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Reduction of tungsten(VI) and molybdenum(V) by allyltrimethylsilane and cyclopentene. Simple high yield syntheses of $MoCl_4(OEt_2)_2$, $MoCl_4(dme)$, $WCl_4(thf)_2$, $WCl_4(dme)$ and $WOCl_3(thf)_2$

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Abstract

Convenient high yield methods to prepare $MoCl_4(OEt_2)_2$, $MoCl_4(dme)$, $WCl_4(thf)_2$, $WCl_4(dme)$ and $WOCl_3(thf)_2$ by reduction of $MoCl_5$ and WCl_6 with olefins such as allyltrimethylsilane or cyclopentene are presented.

Introduction

Molybdenum(IV) and tungsten(IV) halide complexes are important as intermediates or precursors in the preparation of dinitrogen complexes [1], butadiene complexes [2] and various complexes with metal–metal multiple bonds [3]. These metals in the + IV oxidation state also form interesting acetylene complexes [4]. Known methods to prepare WCl_4 and $MoCl_4$ or ligated complexes thereof are based on the reduction of WCl_6 or $MoCl_5$ using reducing agents such as Al at high temperature [5], Zn [6], tetrachloroethane [7], benzene [8], nitriles [9], alkylzinc reagents [10] or $M(CO)_6$ [11]. Some of these methods are tedious to apply on a laboratory scale and in some cases the products are not obtained completely pure so additional purification is required.

As part of an ongoing project related to the olefin metathesis reaction we are interested in the applicability of oxidative additions to tungsten (IV) and molybdenum (IV) centers as a method to obtain imido or alkylidene complexes. Therefore reliable simple high yield methods to prepare MCl_4L_2 or $MCl_4(L\text{-}L)$ complexes with labile monodentate(L) or bidentate(L-L) ligands have been investigated. In the present study the reduction of molybdenum(V) and tungsten(VI) has been carried out using allyltrimethylsilane or cyclopentene as reducing agents and herein simple procedures for the preparation of $MoCl_4(OEt_2)_2$, $MoCl_4(dme)$, $WCl_4(thf)_2$ and $WCl_4(dme)$ are presented. Additionally an improved method to prepare $WOCl_3(thf)_2$ is presented.

Experimental

General procedures

The preparations were carried out under an atmosphere of dried argon using conventional Schlenk technique. Solvents, cyclopentene (Merck), dimethoxyethane and allyltrimethylsilane (Janssen Chimica) were dried and stored over activated molecular sieves. Molybdenumpentachloride (Aldrich) and tungstenhexachloride (Janssen Chimica) were used as received, except in the case of $WCl_4(dme)$ where the tungstenhexachloride was purified from the volatile impurities by a continuous argon flow at 120 °C.

Tungsten and molybdenum were determined gravimetrically as WO_3 and MoO_3. Chlorine was determined by Mohr titration. Elemental analyses were done by Mikro Kemi AB, Uppsala, Sweden. IR spectra were recorded on a Nicolet 20 SXC FT-IR spectrometer as Nujol mulls.

Tetrachloro(1,2-dimethoxyethane-O,O')molybdenum(IV)

$MoCl_5$ (2.3 g, 8.4 mmol) was partly dissolved in dimethoxyethane (20 cm^3) giving a brown solution and evolution of heat. After cooling to −78 °C allyltrimethylsilane (2.7 cm^3, 17.0 mmol) was added, whereupon a brown solid immediately started to form. After letting the reaction mixture reach room temperature and the reaction to continue for 1 h, the precipitate formed was collected by Schlenk filtration, washed with diethyl ether (3×5 cm^3) and dried under vacuum. Yield 1.6 g. Cooling the filtrate at −30 °C gave another crop of 0.3 dark brown crystals. Total yield 1.9 g, 69%.

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Anal. Found: C, 14.5; H, 3.1; Cl, 43.0; Mo, 29.4. Calc.: C, 14.6; H, 3.1; Cl, 43.3; Mo, 29.3%. IR (cm^{-1}): 1187w, 1156vw, 1056m, 1016s, 993m, 980sh, 845s, 803w, 565vw, 418m, 357s, 327s.

Tetrachloro(1,2-dimethoxyethane-O,O')tungsten(IV)

In a Schlenk tube equipped with a reflux-condenser cyclopentene (17 cm^3, 193 mmol) was added to a stirred suspension of WCl_6 (7.45 g, 18.8 mmol) in dichloromethane (20 cm^3). An immediate reaction ensued, giving a dark green solid. Within a few minutes the precipitate dissolved exothermally causing the mixture to boil. The clear yellow–brown solution was filtered when the reaction mixture had reached room temperature (15 min). Dimethoxyethane (10 cm^3) was added to the filtrate and in a slightly exothermic reaction a red–brown solution was obtained, from which a red–brown precipitate immediately started to form. After 30 min reaction the precipitate was filtered off, washed with diethyl ether (3×5 cm^3) and dried under vacuum. Yield 5.95 g, 76%.

