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Carbon–sulfur bond activation of thiophenes by [W(NPh){*o*-$(Me_3SiN)_2C_6H_4$}$(pyridine)_2$]†

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Addition of thiophene, 2-methylthiophene, benzothiophene or 3-methylthiophene to [W(NPh){*o*-$(Me_3SiN)_2C_6H_4$}-$(C_5H_5N)_2$] 1 affords the metallathiacycle complexes [{*o*-$(Me_3SiN)_2C_6H_4$}(NPh)W(SC_4H_4)] 2, [{*o*-$(Me_3SiN)_2C_6H_4$}-(NPh)W(SC_5H_6)] 3, [{*o*-$(Me_3SiN)_2C_6H_4$}(NPh)W(SC_8H_6)] 4 and [{*o*-$(Me_3SiN)_2C_6H_4$}(NPh)W(SC_5H_6)] 5a and 5b, providing the first example of thiophene C–S bond activation by a W(IV) metal complex.

Hydrodesulfurization (HDS), the process by which sulfur is removed from petroleum feedstocks, represents one of the largest-scale industrial processes that utilizes transition metal catalysts. The process involves treatment of crude oil with a high pressure of hydrogen gas (up to 200 atm) in the presence of an alumina-supported catalyst, typically Mo/Co, at elevated temperatures (300–450 °C).[1–5] Of the sulfur containing impurities present in petroleum feedstocks, thiophene and its derivatives are among the most difficult to desulfurize. In order to improve the efficiency of the HDS process, a better understanding of the interaction of thiophenes with transition metal complexes is necessary. As a result, homogeneous modeling of HDS has become an active area of research during the past decade.[4]

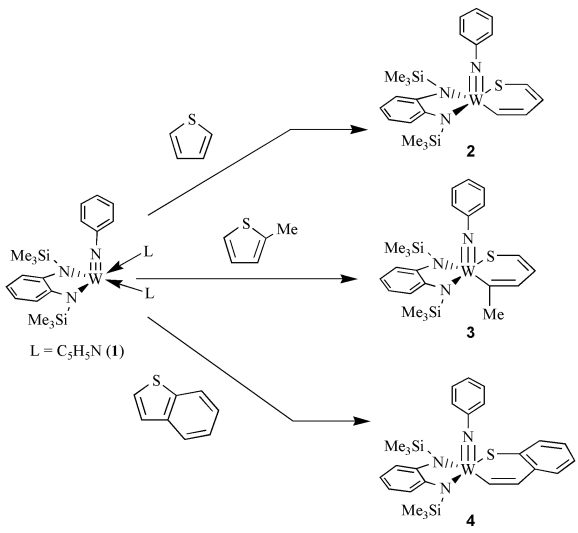
Many research groups have studied the coordination and activation of thiophenes, which are believed to be the initial steps in HDS. A variety of thiophene complexes have been prepared and studied possessing, η^1(S)-coordinated, η^4 and η^5 bound thiophenes.[6–10] In addition, several metal complexes have been found to promote direct C–S bond activation of thiophenes.[4] Surprisingly, thiophene complexes of group 6 metals (Mo and W), an integral component of an industrial HDS catalyst, have been almost non-existent. A recent report by Parkin and coworkers[11] of thiophene and benzothiophene C–S bond activation by the molybdocene complexes $[Me_2Si(C_5Me_4)_2]MoH_2$ and $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ represents the first homogeneous example of such chemistry with molybdenum. The analogous tungsten system has also been shown to facilitate the C–S bond activation of thiophene.[12]

Recently, we have prepared a series of coordinatively unsaturated [W(NPh){*o*-$(Me_3SiN)_2C_6H_4$}L_2] (L = pyridine, 4-picoline or quinoline) complexes.[13] Our investigation of ligand substitution reactions of the W(IV)L_2 complexes with unsaturated substrates has demonstrated the propensity of the W metal center to reduce the coordinated substrate ligand, thereby increasing the W(VI) character of the resulting compounds. These results have prompted us to examine the activity of these W(IV)L_2 complexes towards substrate oxidative addition, specifically the activation of the C–S bonds of thiophene and its derivatives.

Thermolysis (65 °C, 8–12 h) of a toluene solution containing [W(NPh){*o*-$(Me_3SiN)_2C_6H_4$}$(C_5H_5N)_2$] **1** and 2 equivalents of thiophene, 2-methylthiophene or benzothiophene afforded the carbon–sulfur bond activation products [{*o*-$(Me_3SiN)_2C_6H_4$}(NPh)W(SC_4H_4)] **2**, [{*o*-$(Me_3SiN)_2C_6H_4$}(NPh)-W(SC_5H_6)] **3** and [{*o*-$(Me_3SiN)_2C_6H_4$}(NPh)W(SC_8H_6)] **4**, respectively, as a dark red solid in 60–80% isolated yield for **2** and **3**, Scheme 1.‡ Isolation of a pure sample of compound **4** has proved difficult because the complex slowly decomposes during the work-up procedure. As determined by ^{1}H NMR spectroscopy, compound **4** is formed in *ca.* 50% yield.

