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Communications

Activation of Thiophenes by Superacids: Protonation and Polymerization

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Two aspects of thiophene chemistry are of current interest in materials chemistry. Polythiophenes are under intense study for possible applications in electronics and photonics,[1] and metal−thiophene interactions are relevant to the catalytic hydrodesulfurization (HDS) process.[2,3] This communication presents studies at the interface of these otherwise distinct topics, resulting from an examination of the interaction of $TiCl_4$ with thiophenes.

We have found that CH_2Cl_2 solutions of HCl and $TiCl_4$ readily protonate tetramethylthiophene to give salts of $[2\text{-}HC_4Me_4S^+]$. ^{1}H and ^{13}C NMR analysis of these solutions indicate that protonation occurs at the 2-position.[4,5] In the ^{1}H NMR spectrum, all four CH_3 signals are well resolved, two of which are coupled to the unique proton in accord with similar results using more conventional superacids.[6] From these solutions we obtained single crystals of $[2\text{-}HC_4Me_4S^+][Ti_2Cl_9^-]$, thus allowing the first structural analysis of a protonated thiophene (Figure 1). The reflection data refined well, allowing for the identification of the unique H-atom position.[7] The $[2\text{-}HC_4Me_4S^+]$ cation features a tetrahedral carbon, C2, connected to C3 and S via bond lengths closer to values for single bonds, 1.474(7) and 1.804(5) Å, respectively. The C2−C3−C4−S sequence displays a diene-like alternation in bond lengths. The C4−S distance of 1.673(5) Å is shorter than in thiophene (1.71 Å), indicative of an enhanced S−C π-interaction. The $Ti_2Cl_9^-$ anion is unexceptional, consisting of a cofacial bioctahedral arrangement. There is one short Cl···H interaction between a terminal chloride on the anion and the unique hydrogen.

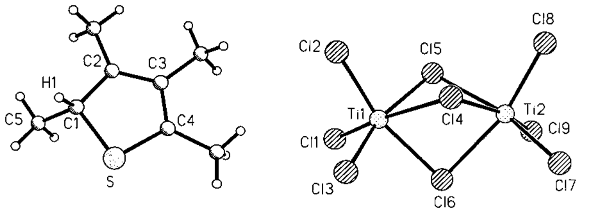

Figure 1. Structure of $[2\text{-}HC_4Me_4S^+][Ti_2Cl_9^-]$. Principal bond lengths (Å): S−C(1), 1.804 (5); C(1)−C(2), 1.474 (7); C(2)−C(3), 1.370 (7); C(3)−C(4), 1.405 (7); C(4)−S, 1.673 (5).

To better understand the $TiCl_4/HCl/C_4Me_4S$ reaction, we examined the interaction of C_4Me_4S and $TiCl_4$ in the absence of acids. Floriani and co-workers had shown that hexamethylbenzene reacts with $TiCl_4$ to give $[(\eta^6\text{-}C_6Me_6)TiCl_3^+][Ti_2Cl_9^-]$.[8] NMR studies suggest that the analogous $[(\eta^5\text{-}C_4Me_4S)TiCl_3^+]$ is formed when CH_2Cl_2

[†] Department of Chemistry, University of California, Davis, CA.

[1] (a) Katz, H. E.; Torsi, L.; Dodabalapur, A. *Chem. Mater.* **1995**, *7*, 2235. (b) Shi, G.; Jin, S.; Li, C. *Science* **1995**, *267*, 994. (c) Torsi, L.; Dodabalapur, A.; Lovinger, A. J.; Katz, H. E.; Ruel, R.; Davis, D. D.; Baldwin, K. W. *Chem. Mater.* **1995**, *7*, 2247. (d) Roncali, J. *Chem. Rev. (Washington, D.C.)* **1992**, *72*, 771. (e) Faid, K.; Fretchette, M.; Ranger, M.; Mazerolle, L.; Levesque, I.; Leclerc, M.; Chen, T.; Rieke, R. D. *Chem. Mater.* **1995**, *7*, 1390.

[2] (a) Gates, B. C. *Catalytic Chemistry*; John Wiley & Sons: New York, 1992. (b) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1996**, *8*, 945.

[3] Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed; John Wiley & Sons: New York, 1994; Vol. 3, p 1433.

[4] Yuan, Y.; Gunig, E.; Miller, L. L. *Chem. Mater.* **1995**, *7*, 255.

