# Selective Synthesis of Tungsten(VI) Mono(catecholato) Complexes Using 1,2-Bis(trimethylsiloxy)benzenes: Molecular Structure of $WCl_4(O_2C_6H_4)$

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Reaction of tungsten hexachloride with 1,2-bis(trimethylsiloxy)benzenes (**1**) selectively gives mono(catecholato)tetrachlorotungsten(VI) complexes, $WCl_4(O_2$-1,2-$C_6H_3R$-4) (**2a**: R = H; **2b**: R = Me; **2c**: R = Bu$^t$). $^1H$ NMR spectra of these complexes show significant upfield shifts of signals of aromatic protons. The distorted octahedral geometry of **2a** was revealed by X-ray crystallography.

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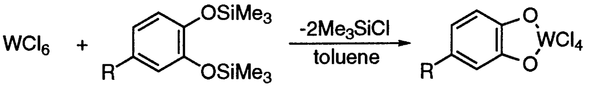
High valent tungsten complexes bearing alkoxide and aryloxide ligands are of great interest as ring-opening metathesis polymerization catalysts.[1,2] The catalytic behavior of such catalyst systems can be controlled by the steric and electronic effects of the ligands. For example, we have reported that the high polymerization of alkylacetylenes was made possible by the combined bulkiness of the alkyl group on the acetylene and that of the metal center of $WCl_{6-n}(OC_6H_3Me_2\text{-}2,6)_n$/cocatalyst (n = 1—4) system.[3,4] Following this study, we tried to prepare tungsten catecholate complexes to investigate the chelating effect of the ligands on the property of the catalyst systems. Among the mono-, bis- and tris(catecholate) compounds of tungsten, our target compounds are mono(catecholato)tetrachlorotungsten(VI) derivatives, $WCl_4$(cat) (cat = catecholate derivatives), because the catalytic activities of mono(catecholate) comlexes should be higher than those of bis- and tris(catecholate) analogues.[3]

The previous synthetic methods for metal catecholates involve the alcoholysis of metal halides,[5,6] condensation of catechols with metal-oxo groups,[7] the reaction of metal carbonyl with ammonium salt of catechol,[8] and the oxidative addition of quinones to low valent metal complexes.[9,10] Among these synthetic methods, only the reported route to $WCl_4$(cat) is the reaction of tungsten chlorides such as $WCl_4L_2$ ($L_2$ = $(OEt_2)_2$, $(THF)_2$, DME), $WCl_5$, and $WCl_6$ with tetrachloro-1,2-benzoquinone or 9,10-phenanthrenequinone,[9] however the handling of simpler 1,2-benzoquinone derivatives such as unsubstituted 1,2-benzoquinone is troublesome due to their thermal instability. We presumed that the reaction of $WCl_6$ with 1,2-bis(trimethylsiloxy)benzene or its alkyl-substituted ones would smoothly proceed to give $WCl_4$(cat), because the 1:1 and 1:2 reactions of early transition metal chlorides with 2,6-dimethylphenyl trimethylsilyl ether selectively yield the corresponding mono- and bis(aryloxide) complexes.[11] In this paper, we report a selective synthesis of a series of mono(catecholato)tetrachlorotungsten(VI) complexes from the reaction of $WCl_6$ with 1,2-bis(trimethylsiloxy)benzenes.

1,2-Bis(trimethylsiloxy)benzenes (**1**) were prepared by similar method as applied for mono(trimethylsiloxy)benzene derivatives.[11] A 1:1 mixture of $WCl_6$ and **1a** was refluxed in toluene for 2 h to give a red purple solution. Evaporation of the solvent gave a crude powdery product. Recrystallization from toluene-hexane gave dark green prisms of **2a** in 41% yield. Similarly complexes **2b** and **2c** were prepared in 23% and 57% yield, respectively. Complexes **2a**, **2b**, and **2c** were characterized by elemental analysis, electrospray ionization mass spectrometry (ESI-MS), and $^1H$ NMR.[12]



