# Synthesis of Tungsten Thienyl Complexes via C–H Bond Activation of Thiophenes

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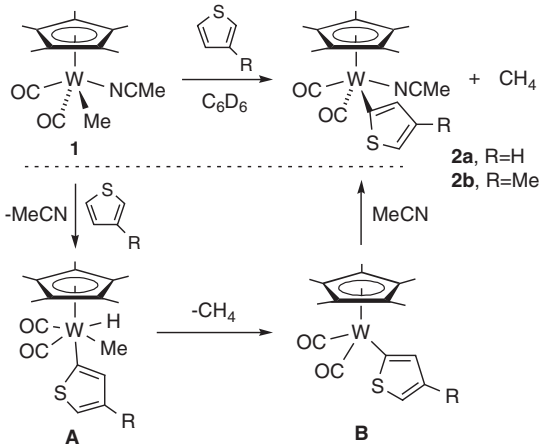
The reactions of *cis*-Cp*W(CO)$_2$(MeCN)Me (**1**) with thiophene or 3-methylthiophene resulted in selective α-C–H bond activation to give *cis*-Cp*W(CO)$_2$(MeCN)R [R = 2-C$_4$H$_3$S (**2a**), 2-C$_4$H$_2$S-4-Me (**2b**)]. **2a** reacted with 3-methylthiophene to afford thienyl exchange products **2b** and thiophene in addition to decomposition products. Reversibility of the exchange reaction was shown by the reaction of **2b** with thiophene.

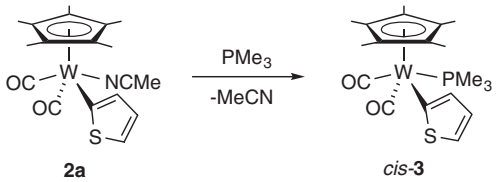
In relation to hydrodesulfurization,[1] recent extensive experimental and theoretical studies on the reactions of transition metal complexes with thiophenes revealed that they display a variety of reaction modes such as $\eta^1$-S coordination, C–S bond activation, C–H bond activation, etc. depending upon their electronic and steric properties.[1–3] In the course of our recent studies on Si–H bond activation by *cis*-Cp*W(CO)$_2$(MeCN)Me (**1**) and related complexes,[4] we became interested in its capability to activate C–S and/or C–H bonds of thiophenes. Here we describe the reactions of **1** with thiophenes leading to selective α-C–H bond activation.

The NMR tube reaction of **1** with thiophene (5 equiv) in C$_6$D$_6$ at room temperature led to the immediate production of *cis*-Cp*W(CO)$_2$(MeCN)(2-C$_4$H$_3$S) (**2a**, >90%)[5] and methane (δ 0.15) (Scheme 1). The $^1$H NMR spectrum of **2a** shows three characteristic doublet of doublets (δ 7.35, 7.49, and 7.62) due to the 2-thienyl protons in addition to coordinated MeCN (δ 1.08) and Cp* (δ 1.70) signals. The cis arrangement of the CO ligands is shown by two CO signals (δ 251.4 and 257.8) in the $^{13}$C NMR spectrum of *cis*-Cp*W(CO)$_2$(CD$_3$CN)(2-C$_4$H$_3$S) (**2a**-$d_3$) in CD$_3$CN.[5] Similar reaction using 3-methylthiophene resulted in the selective formation of *cis*-Cp*W(CO)$_2$(MeCN)(2-C$_4$H$_2$S-4-Me) (**2b**), which shows two thienyl proton signals as singlets (δ 7.19 and 7.37). Complexes **2a** and **2b** were isolated as air-sensitive yellow solids in 50 and 57% yields, respectively, in preparative reactions.




**Scheme 1.**

Although X-ray quality crystals of **2a** were not obtained, the cis-dicarbonyl 2-thienyl structure was confirmed by X-ray analysis of the stereospecific acetonitrile-substitution product, *cis*-Cp*W(CO)$_2$(PMe$_3$)(2-C$_4$H$_3$S) (*cis*-**3**), formed in the reaction of **2a** with PMe$_3$ (Scheme 2).[6,7] The ORTEP drawing and selected bonding parameters are shown in Figure 1.[8]




