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Supramolecular assemblies of tungsten complexes with unusual chelating groups†

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Abstract—Metal complexes of ligands with η^1-*O* coordinated carbonyl moieties are well-known throughout the inorganic literature. However, metal complexes containing authentic acid chloride ligands have not previously been isolated. The synthesis and characterization of compounds with the formula $W(X)Cl_3(OPh\text{-}2\text{-}COCl)$ (**2**) [X = O (**2a**), $NC_6H_3\text{-}2,6\text{-}(CH_3)_2$ (**2b**), and Ph_2C_2 (**2c**)] are reported. The crystal structures of **2a** and **2c** were solved, showing the interaction of the acid chloride carbonyl moiety with the tungsten center. Complex **2c** adopts a channelled structure having six-fold symmetric voids in the solid state. As was anticipated, the coordinated acid chloride of **2a** reacts readily with nucleophiles to produce the ester $WOCl_3(OPh\text{-}2\text{-}COPr^n)$ (**3**) and the amide $WOCl_3(OPh\text{-}2\text{-}CONHBu^t)$ (**4a**). A related amide complex $WOCl_3(OPh\text{-}2\text{-}CONH_2)$ (**4b**), synthesized by the reaction of $WOCl_4$ with salicylamide, displays an infinite-chain structure supported by hydrogen bonding between the amide group and the oxo ligand of an adjacent tungsten complex. The η^1-*O* coordinated nitro compounds $W(X)Cl_3(OPh\text{-}2\text{-}NO_2)$ (**5**) [X = O (**5a**), $NC_6H_3\text{-}2,6\text{-}(CH_3)_2$ (**5b**), and Ph_2C_2 (**5c**)] have also been isolated and the crystal structure of **5c** is reported. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: tungsten; salicylate; acid chloride; hydrogen bonding; materials.

During the 100 years of research that have gone into the development of the field of coordination chemistry, it has become apparent that virtually every generalization about the nature of metal ligand bonding is confounded by a range of exceptions. For example, arguments can be made regarding the tendency of carbon monoxide and other π-acceptor ligands to bind to transition metals with low formal oxidation states, but there are noteworthy examples of carbonyl ligand binding to formally highly oxidized metals. Although suitable ligands for supporting early transition metals in ultimate or penultimate formal oxidation states are typically ionic and strongly electron donating species such as halide, oxide, alkyl amide (R_2N^-), alkyl imido ($R\text{-}N^{-2}$) [1], alkoxide [2,3,4,5], thiolate [6], β-diketonate, cyclopentadienide and carboxylate [7] ligands, there are numerous examples of neutral σ-donor and π-acceptor ligands that support such complexes. While very weakly binding, the η^1-*O* coordinated carbonyl moieties is a class of ligands that pervades the literature in transition metal complexes for both high and low formal oxidation states.

Carboxylates [7], esters, aldehydes [8], ketones, and amides [9] are particularly common as η^1-*O* bound ligands, and are frequently encountered in association with highly Lewis acidic materials. The importance of such functional groups perhaps stems either from their ubiquitous presence in biological systems [10], or from their involvement in industrially important catalytic processes [11]. The stabilization of complexes containing such extraordinarily weak σ-donor ligands is usually accomplished by incorporating that σ-donor into ligand with another coordinating moiety, predisposing the system to a chelating interaction.

One ligand moiety in the group of carbonyl compounds for which there were previously no examples is the acid chloride. Access to a group of stable metal acid chlorides could provide a ready pathway for ligand-based electrophilic attachment of metals to tar-

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† Dedicated to Prof. D. C. Bradley on the occasion of his 73rd birthday.

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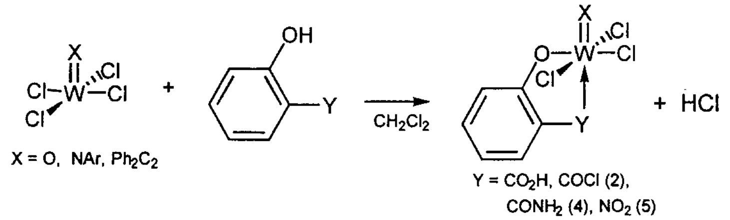
get molecules. Two other functional groups whose coordination chemistry has not been greatly elaborated for high oxidation state metals are nitro groups and primary or secondary amides (Fig. 1). Both η^1-*O* nitro and amide substituents provide the opportunity for constructing hydrogen bonded motifs of transition metal complexes for use in a range of materials applications.

In this paper, we report the synthesis of η^1-*O* coordinated complexes of these ligands with tungsten(VI) complexes, specifically those containing an oxo, aryl imido or η^2-diphenylacetylene units. We have begun to examine both the reactivity of these complexes and their potential to organize stable early transition metal compounds into inorganic/organic hybrid supramolecular materials.

RESULTS AND DISCUSSION

Synthesis and characterization of W(=X)Cl_3(OPh-2-Y) *complexes*

The complexes were synthesized in the same manner as analogous biphenolate and salicylate complexes [12]. The parent metal complex W(=X)Cl_4 was combined with the appropriate phenol in dichloromethane at ambient temperature [Eq. (1)] yielding the chelated phenoxide complex. The compounds were isolated as deep red to red-orange crystalline materials from dichloromethane/hexane solutions.



(1)

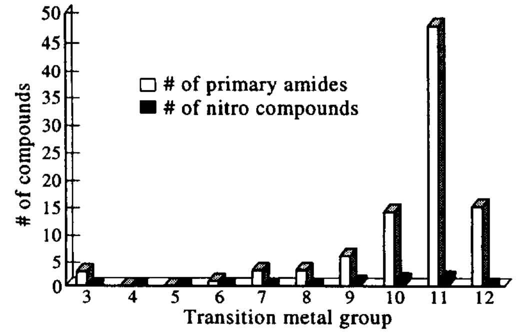
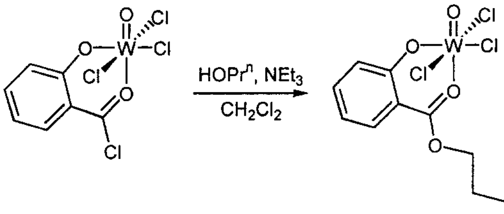


Fig. 1. Frequency of primary amides and nitro groups as η^1-*O* ligands in the Cambridge Structural Database (CSD) [13].