[5] ^{1}H NMR (CD_2Cl_2) δ 5.05 (m, 1H, $SC_3Me_3C\mathit{H}Me$), 3.09 (d, J = 3.42 Hz, 3H, $SC_3\mathit{Me}_3CHMe$), 2.57 (s, 3H, $SC_3\mathit{Me}_3CHMe$), 2.27 (s, 3H, $SC_3\mathit{Me}_3CHMe$), 1.87 (d, J = 7.81 Hz, 3H, $SC_3Me_3CH\mathit{Me}$).

[6] Hogeveen, H. *Recueil* **1966**, *85*, 1072.

[7] For $C_8H_{13}Cl_9STi_2$: monoclinic $P2_1/n$, a = 9.441(5), b = 11.708(5), c = 18.214(13) Å, $\alpha = \gamma = 90°$, β = 91.18(4)°, Z = 4, V = 2013(2) Å^3, T = 130 K, ρ_{calcd} = 1.835 Mg/m^3, for 3539 independent reflections (Mo Kα; R_{int} = 1.45%; 184 parameters refined) R_w (based on F) = 3.72% (0.0° ≤ 2θ ≤ 50.0°).

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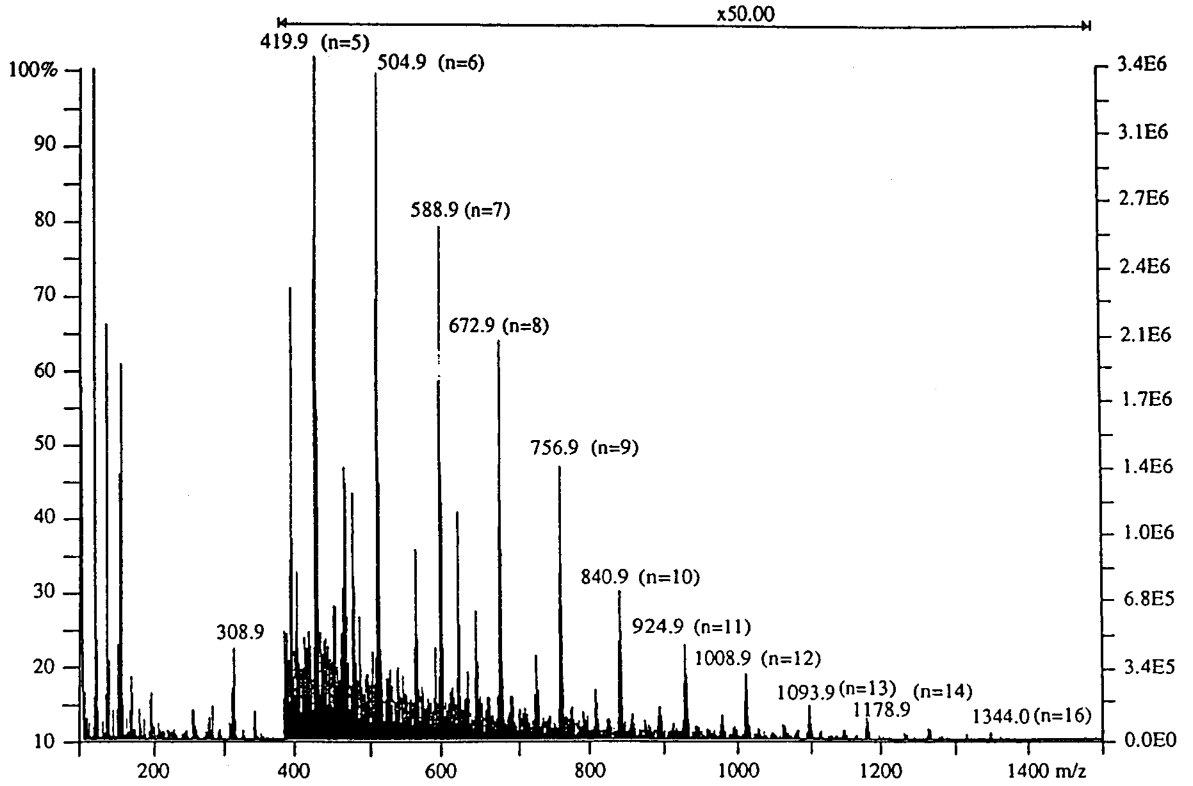
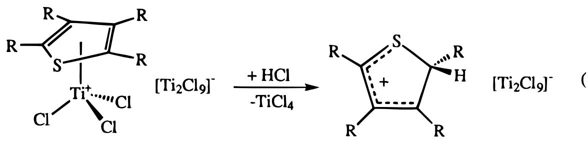


Figure 2. Positive ion FAB mass spectrum of $C_{4n}H_{4n}S_n$ (3-nitrobenzyl alcohol matrix).

solutions of C_4Me_4S are treated with excess $TiCl_4$ at low temperatures. Addition of hexanes to these solutions precipitates analytically pure red crystals of $[(\eta^5\text{-}C_4Me_4S)TiCl_3^+][Ti_2Cl_9^-]$.[9] This species is unstable in solution and decomposes upon prolonged exposure to a vacuum, indicative of its reversion to $TiCl_4$ and C_4Me_4S. NMR studies show that solutions of this salt react with HCl to give the aforementioned $[2\text{-}HC_4Me_4S]Ti_2Cl_9$. This experiment illustrates the competition between $TiCl_3^+$ and H^+ for the weakly basic heterocycle (eq 1).



