Tungsten Oxo Salicylate Complexes from Tungsten Hexachloride Reactions Systems

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Received December 27, 2000

Tungsten hexachloride is a potent halogen-transfer agent, capable of reacting directly with salicylic acid to generate a tungsten oxo fragment and salicoyl chloride. As a result, oxo complexes dominate the chemistry of tungsten(VI) salicylates. Both mono- and disalicylate substituted tungsten oxo complexes are accessible. The Brønsted free acid W(═O)Cl(Hsal)(sal) complex is a sparingly soluble, presumably polymeric material that can be dissolved in THF. The THF adduct has been characterized by NMR spectroscopy, although an X-ray crystallographic study indicates that the product cocrystallizes with a structurally analogous d^1 WCl_2(Hsal·THF)(sal) byproduct. The remaining chloride ligand in W(═O)Cl(Hsal)(sal) is replaced by a bridging oxo unit when the reaction contains a significant excess of salicylic acid. The product "linear" oxo bridged ditungsten complex, [W(═O)(Hsal)(sal)]$_2$O, forms intramolecular hydrogen bonds, accounting for its high solubility in noncoordinating solvents. An X-ray study shows that the intramolecular Hsal·sal hydrogen bonding in this complex accommodates a more linear W−O−W arrangement than does a previously observed class of isostructural diolate derivatives. Tungsten oxo tetrachloride, formed in the initial reaction between salicylic acid and WCl_6, also reacts with the salicoyl chloride byproduct to generate tungsten salicoylate (OAr-2-COCl) complexes.

Introduction

Six coordinate complexes of tungsten (VI), bearing a range of uni- and dinegative ligands, have been widely studied over the past twenty years.[1−34] We have been intrigued by the hydrogen bonding behavior of Brønsted acid complexes of the tungsten oxo, aryl imido, and acetylene derivatives—specifically, complexes containing salicylate (Hsal) or phenol−phenolate (HOArO) monoanions.[32−36] Systematic variation of the steric and electronic environment at the metal by changing the identity or substitution pattern of the appended ligands provides an opportunity to study the influence of the high oxidation state metal on the acidity of the metal bound functionality in non-

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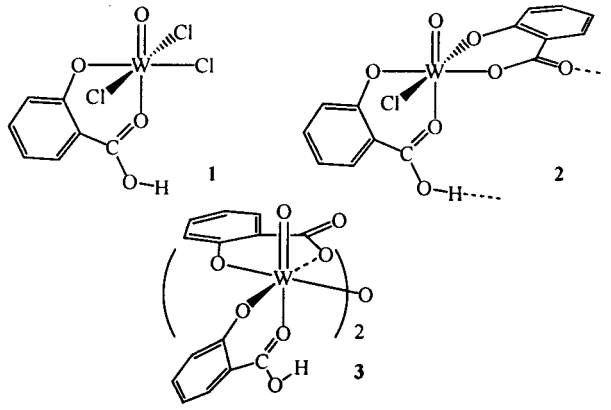
10.1021/ic001456k CCC: $20.00
Published on Web 08/17/2001

aqueous solvents. These compounds also form building blocks for hydrogen bonded inorganic/organic hybrid materials.[33−36] While investigating the synthesis of simple monosalicylate $W(=X)Cl_3(Hsal)$ (1) complexes,[33] we encountered a surprisingly diverse range of tungsten salicylate derivatives, including **2** and **3**, that derive from reactions employing tungsten hexachloride as the metal precursor. During reactions with salicylic acid (H_2-sal), we repeatedly observed the incorporation of both bridging and terminal oxo ligands at the metal, producing complexes characterized as structures **1**, **2**, and **3**.



The reaction between carboxylate derivatives and metal halides is a little exploited method for the synthesis of metal oxygen multiple bonds.[37−40] This paper describes our efforts to define the origin of the ubiquitous oxo ligands in these products and to understand the reaction pathways that produce the observed oxo products. Our results re-emphasize the potency of WCl_6 as a chlorine transfer agent and infer the intermediacy of electron transfer in the substitution reactions.

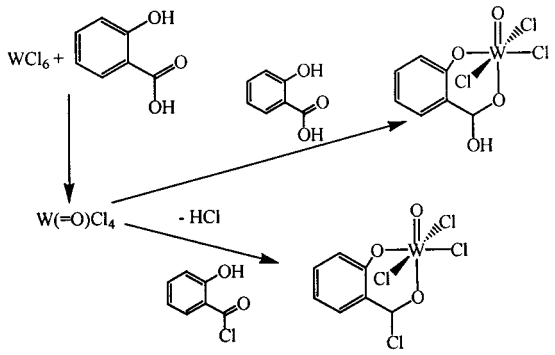
Results and Discussion

Tungsten hexachloride reacts with a stoichiometric quantity of salicylic acid in dichloromethane solution at room temperature, generating a very dark red solution that evolves gaseous HCl. The ^{1}H NMR spectrum of the product mixture indicates that it contains products having three different salicylate chemical environments. This mixture was separated partially by dissolution in hexane. By comparing the spectra of the original and fractionated mixtures to that of pure $W(=O)Cl_3$(Hsal) (**1**), it is possible to assign one of the three sets of salicylate multiplets to this complex. **1** is a dimeric Brønsted acid in solution and can be prepared in high yield directly from reactions between $W(=O)Cl_4$ and salicylic acid in nonpolar media.[10,32−35]

