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Reactions of tris(1,2-ethanediolato)tungsten(VI) with phenyl acetates. X-ray structures of three products

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Abstract

Tungsten(VI) complex $[W(eg)_3]$ (eg=ethanediolate dianion) reacts with phenyl acetates leading to the displacement of one or three diolato ligands. Two types of phenoxides, $[W(O-C_6H_4R-4)_6]$ (R=H, Me, Cl) and $[W(eg)_2(OC_6H_3R_2'-2,6)_2]$ (R'=Me, ^{*i*}Pr) are formed, depending on the nature of phenyl group. The X-ray crystal structure determinations of $[W(OC_6H_5)_6]$, $[W(eg)_2(OC_6H_3Me_2-2,6)_2]$ and $[W(eg)_2(OC_6H_3'Pr_2-2,6)_2]$ confirmed the nature of the compounds. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Metal alkoxides and phenoxides are widely studied due to their many applications in organometallic and catalytic chemistry [1,2]. The general advantage of phenoxide ligands when compared with alkoxide ligands is that changing the substituents on the ring can easily vary their electron-withdrawing properties [3,4]. Changing the bulkiness of the substituents in the ortho position on the ring can also modify steric effects in the close neighborhood of the metal. These properties are one of the reasons why phenoxide ligands have been very widely used in the field of organometallic chemistry related to metathesis [5]. For example, tungsten phenoxides of the type $[WCl_{6-x}(OAr)_x]$ and $[WOCl_{4-y}(OAr)_y]$ are used as air-stable precursors for two-component catalyst systems, typically in the presence of tin or lead organometal reagents [1,3].

The reaction of a metal alkoxide with alkyl or phenyl esters can be presented by the following scheme:

$$M(OR)_n + xR'C(O)OR'' \leftrightarrow$$

 $\mathbf{M}(\mathbf{OR})_{n-x}(\mathbf{OR}'')_x + x\mathbf{R}'\mathbf{C}(\mathbf{O})\mathbf{OR}.$ (1)

This reaction, transesterification, has proved useful in the preparation of phenoxides, e.g. Nb and Ta pentaphenoxides are prepared from metal isopropoxides and phenyl acetate [6,7]. It is a very practical method especially if suitable metal alkoxides can be easily prepared from oxides, because it makes it possible to avoid the use of air and moisture sensitive metal chlorides. Transesterification is also known to be less prone to steric factors than alcohol exchange [2].

Tungsten phenoxides are commonly prepared by a phenolysis reaction of WOCl₄ or WCl₆, which both are sensitive to air and moisture [8,9]. In the course of our studies on the coordination chemistry of tungsten(VI), we have used the trisdiolato complex $[W(eg)_3]$ (eg = 1,2-ethanediolate dianion) as air-stable starting material. In continuation of these studies, we have now prepared W(VI) phenoxides $[W(O-C_6H_4R-4)_6]$ (R = H, Me, Cl) and $[W(eg)_2(OC_6H_3R_2'-2,6)_2]$ (R'=Me, ⁱPr).

2. Results and discussion

Treatment of $[W(eg)_3]$ with various phenyl acetates ArOAc in chlorobenzene solutions led to the formation of tungsten(VI) phenoxides $[W(eg)_{3-x}(OAr)_{2x}]$ (x=1 or 3). Several different substituted phenyl acetates were used, and it was found that the number of diolato ligands that may be substituted in $[W(eg)_3]$ is strongly dependent on the nature and position of the substituents on the aromatic ring. Depending on the phenyl group, two types of phenoxides $[W(OAr)_6]$ and $[W(eg)_2(OAr)_2]$ were synthesized.

2.1. Syntheses of $[W(OAr)_6]$ complexes

The complexes $[W(O-C_6H_4R-4)_6]$ (R = H (1), Me (2), Cl (3)) have earlier been prepared from WOCl₄ and

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Table 1

the corresponding phenols in chlorobenzene solution [8]. We obtained these compounds according to the following reaction using one equivalent of $[W(eg)_3]$ with six equivalents of phenyl acetate in chlorobenzene at reflux temperature:

$$[W(eg)_3] + 6RC_6H_4OAc \rightarrow$$
$$[W(O-C_6H_4R)_6] + 3Ac_2eg. (2)$$

The reaction of $[W(eg)_3]$ in the presence of less than six equivalents of phenyl acetate with no 2,6-disubstitution does not lead to the corresponding $[W(eg)_2(OAr)_2]$ or $[W(eg)(OAr)_4]$ complexes, but gives $[W(OAr)_6]$ and some unreacted trisdiolato complex. Complexes 1–3 are intense red solids, stable in air and soluble in hydrocarbons and chlorinated solvents.

