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COMMUNICATION

A NEW SYNTHETIC ROUTE TO *CIS*-DICHLOROBISDIOLATOTUNGSTEN(VI) COMPLEXES

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Abstract—The substitution of a diolato ligand by two chlorides around a tungsten(VI) centre was carried out by thionyl chloride in dichloromethane. The preparation and structure of *cis*-$[WCl_2(pin)_2]$ (pin = 2,3-dimethyl-2,3-butanediolato) is described.

Although the early transition metal alkoxides are generally prepared from corresponding metal halides, they can also be converted back to the mixed-ligand halo alkoxide compounds. Direct addition of anhydrous hydrogen halide is the most straightforward way to stepwise substitute alkoxide ligands by halides,[1-3] but sometimes it is too violent or difficult to control. Substitution reactions have been successfully carried out by several halogenation reagents, for example by acyl and silyl halides and phosphorus trihalides.[4,5] Solutions of metal alkoxides generally contain trace quantities of the corresponding alcohols, which can react with the halogenation reagent (Scheme 1). So it is possible that the halogenation step is virtually caused by hydrogen halide.

We are currently studying tungsten(VI) diolato complexes in relation to the olefin metathesis reaction. In this paper we report a new synthetic route to dichlorobisdiolato tungsten complexes, which are possible starting materials for organometallic catalysts. The three-step, high yield, synthesis of $[WCl_2(pin)_2]$ (**1**) starting from tungstic acid is shown in Scheme 2. **1** has earlier been prepared by oxidative addition of chlorine to $[W(Ph_2C_2)(pin)_2]$[6] and also by alcoholysis reaction of $WNCl_3$ with H_2pin.[7]

A possible reaction mechanism for the last step in the preparation of **1** includes reaction of $SOCl_2$ with free diol leading to the formation of hydrogen chloride and liberation of diol (Scheme 3). Liberated 1,2-ethanediol (H_2eg) reacts with thionyl chloride, which prevents the alcoholysis of dichloro tungsten(VI) complex. This seems to be a crucial step, because our attempts to substitute the eg ligand in $[W(eg)(pin)_2]$[8] by using hydrogen chloride has failed.

Reaction[†] of $[W(eg)(pin)_2]$ in dichloromethane

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[†] *Synthesis.* 1.0 mmol of $[W(eg)(pin)_2]$ (478 mg) was dissolved in 1.0 cm^3 of CH_2Cl_2 and 2.1 mmol of $SOCl_2$ (0.15 cm^3) was added. The yellow solution was stirred for 2 h until some yellow precipitation was formed. Volatiles were evaporated and the residue was dissolved in 0.5 ml of CH_2Cl_2. 340 mg (70%) of yellow prisms crystallised in 255 K during 3 days. NMR ($CDCl_3$, TMS as internal standard): ^1H, δ 1.66, 1.62, 1.40, 1.38; ^{13}C, δ 105.8, 104.2, 26.0, 25.6, 24.8, 24.5. (Found: C, 29.2; H, 4.9; $C_{12}H_{24}Cl_2O_4W$ requires C, 29.6; H, 4.9%.)

Crystal Data for $C_{12}H_{24}Cl_2O_4W$: $M_r = 487.08$, pale-yellow, prisms, crystal size $0.200 \times 0.150 \times 0.200$ mm, orthorhombic, space group *Pbca* (no. 61), $a = 12.442(2)$, $b = 22.348(2)$, $c = 12.098(2)$ Å, $U = 3363.8(6)$ Å^3, $Z = 8$, $D_c = 1.923$ g cm^{-3}, $F(000) = 1888$, μ(Mo-K_α) = 73.41 cm^{-1}. Data were collected at 21° [1697 reflections with $I > 3.00\sigma(I)$] on a Rigaku AFC5S diffractometer using Mo-K_α radiation ($\lambda = 0.71069$ Å); $2\theta_{max} = 50°$. The structure was solved by the Patterson method and refined to $R = 0.032$ and $\omega R = 0.038$ (heavy atoms anisotropic and hydrogen atoms in calculated positions with fixed temperature factors, absorption correction was applied) using TEXSAN-TEXRAY[12] system $\{R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $\omega R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F)\}$. Atomic coordinates, thermal parameters and bond lengths have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem Soc., Dalton Trans.* 1994, **1**, pp. xxiii–xxviii.