There is a considerable interest in compound **2**, as no acid chloride complexes have been reported previously. X-ray crystallographic studies of **2a** and **2c** will be discussed below. Given the inherent electrophilicity of both the tungsten and carbonyl moieties in complex **2**, either site may be attacked by nucleophiles. This behavior was examined through reactions of **2a** with alcohols or amines. Complex **2a** reacts with η-propanol to yield **3** with and fumes of HCl [Eq. (2)]. The reaction produces an ester which is isolated in modest yield (54%). The regiochemistry of propyl attachment is confirmed by a heteronuclear multiple bond connectivity (HMBC) NMR experiment [14]. HMBC shows coupling between the ^{1}H nuclei on the



(2)

a carbon of the *n*-propyl group to the carbonyl carbon of the ester. Low yields of amide products, such as the *N*-*t*-butyl salicylamide complexes (**4a**), can be obtained through similar reactions between **2a** and amines. It is unclear whether the low yields observed in these reactions are due to the formation of side products or to difficulty in separating the amide product from *t*-butylammonium chloride (*vide infra*).

The unsubstituted salicylamide complex **4b** is readily prepared through the combination of $WOCl_4$ with salicylamide in a method analogous to the preparation of the salicylic acid compounds [12]. Because amides are well known synthons for supramolecular assembly in biological [15] and inorganic systems [16], complex **4b** also has potential for building similar structures. The poor solubility of **4b** in non-donor solvents like dichloromethane, chloroform, and toluene is probably caused by intermolecular associations in the solid state. Complex **4b** is more soluble in ether, THF, and very soluble in DMF. The amide groups are not likely to engage in hydrogen bonding with the carbonyl in an adjacent tungsten complex, due to steric hindrance generated by η^1-*O* coordination of the amide. However, the terminal oxo group is accessible and does form a hydrogen bond with an adjacent amide molecule (*vide infra*).

Efforts were made to employ the nitro complexes **5** as hydrogen bond acceptors with hydrogen bond donors complexes. Given the fact that the amide N-H groups in **4b** will hydrogen bond to an oxo moiety, a carboxylic acid should also form a hydrogen bond with the oxo group of **5a**. Crystallization of an equimolar mixture of $WOCl_3(OPh\text{-}2\text{-}NO_2)$ (**5a**) and $WOCl_3(Hsal)$ in dichloromethane yielded only powdered $WOCl_3(Hsal)$. Apparently, neither the nitro nor the terminal oxo groups of **5a** are sufficiently basic to bind the $WOCl_3(Hsal)$ acid. It may be that the hydrogen bond donor (the Hsal complex) simply does not have the proper complementarity to form a hydrogen bond with the nitro group or the oxo group [17]. Alternatively, the formation of strong intermolecular hydrogen bonding in the $WOCl_3(Hsal)$ lattice may favor the fractionation of the pure acid from **5a**. We are currently examining other hydrogen bond donors that will complement the use of **5** as a Brønsted base in supramolecular assemblies.

X-ray structure data

Compounds **2a, 2c, 4b,** and **5c,** have been characterized by X-ray crystallography. Selected bond distances and angles comparing these complexes are listed in Table 1. It is interesting to note the similarities of the nitro compound **5c** (Fig. 2) to the salicylic acid [12] and acid chloride **2c** (Fig. 3) complexes, the latter two having an obvious structural similarity. The $W—C_{C\equiv C}$ distances of all three diphenylacetylene compounds are identical within the 3σ crystallographic convention. The $W—O_{trans}$ distances of **2c** and **5c** are slightly longer than that of the salicylate

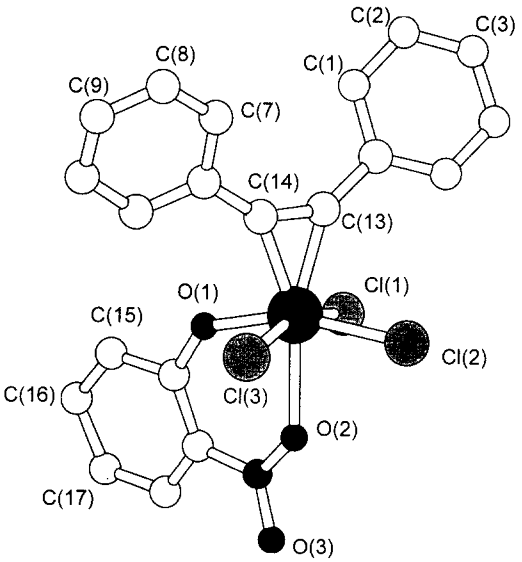
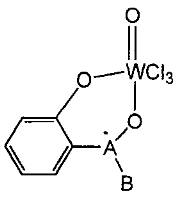


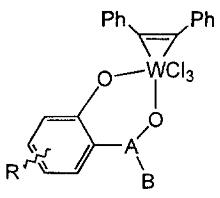
Fig. 2. Ball and stick diagram of the molecular structure of $W(\eta^2\text{-}Ph_2C_2)Cl_3(OPh\text{-}2\text{-}NO_2)$ (**5c**).