2.2. Syntheses of $[W(eg)_2(OAr)_2]$ complexes

Mixed-ligand complexes $[W(eg)_2(OC_6H_3R_2'-2,6)_2]$ (R'=Me (4), ^{*i*}Pr (5)) were obtained by reaction of $[W(eg)_3]$ with two equivalents of phenyl acetates which were disubstituted in the 2,6-positions by methyl or *iso*-propyl groups,

$$[W(eg)_{3}] + 2R_{2}'C_{6}H_{4}OAc \rightarrow$$
$$[W(eg)_{2}(OC_{6}H_{3}R_{2}')_{2}] + Ac_{2}eg. \quad (3)$$

Complexes 4 and 5 are intense yellow solids, stable in air at room temperature and soluble in hydrocarbons, chlorinated solvents and ethers, slightly soluble in ethanol and non-soluble in water. They are also stable in wet ethanol although W(VI) complexes with eg ligands are usually hydrolysed easily [10]. However, they decompose rapidly in basic or acidic solutions.

Our attempts to prepare tetraphenoxides [W(eg) $(OC_6H_3R_2'-2,6)_4$] were unsuccessful, as the reaction of four equivalents of 2,6-disubstituted phenyl acetate with [W(eg)_3] gives [W(eg)_2(OC_6H_3R'_2-2,6)_2] and unreacted phenyl acetate. Under our experimental conditions, 2,6-dichlorophenyl, 2,4,6-trichlorophenyl or 2,4,6-tri-nitrophenyl acetates did not show any reactivity.

2.3. X-ray crystal structures

The main structural parameters of complex **1** are shown in Table 1. The compound forms monomeric molecules in which the central tungsten atom is octahedrally surrounded by six oxygen atoms (Fig. 1). The structure is closely similar to that of complex **2** described by Errington *et al.* [11]. The O–W–O angles of octahedral W(VI) are more regular than in [W(OPhMe-4)₆] as the acute angles in **1** vary from 87.5(2) to 92.6(2)° while in **2** they vary from 86.1(2) to 94.7(1)°. The reason for the variation is probably a steric packing one because the OPh ligand is smaller than the OPhMe-4 ligand. In complex **1**, the W–O distances range from 1.883(4) to 1.917(4) Å being

| W-O(1) | 1.883(4) | O(2)-W-O(6) | 90.9(2) |
|-------------|----------|---------------|----------|
| W-O(2) | 1.884(4) | O(3)-W-O(4) | 88.0(2) |
| W-O(3) | 1.897(4) | O(3)-W-O(5) | 92.6(2) |
| W–O(4) | 1.908(4) | O(3)-W-O(6) | 91.8(2) |
| W-O(5) | 1.905(4) | O(4)-W-O(5) | 89.4(2) |
| W–O(6) | 1.917(4) | O(4)-W-O(6) | 89.1(2) |
| | | O(5)-W-O(6) | 175.2(2) |
| O(1)-W-O(2) | 90.5(2) | | |
| O(1)-W-O(3) | 179.1(2) | W-O(1)-C(1) | 146.6(4) |
| O(1)–W–O(4) | 92.6(2) | W-O(2)-C(7) | 147.8(4) |
| O(1)–W–O(5) | 88.0(2) | W-O(3)-C(13a) | 151.0(5) |
| O(1)–W–O(6) | 87.5(2) | W-O(3)-C(13b) | 136.8(8) |
| O(2)–W–O(3) | 88.9(2) | W-O(4)-C(19) | 143.6(4) |
| O(2)–W–O(4) | 176.9(2) | W-O(5)-C(25) | 137.5(4) |
| O(2)–W–O(5) | 90.8(2) | W-O(6)-C(31) | 134.8(4) |

ding distances (Å) and angles (°) for complex



Fig. 1. ORTEP drawing of $[W(OC_6H_5)_6]$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

slightly longer than in the heteroleptic complexes $[W(OPh'Pr_2)_3Cl_3]$ [9] (1.832(2)–1.848(2) Å) and *trans*- $[W(OPhMe_2)_2Cl_4]$ [12] (1.860(7) Å). The W–O distances in the W(V) complex anion $[W(OPh)_6]^-$ span from 1.932(5) to 1.956(4) [13]. Longer W–O distances are due to a lower charge on the tungsten ion and a negative charge of the complex unit. The W–O–C angles in 1 range from 136.8(8) to 151.0(5)° showing a weak correlation with W–O distances.

