(\text{CH}_3)_2$ ), 3.4-3.6 (m, 4H,  $\text{SCHMe}_2$ );  $^1\text{H}$  nmr (deuterioacetone):  $\delta$  1.37 (d,  $J = 6.7$  Hz, 24H,  $\text{SCH}(\text{CH}_3)_2$ ), 3.51 (m, 4H,  $\text{SCHMe}_2$ ); ms: FAB  $m/z$  671.9 (M + H $^+$ ).

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{28}\text{N}_4\text{S}_6\text{Pd}$ : C, 42.94; H, 4.20; N, 8.35. Found: C, 42.64; H, 4.12; N, 8.45.

## X-ray Crystallographic Data of **2** and Structure Determination.

A single crystal of **2** with approximate size of  $0.4 \times 0.3 \times 0.3$  mm was employed for the X-ray analysis. The crystal belongs to the orthorhombic system, space group Pccn (No. 56) with  $a = 9.9765(8)$ ,  $b = 23.434(8)$ ,  $c = 26.137(5)$  Å;  $Z = 8$ ;  $V = 6111(7)$  Å $^3$ ;  $D_c = 1.459$  g  $\text{cm}^{-3}$ . The X-ray intensities were measured on a Rigaku AFC5R diffractometer by  $\omega$ -2 $\theta$  scan mode. The total of 4035 reflections was collected in the range of  $3 < \theta < 25^\circ$  using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å) and 2426 reflections with  $I > 3\sigma(I)$  were used for the structure determination. The structure was solved by patterson method using the TEXSAN crystallographic software package of Molecular Structure Corporation [12]. All non-hydrogen atoms were found by the successive difference Fourier syntheses and all hydrogen atoms were included at calculated positions. One of two uncoordinated isopropylthio groups was found to be disordered with occupancy factor of 0.667 and 0.333. The structure was refined by full-matrix least-squares with isotropic thermal parameters for hydrogen atoms and carbon atoms of disordered isopropylthio group and with anisotropic thermal parameters for other non-hydrogen atoms. The final R and Rw values were 0.027 and 0.025 respectively. Further details of the crystal structure investigation are available on request from the authors.

## Reaction of the Complex **2** with Aniline.

Aniline (0.027 ml, 0.03 mmole) was added to a solution of complex **2** (20 mg, 0.030 mmole) in benzene (5 ml) at room temperature and the mixture was stirred under nitrogen for 1 hour. After evaporating the solvent under reduced pressure, the residue was applied to preparative tlc separation with methylene dichloride-hexane (2:3) as an eluent to give the compound **3** in 100% yield.

*N*-Phenyl-1,4,6-tris(isopropylthio)thieno[3,4-*c*]thiophen-3(1*H*)-imine (**3**).

This compound was obtained as a pale yellow oil; ir (neat):  $\nu$  3050, 2960, 2910, 2855, 1620 (C=N), 1580, 1520, 1485, 1440, 1380, 1365, 1240, 1220, 1150, 1050, 1015, 990, 905, 840, 765, 725; uv (hexane):  $\lambda$  max nm (log  $\epsilon$ ) 253 (4.42), 335 (4.00);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.22, 1.33, 1.34, 1.35, 1.45, and 1.51 (d,  $J = 6.7$  Hz, each 3H, SCHMeMe), 3.15, 3.35, and 3.62 (sep,  $J = 6.7$  Hz, each 3H, SCHMe<sub>2</sub>), 5.67 (s, 1H, 1-H), 7.06-7.38 (m, 5H, phenyl); ms:  $m/z$  453 ( $M^+$ ).

*Anal.* Calcd. for C<sub>21</sub>H<sub>27</sub>NS<sub>5</sub>: C, 55.59; H, 6.00; N, 3.09. Found: C, 55.81; H, 6.30; N, 3.14.

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