Table 1. Selected bond distances (Å) and angles (°) for comparison in selected $W(X)Cl_3(OPh\text{-}2\text{-}Y)$ compounds

	Oxo		Diphenylacetylene		
Y =	$-CO_2H\cdots$dme	$-COCl$ (**2a**)	$-COCl$ (**2c**)	$-CO_2H$	$-NO_2$ (**5c**)
$W—Cl_{avg}$	2.32(2)	2.31(2)	2.36(4)	2.36(3)	2.34(3)
$W{=}O$	1.68(1)	1.657(7)	—	—	—
$W—C_{avg}$	—	—	2.026(7)	2.014(10)	2.016(9)
$W—O_{trans}$	2.21(2)	2.318(6)	2.271(4)	2.211(6)	2.274(7)
$W—O_{Ph}$	1.88(1)	1.873(6)	1.905(5)	1.928(6)	1.933(6)
$W—O_{Ph}—C$	139(2)	141.75	137.3(4)	136.7(5)	135.0(6)
O—A—B	121.5(7)	116.9(7)	115.4(6)	119.6(8)	118.6(9)
W—O—A—B	174.0(7)	176.4(4)	172.6	174.9	175.3



A = C, B = OH
A = C, B = Cl (2a)



A = C, B = OH, R = 5-Cl
A = C, B = Cl, R = H (2c)
A = N, B = O, R = H (5c)

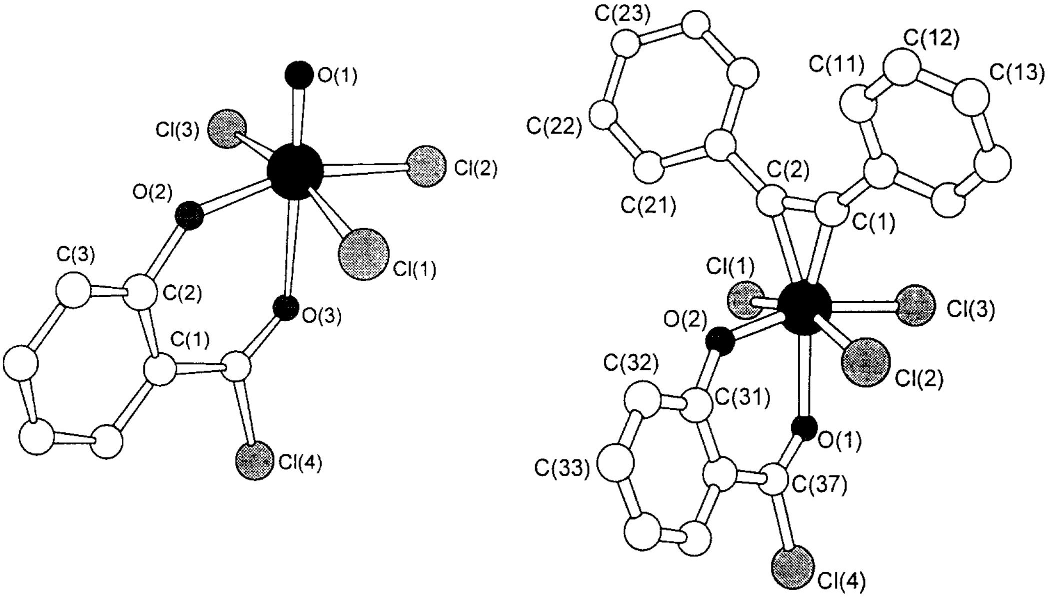
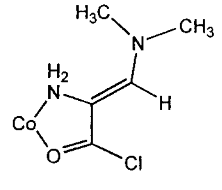


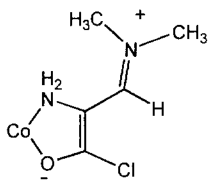
Fig. 3. Ball and stick diagrams of the molecular structures of WOCl$_3$(OPh-2-COCl) (**2a**) and W(η^2-Ph$_2$C$_2$)Cl$_3$(OPh-2-COCl) (**2c**).

(Y = -CO$_2$H) by about 0.061(2) Å. This is probably due to the reduced σ-donor ability of the acid chloride and nitro groups compared to the acid. In all of the complexes, the W—O$_{trans}$ bonds are severely weakened by the *trans* influence of the multiply bonded oxo or acetylene units. The η^1-*O* coordination of the respective groups does not seem to generate significant strain within the chelant moiety. The bond angles and distances in the carboxylate, acid chloride, and nitro groups are consistent with sp^2 hybridized central atom. Also noted in the table are the dihedral angles created by the chelant moiety and the tungsten center. As expected, these angles show the nearly planar arrangement of the coordinating group. The nitro group in **5c** has equal N—O bond lengths of 1.238(10) and 1.233(9) Å indicating that there is significant delocalization in this subunit. This is counter to the expectation that the bonded N—O unit will donate more electron density to tungsten and thereby exhibit greater N—O single bond character than the uncoordinated N—O group. The W—O interaction is evidently too weak to significantly perturb bonding in the NO$_2$ unit.

Relatively few coordination compounds containing acid chloride or nitroarene ligands exist for comparison with **2c** and **5c**. Even fewer examples of these complexes are observed among the early transition metals. A cobalt(III) complex of 3-(dimethylamino)-2-aminoacrylyl chloride (**I**) is the only example of an η^1-*O* bonded acid chloride [18]. Like the *o*-hydroxybenzoylchloride ligand in **2c**, the 3-(dimethylamino)-2-aminoacrylyl chloride binding to cobalt is stabilized *via* a chelate interaction. the acid chloride functionality in **2**, the chemistry of **I** is atypical of acid chlorides [19]. The complex is unreactive to water and actually crystallizes as a hydrated salt. The reduced electrophilicity of the acid chloride carbon has its origins in strong π-donation by the dimethylamino group, which results in a ligand having primarily enolate character (**II**).