A similar reaction of WCl_6 and salicylic acid in a 1:2 molar ratio forms two of the products observed previously in comparable amounts. One of these compounds is **1**, while the other forms colorless crystals that can be purified by distillation from the reaction mixture. This crystalline product reacts with water yielding salicylic acid and HCl and is unequivocally identified as salicoyl chloride, *o*-C_6H_4(OH)(COCl), by its NMR spectra and melting point.[41]

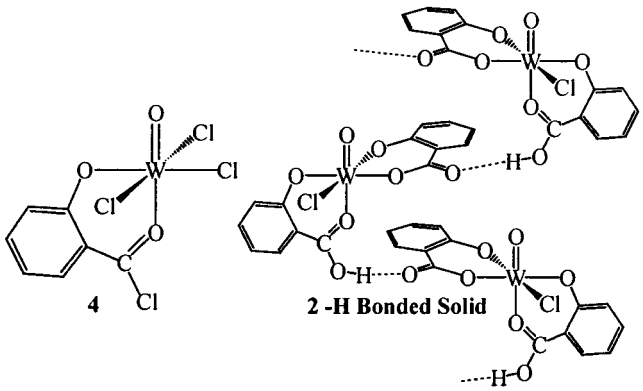
Based on this observation, it is evident that the carboxylic acid group of the salicylic acid reactant is the principle source

Scheme 1



of the oxo ligand transferred to tungsten in these reactions (Scheme 1). Hydrated salicylic acid was eliminated as the possible source of oxygen for the oxo ligand by scrupulously drying the acid precursor prior to the reaction. Attempts to induce oxo complex formation through the addition of stoichiometric quantities of water to tungsten chloro salicylate reaction mixtures produced free salicylic acid rather than any discrete tungsten oxo salicylate complexes (vide infra). Throughout our studies of reactions with WCl_6, we found consistently that simple $W(sal)_3$ complexes of tungsten(VI) were inaccessible by routes previously used for the synthesis of analogous complexes containing chelating diolate ligands.[17]

The observed oxo group transfer by salicylic acid is consistent with the reported formation of acetyl chloride when methyl acetate is reacted with WCl_6 and with observations of other chlorine atom transfer reactions involving WCl_6.[39,42,43] An η^1-tungsten salicylate ester is a potential intermediate in oxo transfer process, by analogy with the known chemistry of PCl_5. Like the chemistry of traditional chlorinating reagents, including PCl_5, the initial oxygen atom transfer step greatly reduces the halogenating aptitude of the tungsten.[44,45] There was no evidence for the formation of significant quantities of tungsten dioxo products, even in the presence of a significant excess of salicylic acid. In addition to salicoyl chloride and **1**, $W(=O)Cl_3(OC_6H_4$-COCl) (**4**) is identifiable in the product mixtures by its distinctive ^{1}H NMR spectrum.[34]



The ease of oxo transfer and the possible intermediacy of an η^1-benzoate intermediate raise questions about the chemose-

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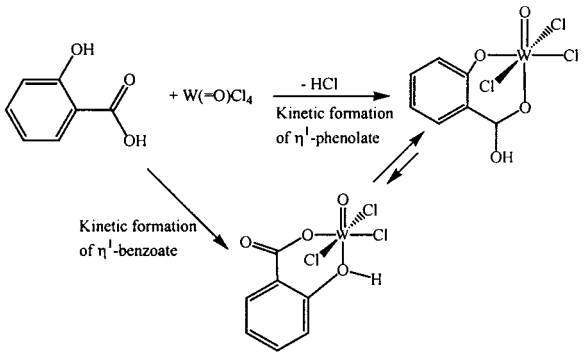
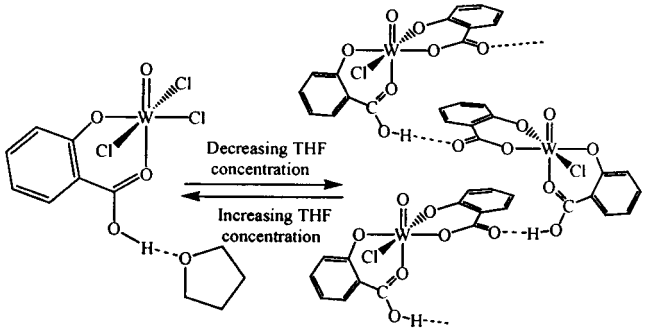
Scheme 2



Scheme 3



lectivity of reactions between salicylic acid and tungsten halides (Scheme 2). The sal monoanions prefer the (η^1-phenolate) structure observed in **1** and **4**. Despite this preference, we cannot determine whether the η^1-phenolate or the η^1-benzoate form of the salicylate complex is the kinetic substitution product, because Griffiths and Williams have detected exchange between these two bonding modes of Hsal in another system.[9] Initial formation of an η^1-benzoate intermediate is consistent with the expectation that the more acidic carboxylic acid proton is likely to be the most active in the protonolysis reaction.

A solid-phase reaction between WCl_6 and an excess of salicylic acid heated with a 140−160 °C oil bath yields W(═O)Cl(Hsal)(sal) (**2**). Only W(═O)Cl_3(Hsal) is isolated from similar solid-phase reactions between W(═O)Cl_4 and salicylic acid (1:6). Reactions involving W(═O)Cl_4 also require salicylic acid to reach its melting point before the HCl evolution. The marked differences in the reactivity and product distribution observed in the substitution of WCl_6 suggests that it may have access to a different substitution pathway than W(═O)Cl_4.

