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REDUCTION OF WCl_6 BY ALLYLTRIMETHYLSILANE. A CONVENIENT METHOD TO PREPARE $WCl_5(OEt_2)$ AND SOME OTHER DERIVATIVES OF WCl_5

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Abstract—WCl_6 was reacted with excess allyltrimethylsilane in diethyl ether solution at low temperature. The main product in the reaction was shown to be $WCl_5(OEt_2)$ which was isolated as black–green air- and moisture-sensitive crystals. $WCl_5(OEt_2)$ was reacted with different Lewis bases, e.g. pyridine and 9-fluorenone to yield the new compounds WCl_5 (pyridine) and WCl_5(9-fluorenone). The latter most likely being an oxygen bonded complex.

Tungsten is one of the transition metals that can be used as a catalyst for the metathesis of olefins.[1,2] Well-defined tungsten based metathesis catalysts, e.g. isolated tungsten carbene complexes have been developed in recent years.[3–5] An active but poorly defined catalyst can also be prepared *in situ* by reacting WCl_6 with an alkylating co-catalyst, e.g. alkyl-tin, alkyl-lithium or alkyl-alumina reagents.[2] Considerable efforts have been devoted to elucidate the nature of the active catalyst in these latter systems, i.e. to determine the actual oxidation state of the metal and the ligands in the coordination sphere of the metal. The reduction of tungsten(VI) as an important reaction path when alkyl-tin reagents are used as co-catalysts has been demonstrated[6,7] and the reducing properties of $SnBu_4$ have also been used[8] to prepare WCl_5 from WCl_6.

Allyltrimethylsilane has been found to undergo slow self-metathesis and fast cross-metathesis without an added co-catalyst.[9,10] Likewise ring-opening polymerizations have been performed using WCl_6/allyltrimethylsilane as the catalyst system.[11,12]

A mechanism involving metalla-carbene and metalla-cyclobutane complexes is the accepted mechanism of the metathesis reaction.[2] How an initiating metalla-carbene is formed in the system of WCl_6/allyltrimethylsilane is still an unanswered question. Based on the organic products propene and chlorotrimethylsilane, found after reaction of WCl_6 with allyltrimethylsilane, suggestions involving double allylation of tungsten and subsequent α-hydrogen transfer and propene elimination have been put forward as a route to form a carbene.[13,14] As indicated by the other organic products, allylchloride and 1,5-hexadiene, reductive elimination reactions are in this case competing reactions not leading to an active carbene but to reduced tungsten.

In the course of a project aiming at the metathesis of functionalized olefins we have continued the study of allyltrimethylsilane and its reactions with WCl_6 to eventually identify or isolate tungsten-σ-allyl or carbene complexes in the reaction mixture. Based on the observed reduction of tungsten(VI) by tetra-alkyl-tin compounds[6–8] or by cyclic olefins[15,16] we have also considered reduced tungsten as a likely product of the reaction. The work presented here describes the isolation and the identification of $WCl_5(OEt_2)$ and some complexes of tungsten(V).

RESULTS AND DISCUSSION

Reaction between WCl_6 *and allyltrimethylsilane*

The treatment of WCl_6 partly dissolved in diethyl ether at $-25°C$ with excess (4 equiv.) allyltrimethylsilane leads to a colour change in the solution and a dissolution of the undissolved WCl_6.

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After *ca* 2 h a green precipitate is formed. Continued reaction overnight leads to a dark orange solution and a fluffy green precipitate (**I**). Schlenk filtration to remove the precipitate gives a clear solution. Slow evaporation at low temperature (−30°C) of the ether solvent leads to the deposition of large black–green crystals (**II**) with a metallic lustre. Several crops with the same appearance can be isolated in this way. GC-MS analysis of the organic evaporate reveals the presence of unreacted allyltrimethylsilane together with propene, allylchloride, chlorotrimethylsilane and 1,5-hexadiene. No attempt was made to quantify the relative amount of these products. The relative amount of the green (**I**) and black–green (**II**) materials varies from one experiment to another but in no case does the amount of **I** exceed more than 10% of the total isolated solid material. Both the isolated solids are extremely air- and moisture-sensitive which precludes full spectroscopic characterizations and a precise elemental analysis.

Since direct spectroscopic and analytical methods gave no decisive information on the composition of the solids indirect methods to characterize the major product **II** were sought for. In the search for more stable adducts, reduced tungsten, i.e. tungsten(V) or (IV) was considered as the likely parent compound.