I



II

Monodentate nitroarene complexes are also very rare for the early transition metals (see Fig. 1), although a range of examples have been structurally characterized for Group 9 and 10 metals [20]. Nitro group coordination in these complexes is stabilized by the formation of either *o*-nitrophenolate or *o*-nitrophenyl chelates. Typical M—O distances in four and six coordinate palladium and rhodium complexes are 2.135(4) and 2.138(3) Å, respectively. These M—O distances are slightly shorter than the distance found in **5c**. The Pd—O bond of the *o*-nitrophenyl chelate is easily disrupted through the addition of phosphine and pyridine ligands, indicating that coordination of the nitro group to the palladium is extremely weak [20]. The nitro group of **5c** can also be compared with the coordination of nitrate ion [21]. The coordination of the *o*-nitrophenolate anion is naturally restricted to an η^1-*O* mode by the six-membered ring formed by the phenolate unit. Crystallographically characterized metal nitrates are analyzed by a comparison of the metal oxygen distances, where M—O_{short} is the distance to the closer oxygen and M—O_{long} is the distance to the further oxygen [21]. The W—O_{short} distance in **5c** of 2.274(7) Å is longer than the characteristic M—O_{short} distance for third row transition metal nitrates. This long bond results from the strong *trans* influence of the acetylene ligand and the poor localization of negative charge density on the oxygens of the nitro group. The W—O_{long} distance is 4.342(7) Å, significantly longer than any reported for simple nitrate salts (M—O_{long} = 3.5 Å). The geometrical constraints imposed by the chelate ring will only permit η^1-*O* coordination mode of the NO_2 group.

The complexes all crystallize in different space groups, the most unusual being $R\bar{3}$ for **2c**. This complex crystallizes in a three-fold symmetric group due to π-interactions [22] between the salicoyl and acetylene units of neighboring molecules. The diphenylacetylene ligand is involved in two types of interactions: (1) π-stacking of C(21)—C(26) ring of the diphenyl acetylene to the C(31)—C(36) ring in an adjacent salicoyl chloride ligand at a distance of 3.749 Å and an interplanar angle of 0° and (2) a C—H···π interaction of the other acetylene phenyl group [C(11)—C(16)] to C(32) of a different salicoyl chloride unit at a distance of 3.654 Å and an angle of 132.9°. With an additional contact of a C—H···π interaction with another adjacent aryl ring C(13)—H(13)···[C(11)—C(26)] at a distance of 3.654 Å and a C—H···centroid angle of 117.3°, the molecule forms an unusual lattice structure that is highly ordered. The hexagonal crystallographic axis corresponds to the *c*-axis of the cell, generating a hexagonal-shaped channel (Fig. 4). The channel has a diameter of approximately 5–6 Å (accounting for large atom radii and hydrogen atoms) and is devoid of solvent molecules. The closest distance between carbon nuclei across the channel is 8.5 Å, while the closest carbon–chlorine distance is 7.8 Å. The absence of solvent is confirmed by NMR characterization of the bulk material. This is an unusual channel structure for a non-covalently bonded system [23]. Future studies will address the idea that molecules assembled by multiple π-interactions can be used to construct other materials containing large unoccupied void volumes.

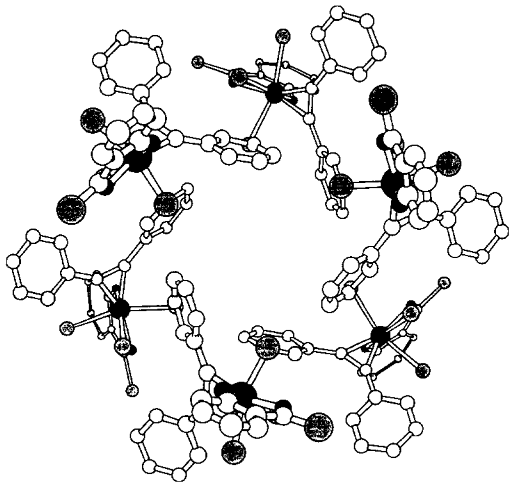


Fig. 4. View of W(η^2-Ph_2C_2)Cl_3(OPh-2-COCl) (**2c**) down the *c* crystallographic axis.

The acid chloride complex **2a** does not exhibit the same channel structure as **2c**. Its structure is typical of tungsten oxo compounds [24], with relevant bond distances and angles listed in Table 1. The only significant structural differences between the two oxo complexes in Table 1 is in the oxo ligand and the chelant moiety. The terminal oxo group bonds at a slightly shorter distance in **2a** than in related salicylate complexes [12]. This may be due to the decreased electron donating ability of the acid chloride compared to the acid, which allows the oxo ligand to interact more strongly with tungsten. This hypothesis is verified by the fact that the W—$O_{carbonyl}$ bond length is much longer in the acid chloride than the corresponding acid (by 0.108 Å). In all other respects, such as W—Cl and W—O_{Ph} bond lengths and corresponding bond angles, the molecular units of **2a** and **2c** are quite similar. Also, complex **2a** bears resemblance to **2c** in the intermolecular associations that are formed. The oxo group forms a 3.39(1) Å C—H···O hydrogen bond with the hydrogen atom on C(3) [25]. The C—H···O interaction lies along the *a* direction of the unit cell. Yet another close contact is observed between Cl(3) and the carbonyl carbon C(7) of an adjacent molecule. The atoms are separated by 3.488(9) Å, at an angle of 90° between the metal chloride bond and the plane of the acid chloride group. The two molecules involved in this interaction are related by the screw-axis in the crystal. The atomic organization of this contact is reminiscent of a nucleophilic substitution at a carbonyl carbon [26]. Lastly, the aromatic rings of the salicoyl chloride ligands stack at a distance of 4.033(6) Å and an interplanar angle of 0° [22].

The structure of the amide **4b** is a classic octrahedral tungsten oxychloride complex (Fig. 5, Table 2). It displays the *trans* effect typical of an oxo ligand with a long bond to the neutral η^1-*O* amide group [W—O_{amide} = 2.271(4) Å]. While the molecular unit appears to be rather mundane, the intermolecular interactions are quite fascinating. There is a hydrogen bond from the amide group of one tungsten atom to the oxo group of the adjacent molecule. This N—H···O_{oxo} interaction is 3.067(9) Å, with an apparent N—H···O angle of 117.7(10)° (Fig. 6). Actually, N—H···O interactions of this type are very common in organometallic coordination chemistry [9]. An average N—H···O distance of the interaction described here is 3.02(1) Å, with an angle of 155.9(5)°. The hydrogen bond between the amide and oxo group in **4b** continues through the lattice, making an infinite