There is some free space around the second coordination sphere of W(VI) in 1 as two phenyl groups show two different orientations in the solid state. One shows two rotamers in a 1:1 ratio with a rotation angle of $23(1)^{\circ}$.

Table 2

and 5

The other is in two positions in a 0.60–0.40 ratio in a plane with different W–O–C angles, as shown in Fig. 1. Compound $[NEt_4][W(OPh)_6]$ consist of two crystallographically independent anions of which one also contains disordered phenoxide ligands [13].

The compounds 4 (Fig. 2) and 5 (Fig. 3) are six-coor-



Fig. 2. ORTEP drawing of $[W(eg)_2(OC_6H_3Me_2-2,6)_2]$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP drawing of $[W(eg)_2(OC_6H_3^iPr_2-2,6)_2]$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

| | 4 | 5 |
|---------------------|--|-----------|
| W-O(1) | 1.923(4) | 1.919(4) |
| W-O(2) | 1.916(4) | 1.907(4) |
| W-O(3) | 1.925(4) | 1.924(4) |
| W–O(4) | 1.907(5) | 1.922(4) |
| W-O(5) | 1.894(4) | 1.892(4) |
| W-O(6) | 1.884(4) | 1.887(4) |
| O(1)-W-O(2) | 78.5(2) | 78.6(2) |
| O(1)-W-O(3) | 166.4(2) | 163.2(2) |
| O(1)-W-O(4) | 93.0(2) | 90.0(2) |
| O(1)-W-O(5) | 84.4(4) | 84.6(2) |
| O(1)-W-O(6) | 104.4(2) | 107.6(2) |
| O(2)-W-O(3) | 90.7(2) | 89.9(2) |
| O(2)-W-O(4) | 90.4(2) | 92.2(2) |
| O(2)-W-O(5) | 162.9(2) | 162.7(2) |
| O(2)-W-O(6) | 92.8(2) | 92.6(2) |
| O(3)-W-O(4) | 78.7(2) | 78.1(2) |
| O(3)-W-O(5) | 106.3(2) | 107.4(2) |
| O(3)-W-O(6) | 84.2(2) | 84.8(2) |
| O(4)-W-O(5) | 91.1(2) | 91.8(2) |
| O(4)-W-O(6) | 162.7(2) | 162.3(2) |
| O(5)-W-O(6) | 90.9(2) | 88.6(2) |
| W-O(1)-C(1) | $122.2(7)^{a}, 110(2)^{b}$ | 117.7(4) |
| W-O(2)-C(2) | 115.0(10) ^a , 126(2) ^b | 120.3(4) |
| W-O(3)-C(3) | 118.9(4) | 118.8(5) |
| W-O(4)-C(4) | 119.0(4) | 120.4(5) |
| W-O5-C(5) | 148.0(4) | 146.4(4) |
| W-O6-C(11) | 147.5(4) | 145.2(4) |
| O(1)-C(1)-C(2)-O(2) | $-35(3)^{a}, 38(7)^{b}$ | -32.1(8) |
| O(3)-C(3)-C(4)-O(4) | 30.8(9) | -19.5(11) |

Selected bonding distances (Å) and angles (°) for complexes 4

^a Refers C(1a) and C(2a).

^b Refers C(1b) and C(2b).

dinated W(VI) complexes with two bidentate eg ligands and two phenolate ligands in *cis*-positions. In compound **4** one eg ligand adopts two conformations **A** and **B** in a 0.72(2):0.28(2) ratio. In **5** the phenolate ligand is more hindered and the eg ligands adopt only one conformation. Otherwise the structures of both compounds are quite similar as seen from the bond parameters in Table 2. The W–O(diolato) bonds are slightly longer than the W–O(phenolate) bonds.