Direct spectroscopic characterization of **2** is difficult, because it is sparingly soluble in common nonprotic solvents except THF. Mass spectrometric studies of **2** are consistent with the assigned formulation. It seems reasonable that W(═O)Cl(Hsal)(sal) forms an extended hydrogen-bonded network (**2**−**H-Bonded Solid**) in the solid state like its isoelectronic counterpart [pyH][W(═O)$_2$(Hsal)(sal)] prepared in Williams' group.[11] This would account for the reduced solubility of **2** in solvents except for strong Lewis bases. The ^{1}H NMR spectrum of the THF adduct in $CDCl_3$ is complex, with intense THF peaks and an unexpectedly large number of multiplets attributable to salicylate ligands. The complexity of the spectrum results from an equilibrium between a monomeric THF adduct and associated THF substituted oligomers of varying nuclearity (Scheme 3). Consistent with this proposal, the appearance of the ^{1}H NMR spectrum of W(═O)Cl(Hsal·THF)(sal) (**2·THF**) is highly dependent on the concentration of both **2** and THF. The addition of several drops of THF to the NMR samples results in complete dissolution of solid residues and the simplification of the spectrum to that expected of a mono-THF adduct.

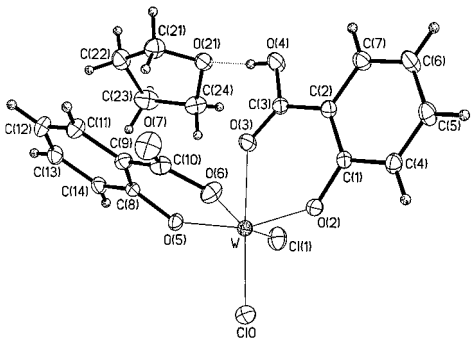
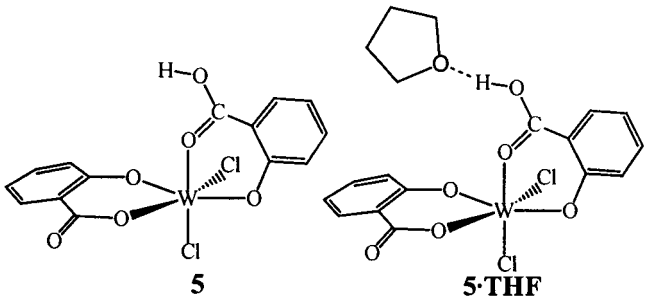


Figure 1. Thermal ellipsoid representation of the molecular structure of $WCl_{1.84}O_{0.16}$(Hsal·THF)(sal) **(7·THF)$_{0.16}$(10·THF)$_{0.84}$.**

Table 1. Selected Bond Distances (Å) and Angles (deg) for W(═O)$_{0.14}$Cl$_{1.86}$(Hsal·THF)(sal) **(7·THF)$_{0.16}$(10·THF)$_{0.84}$**

W−Cl(1)	2.3248(10)	W−ClO	2.1158(10)
W−O(2)	1.896(3)	W−O(3)	2.252(3)
W−O(5)	1.885(2)	W−O(6)	1.960(3)
O(4)−C(3)	1.282(4)	O(3)−C(3)	1.246(4)
O(4)−O(21)	2.54	C(10)−O(7)	1.203(4)
Cl(1)−W−ClO	97.36(4)	Cl(1)−W−O(2)	93.71(9)
O(2)−W−ClO	98.53(8)	O(3)−W−Cl(1)	80.66(8)
O(3)−W−ClO	177.65(7)	O(2)−W−O(3)	80.39(10)
O(5)−W−Cl(1)	90.34(8)	O(5)−W−ClO	100.43(8)
O(5)−W−O(2)	159.94(11)	O(5)−W−O(3)	80.90(10)
O(6)−W−Cl(1)	161.27(9)	O(6)−W−ClO	101.23(9)
O(6)−W−O(2)	85.77(12)	O(6)−W−O(3)	80.80(11)
O(6)−W−O(5)	84.16(11)	W−O(6)−C(10)	136.1(2)
W−O(3)−C(3)	131.0(2)	W−O(2)−C(1)	139.2(2)
W−O(5)−C(8)	133.8(2)		

A small quantity of red crystalline material was obtained from a THF solution of W(═O)Cl(Hsal)(sal) upon addition of hexane cosolvent. Although bulk samples of the precursor analyze as W(═O)Cl(Hsal)(sal), an X-ray study identified the crystals as a cocrystallized mixture of **2·THF** and a structurally homologous d^1 WCl_2(Hsal·THF)(sal) complex (**5·THF**).



The substitution of a chloride complex for a structurally similar complex containing an oxo ligand is in keeping with Parkin's studies of the origin of "bond stretch isomerism."[46] W(═O)-Cl(Hsal)(sal) and WCl_2(Hsal)(sal) should differ only in a presumed 0.35 Å shortening of the tungsten oxygen double bond in **7** compared to the corresponding tungsten chlorine bond in **5**.