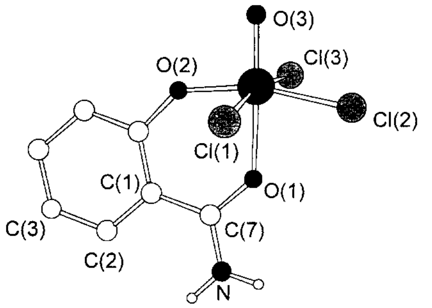
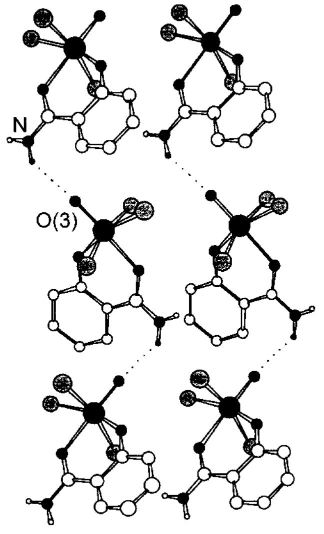


Fig. 5. Ball and stick diagram of the molecular structure of $WOCl_3(OPh\text{-}2\text{-}CONH_2)$ (**4b**).

Table 2. Pertinent bond distances (Å) and angles (°) in $WOCl_3(OPh\text{-}2\text{-}CONH_2)$ (**4b**)

W—Cl (avg)	2.329(15)	O(1)—WCl (avg)	83.3(4)
W—O(1)	2.147(9)	O(3)—W—Cl (avg)	97.6(15)
W—O(2)	1.875(8)	W—O(2)—C(6)	139.3(7)
W—O(3)	1.676(9)	N—C(7)—O(1)	117.9(11)
N—C(7)	1.290(15)		
O(1)—C(7)	1.285(15)		

one dimensional chain of hydrogen bonds. These one dimensional chains of complexes are arranged in a herringbone pattern. These strands are in turn held together by two other non-covalent interactions: (1) A close contact, possibly a van der Walls interaction, between a chloride ligand [Cl(3)] and an adjacent arene ring at a distance of 3.434 Å with an 89.9° contact angle, and (2) A C—H···Cl interaction between C(3) of the arene ring and Cl(1) of a nearby complex at a distance of 3.696 Å and an angle of 118.1°. Hydrocarbon C—H···Cl interactions are well known and have been observed in the assembly of other hydrogen bonded complexes [27]. All of these interactions help to stabilize the crystal lattice, which contributes to the poor solubility of **4b** in non hydrogen bonding solvents (*N*- or *O*-atom donor solvents). According to the Cambridge Structural Database (CSD), only one other group 6 complex with a coordinating primary amide moiety has been documented: $MoO_2Cl_2(CH_3CONH_2)$ [28]. This complex shows an analogous intermolecular oxo-amide hydrogen bond motif in the solid state at a distance of 3.042 Å and an angle of 158°.



N-H···O(3) distance = 3.067(9) Å
angle = 117.7(10)°

Fig. 6. Infinite chain of hydrogen bonding by N—H···O=W groups in $WOCl_3(OPh\text{-}2\text{-}CONH_2)$ (**4b**).

EXPERIMENTAL

General procedures

All experiments were performed under a nitrogen atmosphere in a HE-553-2 Vacuum Atmospheres dry box or using standard Sclenk techniques. Benzene, toluene, hexane, and diethyl ether were purified by distillation over Na/benzophenone. Dichloromethane and *t*-butylamine were purified by distillation over CaH_2, followed by purging with dry nitrogen. NMR solvents (Cambridge Isotope Laboratories) were dried with 5 Å molecular sieves and degassed with dry nitrogen prior to use. Salicylic acid (H_2sal), and 2-nitrophenol ($HOPh\text{-}2\text{-}NO_2$) were used as received from Aldrich. Thionyl chloride was used as received from Eastman-Kodak. $W(=NC_6H_3\text{-}2,6\text{-}Me_2)Cl_4$ and $W(\eta^2\text{-}Ph_2C_2)Cl_4$ were prepared using published procedures. $WOCl_4$ was received as a gift from Hercules Research Company.

NMR spectra were recorded on Bruker AM-500 or DRX-400, Varian XL-300, or General Electric QE-300 spectrometers. ^1H and ^{13}C data are listed in parts per million (ppm) downfield from tetramethylsilane with ^1H data referenced by the solvent's residual proton peak. All NMR spectra are recorded at ambient temperature (~20°C) in $CDCl_3$ unless otherwise noted. All coupling constants are linked in hertz (Hz). Elemental analyses were performed by Desert Analytics (P.O. Box 41838, Tucson, AZ 85717).

Preparation of salicoyl chloride (HOPh-2-COCl) (**1**)

This procedure is based on several literature methods [29]. Salicylic acid (10.0 g, 72.4 mmol) was placed in a 250 cm^3 flask with a magnetic stirbar. A small amount of aluminum chloride (0.3 g, 2.25 mmol) was added, followed by dry benzene (60 cm^3). The mixture was fitted with a reflux condenser and thionyl chloride (7.92 cm^3, 108.6 mmol, 1.5 equiv.) was added by syringe. As the yellow mixture was refluxed for 5 h, it became orange colored. The volume was then reduced to 30 cm^3 *in vacuo* and was stirred overnight. The volume of the viscous solution was further reduced *in vacuo* until the exterior of the flask was no longer cool to the touch. This gelatinous product was vacuum distilled twice into a liquid nitrogen cooled flask (to insure the complete removal of the solvent). The product is a colorless, non-viscous liquid at room temperature, whose density (1.3112 g/cm^3) and freezing point (18°C) match the literature values [30]. This material was stored at -20°C to prolong shelf life as autocondensation occurs more quickly at room temperature. The solid was melted immediately prior to each use and handled under nitrogen to prevent hydrolysis. Yield: 34% (2.90 cm^3, 3.80 g, 24.3 mmol).