3. Conclusion

The tungsten(VI) complex $[W(eg)_3]$ (eg = ethanediolate dianion) reacts with simple phenyl acetates leading to the displacement of all diolato ligands and formation of tungsten(VI) hexaphenoxides $[W(OAr)_6]$. Phenyl acetates with 2,6-disubstitution (dimethyl or di-*iso*-propyl) can

form complexes having the formula $[W(eg)_2(OC_6H_3R_2'-2,6)_2]$.

According to X-ray studies, two phenoxide ligands in the mixed complexes are in *cis*-positions.

4. Experimental

Chemicals were from commercial origins and were used without subsequent purification. [W(eg)₃] was prepared as described earlier [14]. Substituted phenyl acetates were prepared from phenols and acetic anhydride. ¹H NMR spectra were recorded on a JEOL GSX-400 spectrometer. The products are pure according to NMR measurements. The C and H elemental analyses failed due to incomplete decomposition of the compounds during the analysis.

4.1. Preparation of $[W(OC_6H_5)_6]$ (1)

[W(eg)₃] (0.72 g, 2.0 mmol) and PhOAc (1.6 g, 12.5 mmol) were dissolved in 50 ml of chlorobenzene and the mixture was allowed to reflux for six hours. During this period the color of the solution turned intense red. The solution was filtered and the filtrate was washed twice with 10% aqueous NaOH (25 ml) and twice with water (25 ml). Volatiles were evaporated in vacuum and the red residue was dissolved in acetonitrile. Slow evaporation of solvent led to crystallization of [W(OPh)₆] as red needles (720 mg, 48%). m.p. 97°C (lit. 95–96°C [8]). NMR (solvent CDCl₃, standard SiMe₄): $\delta_{\rm H}$ 7.13 (m, 2H), 6.79 (m, 3H).

4.2. Preparation of $[W(OC_6H_4Cl-4)_6]$ (2)

4-ClPhOAc (1.1 g, 6.5 mmol) was added to the solution of [W(eg)₃] (0.36 g, 1.0 mmol) in chlorobenzene (50 ml). The reaction mixture was stirred under reflux for eight hours. Washing of the filtered solution with 10% aqueous NaOH (25 ml) and water (2 × 25 ml) followed by evaporation and crystallization from hexane yielded 620 mg (65%) of dark red microcrystals. m.p. 155–156°C (lit. 157–158°C [8]). NMR (solvent CDCl₃, standard SiMe₄): $\delta_{\rm H}$ 7.31 (m, 2H), 6.90 (m, 2H).

4.3. Preparation of $[W(OC_6H_5Me-4)_6]$ (3)

4-MePhOAc (1.0 g, 6.8 mmol) and $[W(eg)_3]$ (0.36 g, 1.0 mmol) were dissolved in chlorobenzene, and the reaction solution was allowed to reflux for eight hours. The solution was then filtered and the filtrate was washed with NaOH-solution (10%, 25 ml) and water (2 × 25 ml). Evaporation and crystallization from acetonitrile yielded 410 mg of dark red crystals (67%). m.p. 130°C (lit. 130–

131°C [8]). NMR (solvent CDCl₃, standard SiMe₄): $\delta_{\rm H}$ 7.05 (m, 2H), 6.81 (m, 2H), 2.27 (d, J = 5 Hz, 3H).

4.4. Preparation of $[W(eg)_2(OC_6H_3Me_2-2,6)_2]$ (4)

0.36 g (1.0 mmol) [W(eg)₃] and 0.36 g (2.2 mmol) 2,6-Me₂PhOAc were dissolved in 50 ml of chlorobenzene and the reaction mixture was stirred under reflux for six hours. The yellow solution was filtered and the solvent was evaporated yielding yellow microcrystals. Crystals for X-ray analysis were grown from ether by slow evaporation (415 mg, 68%). The crystals decompose at temperatures over 200°C in air. NMR (solvent CDCl₃, standard SiMe₄): $\delta_{\rm H}$ 7.13 (d, J=8 Hz, 2H), 6.96 (t, J=8 Hz, 1H), 5.43 (m, 1H), 5.29 (m, 2H), 5.17 (m, 1H), 1.17 (q, 6H).