Characterization of the reaction products by ^{1}H NMR spectroscopy was straightforward due to the distinct resonances and coupling constants associated with the thiophene ring protons, which are similar for all three compounds. For example, the ^{1}H NMR spectrum of **2** displays two resonances (δ 0.39 and 0.50), which correspond to the inequivalent Me_3Si groups. The metallathiacycle protons are shifted downfield with respect to free thiophene and appear as a doublet of doublets (δ 6.70, $^3J_{HH}$ 7, 9 Hz) corresponding to the β-CH, a doublet (δ 8.01, $^3J_{HH}$ 9 Hz) with ^{183}W satellites ($^2J_{WH}$ 8 Hz) for the α-CH, a doublet of doublets (δ 8.20, $^3J_{HH}$ 13, 7 Hz) for the γ-CH, and a doublet (δ 9.00, $^3J_{HH}$ 13 Hz) for the δ-CH adjacent to the S atom.

Compound **4** displays two doublet resonances corresponding to the α (δ 8.50, $^3J_{HH}$ 13 Hz) and β (δ 8.65, $^3J_{HH}$ 13 Hz) protons, respectively. The resonance at δ 8.50 has ^{183}W satellites ($^2J_{WH}$ 10 Hz), confirming the suggested C(vinyl)–S insertion product. The absence of a proton resonance in the ^{1}H NMR spectrum of **3** with ^{183}W satellites or in the vicinity of that observed for the α-CH proton of compound **2** suggests preferential activation of the (Me)C–S bond in the reaction of **1** with 2-methylthiophene. The observed downfield shift of the metallathiacycle protons for compounds **2**, **3** and **4** contrasts with the reported upfield shift with respect to free thiophene found for the complex $(C_5H_5)_2W(SC_4H_4)$.[12] This is presumably due to the increased electron deficiency of the d^0 W(VI) center in compounds **2**, **3** and **4** relative to the d^2, Cp_2W(IV) system.



Scheme 1 C–S bond activation products.

† Electronic supplementary information (ESI) available: experimental section, proton NMR spectra for **2**, **3** and **5a**,**b** and crystallography. See http://www.rsc.org/suppdata/cc/b1/b101955b/

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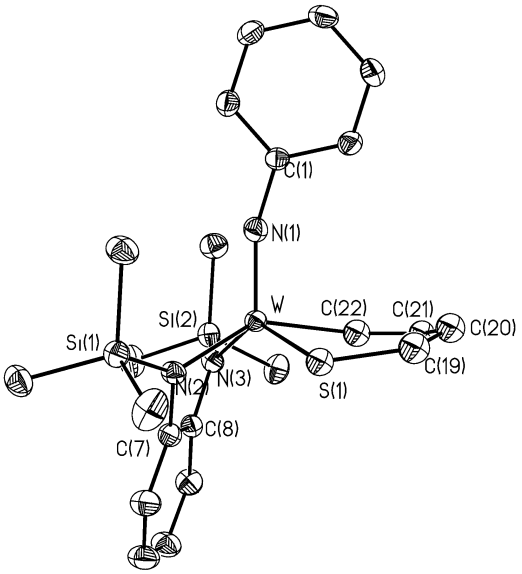
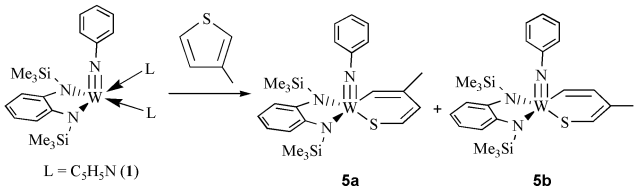


Fig. 1 Molecular structure of **2**, showing 50% thermal ellipsoids and the atom labeling scheme. The H atoms and the minor part of the disordered metallathiacycle are removed for clarity. Selected bond distances (Å) and angles (°): W–N(1) 1.734(3), W–N(2) 2.016(3), W–N(3) 2.008(3), W–S(1) 2.371(3), W–C(22) 2.196(9), S(1)–C(19) 1.722(12), C(19)–C(20) 1.192(16), C(20)–C(21), 1.600(16), C(21)–C(22) 1.289(14); W–N(1)–C(1) 162.4(3), N(1)–W–N(2) 116.06(13), N(1)–W–N(3) 117.02(14), N(1)–W–S(1) 104.49(13), N(1)–W–C(22) 98.0(3), C(22)–W–S(1) 83.7(3).