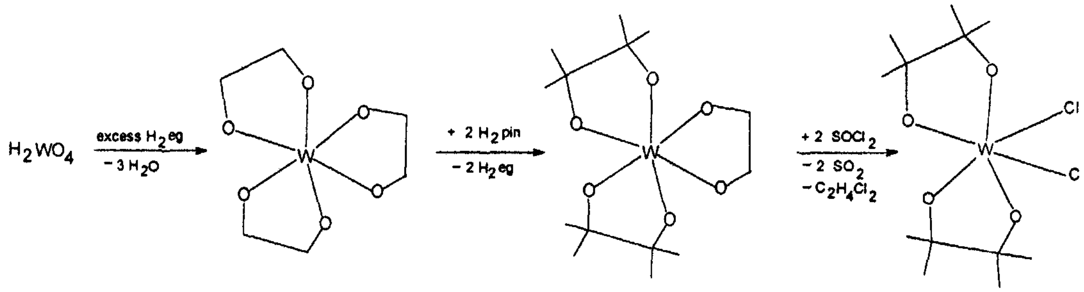
$$ROH + EX \rightarrow ROE + HX;$$

$$E = RCO,\ Me_3Si,\ PX_2$$

Scheme 1.

solution under a nitrogen atmosphere with 2 equivalents of $SOCl_2$ led to the formation of a yellow solution and the precipitation of a yellow powder. Recrystallisation from CH_2Cl_2 gave crystals suitable for X-ray analysis. Compound **1** was soluble in chloroform, acetonitrile and tetrahydrofuran, but only slightly soluble in alcohols. It can be washed with ethanol without alcoholysis reaction. **1** is stable in air in the solid state for a week, but in CH_2Cl_2 solution it turns blue during a few days. The chloro ligands are tightly bonded to tungsten(VI) since silver chloride does not precipitate in the presence of silver nitrate and **1** in acetonitrile at room temperature.

1 crystallises as monomeric distorted octahedral tungsten(VI) species (Fig. 1). The tungsten(VI) ion is surrounded by oxygen atoms of two chelating diolato(2−) ligands and by two chlorides which are in *cis* positions. Original configurations of pin ligands of [W(eg)(pin)$_2$] has prevailed during chlorination reaction. The W—O distances (range 1.874(7)–1.892(8) Å) are slightly shorter than those found in trisdiolato complexes.[8, 9] W—Cl distances (2.355(3) and 2.356(3) Å for Cl(1) and Cl(2), respectively) are typical for alcoholato chloro tung-



Scheme 2.