A thermal ellipsoid representation of the structure of W(═O)$_{0.14}$Cl$_{1.86}$(Hsal·THF)(sal) **(2·THF)$_{0.14}$(5·THF)$_{0.86}$** is shown in Figure 1. Table 1 contains a compilation of selected bond distances and angles. The THF adduct is mononuclear and possesses an octahedral coordination environment around the metal atom. It is noteworthy that the quantity of the d^1 dichloride

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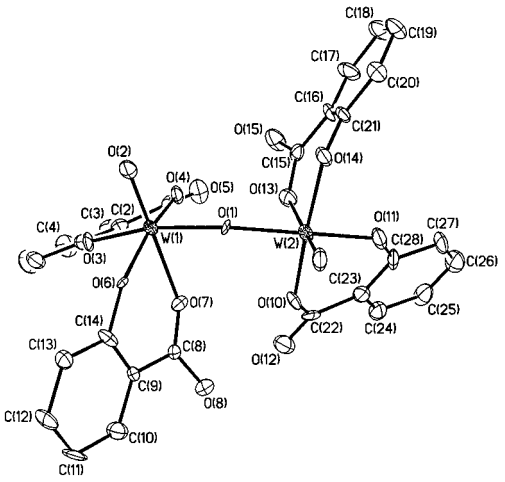
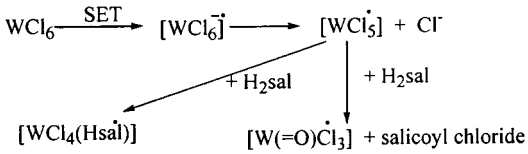


Figure 2. Thermal ellipsoid representation of the molecular structure of $[W(=O)(Hsal)(sal)]_2O$ (**8**). Representations of hydrogen atom positions have been omitted for clarity.

Scheme 4



complex in the crystal is approximately five times that of the d^0 oxochloride complex. The structure is characterized by the shortened W−ClO distance of 2.116(1) Å, and a long *trans*-W−O(3) distance of 2.252(3) Å to the weakly donating carbonyl oxygen of the protonated carboxylic acid group.[16,32] O(2), O(5), O(6), and Cl(1) are all bent away from Cl/O out of the square plane between 7.3 and 11.2°, although it seems unlikely that Cl/O is producing a significant trans-effect.[47]

The existence of a d^1 $WCl_2(Hsal)(sal)$ product is in keeping with the known reactivity of WCl_6. Bell demonstrated that WCl_6 is prone to single electron-transfer reactions during substitution by phenolic ligands.[4] These studies have also proven that the d^1 complexes are labile and undergo more rapid isomerization reactions than the analogous d^0 complexes. We hypothesize that an electron transfer-induced process may be an important or predominant initial step in the reaction between WCl_6 and salicylic acid (Scheme 4), but have not tested this assumption due to the complexity of this system. These results are consistent with the increased reactivity of WCl_6 in substitution reactions compared with $W(=O)Cl_4$.

A solid-state reaction between WCl_6 and excess salicylic acid, warmed in a 200 °C oil bath, reduces the yield of W(═O)Cl-(Hsal)(sal) to a trace and forms a complicated product mixture. In addition to salicylate complexes, phenol is formed through the decarboxylation of salicylic acid. A red crystalline substance was isolated from this mixture. Unlike products containing intermolecular hydrogen bonds, such as **2** and **5**, this complex is very soluble in methylene chloride and toluene. The product shows a nonconcentration dependent ^1H NMR spectrum with two sets of multiplets for salicylate ligands. Single crystals of this product, which analyzed as $[W(=O)(Hsal)(sal)]_2O$, were obtained for X-ray analysis.

Figure 2 shows a thermal ellipsoid representation of $[W(=O)(Hsal)(sal)]_2O$ (**3**), while selected bond distances and angles are shown in Table 2. The complex exists as an oxo bridged dimer of W(═O)(Hsal)(sal) subunits. The like stereochemistry of the two tungsten centers gives the molecule virtual C_2 symmetry. Furthermore, this stereochemical complementarity allows an Hsal ligand from one tungsten center to hydrogen bond to the carboxylate unit of the sal ligand on the other tungsten center. A similar compound can be isolated from syntheses employing 3,5-di-*tert*-butylsalicylic acid with $W(=O)Cl_4$ in refluxing chlorobenzene. The hydrogen-bonded protons in these oxo bridged species cluster in a distinctive chemical shift range around $\delta = 17$. The intramolecular hydrogen bonding observed in this structure explains both the solubility of **3** in nonpolar solvents and its inability to strongly bind organic Lewis bases, including diethyl ether and tetrahydrofuran.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Structure of $[W(=O)(Hsal)(sal)]_2O$ (**8**)

W(1)−O(2)	1.680(9)	W(1)−O(1)	1.8859(7)
W(1)−O(6)	1.9003(6)	W(1)−O(3)	1.932(11)
W(1)−O(4)	1.978(9)	W(1)−O(7)	2.219(9)
W(2)−O(9)	1.647(10)	W(2)−O(1)	1.8902(7)
W(2)−O(14)	1.900(9)	W(2)−O(11)	1.948(9)
W(2)−O(10)	1.957(9)	W(2)−O(13)	2.212(10)
O(3)−C(7)	1.335(11)	O(4)−C(1)	1.31(2)
O(5)−C(1)	1.23(2)	O(6)−C(14)	1.334(6)
O(7)−C(8)	1.27(2)	O(8)−C(8)	1.30(2)
O(10)−C(22)	1.32(2)	O(11)−C(28)	1.324(11)
O(12)−C(22)	1.23(2)	O(13)−C(15)	1.26(2)
O(14)−C(21)	1.355(11)	1.30(2)	
O(2)−W(1)−O(1)	98.3(4)	O(2)−W(1)−O(6)	96.9(3)
O(1)−W(1)−O(6)	97.21(3)	O(2)−W(1)−O(3)	99.5(5)
O(1)−W(1)−O(3)	160.3(3)	O(6)−W(1)−O(3)	88.8(3)
O(2)−W(1)−O(4)	99.9(4)	O(1)−W(1)−O(4)	86.7(3)
O(6)−W(1)−O(4)	162.1(2)	O(3)−W(1)−O(4)	82.1(4)
O(2)−W(1)−O(7)	176.5(4)	O(1)−W(1)−O(7)	80.7(3)
O(6)−W(1)−O(7)	80.0(2)	O(3)−W(1)−O(7)	82.0(4)
O(4)−W(1)−O(7)	83.4(3)	O(9)−W(2)−O(1)	96.8(4)
O(9)−W(2)−O(14)	95.6(4)	O(1)−W(2)−O(14)	97.9(3)
O(9)−W(2)−O(11)	101.4(5)	O(1)−W(2)−O(11)	160.7(3)
O(14)−W(2)−O(11)	86.8(4)	O(9)−W(2)−O(10)	101.9(5)
O(1)−W(2)−O(10)	87.8(3)	O(14)−W(2)−O(10)	160.9(4)
O(11)−W(2)−O(10)	82.2(4)	O(9)−W(2)−O(13)	175.8(4)
O(1)−W(2)−O(13)	80.9(3)	O(14)−W(2)−O(13)	81.3(4)
O(11)−W(2)−O(13)	81.2(4)	O(10)−W(2)−O(13)	81.6(4)
W(1)−O(1)−W(2)	162.97(2)	C(7)−O(3)−W(1)	134.0(8)
C(1)−O(4)−W(1)	134.2(9)	C(14)−O(6)−W(1)	137.1(3)
C(8)−O(7)−W(1)	129.7(8)	C(22)−O(10)−W(2)	133.1(9)
C(28)−O(11)−W(2)	130.7(8)	C(15)−O(13)−W(2)	129.6(9)
C(21)−O(14)−W(2)	134.1(7)		