**Scheme 2.**

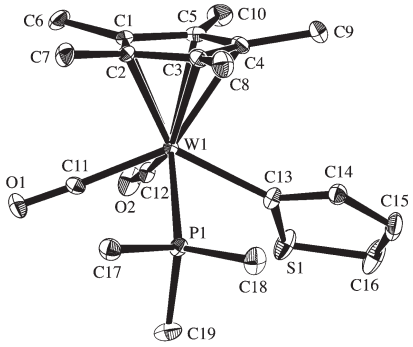


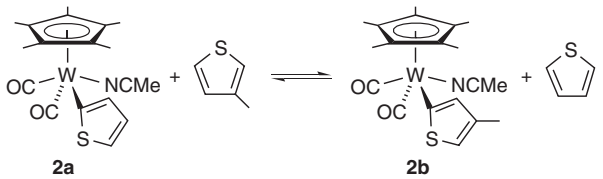

**Figure 1.** ORTEP drawing of *cis*-**3**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1–P1, 2.479(1); W1–C11, 1.955(4); W1–C12, 1.946(5); W1–C13, 2.238(4); S1–C13, 1.744(5); S1–C16, 1.722(6); C13–C14, 1.385(6); C14–C15, 1.433(7); C15–C16, 1.338(9); P1–W1–C11, 75.6(1); P1–W1–C13, 76.6(1); C11–W1–C12, 73.7(2); C12–W1–C13, 82.4(2); C13–S1–C16, 95.0(3); S1–C13–C14, 106.7(3); C13–C14–C15, 114.5(5); C14–C15–C16, 114.1(5); S1–C16–C15, 109.6(4).

When a solution of *cis*-Cp*W(CO)$_2$(CD$_3$CN)Me (**1**-$d_3$) and thiophene in CD$_3$CN was monitored by $^1$H NMR spectroscopy, no reaction was observed after 3 h in contrast to the rapid reaction in C$_6$D$_6$. This observation suggests the intermediacy of coordinatively unsaturated Cp*W(CO)$_2$Me generated from **1** upon release of the MeCN ligand. A plausible mechanism for the formation of **2** based on oxidative addition/reductive elimination sequence is shown in Scheme 1,[9] where an α-C–H bond of thiophene is cleaved by Cp*W(CO)$_2$Me. The resulting activation product **A** undergoes reductive elimination of methane to produce 16e intermediate **B**, whose vacant coordination site is occupied by MeCN to afford **2a**. In the reaction with 3-methylthiophene, regiospecific α-C–H bond activation occurs at the sterically less hindered 5-position of the thiophene ring to give **2b**.

In C$_6$D$_6$, **2a** gradually decomposed by releasing the MeCN ligand to give a complex mixture containing Cp*W(CO)$_3$(2-C$_4$H$_3$S) (**4a**)[10] as a major component (ca. 10% at 35% decomposition after 5 h) along with several unidentified products.

When the reactivity of **2a** toward thiophene was examined in $C_6D_6$, similar decomposition products were only observed. Interestingly, however, the decomposition was slowed compared to that in the absence of thiophene, suggesting that thiophene might interact with **2a** to restrain the decomposition.

To get information on the interaction, **2a** was treated with neat 3-methylthiophene (30 equiv) to minimize the decomposition (Scheme 3). After 3 days at room temperature, thienyl exchange products **2b** (16%) and free thiophene (16%) were formed in addition to unchanged **2a** (47%), although decomposition was not completely suppressed as shown by the formation of **4a** (11%) and minor unidentified products. Reversibility of the exchange reaction is demonstrated by the reaction of **2b** with thiophene (30 equiv) to give **2a** (33%) and free 3-methylthiophene (32%) along with unchanged **2b** (49%) and decomposition products including $Cp^*W(CO)_3(2\text{-}C_4H_2S\text{-}4\text{-}Me)$ (**4b**)[10] (6%) under the same conditions. In contrast to the fairly clean reaction of **1** with the thiophenes, the reactions of **2a**,**b** suffered from the formation of decomposition products probably due to the lesser reactivity caused by steric hindrance of the thienyl ligands. The higher yields of the exchange products and the lower yields of decomposition products in the reaction of **2b** with thiophene compared to the reaction of **2a** with 3-methylthiophene can be related to the higher reactivity of thiophene compared to 3-methylthiophene toward C–H bond activation by **1**. In the competitive reaction of **1** with a 1 : 1 mixture of the thiophenes (10 equiv each) in toluene-$d_8$ from $-78\,^\circ C$ to room temperature, **2a** and **2b** were formed in a 2.8 : 1 ratio.