Preparation of $\mathrm{WOCl_3(OPh\text{-}2\text{-}COCl)}$ (**2a**)

$\mathrm{WOCl_4}$ (2.5017 g, 7.32 mmol) was slurried in dichloromethane (20 cm^3) in a 50 cm^3 Schlenk flask with a magnetic stirbar. Salicoyl chloride (0.87 cm^3, 7.28 mmol) was added slowly by syringe. The slurry became blood red upon addition of the first drop of salicoyl chloride. The addition of salicoyl chloride produced copious amounts of HCl over the 5 min required to add the liquid. The reaction was stirred an additional 25 min then the solvent was removed *in vacuo*. The product was recrystallized from toluene layered with hexane to yield a deep crimson microcrystalline material. X-ray quality crystals were recrystallized from dichloromethane layered with hexane. Yield: 96% (3.1811 g, 7.07 mmol). NMR data: ^{1}H (300 MHz): 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 (500 MHz, $\mathrm{CDCl_3}$): δ 178.86 (-$\underline{\mathrm{C}}$OCl), 159.67, 140.25, 136.16, 129.40, 123.59 123.10. Mass spectrum (EI): 460 [$\mathrm{M^+}$], 427 [$\mathrm{WOCl_3(OPh\text{-}2\text{-}COCl)^+}$], 307 [$\mathrm{WOCl_3^+}$], 272, 240 [$\mathrm{C_{14}H_8O_4^+}$], 120 [$\mathrm{C_6H_4CO_2^+}$], 92 [$\mathrm{C_6H_4O^+}$], 64 [$\mathrm{COCl^+}$]. Anal. calcd for $\mathrm{C_7H_7O_3WCl_4}$. Calc.: 18.21% C; 0.87% H. Found: 18.89% C; 0.62% H.

Preparation of $\mathrm{W({=}NC_6H_3\text{-}2,6\text{-}Me_2)Cl_3(OPh\text{-}2\text{-}COCl)}$ (**2b**)

This compound was prepared in a manner similar to **2a**. $\mathrm{W({=}NC_6H_3\text{-}2,6\text{-}Me_2)Cl_4}$ (1.6070 g, 3.61 mmol) was slurried in dichloromethane (30 cm^3) and salicoyl chloride (0.43 cm^3, 3.60 mmol) was added by syringe. The product was recrystallized from dichloromethane and isolated as a black microcrystalline material. Yield: 76% (1.5550 g, 2.75 mmol). NMR data: ^{1}H (400 MHz): δ 8.41 (H, dd, 6-H of -OPh-2-COCl), 7.93 (H, dt, 5-H), 7.35 (H, t, 4-H), 7.31 (2H, d, *m*-H's of imido), 7.08 (H, d, 3-H of -OPh-2-COCl), 6.74 (H, t, *p*-H of imido), 3.22 (6H, s, $\mathrm{NC_6H_3\text{-}2,6\text{-}(C\underline{H}_3)_2}$). ^{13}C: δ 180.73 (-$\underline{\mathrm{C}}$OCl), 162.52, 150.13, 144.69, 141.33, 136.24, 133.15, 126.89, 126.42, 122.83, 121.56, 18.44 ($\mathrm{NC_6H_3\text{-}2,6\text{-}(\underline{C}H_3)_2}$). Anal. $\mathrm{C_{15}H_{13}NO_2WCl_4}$. Calc.: 31.89% C; 2.32% H; 2.48% N; 25.10% Cl. Found: 31.53% C; 2.02% H; 2.37% N; 25.28% Cl.

Preparation of $\mathrm{W(\eta^2\text{-}Ph_2C_2)Cl_3(OPh\text{-}2\text{-}COCl)}$ (**2c**)

This compound was also prepared in a manner similar to **2a**. $\mathrm{W(Ph_2C_2)Cl_4}$ (1.2087 g, 2.40 mmol) was slurried in 30 cm^3 dichloromethane and salicoyl chloride (0.28 cm^3, 2.35 mmol) was added by syringe. The solution was filtered through Celite and the volume reduced *in vacuo* to yield purplish–black blocks suitable for X-ray diffraction. Yield: 70% (1.0520 g, 1.69 mmol). NMR data: ^{1}H (400 MHz): δ 8.45 (H, dd, 6-H of -OPh-2-C = OCl), 8.16 (4H, *o*-H's of $\mathrm{Ph_2C_2}$), 7.84 (H, dt, 5-H, of -OPh-2COCl), 7.77 (4H, t, *m*-H's of $\mathrm{Ph_2C_2}$), 7.63 (2H, t, *p*-H's of $\mathrm{Ph_2C_2}$), 7.36 (4-H of -OPh-2-COCl), 6.94 (3-H of -OPh-2-COCl). ^{13}C (partial): δ 179.79, (-$\underline{\mathrm{C}}$OCl), 163.20, 141.41, 138.17, 136.41, 134.72, 134.11, 129.43, 125.44, 122.35, 119.47. Anal. calcd for $\mathrm{C_{21}H_{14}O_2WCl_4}$. Calc.: 40.42% C; 2.26% H; 22.73% Cl. Found: 40.34% C; 1.98% H; 22.38% Cl.

Preparation of $\mathrm{WOCl_3(OPh\text{-}2\text{-}COOPr^n)}$ (**3**)

A 50 cm^3 Schlenk flask was charged with **2a** (0.8061 g, 1.79 mmol), a magnetic stirbar, and dichloromethane (25 cm^3). In a separate Schlenk flask, 1-propanol (0.13 cm^3, 1.74 mmol) and triethylamine (0.25 cm^3, 1.79 mmol) were mixed with dichloromethane (10 cm^3). The solution of **2a** was cooled to -78°C and the 1-propanol/triethylamine solution was added dropwise over 15 min. Fumes evolved during the addition (presumably HCl). After stirring an additional 45 min at -78°C, the reaction was allowed to warm to room temp (over thirty minutes) and stripped to dryness *in vacuo*. The dark red residue was taken up in hot hexane (5 × 10 cm^3) and filtered through Celite. The hexane was concentrated and allowed to cool, producing crystals of **3**. Yield: 54% (0.4673 g, 0.09 mmol). NMR data: ^{1}H (400 HMz): δ 8.24 (H, dd, 6-H), 7.86 (H, dt, 5-H) 7.35 (H, t, 4-H), 7.18 (H, d, 3-H), 4.65 (2H, t, $\mathrm{OC\underline{H}_2CH_2Ch_3}$), 1.96 (2H, q, $\mathrm{OCH_2C\underline{H}_2CH_3}$), 1.11 (3H, t, $\mathrm{OCH_2CH_2C\underline{H}_3}$). ^{13}C: δ 169.77 (ester), 160.65, 137.37, 131.75, 129.30, 123.17, 118.94, 71.98 ($\mathrm{O\underline{C}H_2CH_2CH_3}$), 22.26 ($\mathrm{OCH_2\underline{C}H_2CH_3}$), 10.64 ($\mathrm{OCH_2CH_2\underline{C}H_3}$).