Anal. Found: C, 11.6; H, 2.5; Cl, 33.8; W, 44.3. Calc.: C, 11.6; H, 2.4; Cl, 34.1; W, 44.2%. IR (cm^{-1}): 1184w, 1152w, 1102w, 1051m, 1006s,br, 975s,br, 843s,br, 804m, 435m, 418sh, 356s, 323s.

Tetrachlorobis(tetrahydrofuran)tungsten(IV)

A solution containing reduced tungsten was prepared in a manner strictly analogous to that used to prepare tetrachloro(1,2-dimethoxyethane-*O,O'*)tungsten(IV) using cyclopentene (27 cm^3, 306 mmol), unsublimed WCl_6 (11.8 g, 29.8 mmol) and dichloromethane (35 cm^3). After cooling the filtrate to ice-bath temperature tetrahydrofuran (25 cm^3) was added dropwise, giving a red–brown solution, which after a few minutes at room temperature turned green as a yellow solid precipitated. After 1 h the yellow solid was isolated by Schlenk filtration, washed with dichloromethane (3×10 cm^3) and dried under vacuum. Yield 5.05 g, 36%.

Anal. Found: C, 20.3; H, 3.4; Cl, 30.4; W, 39.2. Calc.: C, 20.5; H, 3.4; Cl, 30.2; W, 39.0%. IR (cm^{-1}): 1167w, 1043mw, 991m, 949mw, 918mw, 817s, 315s, 253m.

Tetrachlorobis[1,1'-oxybis(ethane)]molybdenum(IV)

$MoCl_5$ (9.3 g, 34.0 mmol) was partly dissolved in diethyl ether (50 cm^3) giving a red–brown suspension. After cooling to −78 °C, allyltrimethylsilane (11 cm^3, 69.2 mmol) was added, whereupon a red–brown solid immediately started to form. The reaction mixture was stirred for 2 h at room temperature, the product filtered off, washed with diethyl ether (3×10 cm^3) and dried under vacuum. Yield 11.2 g, 85%.

Anal. Found: Cl, 36.8; Mo, 25.0. Calc.: Cl, 36.7; Mo, 24.9%. IR (cm^{-1}): 1184m, 1142w, 990s, 976sh, 865ms, 824m, 736s, 530m, 457m, 347s, 268m, 247w.

Trichlorooxobis(tetrahydrofuran)tungsten(V)

Allyltrimethylsilane (25 cm^3, 157 mmol) was added to a stirred suspension of WCl_6 (16.05 g, 40.5 mmol) in diethyl ether (100 cm^3) at room temperature. By continuous stirring for 90 min the WCl_6 dissolved and a light green precipitate formed. The solution was filtered and cooled on an ice-bath. Tetrahydrofuran (60 cm^3) was slowly added to the stirred solution, giving immediate formation of a black crystalline precipitate which reacted further to give a black oil. The reaction was allowed to reach room temperature and soon turquoise crystals began to form. After 90 min the product was separated by Schlenk filtration, washed with diethyl ether (6×6 cm^3) and dried under vacuum. Yield: 12.45 g, 68%.

Anal. Found: W, 40.6; Cl, 23.8. Calc.: W, 40.8; Cl, 23.6%. IR (cm^{-1}): 1177m, 1136w, 1048m, 1003sh, 989s, 956m, 925m, 917m, 845sh, 826s, 675m, 574w, 352s, 332s, 323s, 253m, 227m.

Results and discussion

The reduction of $MoCl_5$ in diethyl ether or dimethoxyethane (dme) solution using allyltrimethylsilane as the reducing agent proceeds smoothly to give $MoCl_4(OEt_2)_2$ and $MoCl_4(dme)$ in high yields. Both compounds are almost insoluble in diethyl ether. Excess reducing agent and the organic products from the reduction are therefore easily removed and the products are obtained analytically pure by washing with diethyl ether. A similar method to prepare $MoCl_4(OEt_2)_2$ using norbornene as reducing agent has been described [12] and a recent report [13] describes the preparation of $MoCl_4(dme)$ from $MoCl_5$ in toluene/dme mixture. In the latter reaction dme was the suggested reducing agent, but based on the known reduction of Mo(V) with benzene [8] we find it more likely that toluene is the reducing agent. $MoCl_4(OEt_2)_2$ undergoes elimination of diethyl ether by storage at room temperature; molybdenum and chlorine analyses of freshly prepared samples are in agreement with the formula $MoCl_4(OEt_2)_2$ while samples kept under inert atmosphere for some days give carbon and hydrogen analyses corresponding to the formula $MoCl_4(OEt_2)$ (*Anal.* Found: C, 15.2; H, 3.4. Calc.: C, 15.4; H, 3.2%).