**1a**: R = H
**1b**: R = Me
**1c**: R = Bu$^t$

**2a**: R = H
**2b**: R = Me
**2c**: R = Bu$^t$

The most remarkable feature of these complexes is significant upfield shifts of the signals of the aromatic protons in $^1H$ NMR spectra (Figure 1). The resonances of 3,6-protons and 4,5-protons of **2a** in $CDCl_3$ appeared at δ 6.47 and 5.69, respectively, which are upfield shifted by 1.03 and 1.17 ppm to δ 5.44 and 4.52 in $C_6D_6$. The solvent effect of $C_6D_6$ on the chemical shifts of the aromatic protons in **2a** is greater than those observed in a mono(aryloxo)tungsten(VI) complex, $WCl_5(OC_6H_3Me_2\text{-}2,6)$[11,13] ($^1H$ NMR in $CDCl_3$: δ 7.38 (3,5-H), 6.28 (4-H); in $C_6D_6$: δ 6.57 (3,5-H), 5.52 (4-H); upfield shifts: 0.81 and 0.76 ppm), which might have higher Lewis acidity than **2a**. The greater paramagnetic shift is caused by the electron-deficient metal center through π-conjugation with the catecholate ligand.

In toluene solution, the UV-visible spectra of **2a** showed an intense peak at $\lambda_{max}$ = 501 nm. When **2a** was dissolved in THF, two absorption bands were observed at $\lambda_{max}$ = 394 and 668 nm at first, both of which disappeared in a few minutes with a set of color change from purple to green and finally colorless. This might be attributed to decomposition through some kinds of charge transfer from THF.

The molecular structure of compound **2a** is shown in Figure 2.[14] The tungsten atom adopts a distorted octahedral geometry having two oxygen atoms in *cis* position. The narrow O1–W–O1* angle (76.5(3)°) and the wide Cl1–W–Cl1* angle (106.8(2)°) result from the chelating coordination of the catecholate ligand. There is a 2-fold axis in **2a** through W1 and

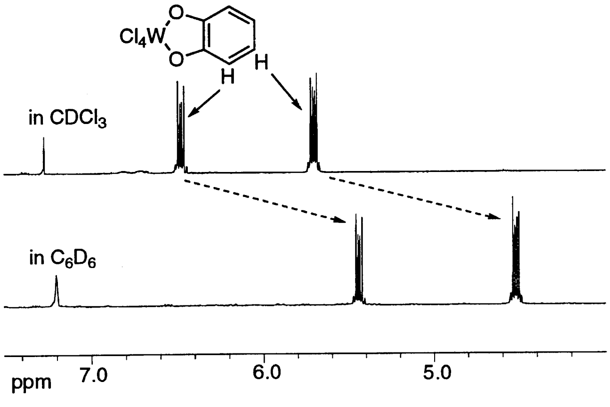


**Figure 1.** $^1H$ NMR spectra of **2a** in $CDCl_3$ and $C_6D_6$.

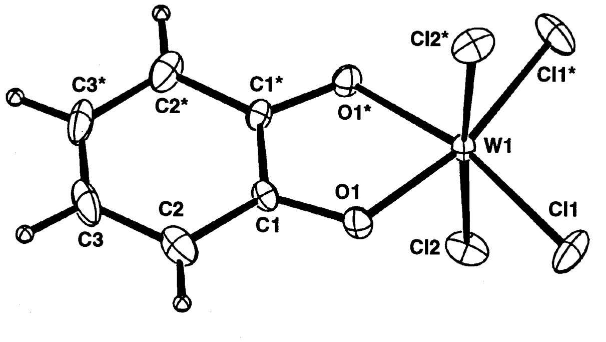


**Figure 2.** A drawing of **2a** with the numbering scheme. Thermal ellipsoids scaled at 20% probability level. Selected bond distances (Å) and angles (degree): W(1)–Cl(1) 2.250(3), W(1)–Cl(2) 2.312(2), W(1)–O(1) 1.932(6), O(1)—C(1) 1.326(9), Cl(1)–W(1)–Cl(1)* 106.8(2), Cl(1)–W(1)–Cl(2) 88.8(1), Cl(1)–W(1)–Cl(2)* 88.7(1), Cl(1)–W(1)–O(1) 88.3(2), Cl(1)–W(1)–O(1)* 164.9(2), Cl(2)–W(1)–Cl(2)* 175.8(2), Cl(2)–W(1)–O(1) 91.3(3), Cl(2)–W(1)–O(1) 92.0(3), O(1)–W(1)–O(1) 76.5(3), W(1)–O(1)–C(1) 118.9(5)