An X-ray diffraction study of a single crystal of **2** grown from a concentrated pentane solution at −40 °C confirmed the nature of the C–S bond activation product. Due to disorder in S1 and C22, the positions of the metallathiacycle atoms were solved independently in two parts. A molecular drawing of **2** with selected bond lengths and angles for the major part are shown in Fig. 1.§ Compound **2** adopts a five-coordinate, distorted square pyramidal geometry with the imido ligand occupying the apical position. The short W–N(imido) bond length of 1.734(3) Å, consistent with a W–N triple bond and the W–N(amido) bond lengths of 2.016(3) and 2.008(3) Å are similar to that observed for other W(VI) complexes.[14] The average bond lengths for the thiophene fragment of the complex suggest localized bonding within the metallathiacycle.

Thiophenes are known to interact with a metal center in a number of different modes however; a η^1-S-bound thiophene[6–10] is believed to be a prerequisite for C–S bond activation. Although the initial interaction of thiophene and its derivatives with compound **1** has not been directly observed, the ability of **1** to accommodate additional ligands has been demonstrated.[13] Compound **1** rapidly forms octahedral complexes with the addition ligands such as CO and PMe_3. For the reaction of the σ-donor ligand PMe_3 with **1**, the complex $[W(NPh)\{o\text{-}(Me_3SiN)_2C_6H_4\}(C_5H_5N)(PMe_3)_2]$ is the preferred product, suggesting labilization of one of the pyridine ligands upon coordination of the first PMe_3 ligands. Although thiophenes are weaker donor ligands than PMe_3, under the thermolysis conditions for the reaction of thiophenes with **1**, labilization of a pyridine ligand would generate the open coordination site necessary for C–S bond activation. Although no direct evidence for such a mechanism has been observed, it must be considered given the reactions of **1** with PMe_3.

Compound **1** also reacts with 2 equivalents of 3-methylthiophene. Unlike the previously described examples, 3-methylthiophene generates a mixture of the two possible C–S bond activation products, $[\{o\text{-}(Me_3SiN)_2C_6H_4\}(NPh)W(SC_5H_6)]$ **5a** and **5b**, Scheme 2.‡ As determined by ^{1}H NMR spectroscopy, the products are formed in a 60:40 ratio with **5a** as the major component. A similar product mixture was observed for the reaction of $Cp^*Rh(Ph)(H)(PMe_3)$ with 3-methylthiophene.[15] The observed product selectivity in the reaction of **1** with benzothiophene arises from steric congestion on one side of the thiophene ring, whereby C–S bond activation opposite the substituent is preferred. For the reaction of 3-methylthiophene with **1**, both C–S bonds are accessible as demonstrated by the formation of both **5a** and **b**.



Scheme 2 Product mixture generated from 3–methylthiophene C–S bond activation.

In summary, we have demonstrated that the chelate stabilized W(IV)L_2 complex $[W(NPh)\{o\text{-}(Me_3SiN)_2C_6H_4\}(C_5H_5N)_2]$ **1** facilitates the C–S bond activation of both thiophene and substituted thiophenes. To our knowledge, this reactivity is the first example of thiophene C–S bond activation by a W(IV) species. Currently we are investigating other substrates, such as more highly substituted thiophenes and nitrogen and oxygen containing heterocycles, to determine the scope of this reactivity.

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Notes and references

‡ All reactions and manipulations were carried out using standard Schlenk techniques or in a dry box under atmospheres of argon or nitrogen. *Synthesis* of compounds **2**–**5a**,**b**: to a purple toluene solution of **1** were added 2 equivalents of the appropriate thiophene. Thermolysis (65 °C) of the reaction mixtures for 8–12 h resulted in a color change from purple to red. After removal of the reaction solvent *in vacuo*, the crude products were extracted with cyclohexane and dried *in vacuo*.

§ *Crystal data* for **2**: $C_{22}H_{31}N_3SSi_2W$, M = 609.59, triclinic, space group $P\bar{1}$, a = 9.4647(4), b = 11.7141(5), c = 12.4830(5) Å, α = 101.246(1), β = 111.655(1), γ = 93.904(1)°, V = 1246.64(9) Å^3, Z = 2, T = 173(2) K, final $R1$ = 0.0264, $wR2$ = 0.0647, GOF (on F^2) = 1.024.

The structure was solved by the Direct Methods in SHELXTL5, and refined using full-matrix least squares.[16] The non-H atoms, except the disordered, were treated anisotropically, whereas the methyl hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The S1–C22 chain is found to be disordered by a 180° rotation and was refined in two parts; the major part is represented by the S1–C22 chain and the minor part by S1′–C22′. Their site occupation factors were dependently refined to 0.55(1) for the major part and, consequently, 0.45(1) for the minor part. All atoms of the disorder were refined with isotropic thermal parameters. The W–S1 and W–S1′ bonds were constrained to be equivalent during refinement. Similarly, W–C22 and W–C22′ were also constrained to remain equivalent.

CCDC reference number 162416. See http://www.rsc.org/suppdata/cc/b1/b101955b/ for crystallographic data in CIF or other electronic format.

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