**2a** **2b**

**Scheme 3.**

Similarly to the case of **1**-$d_3$, in $CD_3CN$ **2a**-$d_3$ and **2b**-$d_3$ are stable and did not react with 3-methylthiophene and thiophene, respectively, suggesting $Cp^*W(CO)_2(2\text{-}C_4H_3S)$ and $Cp^*W(CO)_2(2\text{-}C_4H_2S\text{-}4\text{-}Me)$ for the intermediates to activate the C–H bonds of the thiophenes in the thienyl exchange reactions. In the reaction of **2a** with thiophene in $C_6D_6$, the corresponding process would reproduce **2a** and thiophene to prevent the decomposition to some extent. Thus, acetonitrile tungsten complexes **1** and **2** were found to undergo C–H bond activation of thiophenes, and provide rare examples of tungsten complexes active for C–S and/or C–H bond cleavage of thiophenes.[11]

C–H bond activation of thiophene is often accompanied by C–S bond activation, but **1** and **2** lack the latter reactivity. One reason for this seems to be larger steric crowding at their metal centers compared to those of complexes showing C–S bond activation reactivity: $Cp^*W(CO)_2R$ (R = Me, $2\text{-}C_4H_3S$, $2\text{-}C_4H_2S\text{-}4\text{-}Me$) from **1** and **2** vs $Cp^*Rh(PMe_3)$ from a typical C–S bond activator $Cp^*Rh(PMe_3)(Ph)H$,[12] for example. It has been suggested that large steric crowding at a metal center favors C–H bond activation, although the change of electron density on a metal center also affects the reactivity.[2] Further reactivity studies of **2** are now under way.

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**References and Notes**


1 For recent reviews, see: a) R. J. Angelici, *Polyhedron*, **16**, 3073 (1997). b) W. D. Jones, D. A. Vicic, R. M. Chin, J. H. Roache, and W. Myers, *Polyhedron*, **16**, 3115 (1997). c) R. J. Angelici, *Organometallics*, **20**, 1259 (2001).

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3 A. L. Sargent and E. P. Titus, *Organometallics*, **17**, 65 (1998) and the references cited therein.

4 a) H. Sakaba, K. Ishida, and H. Horino, *Chem. Lett.*, **1998**, 149. b) H. Sakaba, M. Tsukamoto, T. Hirata, C. Kabuto, and H. Horino, *J. Am. Chem. Soc.*, **122**, 11511 (2000).

5 In the following NMR data, 2-thienyl and 4-methyl-2-thienyl ligands are abbreviated as T and MT, respectively. Satisfactory elemental analyses were obtained for **3** and **4a**,**b**, but could not for air-sensitive **2a**,**b**. **2a**,**b**-$d_3$ were obtained by dissolving **2a**,**b** in $CD_3CN$. **2a**: $^1$H NMR (400 MHz, $C_6D_6$) δ 1.08 (s, 3H, MeCN), 1.70 (s, 15H, $Cp^*$), 7.35 (dd, $J$ = 4.9, 3.2 Hz, 1H, T), 7.49 (dd, $J$ = 3.2, 0.7 Hz, 1H, T), 7.62 (dd, $J$ = 4.9, 0.7 Hz, 1H, T). **2a**-$d_3$: $^{13}$C NMR (100 MHz, $CD_3CN$) δ 4.7 (septet, $J_{CD}$ = 21 Hz, *C*$D_3$CN), 10.6 ($C_5$*Me*$_5$), 104.9 (*C*$_5$Me$_5$), 129.3 (T), 130.3 (T), 137.2 (T), 140.3 ($CD_3$*C*N), 149.3 (T), 251.4 (CO), 257.8 (CO). **2b**: $^1$H NMR (400 MHz, $C_6D_6$) δ 0.97 (s, 3H, MeCN), 1.72 (s, 15H, $Cp^*$), 2.33 (s, 3H, MT-Me), 7.19 (s, 1H, MT), 7.37 (s, 1H, MT). **2b**-$d_3$: $^{13}$C NMR (100 MHz, $CD_3CN$) δ 4.8 (septet, $J_{CD}$ = 21 Hz, *C*$D_3$CN), 10.7 ($C_5$*Me*$_5$), 15.3 (MT-*Me*), 105.0 (*C*$_5$Me$_5$), 126.2 (MT), 139.9 (MT), 140.2 ($CD_3$*C*N), 140.5 (MT), 150.2 (MT), 251.4 (CO), 258.0 (CO).