the center of C3 and C3*. The significantly short W1–O1 distance of 1.932(6) Å indicates the strong π-donation from catecholate to tungsten. The extended dπ-pπ conjugation through the chelating catecholate ligand is realized by the planar $WO_2C_6H_4$ unit. It is notable that the W1–Cl1 distance trans to oxygen atom (2.250(3) Å) is apparently shorter by 0.06 Å than the W1–Cl2 distance trans to chlorine atom (2.312(2) Å), when we consider that the W–Cl distances trans to oxygen are usually comparable or slightly longer than those trans to chlorine .[11,15,16] When we assume xy plane on the $WO_2C_6H_4$ unit, $d_{yz}$ and $d_{zx}$ orbitals are not available for π-donation from Cl2 and Cl2* due to strong π-donation from O1 and O1*, while $d_{xy}$ orbital is available for π-donation from Cl1 and Cl1*.

Our preliminary experiments revealed that these catecholate complexes have catalytic activities for the polymerization of *t*-butylacetylene (catalyst **2a**: in toluene at 60 °C for 24 h; polymer yield 84%, $M_n = 1.2 \times 10^5$, $M_w/M_n = 2.5$, *cis*-68%). However, their activities were lower compared to monodentate aryloxide complexes such as $WCl_4(OC_6H_3Me_2\text{-}2,6)_2$. This can result from higher electron density at the metal center in **2**. Thus the dπ-pπ conjugation significantly affects the activity of the catalyst system. When complex **2a** was combined with $Et_3Al$, poly(*t*-butylacetylene) with higher *cis*-content (*cis*-86%) was obtained. Further studies on catalysis and reactivity of **2** are in progress.

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12 **1a**: $^1H$ NMR (270 MHz, $CDCl_3$, 30 °C) δ 6.84 (s, 4H, aromatic protons), 0.26 (s, 18H, $OSiMe_3$). **1b**: $^1H$ NMR (270 MHz, $CDCl_3$, 30 °C) δ 6.71 (d, 1H, 5-H), 6.63 (m, 2H, 3- and 6-H), 2.23 (s, 3H, 4-Me) 0.24 (s, 18H, $OSiMe_3$). **1c**: $^1H$ NMR (270 MHz, $CDCl_3$, 30 °C) δ 7.27 (m, 2H, 3- and 6-H), 7.18 (d, 1H, 5-H), 1.69 (s, 9H, 4-Bu$^t$) 0.67 (s, 18H, $OSiMe_3$).
**2a**: mp 123—124 °C. ESI-MS for $^{184}W$: 434 ($M^-$). $^1H$ NMR (270 MHz, $C_6D_6$, 30 °C) δ 5.44 (dd, 2H, 3,6-H), 4.52 (dd, 1H, 4,5-H). **2b**: mp 134—136 °C. ESI-MS for $^{184}W$: 448 ($M^-$). $^1H$ NMR (270 MHz, $C_6D_6$, 30 °C) δ 5.30 (s, 1H, 3-H), 5.25 (d, 1H, 6-H), 3.78 (d, 1H, 5-H), 3.73 (s, 3H, 4-Me). **2c**: mp 123—124 °C. ESI-MS for $^{184}W$: 490 ($M^-$). $^1H$ NMR (270 MHz, $C_6D_6$, 30 °C) δ 5.79 (s, 1H, 3-H), 5.44 (d, 1H, 6-H), 4.29 (d, 1H, 5-H), 0.84 (s, 9H, 4-Bu$^t$).

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14 Crystal and refinement data for **2a**: $C_6H_4O_2WCl_4$, formula weight = 433.76, space group $P4_12_1$ (tetragonal), $a$ = 9.560(2), $c$ = 11.490(3) Å, $V$ = 1050.2(5) $Å^3$, $Z$ = 4, $d_{calc}$ = 1.372 $gcm^{-3}$, unique reflections = 3319, used reflections = 763 ($I > 3\sigma(I)$), $R$ = 0.0280, $R_w$ = 0.0310.

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