Tungsten(IV) has been isolated as its THF adduct,[17] $WCl_4(THF)_2$, and tungsten(IV) also forms isolable complexes with other Lewis bases, e.g. pyridine[18–20] and bipyridine.[21] Chloro complexes of tungsten(IV), e.g. WCl_6^{2-} are also known.[18] Tungsten(V) forms stable chloro complexes[22] but no simple stable Lewis base adducts besides WCl_5(bipyridine).[8] A brief note[23] describing some benzoic ester derivative is also known.

Complexes with nitrogen donor ligands

Compound **II** dissolves in neat pyridine. An orange solution is thus obtained which within 45 min deposits a small amount of an orange solid. Heating the mixture at reflux results in a dark red solution and more of the orange solid (**III**). After isolation of the solid from the hot solution the elemental anslysis and the IR spectrum reveals that this is the known *trans*-$WCl_4(pyridine)_2$.

Treatment of an etheral solution of **II** with one equiv. of pyridine at room temperature results in immediate darkening of the solution. Within a few minutes stirring a dark green precipitate (**IV**) forms. No definite conclusion as to the formulation of (**IV**) is obtained by elemental analysis.

Comparing the IR spectra of **III** and **IV** disclose similarities, i.e. coordinated pyridine in both substances as demonstrated by the three bands at 444, 683 and 1607 cm^{-1} in the spectrum of **III** and at 440, 680 and 1607 cm^{-1} in the spectrum of **IV**, but also differences in the region of metal halide vibrations. In the spectrum of **III** an intense band at 311 cm^{-1} is present, which is most likely the W—Cl stretch in a *trans*(*D*4*h*) arrangement of the two chloride ligands, while in the spectrum of **IV** two intense bands at 348 and 322 cm^{-1} are present.

On addition of allyltrimethylsilane (1.3 equiv.) to an ether solution of **II** at room temperature before the addition of pyridine (1 equiv.) a dark solution is obtained. From this solution dark black–green crystals (**V**) separate within minutes. Elemental analysis of this product is in accordance with the formula WCl_5(pyridine).

The IR spectrum of **V** is in many respects similar to the spectra of **III** and **IV**. The bands at 438, 687 and 1607 cm^{-1} showing coordinated pyridine are almost unshifted relative to those of **III** and **IV**. One intense band at 334 cm^{-1}, a shoulder at 350 cm^{-1} and a medium band at 392 cm^{-1} are present in the metal halide stretching region.

If it is considered that pyridine in its reaction with high valent metal ions possesses reducing properties[24,25] as well as complexing properties, the formation of the products **III**, **IV** and **V** can be rationalized. Excess pyridine and heating promotes the reduction to tungsten(IV) as in **III**, while stoichiometric amounts of pyridine at room temperature bring about only partial reduction leading to some kind of mixed tungsten(V)/(IV) product (**IV**) with coordinated pyridine. The isolation of analytically pure WCl_5(pyridine), which is a rare example of tungsten(V) nitrogen-coordinated complex, when allyltrimethylsilane is used as a co-reactant is most likely due to some kind of stabilizing effect of the olefin prohibiting the reduction to tungsten(IV). WCl_5(pyridine) is soluble in solvents such as toluene, benzene and chlorobenzene. In all these solvents red solutions are obtained, but the parent compound cannot be recovered.

As is the case with pyridine, bipyridine reacts with an ether solution of **II** at room temperature to yield a yellow–brown precipitate analysing approximately to a mixture of WCl_5(bipyridine) and WCl_4(bipyridine). This is in accordance with the observation in the case of pyridine and further studies were therefore not pursued. An impure compound of the formula WCl_5(bipyridine) was prepared recently[8] and described as being brick-red.

Chloro-complexes

Compound **II** dissolves in CH_2Cl_2 to produce a clear green solution. On addition of tetraphenylarsonium chloride in CH_2Cl_2 a red–brown solution is obtained. Within minutes of stirring a brown solid deposits. Brown crystals (**VI**) are isolated by cooling to -30°C and subsequent filtration. The elemental analysis and the IR spectrum shows that this is the known[22] $[WCl_6][AsPh_4]$. In a similar way the green tetramethylammonium salt is obtained.

The formation of the hexachloro coordinated anion WCl_6^- from (**II**) is strong evidence that (**II**) is a chloro complex of tungsten(V), most likely the ethyl ether adduct $WCl_5(OEt_2)$. A high excess of Cl^- has been observed to induce reduction of metal halides[24] but we are convinced that this is not the case in the present study.

Complexes with oxygen donors

Having reached a likely formulation of (**II**) we found it interesting to try to substitute diethyl ether by other oxygen donors.