(1)

Given the successes with the $C_4Me_4S/TiCl_4/HCl$ system, we have investigated the corresponding chemistry of the parent thiophene. Previous studies, beginning with the discovery of thiophene,[10] had shown that thiophene was sensitive to strong acids to give insoluble "polymers" as well as trimeric and tetrameric species.[11] Dichloromethane solutions of thiophene and $TiCl_4$ (0.6 M) react to give yellow solutions. Attempts to isolate adducts from such solutions were unsuccessful; evaporation of the solution left no residue, indicating that $[(C_4H_4S)TiCl_3^+]Ti_2Cl_9^-$, if it forms, is less stable than the C_4Me_4S derivatives. Addition of gaseous HCl to this $TiCl_4/C_4H_4S$ solution at −78 °C, followed by warming to room temperature, led to a darkening of the solution and the formation of a brilliant red precipitate. Similar reactions can be conducted without solvent using only thiophene and $TiCl_4$, in which case the addition of HCl converts the solution into a red paste. Water discharges the red color, giving a yellow precipitate. Extraction of this solid with CH_2Cl_2 (CS_2 and benzene can also be used) followed by addition of hexanes to the organic phase affords a pale yellow solid (mp 145−151 °C) analyzing as $C_{4n}H_{4n}S_n$.[12] The polymerization is more conveniently conducted using HOTf instead of gaseous HCl. For example starting with 3.6 g of thiophene and 4.3 g of $TiCl_4$ followed by an excess of HOTf gave 2.5 g of polymer.

Size exclusion chromatographic (SEC) analysis showed that the solid has a number-average molecular weight (M_n) of 1800 and a weight-average molecular weight (M_w) of 3300. The polymer can be readily fractionated to give samples with M_n (M_w) values that range from 3500 (5000) to 1000 (1200). A M_n of 3500 corresponds to a degree of polymerization (dp) of 41.

The identification of the product as $C_{4n}H_{4n}S_n$ is supported by positive ion FAB MS data for a low molecular weight fraction which showed peaks from $[1344-n(84)]^+$ for $5 \leq n \leq 16$, i.e., integral multiples of thiophene (Figure 2). MS/MS measurements on the $[(C_4H_4S)_7]^+$ peak ($m/z = 588$) showed that the progression $[1344-n(84)]^+$ is not due to fragmentation but reflects the polydispersity of the sample. Also observed is a set of weaker peaks for $[(C_4H_4S)_n-H_2S]^+$ resulting from the fact that the $C_4H_4S/TiCl_4/HCl$ reaction evolves some H_2S. The mechanism of this side reaction remains unknown.

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(8) Solari, E.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C.; Rosi, M.; Sgamellotti, A. *Inorg. Chem.* **1994**, *33*, 2018.

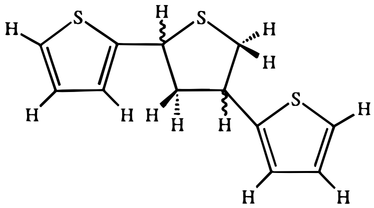
(9) Anal. Calcd (found) for $C_8H_{12}Cl_{12}STi_3$: C, 13.54 (13.74); H, 1.70 (1.74); Cl, 59.97 (59.59); S, 4.52 (4.65); Ti, 20.26 (20.24).

(10) Meyer, V. *Berichte* **1883**, *16*, 1465.

(11) Meisel, S. L.; Johnson, G. C.; Hartough, H. D. *J. Am. Chem. Soc.* **1950**, *72*, 1910. Curtis, R. F.; Jones, D. M.; Ferguson, G.; Hawley, D. M.; Sime, J. G.; Cheung, K. K.; German, G. *J. Chem. Soc., Chem. Commun.* **1969**, 165.