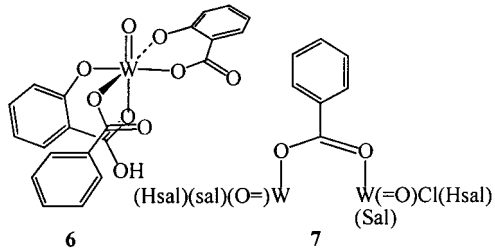
The structural characteristics of $[W(=O)(Hsal)(sal)]_2O$ correspond closely to the structures of other salicylate complexes.[9−11,32−35] The short average W═O distances of 1.654 (9) Å and concomitant long average trans W−O distances of 2.216 (9) Å are characteristic of tungsten oxo salicylate complexes.[9−11,32−35] The average $O_{Ar}-W-O_{COO}$ bite angle of the salicylate chelates is 81°. This is characteristic of sal ligands, but is significantly larger than the 75° angles that are characteristically observed for chelating catecholate ligands.[17,18] This relaxed bite angle accommodates the octahedral coordination geometry of the tungsten center better than the more restricted chelating diolates.[17,18] It also accounts for the observation that W−O distances trans to the oxo ligand are 0.1 Å shorter in the salicylate complexes than in their catecholate analogues. The carbonyl group of the protonated Hsal unit coordinates trans to the oxo ligand. The poor σ-donor ability of the η^1-benzoate groups compared to the η^1-phenoxide groups is clearly indicated by their respective W−O distances of 1.967 (10) Å and 1.920 (9) Å. The W−μ-O distances of 1.8859 (7) and 1.8902 (7) Å are within the range observed previously for "linear" oxo bridges

(47) Kerschner, J. L.; Fanwick, PE.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1989**, *28*, 780.

in ditungsten complexes.[17,18] Although these distances are not characteristic of strong π-bonding between tungsten and the bridging oxygen, they are significantly shorter than W−O distances of 1.920 Å observed for non-π-donating aryloxide ligands.[16] Consistent with weak π-donation by the μ-oxo ligand, it is the phenoxide oxygen of the sal ligand that lies trans to the bridging oxo ligand rather than the more weakly σ-donating η^1-benzoate group. Another factor that may favor the placement of the sal carbonyl group cis to the μ-oxo group is the ability of the carbonyl to act as an intramolecular hydrogen bond acceptor.

The intramolecular hydrogen bonding observed in $[W(=O)(Hsal)(sal)]_2O$ is characteristic of intermolecular hydrogen bonds studied in neutral mononuclear tungsten salicylate complexes.[10,32−35] The O−O distances of 2.54 Å (average) reflect strong hydrogen bonding.[16] These hydrogen bonds are achieved with 6° less distortion of the W−μ-O−W angle from linearity than is found in structurally related ditungsten catecholate complexes.[17,18] The carbonyl and carboxylic acid units have greater radial extension from tungsten than analogous alkoxide and alcohol moieties. This allows the tungsten centers in the salicylate complex to maintain greater separation and still support strong directional intramolecular hydrogen bonding. A byproduct of this structural motif is that the dihedral relationship between the tungsten oxo units of 76.4° is much smaller than the average of 95° typically found in known oxo bridged diolate complexes.[17,18]

Tests of several sets of experimental conditions were required to develop a controlled synthesis of **3**. Given the possible involvement of adventitious water, these studies included controlled hydrolysis experiments. Although isostructural diolate complexes, $[W(=O)(Hdiolate)(diolate)]_2O$, were synthesized previously through hydrolysis of $W(diolate)_3$ precursors in wet alcohol,[17] the hydrolysis of W(=O)Cl(Hsal)(sal) with stoichiometric water in THF solution results only in the isolation of salicylic acid. Only very small quantities of $[W(=O)(Hsal)(sal)]_2O$ were observed in the products of other reactions, including those between W(=O)Cl(Hsal)(sal) and hexamethyldisilylsulfide ($(Me_3Si)_2S$), and between $W(=O)Cl_4$ and H_2-sal in varying stoichiometries. Based on these observations, we suggest that the oxo unit replacing the remaining chlorine atom during the formation of **3** again probably originates in salicylic acid reactant. Refluxing 3 equiv of salicylic acid with $W(=O)Cl_4$ for extended periods in chlorobenzene produces modest yields of $[W(=O)(Hsal)(sal)]_2O$. Pure $[W(=O)(Hsal)(sal)]_2O$ is obtained as orange−red crystals containing a nonstoichiometric quantity of solvent through recrystallization from dichloromethane or toluene. Again, it seems plausible that a discrete tungsten η^1-salicylate ester (**6**) is an intermediate in the introduction of the μ-oxo bridge. The formation of a carboxylate bridged intermediate (**7**) could bring the metals into sufficiently close proximity to facilitate the final oxo group transfer step.



