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$WCl_4(DME)$: A Facile Entry into Bis(cyclopentadienyl) Complexes of Tungsten(IV). Synthesis of Bis(cyclopentadienyl)tungsten Dihydride

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Summary: A new simple method of preparing bis(cyclopentadienyl)tungsten dihydride from $WCl_4(DME)$ is presented.

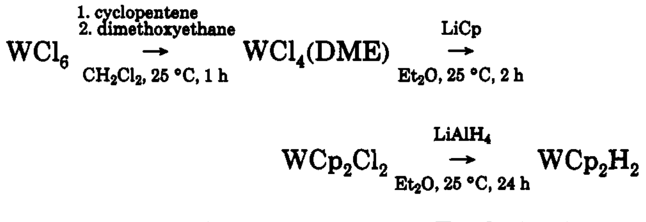
Despite the wealth of chemistry developed around the bent-metallocene complexes $W(C_5H_5)_2X_2$ (X = halide, hydride, alkyl, alkoxide; X_2 = O),[1] no easy synthetic entry into these complexes have been described since the original[2-4] isolation of the dihydride complex (X = H). Most of the work in the field has relied on the preparative method described by Green,[4] which is not always fully reproducible, or on the improved scaled-up version,[5] which is time-consuming. Moreover, in these preparative methods a high excess of sodium cyclopentadienide is used and isolated yields are rather low, which leads to a low utilization of cyclopentadiene. For that reason, these methods are not well suited for an extension into the field of less easily available substituted cyclopentadienyl ligands. Metal-vapor synthesis, i.e. cocondensation of cyclopentadiene or permethylated cyclopentadiene (Cp*) with tungsten atoms, has been applied to prepare Cp_2WH_2[6,7] and $Cp^*{}_2WH_2$.[8] This latter compound was more recently[9] prepared from $Cp^*WCl_4PMe_3$.

A convenient method for the preparation of $WCl_5(OEt_2)$ was described recently,[10] and further extensions of that work resulted in simple straightforward methods for the preparation of $WCl_4(THF)_2$ and $WCl_4(DME)$ in high isolated yields[11] (THF = tetrahydrofuran, DME = dimethoxyethane). Unlike other relatively easily accessible derivatives of tungsten(IV), e.g. $WCl_4(nitrile)_2$[12] or $WCl_4(alkyne)$,[13,14] these ether adducts of tungsten(IV) have prospects of being fully compatible with Grignard or lithium reagents, thus enabling halide/R group (R = alkyl, aryl, Cp, etc.) metathesis to be carried out. To demonstrate that this is the case, the reactions of $WCl_4(THF)_2$ and $WCl_4(DME)$ with LiCp have been studied.

Herein a simple method for the preparation of Cp_2WCl_2 (**I**) and the subsequent conversion of this complex to Cp_2WH_2 (**II**) is presented.

In the case of the two precursor complexes $WCl_4(THF)_2$ and $WCl_4(DME)$ there are a number of possible combinations of Cp reagents and solvents which can be tested in the halide/Cp exchange reaction. The present study has been limited to reactions with LiCp in THF, DME, and diethyl ether. Although homogeneous reactions are generally preferred, the low solubility (except for $WCl_4(DME)$ in DME) of both precursor complexes in ethereal solvents requires the use of heterogeneous reaction conditions. The reaction of $WCl_4(DME)$ in diethyl ether, which is outlined in Scheme I, was found to be superior to all other reactions investigated. At room temperature this reaction proceeds smoothly, furnishing a dark green solid product. The IR spectrum of the isolated product is identical with that reported[15] for the target complex (**I**), but the low solubility of this product precludes further characterization by other spectroscpic methods. The elemental analysis of the compound gives, however, a slightly lower carbon and chlorine content and a slightly higher tungsten content than those calculated for **I**, thus showing that the isolated solid is contaminated with minor amounts of some unidentified impurity. All attempts to obtain an analytically pure product were unsuccessful; the impurity contained in the isolated product cannot be removed by simple washing procedures, and the low solubility of **I** precludes recrystallization. The product is, however, sufficiently pure to be used as the starting material in subsequent reactions, as demonstrated by the preparation of the dihydride **II** (*vide supra*). The isolated yield of the dichloride **I** is high (73%), and attempts to further optimize conditions were therefore considered unnecessary.

Scheme I



$$WCl_6 \xrightarrow[CH_2Cl_2,\ 25\ ^\circ C,\ 1\ h]{1.\ cyclopentene\quad 2.\ dimethoxyethane} WCl_4(DME) \xrightarrow[Et_2O,\ 25\ ^\circ C,\ 2\ h]{LiCp} WCp_2Cl_2 \xrightarrow[Et_2O,\ 25\ ^\circ C,\ 24\ h]{LiAlH_4} WCp_2H_2$$

The corresponding reaction in DME solution is considerably more sluggish. $WCl_4(DME)$ dissolves in DME, and after reaction with LiCp a brown, slightly oily product is obtained. The IR spectrum of this compound shows

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additional bands not assignable to complex I, indicating that the isolated material is of purity lower than that isolated after reaction in diethyl ether. The impurity is, even in this case, insoluble in organic solvents, and further studies in DME solution were not pursued.

$WCl_4(THF)_2$ is virtually insoluble in THF, and as $WCl_4(DME)$ in THF is rapidly and quantitatively converted to $WCl_4(THF)_2$, both these precursors react heterogeneously with LiCp in THF solution. The IR spectrum of the product obtained by reaction in THF is identical with that published for complex I, but the yields are very modest (30–40%).