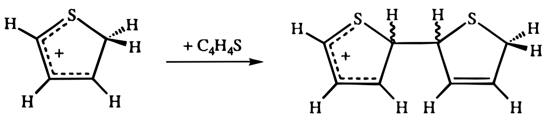
(12) Anal. Calcd (found) for $C_{4n}H_{4n}S_n$: C, 57.01 (57.10); H, 4.80 (4.70); S, 38.10 (37.90).

The ^1H NMR spectrum of the polymer consists of two complex sets of resonances in the regions δ 1.5−5.1 and 6.5−7.5. These are attributed to hydrogen atoms attached to sp^3 and sp^2 carbon atoms, respectively. The ratio of the two regions is 3:1.1, favoring the aliphatic signals. The IR spectrum of the polymer also suggests a combination of sp^3 and sp^2 centers. The spectrum is dominated by a signal at 2930 cm^{-1} that is associated with ν_{C-H} for sp^3 centers; ν_{C-H} for the sp^2 centers is observed at 3066 cm^{-1} and $\nu_{C=C}$ at 1449 cm^{-1}. Kovacic and McFarland appear to have isolated a similar polymer via the reaction of $C_4H_4S_4$ and $AlCl_3$ in CS_2.[13] The polymer structure is related to that of the thiophene trimer (2′,2″-thienyl-2,4-tetrahydrothiophene) generated by the trimerization of thiophene by H_3PO_4−clay mixtures.[11]



Studies on the effects of stoichiometry and substituents provided additional mechanistic insights. Thiophene polymerization was not induced with $TiCl_4$ or HCl/HOTf alone. For a given [HOTf], the M_n dropped strongly at low [Ti]/[C_4H_4S], indicating that titanium is consumed in the polymerization process. For solutions where [Ti]/[C_4H_4S] = 1, the influence of [HOTf] on M_n was negligible from ratios of 0.10 to 0.017. Thiophenes bearing substituents at the 2-position do not polymerize, as was demonstrated by GPC analyses of reactions with 2-methylthiophene and 2,5-dimethylthiophene. $TiCl_4$/HOTf mixtures react with 3-methylthiophene and 3-hexylthiophene to give oligiomers with $M_n \sim 900$ (dp $\sim$ 8) and 700 (dp $\sim$ 4), respectively.

The structure of $C_4Me_4HS^+$ suggests that polymerization is initiated by protonation which converts thiophene into a carbon electrophile[14] which then attacks unprotonated thiophene (eq 2).



(2)

This scenario is also consistent with inhibition by substituents at the 2 and 5 positions, as well as the considerable stability of 2-$HC_4Me_4S^+$. It remains uncertain if $TiCl_4$ assists in the polymerization,[15] but it is clear that $TiCl_4$ binds to the growing polymer, hence the requirement for high concentrations of $TiCl_4$. The affinity of the polymer for $TiCl_4$ was confirmed by treating purified samples of the polymer ($M_n = 2500$) with $TiCl_4$ to give the red adduct with the approximate stoichiometry of $(C_4H_4S)_n(TiCl_4)_{n/3}$.[16] Hydrolysis of this adduct regenerated the polymer without altering its M_n or polydispersity. Tetrahydrothiophene is known to form stable adducts with $TiCl_4$,[17] and the coordinating ability of 2,3-dihydrothiophene has recently been demonstrated.[18] Far-IR measurements of $(C_4H_4S)_n(TiCl_4)_{n/3}$ reveal a broad band at 400 cm^{-1}, typical of ν_{Ti-Cl} for Lewis base adducts of $TiCl_4$.[19]

In summary, protonation of thiophene by the superacid system HCl/$TiCl_4$ gives the $TiCl_4$-bound polymer $C_{4n}H_{4n}S_n(TiCl_4)_{n/3}$. This new material, while structurally complex, merits further study because of its low cost as well as its ability to bind transition metals. The polymerization mechanism implicates the formation of a protonated thiophene $C_4H_5S^+$. This proposal finds support in our isolation of salts of $HC_4Me_4S^+$.

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(14) Belen'kii, L. I. *Heterocycles* **1994**, *37*, 2029.

(15) The activation of unsaturated sulfur compounds via the combined action of Bronsted and Lewis acids: Derouane, D.; Harvey, J. N.; Viehe, H. G. *J. Chem. Soc., Chem. Commun.* **1995**, 993.

(16) Anal. Calcd (found) for $C_{12}H_{12}Cl_4S_3Ti$: C, 32.60 (32.77); H, 2.74 (2.75); S, 21.76 (21.34); Ti, 10.83 (9.70).

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(18) (a) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1989**, *28*, 1751. (b) Sauer, N. N.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 2160.

(19) Fowles, G. W. A; Walton, R. A. *J. Chem. Soc.* **1964**, 4330.