Preparation of $\mathrm{WOCl_3(OPh\text{-}2\text{-}CONHBu^t)}$ (**4a**)

This compound was synthesized in a similar fashion to the ester complex **3**. A toluene solution of *t*-butylamine (0.27 cm^3, 2.57 mmol) was added to a toluene solution of **2a** (0.4673 g, 1.04 mmol) at -78°C. The reaction was filtered to remove the by-product, *t*-butylammonium chloride. The solid salt was washed with hot toluene (2 × 10 cm^3) and the filtrate solution concentrated *in vacuo*. The solution was warmed to 60°C and allowed it to stand, yielding deep red block crystals. The poor yield may be due to association of the product with the *t*-butylammonium chloride. This hypothesis was corroborated by the fact that the precipitate yielded bright red solution upon cleaning the filter frit with acetone. Yield: 11% (0.0580 g, 0.012 mmol). NMR data (300 MHz): ^{1}H: δ 7.73 (H, t), 7.64 (H, d), 7.26 (H, t) 6.98 (H, bs, -CON$\underline{\text{H}}$(CH$_3$)$_3$), 1.60 [9H, s, -CONH(C$\underline{\text{H}}_3$)$_3$].

Preparation of $WOCl_3(OPh\text{-}2\text{-}CONH_2)$ (**4b**)

$WOCl_4$ (2.1900 g, 6.41 mmol) was weighed into a 50 cm^3 Schlenk flask with a magnetic stirbar. Dichloromethane (30 cm^3) was added via cannula, followed by solid salicylamide (0.8795 g, 6.41 mmol) from an addition tube. Upon addition of the salicylamide, a deep reddish-purple color developed and as the reaction proceeded, microcrystals of the same color began to precipitate. The mixture was stirred for eight hours, then the solid microcrystalline product was harvested by filtration (2.465 g 5.57 mmol). The supernatant solution volume was reduced and cooled to −20°C, yielding X-ray quality crystals (0.213 g, 0.48 mmol). Yield: 94% (2.678 g [total], 6.05 mol). NMR data: ^{1}H (300 MHz): δ 7.85 (H, t), 7.75 (H, d), 7.35 (H, t), 7.24 (H, d), 7.03 (H, broad s, CON$\underline{\text{H}}$), 6.61 (H, broad s, CON$\underline{\text{H}}$). The complex was not soluble enough in $CDCl_3$ to obtain a ^{13}C NMR spectrum. Anal. $C_7H_6O_3NWCl_3$. Calc.: 19.01% H, 3.17% N. Found: 19.24% C; 1.29% H, 3.22% N.

Preparation of $WOCl_3(OPh\text{-}2\text{-}NO_2)$ (**5a**)

A 50 cm^3 Schlenk flask was charged with $WOCl_4$ (1.3650 g, 4.00 mmol), a magnetic stirbar, and dichloromethane (30 cm^3). Solid 2-nitrophenol (0.5593 g, 4.02 mmol) was added by addition tube and the solution immediately changed to a deep red color. The mixture was stirred for 6 h, then filtered through Celite. The volume was reduced to 5 cm^3 and allowed to stand, producing blood red blocks. The liquid was decanted and the material dried for 6 h at room temperature (10^{-6} torr). The material appeared glassy rather than microcrystalline. Yield: 75% (1.3270 g, 2.99 mmol). NMR data: ^{1}H (300 MHz): δ 8.40 (H, dd, 6-H), 7.97 (H, dt, 5-H), 7.45 (H, dt, 4-H), 7.29 (H, d, 3-H). ^{13}C: δ 211.08 ($\underline{\text{C}}$-NO$_2$), 195.24, 194.56 (O—C$_{\text{ipso}}$), 185.37, 183.52, 180.78. Anal. calcd for $C_6H_4O_4NWCl_3$. Calc.: 16.22% C; 0.91% H; 3.15% N. Found: 16.16% C; 0.68% H; 3.07% N.

Preparation of $W({=}NC_6H_3\text{-}2,6\text{-}Me_2)Cl_3(OPh\text{-}2\text{-}NO_2)$ (**5b**)

This synthesis was carried out in a manner similar to that of **5a**. The filtrate was concentrated to 20 cm^3 and warmed to 40°C. Thin brown parallel-piped shaped crystals formed after standing overnight at room temperature. Two crops of these crystals yielded only small amounts of material (0.129 g, 0.23 mmol). The supernate was cooled to −20°C to produce more crystals which had a different morphology from the first crops. This material was block shaped and the blocks were clumped together. Both sets of crystals have identical ^{1}H and ^{13}C NMR spectra. Yield: 70% (0.727 g [total], 1.33 mmol). NMR data: ^{1}H (300 MHz): δ 8.32 (H, dd, 6-H), 7.86 (H, dt, 5-H), 7.30 (3H, mult, 4-H of OPh-2-NO$_2$ and *m*-H's of imido), 7.14 (H, d, 3-H), 6.72 (H, t, *p*-H of imido), 3.20 (6H, s, NC$_6$H$_3$-2,6-(C$\underline{\text{H}}_3$)$_2$). ^{13}C: δ 157.05, 149.76, 144.43, 139.46, 136.27, 133.11, 126.96, 126.48, 125.84, 124.13, 18.01 (NC$_6$H$_3$-2,6-($\underline{\text{C}}$H$_3$)$_2$). Analytical Data for $C_{14}H_{13}O_3N_2WCl_3$. Calc.: 30.71% C; 2.39% H; 5.12% N. Found: 30.40% C; 2.21% H; 4.98% N.