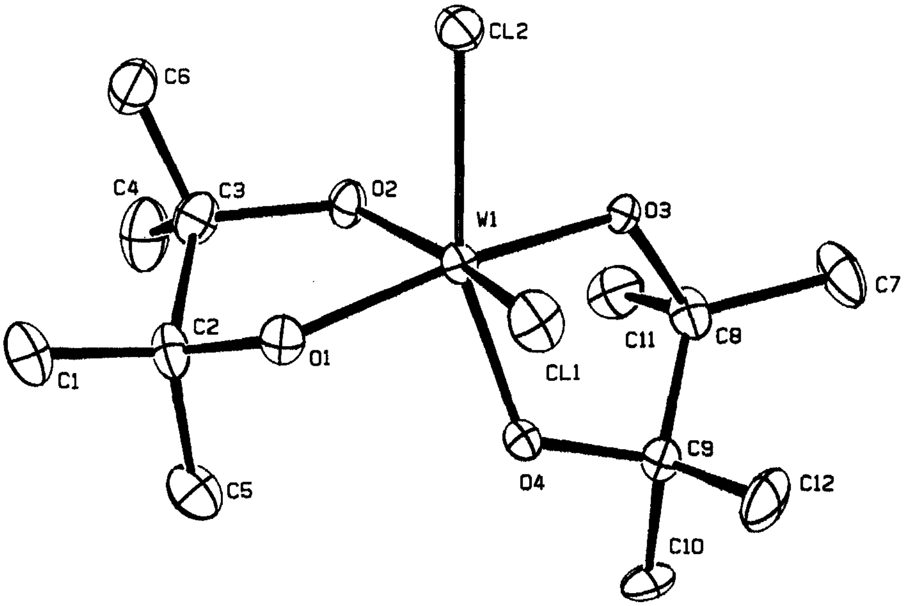
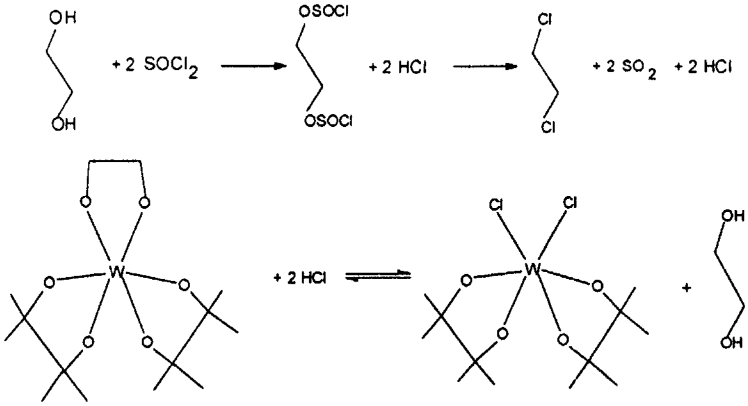


Fig. 1. An ORTEP[13] drawing of compound **1**. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (°): W(1)—Cl(1) 2.355(3), W(1)—Cl(2) 2.356(3), W(1)—O(1) 1.892(8), W(1)—O(2) 1.874(7), W(1)—O(3) 1.880(7), W(1)—O(4) 1.882(8); Cl(1)—W(1)—Cl(2) 84.2(1), O(1)—W(1)—O(2) 78.2(3), O(3)—W(1)—O(4) 77.6(3).



(3a)

(3b)

Scheme 3.

sten(VI) complexes.[10,11] IR spectrum of **1** consists of strong peaks at 390 and 343 cm^{-1} which are assigned as W—Cl stretchings. In middle-IR similar vibrations of 2,3-dimethyl-2,3-butanediolato ligand as found in [W(eg)(pin)$_2$] and [W(pin)$_3$] are seen. ^{1}H NMR and ^{13}C NMR spectra are comparable to those reported by earlier authors.[6]

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REFERENCES

1. M. D. Atherton and H. Sutcliffe, *Inorg. Chim. Acta* 1988, **143**, 213.
2. D. C. C. Crans, H. Chen and R. A. Felty, *J. Am. Chem. Soc.* 1992, **114**, 4543.
3. A. D. Horton and R. R. Schrock, *Polyhedron* 1988, **7**, 1841.
4. D. C. Bradley, F. M. A. Halim and W. Wardlaw, *J. Chem. Soc.* 1950, 3450.
5. M. H. Chisholm, D. L. Clark, R. J. Errington, K. Folting and J. C. Huffman, *Inorg. Chem.* 1988, **27**, 2071.
6. K. H. Theopold, S. J. Holmes and R. R. Schrock, *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 1010.
7. S. Buth, S. Wocaldo, B. Neumüller, F. Weller and K. Dehnicke, *Z. Naturforsch.* 1992, **47b**, 706.
8. A. Lehtonen and R. Sillanpää, *Polyhedron* 1994, **13**, 2519.
9. J. Scherle and F. A. Schröder, *Acta Cryst.* 1974, **B30**, 2772.
10. B. L. Handy, *Acta Crystallogr.* 1975, **B31**, 300.
11. F. Quignard, M. Leconte, J.-M. Basset, L.-Y. Hsu, J. J. Alexander and S. G. Shore, *Inorg. Chem.* 1987, **26**, 4272.
12. TEXSAN-TEXRAY: Structure Analysis Package, Molecular Structure Corporation, Texas (1989)
13. C. K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976)