6 The reaction of **2a** with $PMe_3$ in $C_6D_6$ exclusively afforded *cis*-**3**, which subsequently underwent slow isomerization to form an equilibrium mixture with its trans isomer. An equilibrium ratio of *cis*-**3** : *trans*-**3** = 4.6 : 1 was obtained after 2 days at room temperature. *Cis*-**3** was isolated as yellow crystals in 46% yield in a preparative reaction. *cis*-**3**: $^1$H NMR (400 MHz, $C_6D_6$) δ 0.95 (d, $J_{PH}$ = 8.8 Hz, 9H, $PMe_3$), 1.73 (s, 15H, $Cp^*$), 6.99 (dd, $J_{HH}$ = 3.1 Hz, $J_{PH}$ = 2.4 Hz, 1H, T), 7.12 (dd, $J_{HH}$ = 4.9, 3.1 Hz, 1H, T), 7.48 (dd, $J_{HH}$ = 4.9 Hz, $J_{PH}$ = 1.8 Hz, 1H, T); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 11.4 ($C_5$*Me*$_5$), 18.0 (d, $J_{PC}$ = 31.4 Hz, $PMe_3$), 103.1 (*C*$_5$Me$_5$), 131.1 (T), 131.2 (T), 136.5 (d, $J_{PC}$ = 29.2 Hz, T), 140.6 (d, $J_{PC}$ = 7.5 Hz, T), 238.5 (br, CO), 250.2 (br, d, $J_{PC}$ = 24 Hz, CO). *trans*-**3**: $^1$H NMR (400 MHz, $C_6D_6$) δ 1.16 (d, $J_{PH}$ = 8.8 Hz, 9H, $PMe_3$), 1.60 (s, 15H, $Cp^*$), 7.24 (dd, $J_{HH}$ = 4.9, 3.2 Hz, 1H, T), 7.52 (d, $J_{HH}$ = 4.9 Hz, 1H, T), 7.61 (d, $J_{HH}$ = 3.2 Hz, 1H, T); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 11.0 ($C_5$*Me*$_5$), 19.5 (d, $J_{PC}$ = 31.4 Hz, $PMe_3$), 102.3 (*C*$_5$Me$_5$), 128.9 (T), 131.8 (d, $J_{PC}$ = 9.7 Hz, T), 132.0 (T), 140.6 (d, $J_{PC}$ = 2.2 Hz, T), 237.3 (d, $J_{PC}$ = 20.1 Hz, CO).

7 Crystal data for *cis*-**3**: $C_{19}H_{27}O_2PSW$, monoclinic, space group $P2_1/a$ [No. 14], $a$ = 16.016(1), $b$ = 8.4880(8), $c$ = 16.517(3) Å, $\beta$ = 115.725(2)°, $V$ = 2022.8(4) Å$^3$, $Z$ = 4, μ(Mo Kα) = 59.08 cm$^{-1}$, Rigaku/MSC Mercury CCD diffractometer, $R$ = 0.019 ($R_W$ = 0.022) for 3284 observed reflections [$I > 3.00\sigma(I)$].

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9 σ-Bond metathesis might be conceivable as another possible mechanism.

10 **4a**,**b** were identified by spectral comparison with authentic samples prepared by the reactions of **2a**,**b** with CO (1 atm) in benzene. **4a**: $^1$H NMR (400 MHz, $C_6D_6$) δ 1.52 (s, 15H, $Cp^*$), 7.11 (dd, $J$ = 5.1, 3.4 Hz, 1H, T), 7.30 (dd, $J$ = 3.4, 0.7 Hz, 1H, T), 7.43 (dd, $J$ = 5.1, 0.7 Hz, 1H, T); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 10.1 ($C_5$*Me*$_5$), 104.9 (*C*$_5$Me$_5$), 125.6 (T), 129.8 (T), 134.0 (T), 141.2 (T), 222.0 (CO) 232.5 (CO). **4b**: $^1$H NMR (400 MHz, $C_6D_6$) δ 1.55 (s, 15H, $Cp^*$), 2.19 (s, 3H, MT-Me), 7.01 (s, 1H, MT), 7.15 (s, 1H, MT); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 10.2 ($C_5$*Me*$_5$), 15.2 (MT-*Me*), 104.9 (*C*$_5$Me$_5$), 126.1 (MT), 130.0 (MT), 140.2 (MT), 143.8 (MT), 221.9 (CO), 232.7 (CO).

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