On dissolution of **II** in THF by dropwise addition of THF to solid **II** heat is evolved and a yellow suspension is initially obtained. Further addition of THF gives a clear green solution. On continued stirring of this solution at room temperature it gradually changes to finally reach a turquoise colour. By reducing the volume and cooling to -25°C very air-sensitive turquoise crystals of **VII** deposit. The elemental analysis and IR spectrum reveal that this is $WOCl_3(THF)_2$. Precedence for oxygen abstraction reactions from THF can be found[26] although hexamethyldisiloxane seems to be the preferred reagent for this kind of reaction.[8,27] Other oxygen donors react differently. We have studied the reaction of **II** with 9-fluorenone, an example outside the ether class.

Dropwise addition of 9-fluorenone in CH_2Cl_2 into a solution of **II** in the same solvent gives an immediate precipitation of a dark solid. Isolation by filtration gives green–black crystals (**VIII**) which analyse for WCl_5(9-fluorenone). The formation of this compound does not necessarily implicate that 9-fluorenone is a better donor than diethyl ether with respect to tungsten(V). The low solubility of the fluorenone adduct shifts the equilibrium towards the formation of the fluorenone adduct.

All the reactions described and the products isolated in these reactions clearly demonstrate that the parent compound (**II**) must be WCl_5, probably as its diethyl ether solvate. Further proof for this is found in the UV spectrum of **II**. This spectrum shows an absorbance maximum at 298 nm which is in accordance with published data.[28] The reactions carried out also show that care must be taken if adduct formation is used as a method to characterize an unknown compound.

The reaction between WCl_6 and allyltrimethylsilane is in our opinion a convenient entry into tungsten(V) chemistry, easier than the older high temperature methods[29–33] to use. The method is easily applicable for the synthesis of quantities of about 10 g. The solubility of $WCl_5(OEt_2)$ in organic solvents makes this useful as a precursor for other tungsten(V) compounds.

Regarding the actual mechanism by which WCl_5 is formed in the present case, this is still an open question. The results presented here do not allow a distinction between direct reduction and a reaction path involving allylation of WCl_6 and subsequent reductive elimination as suggested in earlier studies. A direct reduction can proceed via chlorine radical transfer from WCl_6 to allyltrimethylsilane resulting in WCl_5, chlorotrimethylsilane and an allyl radical. Further reactions as dimerization of allyl radicals, recombination of allyl and chlorine radicals and hydrogen abstraction from a hydrogen source in the system could equally well, as the indirect reduction, explain the organic products 1,5-hexadiene, allylchloride and propene. The present study reveals, however, no formation of tungsten(IV), which must form in a mono-molecular reductive elimination from tungsten(VI).

EXPERIMENTAL

General procedures and chemicals

All preparations and reactions were carried out under an atmosphere of dried nitrogen or argon using conventional Schlenk techniques. Solvents were dried and stored over activated molecular sieves. Allyltrimethylsilane (Janssen Chimica) was distilled prior to use and stored over activated molecular sieves. Tetraphenylarsoniumchloride (Merck) was dried over Sicapent *in vacuo*. Tetramethylammoniumchloride was dried by vacuum treatment at 50°C for 48 h. 2,2-bypiridine (Merck) was recrystallized from ethanol prior to drying over Sicapent *in vacuo*. Tungsten hexachloride (Janssen Chimica) was purified from the volatile impurities by a continuous nitrogen flow at 120°C. Tungsten was determined gravimetrically as WO_3. Chlorine was determined by Mohr titration. Elemental analyses were done by Mikro Kemi AB, Uppsala, Sweden. IR spectra were recorded on a PE 580B spectrometer or on a Nicolet 20 SXC FT-IR spectrometer as Nujol or Fluorolube mulls between CsI windows or as CsI tablets. UV spectra were recorded in standard Schlenk tubes using a Guided

Wave, Model 260 fibre optic spectrophotometer equipped with an adjustable probe head.

Preparations

(1) *(Diethyl ether)pentachlorotungsten* (**II**). Allyltrimethylsilane (11 cm^3, 69 mmol) was added to a suspension of WCl_6 (6.8 g, 17.1 mmole) in diethyl ether (200 cm^3) at -25°C. Upon continuous stirring of the cold mixture WCl_6 gradually dissolved and after 24 h a clear solution and a green precipitate were obtained. The green solid (0.5 g) was separated by Schlenk filtration. Cooling the solution to -25°C and concentration to *ca* 70 cm^3 afforded the first crop (1.9 g) of large black–green crystals. Further concentration to *ca* 20 cm^3 afforded 2.5 g and additional concentration afforded another 0.4 g. Total yield = 4.8 g (64%).