4.5. Preparation of $[W(eg)_2(OC_6H_3^i Pr_2 - 2,6)_2]$ (5)

[W(eg)₃] (0.54 g, 1.5 mmol) and 2,6-^{*i*}Pr₂PhOAc (0.70 g, 3.2 mmol) were dissolved in 50 ml of chlorobenzene and the reaction mixture was allowed to reflux for four hours. The yellow solution was filtered and evaporated to dryness. The oily residue was washed twice with 5 ml of cold heptane and the remaining yellow powder was extracted with ether (30 ml). Yellow crystals precipitated from ether solution at -18° C (540 mg, 55%) and decompose over 200°C. Crystals for X-ray analysis were grown from hot heptane. NMR (solvent CDCl₃, standard SiMe₄): $\delta_{\rm H}$ 7.11 (d, J=8 Hz, 2H), 6.94 (t, J=7 Hz, 1H), 5.43 (m, 1H), 5.27 (m, 2H), 5.15 (m, 1H), 3.61 (m, 2H), 1.17 (q, 12H).

4.5.1. X-ray crystal determinations

Crystal data for compounds 1, 4 and 5, along with other experimental details, are summarized in Table 3. Single-crystal data collections were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo K α radiation ($\lambda = 0.71069$ Å). The unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. Data reduction and subsequent calculations were performed with teXsan for Windows [15]. The data was corrected for Lorenz and polarization effects and for absorption (PSI-scans [16]).

The structures were solved by direct methods using the SIR92 [17] program and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97 [18] program. Non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were included in the calculations at fixed distances from their host atoms. Figures were drawn with Ortep-3 for Windows [19].

| | 1 | 4 | 5 |
|--|--|--------------------------------|--------------------------------|
| Formula | C ₃₆ H ₃₀ O ₆ W | $C_{20}H_{26}O_{6}W$ | $C_{28}H_{42}O_6W$ |
| Μ | 742.45 | 546.26 | 658.47 |
| Crystal size (mm) | $0.25 \times 0.20 \times 0.20$ | $0.22 \times 0.20 \times 0.18$ | $0.20 \times 0.18 \times 0.18$ |
| Crystal description | red, needle | yellow, prism | yellow, prism |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group (No.) | $P2_1/n$ (14) | $P2_{1}/c$ (14) | $P2_1/c$ (14) |
| a (Å) | 13.731(3) | 8.3463(18) | 10.8735(9) |
| <i>b</i> (Å) | 16.215(4) | 19.7436(17) | 18.0693(13) |
| <i>c</i> (Å) | 13.9351(13) | 12.4840(15) | 14.7165(8) |
| β(°) | 90.442(13) | 97.939(13) | 95.665(5) |
| $U(\text{\AA}^3)$ | 3102.5(10) | 2037.5(5) | 2877.3(4) |
| Ζ | 4 | 4 | 4 |
| <i>F</i> (000) | 1472 | 1072 | 1328 |
| $\lambda(Mo K_{\alpha}) (cm^{-1})$ | 37.68 | 57.01 | 40.51 |
| h, k, l ranges | 0-16, 0-19, -17-17 | 0-10, 0-23, -15-15 | 0-13, 0-21, -18-18 |
| Reflections measured | 5708 | 3829 | 5355 |
| Unique reflections | 5470 | 3570 | 5072 |
| Refined parameters/restrains | 182/28 | 263/16 | 316/- |
| $R_1, wR_2 (I > 2\delta)$ | 0.035, 0.077 | 0.031, 0.064 | 0.035, 0.078 |
| R_1 , wR_2 (all data) | 0.072, 0.088 | 0.059, 0.071 | 0.070, 0.087 |
| Goodness of fit on F^2 | 1.041 | 1.041 | 1.014 |
| Maximum, minimum in final diff. map (e \mathring{A}^{-3}) | 0.51, -0.70 | 1.00, -0.89 | 0.90, -1.16 |

| Table 3 | |
|------------------|----------------------|
| Crystal data and | experimental details |

Calculations have been done with SHELX-97 and refinements are based on F^2 . Single-crystal data collections were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo K_x radiation ($\lambda = 0.71069$ Å). The unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. Data reduction and subsequent calculations were performed with teXsan for Windows [15]. The data was corrected for Lorenz and polarization effects and for absorption (PSI-scans [16]). The structures were solved by direct methods using the SIR92 [17] program and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97 [18] program. Non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were included in the calculations at fixed distances from their host atoms. Figures were drawn with Ortep-3 for Windows [19].

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