6 **7**

Conclusions

Tungsten hexachloride is a potent halogen transfer agent, which is capable of reacting directly with salicylic acid to generate salicoyl chloride and both $W(=O)Cl_3(Hsal)$ and $W(=O)Cl_3(OC_6H_4COCl)$. Consequently, oxo complexes dominate the chemistry of these tungsten salicylates. Both mono- and disalicylate substituted tungsten oxo complexes are accessible products of substitution reactions. The W(=O)Cl(Hsal)(sal) complex forms a sparingly soluble, presumably polymeric material that can be dissolved in THF and has been structurally characterized as the THF adduct. A $WCl_2(Hsal\cdot THF)(sal)$ d^1 complex is formed during the synthesis of W(=O)Cl(Hsal·THF)(sal) and cocrystallizes with W(=O)Cl(Hsal·THF)(sal). This product mixture lends some support to the hypothesis that electron-transfer reactions may be involved in substitution reactions involving WCl_6. Reactions under forcing conditions in the presence of excess salicylic acid result in the replacement of the remaining chloride ligand in W(=O)Cl(Hsal)(sal) by a bridging oxo unit. The resulting "linear" oxo bridged ditungsten complex, $[W(=O)(Hsal)(sal)]_2O$, forms intramolecular hydrogen bonds, and consequently it is highly soluble in noncoordinating solvents. The intramolecular Hsal·sal hydrogen bonding scheme accommodates a more linear W−O−W arrangement than a previously observed class of structurally analogous diolate derivatives.

Experimental Section

All experimental procedures were carried out in a nitrogen atmosphere using standard Schlenk and glovebox techniques. Gaseous nitrogen was dried with 5 Å molecular sieves. All commercial solvents were purified using standard methods, distilled under a nitrogen atmosphere, degassed by purging with pure nitrogen, and stored over 5 Å molecular sieves. Starting materials such as salicylic acid, catechol, hexamethyldisilyl sulfide, tungsten hexachloride, and tungsten oxytetrachloride were stored under a nitrogen atmosphere. Chloroform-d_1 was degassed with nitrogen and stored over 5 Å molecular sieves. NMR spectra were obtained on Varian XL-300 and Brucker AM-500 MHz instruments. Mass spectra were obtained on the AutoSpecEQ instrument (positive FAB in NBA); solutions of the samples were prepared in the inert atmosphere. Elemental analyses were performed by Desert Analytics, P.O. Box 41838, Tuscon, AZ 85717.

WCl_6 Reacting with Salicylic Acid (H_2sal). Tungsten hexachloride (1.189 g) was slurried in a Schlenk flask with dichloromethane (10 mL). Salicylic acid (0.414 g) was slurried in a separate flask with dichloromethane (10 mL), and the suspension was added to the WCl_6 slurry through a cannula. The red solution turned very dark, and gaseous HCl formed. After stirring overnight, all of the solids dissolved. The solvent was evaporated in vacuo, leaving a black residue. ^{1}H NMR spectroscopy showed that the products contained salicylate ligands in three different chemical environments. The most soluble component of the mixture was extracted with hexane. After slow evaporation of hexane solution, a small quantity (0.1 g) of a black crystalline material was isolated. This material was identified as $W(=O)Cl_3(OPh\text{-}2\text{-}COCl)$ by comparison to authentic NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (H, dd, 6-position of −OPh-2-COCl), 8.01 (H, dt, 5-position), 7.46 (H, dt, 4-position), 7.22 (H, dd, 3-position). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.86 (carbonyl), 159.67, 140.25, 136.16, 129.40, 123.59, 123.10.

WCl_6 Reacting with Two Equivalents of H_2sal. Tungsten hexachloride (1.0467 g) was slurried in a Schlenk flask with dichloromethane (10 mL). Salicylic acid (0.7291 g) was slurried in a separate flask with dichloromethane (10 mL), and the suspension of acid was added to the WCl_6 slurry via cannula. The red solution turned very dark, and gaseous HCl formed. After stirring overnight, all of the solids dissolved. The solvent was evaporated under vacuum, leaving a dark red solid residue. According to the ^{1}H NMR spectrum, there were two chemical environments for the sal ligand in comparable amounts, one of which