$CpSiMe_3$ has been shown to be a mild Cp transferring reagent, enabling the isolation of the mono(cyclopentadienyl) complex $CpTiCl_3$.[16] This reagent has the advantage that the byproduct of the reaction, $ClSiMe_3$, is highly soluble, which facilitates the purification of the insoluble product. Attempts to use this reagent to possibly isolate $CpWCl_3$ or Cp_2WCl_2 were unsuccessful; the precursor complex $WCl_4(DME)$ was recovered unchanged despite heating at reflux.

The established entry into the type of complexes under discussion gives the dihydride as the initial product,[4,5] which can easily be converted to the dichloride.[5,15,17] $LiAlH_4$ was used as the hydride transfer reagent[15,18] to demonstrate the feasibility of Cp_2WCl_2 obtained by the present method and to give an indication of the time required to obtain the dihydride. From WCl_6, the dihydride II was obtained in 31% sublimed yield (based on WCl_6) within 2 days with less than 4 h of effective working time. This yield is lower than that reported (46%) for the large-scale method.[5]

Attempts to apply a strict one-pot procedure, i.e. to add $LiAlH_4$ without prior isolation of the dichloride I, made the workup procedure more difficult, resulting in a considerably lower yield of the dihydride than a procedure involving isolation of I and brief washing of the product with ethanol to remove coprecipitated LiCl and other impurities before the reaction with $LiAlH_4$. The principles demonstrated in the present work should most likely apply in the synthesis of other tungsten(IV) complexes with more sophisticated cyclopentadienyl ligands, for which a high cyclopentadiene utilization is of importance.

Experimental Section

All preparations were performed under an atmosphere of dried argon using conventional Schlenk techniques. Solvents, except ethanol, were dried by and stored over activated molecular sieves.

LiCp was prepared by the reaction of BuLi (2.5 M in hexane) with cyclopentadiene (from freshly cracked dicyclopentadiene) in heptane at ice-bath temperature. The white product was isolated by filtration, washed with diethyl ether, and dried in vacuo.

$WCl_4(DME)$ was prepared by cyclopentene reduction of WCl_6 followed by addition of dimethoxyethane as described elsewhere.[11]

Tungsten was determined gravimetrically as WO_3. Elemental analyses were by Analyslaboratoriet, Lund, Sweden, and by Mikro Kemi, Uppsala, Sweden.

Infrared spectra were recorded on either a Nicolet 20 SXC FT-IR or a PE 580B spectrometer as Nujol mulls between CsI windows.

NMR spectra were recorded on a Varian Unity 300 spectrometer in C_6D_6.

WCp_2Cl_2. Solid $WCl_4(DME)$ (4.0 g, 9.62 mmol) and LiCp (1.38 g, 19.16 mmol) were charged into a 300-cm^3 Schlenk tube. Diethyl ether (60 cm^3) was added with stirring, at ambient temperature, giving an immediate color change from brown to green.

The suspension was allowed to react overnight. The grayish green solid was isolated by filtration and dried under vacuum. Excess $WCl_4(DME)$ was removed by stirring the finely crushed solid with dimethoxyethane (30 cm^3) for 1 h followed by filtering and drying in vacuo. Additional washing with THF (20 cm^3) and absolute ethanol (40 cm^3), by the same procedure as described for dimethoxyethane, removed the coprecipitated LiCl. Finally, the dark green product was washed, on the filter, with ethanol (20 cm^3) followed by two aliquots of diethyl ether (20 cm^3) and dried in vacuo, giving WCp_2Cl_2 (2.7 g, 73%). Anal. Calcd for $C_{10}H_{10}Cl_2W$: C, 31.2; H, 2.6; Cl, 18.4; W, 47.8. Found: C, 29.4; H, 2.7; Cl, 17.4; W, 47.9. IR (Nujol): as reported in the literature[15] with W–Cl at 284 (vs) and 264 (vs) cm^{-1}.

WCp_2H_2. Diethyl ether (50 cm^3) was added to a mixture of $WCl_4(DME)$ (2.8 g, 6.73 mmol) and LiCp (0.97 g 13.47 mmol) at room temperature with vigorous stirring. An immediate reaction ensured, giving a color change from brown to green. After 2 h the solvent was evaporated and the residue was stirred with ethanol (50 cm^3) for 10 min to dissolve LiCl. The remaining green solid was isolated by Schlenk filtration, washed with three aliquots of diethyl ether (10 cm^3), and dried under vacuum. The solid was transferred to a Schlenk tube, and diethyl ether (50 cm^3) was added. $LiAlH_4$ (2.0 g, 52.70 mmol) was added in small portions to the stirred suspension, followed by additional diethyl ether (50 cm^3). All dihalide dissolved within a few minutes, and the ethereal phase turned orange. The reaction was continued overnight with the Schlenk tube vented through a mercury release valve.

Unreacted $LiAlH_4$ and other solid products were removed by Schlenk filtration and washed with two aliquots of diethyl ether (20 cm^3). The ether solutions were combined and cooled on an ice bath, and the remaining $LiAlH_4$ in solution was hydrolyzed by cautious addition of diethyl ether (100 cm^3) saturated with water followed by water (40 cm^3). Phase separation and extraction of the aqueous phase twice with diethyl ether (50 cm^3) gave an ether solution which was washed once with water (40 cm^3). The small amount of red-brown precipitate formed was removed together with the water. The yellow solid remaining after evaporation of the solvent was sublimed at 120 °C under vacuum, giving bright yellow crystals of WCp_2H_2 (0.9 g, 42%). Anal. Calcd for $C_{10}H_{12}W$: C, 38.0; H, 3.8; W, 58.2. Found: C, 38.2; H, 4.0; W, 57.6. IR (Nujol): as reported earlier[19,20] with W–H at 1895 (br) cm^{-1}. ^1H NMR (benzene-d_6): δ 4.25 (t, 10 H), −12.25 ("9-line", 2 H).

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