Preparation of $W(\eta^2\text{-}Ph_2C_2)Cl_3(OPh\text{-}2\text{-}NO_2)$ (**5c**)

This synthesis was carried out in a manner similar to that of **5a**. The filtrate was concentrated to 5 cm^3 and layered with 7 cm^3 hexane. After standing at room temperature for 3 days, shiny, red–orange, X-ray quality needles were harvested by decanting the supernate solution. Yield: 87% (0.872 g, 1.44 mmol). NMR data: ^{1}H (300 MHz): δ 8.36 (H, dd, 6-H of OPh-2-NO$_2$), 8.17 (4H, dd, *o*-H's of Ph's), 7.79 (5H, t, *m*-H's of Ph's overlapped with 5-H of OPh-2-NO$_2$), 7.65 (2H, t, *p*-H's of Ph's), 7.33 (H, t, 4-H), 7.01 (H, d, 3-H). ^{13}C: δ 252.22 (Ph$_2\underline{\text{C}}_2$), 158.52, 139.81, 138.14, 135.05, 134.79, 134.41, 129.51, 127.36, 125.35, 124.30. Anal. calcd for $C_{20}H_{13}O_3NWCl_3$. Calc.: 39.60% C; 2.33% H; 2.31% N. Found: 39.71% C; 2.07% H, 2.26% N.

Crystallographic structure determinations

Crystal, data collection, and refinement parameters are given in Table 3. Suitable crystals for single-crystal X-ray diffraction were sectioned and mounted in a thin-walled capillary flushed with nitrogen. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20 \leqslant 2\theta \leqslant 25^\circ$) for all structures except **2a** ($48 < 2\theta < 50^\circ$).

The systematic absences in the diffraction data are uniquely consistent with $P2_1/n$ for **2a** and **4b** while **5c** was assigned to *Pccn*. The unit-cell parameters, photographic data, systematic absences and occurrences of equivalent reflections in **2c** are consistent with rhombohedral space groups without *c*-glide absences. The *E*-statistics and the chemical composition suggested the space group, $R\bar{3}$, and this solution gave chemically reasonable and computationally stable results during refinement.

The structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Semi-

Table 3. Summary of X-ray diffraction data for crystallographically characterized compounds

Compound	**2a**	**2c**	**4b**	**5c**
Empirical formula	$C_7H_4Cl_4O_3W$	$C_{21}H_{14}Cl_4O_2W$	$C_7H_6Cl_3NO_3W$	$C_{20.50}H_{15}Cl_4NO_3W$
Formula weight	461.77	623.97	458.30	648.98
Crystal color, habit	Deep red prism	Deep red block	Dark red block	Red thin plate
Space group	$P2_1/n$	$R\bar{3}$	$P2_1/n$	$Pccn$
V, Å^3	1161.2(3)	9997(7)	1111.7(7)	4439(2)
Z (molecule/cell)	4	18	4	8
$R(F)$, %	0.045[b]	0.0351[b]	0.0438[a]	0.0330[b]
Rw (F), %	0.071	0.0755[b,c]	0.0537[a]	0.0710[b,c]
Temperature (°C)	−120	25(2)	23(2)	−35(2)
Radiation	Cu-$K\alpha$ (λ = 1.54178 Å)		Mo-$K\alpha$ (λ = 0.71073 Å)	
a (Å)	11.579(2)	32.453(8)	5.5687(5)	26.590(5)
b [Å)	7.909(2)	—	14.618(2)	10.370(2)
c (Å)	12.705(1)	10.961(4)	13.683(3)	16.097(2)
α (°)	—	—	—	—
β (°)	93.57(1)	—	93.78(1)	—
γ (°)	—	120	—	—

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

empirical ellipsoid absorption corrections were applied to **2c** and **4b**, and a semi-empirical lamina absorption correction was applied to **5c**; all data with a glancing angle of $\leqslant 3°$ to the prominent face [0 0 1] were rejected, affecting 163 reflections. One-half of a molecule of dichloromethane was located on a two-fold axis in **5c**. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were treated as idealized contributions. Several of the remaining peaks from the difference map (1.06 to 1.46 e/Å^3 for **2c**, and 1.01 to 2.56 e/Å^3 for **4b**) were in chemically unreasonable positions (i.e. positions near the heavy atoms: 1.15 Å from W and 1.64 Å from Cl for **2c** and 0.86 to 1.58 Å from W for **4b**) and were considered noise. The structure of **2a** was solved using TeXsan software and Cromer and Waber's neutral atom scattering factors [31]. All software and sources of the scattering factors for **2c, 4b,** and **5c** are contained in either SHELXTL version 4.2 or the SHELXTL version 5.03 program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

CONCLUSIONS

A wide variety of weakly-coordinated functional groups can be used to satisfy the coordination sphere of the W(X)Cl_3(OR) fragment. The electrophilic acid chloride complexes, W(X)Cl_3(OPh-2-COCl), may have synthetic utility for the metallation of alcohols, amines, and nucleophilic metal complexes. Both W(η^2-C_2Ph_2)Cl_3(OPh-2-COCl) and WOCl_3(OPh-2-$CONH_2$) produce interesting lattice structures. W(η^2-C_2Ph_2)Cl_3(OPh-2-COCl) arranges in a three-fold symmetric space group through weak intermolecular contacts involving the aryl subunits of the diphenyl acetylene and salicoyl chloride ligands. These contacts generate a star-shaped void whose internal diameter is 5–6 Å. This is a very unusual feature in non-covalently bonded solids. WOCl_3(OPh-2-$CONH_2$) forms an infinite one-dimensional hydrogen bonded herringbone in the solid phase.

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