Table 3. Crystal Data and Structure Refinement for

	$W(=O)_{0.14}Cl_{1.86}(Hsal\cdot THF)(sal)$	$[W(=O)(Hsal)(sal)]_2O$
empirical formula	$[C_{18}H_{17}Cl_2O_7W]_{0.86}-[C_{18}H_{17}C_lO_8W]_{0.14}$	$C_{29}H_{20}O_{15}W_2$
fw	597.34	1047.05
Temp (K)	218(2)	251(2)
space group	$P2_1/c$	$C2/c$
unit cell dimensions	$a = 9.97010(10)$ Å	$a = 16.983(2)$ Å
	$b = 15.67030(10)$ Å	$b = 21.683(2)$ Å
	$c = 12.5001(2)$ Å	$c = 18.755(3)$ Å
	$\alpha = 90^o$	$\alpha = 90^o$
	$\beta = 93.5660(10)^o$	$\beta = 114.23(1)^o$
	$\gamma = 90^o$	$\gamma = 90^o$
vol (Å^3)	1949.17(4)	6298(2)
Z	4	8
density (calc. g/cm^3)	2.036	2.209
absorption coeff (mm^{-1})	6.220	7.544
Wavelength (Mo Kα,Å)	0.71073	0.71073
final *R* indices	$R1 = 0.0232$	$R1 = 0.0614$
$[I > 2\sigma(I)]^a$		
	$wR2 = 0.0537$	$wR2 = 0.1470$
R indices (all data)	$R1 = 0.0299$	$R1 = 0.0784$
	$wR2 = 0.0594$	$wR2 = 0.1470$

[a] Quantity minimized $= R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$; $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$.

was identified on the basis of its NMR spectrum as $W(=O)Cl_3(Hsal)$. This mixture was treated with hexane, and the resulting solution, after separation from the solid residue, was concentrated under vacuum. The resulting red oil was distilled under vacuum at room temperature, and a white solid condensate formed. This crystalline substance melted at 18.0 °C into a colorless free-flowing liquid and reacted readily with water, yielding salicylic acid and HCl. Its ^{1}H and ^{13}C NMR spectra correspond to those of salicoyl chloride, HOC_6H_4COCl.

W(═O)Cl(Hsal)(sal) (2). Solid WCl_6 (3.1 mmol) and salicylic acid (18.6 mmol) were mixed in a Schlenk tube and heated gradually in an oil bath. Intensive HCl evolution began around 120 °C, but heating was continued until the reaction mixture reached 130−140 °C. After the evolution of HCl stopped, the mixture was heated quickly to 160 °C and cooled to ambient temperature. The cold mixture was treated with diethyl ether, dissolving the salicylic acid. The dark purplish red microcrystalline insoluble material was filtered off, washed with diethyl ether and dichloromethane, and dried in vacuo. The product was highly soluble in tetrahydrofuran, and was stable in dry air, but slowly hydrolyzed by moist air. Yield: 73% (1.15 g). Elemental analysis: found; 33.02% C, 1.37% H; calculated; 33.04% C, 1.77% H. Mass spectrum (positive FAB in NBA, THF solution): 509, 524, 626, 641.

W(═O)Cl(Hsal·THF)(sal) (2·THF). This adduct was prepared by slow crystallization from a mixed THF/hexane solution of W(═O)Cl(Hsal·THF)(sal). Base-free W(═O)Cl(Hsal)(sal) (0.20 g) was dissolved in tetrahydrofuran (7 mL). The resulting dark red solution was then concentrated in vacuo, mixed with hexane (3 mL), and heated in a water bath to redissolve the precipitate. On standing, a dark red crystalline product separated from the supernatant solution. The mother liquor was decanted, and the solid was dried in vacuo. The yield of W(═O)Cl(Hsal·THF)(sal) was relatively low (0.05 g). A small amount of W(═O)Cl(Hsal···THF)(sal), slightly contaminated with the base-free precursor, was obtained from the supernatant solution on addition of more hexane. Total yield of W(═O)Cl(Hsal···THF)(sal) 47% (0.1 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (H, d), 8.09 (H, dd), 7.80 (H, dd), 7.56 (H, dd), 7.20 (H, m), 7.07 (H, t), 7.02 (H, d), 6.77 (H, d), 3.71 (4H, t, O−CH_2 in THF), 1.84 (4H, O−CH$_2$−CH_2 in THF).^{13}C NMR (125 MHz, $CDCl_3$, partial): δ 173.22, 160.55, 136.98, 134.82, 131.83, 131.63, 126.80, 123.15, 122.74, 121.98, 121.50, 119.99, 119.73, 67.95 (O−CH_2 in THF), 25.55 (O−CH$_2$−CH_2 in THF).

[W(═O)(Hsal)(sal)]$_2$O (3). A mixture of $W(=O)Cl_4$ (2.017 g) and salicylic acid (1.631 g), molar ratio 1:2, was stirred in chlorobenzene (10−12 mL) for 30 min. The solution turned dark red; a microcrystalline precipitate and gaseous HCl were formed. The mixture was then heated until visible HCl formation stopped. Upon cooling, a microcrystalline sample presumed to be W(═O)Cl(Hsal)(sal) separated from the red solution. An additional equivalent of salicylic acid (0.815 g) was added, and this mixture was refluxed overnight. Further HCl evolution was observed. After cooling, a precipitate of W(═O)Cl(Hsal)(sal) (^{1}H NMR evidence) was quickly filtered off, the supernatant solution was cooled to −18 °C, and the solution was decanted from the crystalline product. The product was washed with toluene and dried under vacuum. ^{1}H NMR spectra revealed the product to be a mixture of [W(═O)(Hsal)(sal)]$_2$O and H_2sal. The H_2sal was removed by washing with diethyl ether (the dinuclear tungsten product is insoluble in ether). The crude complex was recrystallized from dichloromethane or toluene. Yield: 34% (0.643 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 19.9 (2H, bs), 8.06 (2H, d), 8.00 (2H, d), 7.79 (2H, t), 7.44 (2H, t), 7.25 (2H, d), 7.19 (2H, t), 7.00 (2H, t), 6.55 (2H, d).^{13}C NMR (125 MHz, $CDCl_3$): δ 172.98, 170.15, 161.38, 159.98, 136.43, 136.40, 131.50, 130.953, 125.49, 122.05, 121.42, 120.26, 118.24, 115.16. Mass spectrum (pos. FAB in NBA, CH_2Cl_2): 963.