IR: W—Cl 315(s), 351(sh) cm^{-1} and coordinated ether, 1013 and 999 cm^{-1}. Found: Cl, 40.7. Calc.: Cl, 40.7%.

(2) *Bis(pyridine)tetrachlorotungsten* (**III**). **II** (0.45 g, 1 mmol) was dissolved in pyridine (25 cm^3) to give a clear orange solution. After stirring for 45 min at room temperature a small amount of an orange solid was formed. Heating the reaction mixture under reflux for 1.5 h afforded a dark red solution and an orange solid. The solid was isolated by filtering the hot mixture. The solid was washed with 3 × 5 cm^3 ether and dried *in vacuo*. Isolated yield = 0.20 g.

Found: C, 25.1; H, 2.1; N, 5.8; Cl, 27.7; W, 37.5. $C_{10}H_{10}N_2Cl_4W$ requires: C, 24.8; H, 2.1; N, 5.8; Cl, 29.3; W, 38.0%.

IR: W—Cl 311(s), 330(sh) cm^{-1} and coordinated pyridine, 1607, 683, 444 cm^{-1}.

(3) *(Pyridine)pentachlorotungsten* (**V**). **II** (0.75 g, 1.7 mmol) was dissolved in diethyl ether (30 cm^3) and the solution was filtered to give a clear solution. To this solution 0.36 cm^3 (2.3 mmol) of allyltrimethylsilane was added followed by an addition of 0.16 cm^3 (2 mmol) of pyridine. The solution darkened and dark crystals separated at once. The crystals were collected by filtration and dried *in vacuo*. The crystals were stable in air for a short period.

Found: C, 13.9; H, 1.0; N, 3.2; Cl, 39.0; W, 41.0. $C_5H_5NCl_5W$ requires: C, 13.6; H, 1.1; N, 3.2; Cl, 40.3; W, 41.8%.

IR: W—Cl 334(s), 350(sh), 392(mw) cm^{-1} and coordinated pyridine, 1607, 687 and 438 cm^{-1}.

(4) *Tetraphenylarsonium hexachlorotungstate*(V) (**VI**). Tetraphenylarsoniumchloride (0.8 g, 1.9 mmol) dissolved in CH_2Cl_2 (20 cm^3) was added dropwise to **II** (0.9 g, 2.1 mmol) dissolved in CH_2Cl_2 to give a red solution. After stirring for some minutes a brown solid deposited. Cooling to -30°C and filtration afforded a brown solid (0.6 g). An additional 0.6 g was obtained by addition of CCl_4 (10 cm^3) to the filtrate. The solid can be recrystallized by dissolution in CH_2Cl_2 and precipitated by the addition of CCl_4. Total isolated yield = 1.2 g (81%). M.p. = 255°C (lit.[22] 253–256°C).

Found: C, 36.8; H, 2.5; Cl, 26.3; W, 23.3. $C_{24}H_{20}Cl_6AsW$ requires: C, 36.9; H, 2.6; Cl, 27.3; W, 23.6%.

IR: W—Cl 315(s), 332(sh), 350(m) and 385(w) cm^{-1}.

(5) *Bis(tetrahydrofuran)trichlorooxotungsten* (**VII**). THF (30 cm^3) was added dropwise to solid **II** (0.45 g, 1 mmol). On addition, heat was evolved and an initial yellow suspension was obtained which on further addition gave a green homogeneous solution. Further stirring at room temperature gave a turquoise solution. Reducing the volume to one third of the original volume and cooling to -25°C for 3 days afforded turquoise air-sensitive crystals. These were separated, washed with diethyl ether and dried *in vacuo*.

Found: C, 20.3; H, 3.2; Cl, 23.3. $C_8H_{16}Cl_3OW$ requires: C, 21.3; H, 3.6; Cl, 23.6%.

IR: W—Cl 325(s), 351(m) cm^{-1}; W═O 998(vs), 1003(sh) cm^{-1} and coordinated THF, 1047 cm^{-1}.

(6) *(9-Fluorenone)pentachlorotungsten* (**VIII**). Fluorenone (0.54 g, 3 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added dropwise to a solution of **II** (1.3 g) in CH_2Cl_2 (15 cm^3), whereupon a dark solid deposited. The black–green crystals were separated by filtration and washed repeatedly with diethyl ether before drying *in vacuo*.

Found: C, 29.5; H, 1.6; Cl, 32.5. $C_{12}H_6Cl_5OW$ requires: C, 28.8; H, 1.5; Cl, 32.7%.

IR (Fluorolube): C═O 1550(s,br) cm^{-1}; W—Cl 334(s), 385(m) cm^{-1}.

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