The preparation of analogous tungsten compounds starting from W(VI) involves a two step reduction with W(V) as an intermediate which complicates the reaction. We have shown [14] that WCl_6 is conveniently reduced in diethyl ether solution by allyltrimethylsilane to give the complex $WCl_5(OEt_2)$ in high isolated yield without further reduction to W(IV). Thus, the +V oxidation state is in the case of tungsten stabilized by complexation with the ether. Besides allyltrimethylsilane we have in the present study also used cyclopentene as reducing agent, which is one of those olefins claimed to be effective for the preparation of $WCl_4(OEt_2)$ [12]. In our hands, however, all attempts to conduct the reduction to $WCl_4(OEt_2)_2$ or WCl_4(dme) in the presence of diethyl ether and dme have been unsuccessful leading to $WCl_5(OEt_2)$ in the case of diethyl ether or to a green intractable oil in the case of dme.

Another complication related to the formation of W(V) as an intermediate is the propensity for W(VI) and W(V) to abstract oxygen from ethers especially tetrahydrofuran (thf), e.g. both W(V) and W(VI) react with thf to give $WOCl_3(thf)_2$ [15]. This means that the reduction to tungsten(IV) must be completed before the complexing ether is added, holding in mind that a precipitation of WCl_4 is undesirable because this is a polymer of low reactivity and solubility.

By reaction of WCl_6 with allyltrimethylsilane in CH_2Cl_2 solution a greyish-black precipitate was obtained. This precipitate reacts with thf and dme to give $WCl_4(thf)_2$ and WCl_4dme, respectively, although not in a completely pure state. No formation of $WOCl_3(thf)_2$ was observed in the reaction with thf, which excludes substantial amounts of W(V) in the precipitate. Thus, these observations suggest that the precipitate is a compound of tungsten(IV).

Changing the reducing agent to cyclopentene gave an immediate reaction with very little solid remaining, indicating that in this case a reduced soluble tungsten complex is formed. A tentative formulation of the complex in solution is $WCl_4(\text{cyclopentene})_n$ [12, 16]. The addition of thf or dme to a solution prepared in this way gave an immediate precipitation of the known WCl_4(thf) [10, 17] and the new complex WCl_4(dme), respectively. The addition of diethyl ether has, however, not led to the isolation of an analogous diethyl ether complex and a possible reason can be the weaker donor ability of this ether.

It is worth noting that in the preparation of the two ether complexes, $WCl_4(thf)_2$ and WCl_4(dme), the purification of WCl_6 contaminated with small amounts of $WOCl_4$ or other oxychlorides is not necessary. These impurities are either filtered off before the addition of the ether or kept in solution as their ether adducts.

Additionally we have found that the reaction involving WCl_6 and cyclopentene is sensitive to the concentration of tungsten in solution and to the tungsten to olefin ratio applied. A shining green precipitate was obtained in more dilute ($C_W \approx 0.15$ M) CH_2Cl_2 solution using four equivalents of cyclopentene. This precipitate was subjected to sublimation at 180 °C to give about 30% of analytically pure WCl_5 (found (calc.)(%): W = 50.78 (50.91)) thus showing that WCl_5 is the main product in more dilute solution and also observed previously [18]. On continued reaction, however, the precipitate of WCl_5 initially formed dissolves giving the same soluble form of tungsten (IV) as in the case of the more concentrated solution.

Different methods to prepare $WOCl_3(thf)_2$ are known, [14, 15a, 19], one of these stating that the compound obtained is not very stable [19]. The method described here is an improved version of that given earlier [14]. It gives a very pure product which can be stored under argon at low temperature for several months without noticeable decomposition. A great additional advantage for the preparation of larger quantities is that no purification of WCl_6 is needed for reasons discussed above.

$WOCl_3(thf)_2$ is a convenient starting material for the preparation of other $WOCl_3L_2$ or $WOCl_3$(L-L) complexes, e.g. it dissolves completely in neat dme and on addition of diethyl ether turquoise crystals of $WOCl_3$(dme) [20] precipitate. The reverse reaction is also possible; dissolution of $WOCl_3$(dme) in thf gives an immediate precipitation of $WOCl_3(thf)_2$.

Attempts to carry out similar ligand exchange reactions in the case of molybdenum and tungsten(IV) chloro complexes have been carried out; $MoCl_4(OEt_2)$ reacts with neat dme to give $MoCl_4$(dme), WCl_4(dme) in neat thf gives $WCl_4(thf)_2$, while the reverse reactions do not work either at room temperature or at elevated temperatures.

Comparing the applicability of the two olefins cyclopentene and allyltrimethylsilane the present study shows that for the preparation of the ether complexes of tungsten(IV) cyclopentene is the preferred reducing agent since this gives the soluble form of tungsten(IV).

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