[W(═O)(H-3,5-*t*-Bu$_2$sal)(3,5-*t*-Bu$_2$sal)]$_2$O. A mixture of $W(=O)Cl_4$ (1.0409 g) and 3,5-di-*tert*-butyl salicylic acid (1.5749 g), molar ratio 1:2, was refluxed in chlorobenzene (75 mL) for 18 h. After cooling, the chlorobenzene was removed in vacuo. The residue was extracted with hexane. This solution was cooled to −20 °C overnight, and a red powder deposited from solution. Yield: 66% (1.5107 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 15.92 (2H, bs), 7.24, 7.75, 7.85, 7.98 (2H, d) 1.62, 1.30, 1.29,1.02 (9H, s).^{13}C NMR (125 MHz, $CDCl_3$): δ 174.22, 171.91, 158.62, 157.83, 148.31, 143.90, 141.46, 131.71, 131.45, 126.82, 126.44, 125.61, 118.68, 115.24, 35.934, 35.36, 34.88, 30.74, 31.69, 30.71, 29.90. Elemental Analysis: found; 51.36% C, 5.66% H; calculated; 51.07% C, 5.86% H.

Hydrolysis of W(═O)Cl(Hsal)(sal) and $W(=O)Cl_3$(Hsal). A stoichiometric amount of water (0.0192 g) in THF solution (1.65 mL) was added to a THF solution (12 mL) of W(═O)Cl(Hsal)(sal) (1.087 g) slowly at −78 °C with a rapid stirring. The mixture was stirred for about 2 h, warmed to room temperature, and evaporated in vacuo. A ^{1}H NMR spectrum of the reaction mixture showed no [W(═O)(Hsal)(sal)]$_2$O, but contained new species that exhibited three types of salicylate ligand environments. Unfortunately, these species were unstable in solution and were not isolated in a pure state.

$W(=O)Cl_3$(Hsal) (1.257 g) was dissolved in THF (15−20 mL). The solution was cooled to −78 °C, and a THF solution (2.15 mL) of water (0.0255 g) was added dropwise with stirring. The reaction mixture was stirred overnight and did not change color, although a small amount of light precipitate formed. An aliquot of the solution was transferred to an NMR tube, the solvent was evaporated in vacuo, and the ^{1}H NMR spectrum of the solid residue was obtained in $CDCl_3$. The spectrum showed little difference from that of $W(=O)Cl_3$(Hsal). A second equivalent of water was added to the reaction mixture under the same conditions (−78 °C). This only resulted in an increased amount of the

precipitate. NMR spectra of the organic residues isolated from both of these studies showed H_2sal as the only identifiable product of the reaction.

The Reaction between W(═O)Cl(Hsal)(sal) and $(Me_3Si)_2S$. Hexamethyldisilyl sulfide (0.1051 g) was added dropwise to the stirred suspension of W(═O)Cl(Hsal)(sal) (0.5990 g.) in toluene. After stirring overnight, the appearance of the mixture had not changed significantly. Refluxing for 1 day caused the solution to turn dark brown and form a dark precipitate. The solvent was evaporated in vacuo, and the residue was washed with hexane and dissolved in dichloromethane. After standing for several days, large well-formed crystals of $[W(═O)(Hsal)(sal)]_2O$ formed from solution along with a fine brown precipitate.

Crystallographic Structural Determinations. Crystal, data collection and date refinement parameters for $WO_{0.14}Cl_{1.86}$(Hsal·THF)(sal) **(2·THF)$_{0.16}$(5·THF)$_{0.84}$** and $[W(═O)(Hsal)(sal)]_2O$ (3) are collected in Table 3. Data were collected on a Siemens P4/CCD diffractometer. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI). **(2·THF)$_{0.16}$(5·THF)$_{0.84}$.** The systematic absences in the diffraction data were uniquely consistent with the $P2_1/c$ space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semi-empirical absorption corrections were applied. There is a compositional disorder (86/14), which was labeled CLO and refined as an undersized chlorine atom (0.926). All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. **3.** Photographic data, unit-cell parameters, and systematic absences were consistent with the monoclinic space groups *C*2/*c* or *Cc*. *E*-statistics suggested the centrosymmetric alternative; this was supported by chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semi-empirical absorption corrections were less than satisfactory. Therefore, the empirical absorption correction program, XABS2, which calculates an absorption tensor based on the difference between F_o and F_c was employed.[39] The phenyl rings in the structure were fixed as rigid planar groups to conserve data. There is a solvent molecule of dichloromethane in the asymmetric unit; the chlorine atoms are statistically disordered over two positions with an equal occupancy distribution. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the solvent molecule were ignored because of the disorder, but all other hydrogen atoms were treated as idealized contributions. None of the remaining peaks in the difference map (max = 1.23 e Å^3), which are located near both tungsten atoms (0.9−1.3 Å), were in chemically reasonable positions.

Acknowledgment. The authors acknowledge the Petroleum Research Fund administered by the American Chemical Society for supporting this research. We thank Hercules Corporation for gifts of tungsten precursors and a Vacuum Atmospheres Inc. inert atmosphere box in support of this work.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures $[W(═O)(Hsal)(sal)]_2O$ (**3**) and $WO_{0.14}Cl_{1.86}$(Hsal·THF)(sal) **(2·THF)$_{0.16}$(5·THF)$_{0.84}$**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001456K