Photochemical Synthesis Method of Tungsten(II) Complexes [$WCl_2(CO)_3(PPh_3)_2$] and [$WCl_2(CO)_2(dppe)$]

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Abstract

The photochemical oxidation reaction of $W(CO)_6$ to [$W(CO)_4Cl_2$]$_2$ with CCl_4 was applied in the synthesis of [$WCl_2(CO)_3(PPh_3)_2$] and [$WCl_2(CO)_2$(dppe)].

Introduction

The photochemical oxidation reactions mechanism of organometallic complexes by halocarbons are broadly investigated [1–5] because of their possible application in the synthesis of high oxidation state of organometallic complexes as well as in the identification of intermediate species formed in photocatalytic reactions in halocarbon solvents.

Photogeneration of a catalyst for olefin metathesis from $W(CO)_6$ in CCl_4 is an exemplary process [5–7]. In that system the formation of intermediates [$W(CO)_5Cl$] [7], [$W(CO)_4Cl_2$] [8], [$Cl_2C{=}W(CO)_4$] [9] and [$Cl_2C{=}W(CO)_3Cl_2$] [10] is postulated. The olefin metathesis reaction is initiated most likely by the formed dichlorocarbene compounds. We failed, however, in characterization of such compounds.

Many complexes containing the dichlorocarbene ligand with Fe [11, 12], Os [13], Ir [14], Ru [15] are recognized.

Stability of such carbene complexes containing the phosphine ligand could be explained in terms of the donor–acceptor properties of the latter. Phosphine, an acceptor less powerful than CO, allows the shift of greater electron density over the electron deficient dichlorocarbene ligand, and hence the stronger π-back bonding. That was the reason why in the investigated photochemical reaction of $W(CO)_6$ with CCl_4, a phosphine was used as the ligand stabilizing the produced intermediate complexes.

Experimental

General Procedures and Materials

All operations were carried out under argon purified by passage through BTS catalyst using standard Schlenk tube techniques. Solvents applied were dried, distilled and deoxygenated.

$W(CO)_6$, PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe) were commercial products, used without purification. [$W(CO)_5PPh_3$] was prepared according to literature procedures [16].

All the photochemical reactions were carried out in a glass reactor with a quartz window. A mercury lamp HBO 200 was used as the light source.

Infrared spectra were obtained with a Specord 75–IR instrument.

^1H, ^{13}C NMR spectra were taken of saturated solutions of the complexes in $CDCl_3$ using a Tesla 100 spectrometer.

Synthesis

Bis(triphenylphosphine)tungsten tricarbonyl dichloride (A)

$W(CO)_6$ (1 g, 2.8 mmol) and PPh_3 (1.6 g, 6 mmol) were dissolved in C_6H_{12} and CCl_4 (10:1, 100 cm^3) with continuous stirring under a stream of argon. The mixture was irradiated for 2 h. An amorphous, yellow precipitate settled down. This was filtered off, washed with 20 cm^3 C_6H_{12}, 20 cm^3 CCl_4, twice with 20 cm^3 CH_3CN and dried *in vacuo* (yield = 1.6 g, 65%).

Anal. Calc. for $C_{39}H_{30}O_3P_2Cl_2W$: C, 54.26; H, 3.50; P, 7.80; Cl, 8.21; W, 21.29. Found: C, 55.01; H, 3.60; P, 8.27; Cl, 9.37; W, 21.83%.

IR (KBr): ν(CO) 2015s, 1935vs, 1890s. ^1H NMR ($CDCl_3$): δ (ppm) 7.46; 7.56 (phenyl). ^{13}C NMR ($CDCl_3$): δ (ppm) 197.2 (CO); 128.30; 131.27; 135.76 (phenyl). The compound is diamagnetic in the range 81–296 °C.

(Ethylene bis-diphenylphosphine)tungsten dicarbonyl dichloride (B)

$W(CO)_6$ (1 g, 2.8 mmol) and $PPh_2{-}CH_2{-}CH_2{-}PPh_2$ (1.2 g, 3 mmol) were dissolved in C_6H_{12} and CCl_4 (10:1, 100 cm^3) with continuous stirring under a stream of argon. The mixture was irradiated for 2 h. A yellow, amorphous precipitate settled down. This was filtered off, washed with 20 cm^3 C_6H_{12} and twice with 20 cm^3 CCl_4. The obtained compound was

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triply recrystallized from $CHCl_3$/hexane (yield = 1 g, 50%).

Anal. Calc. for $C_{28}H_{24}O_2P_2Cl_2W$: C, 47.42; H, 3.41; P, 8.73; Cl, 9.09; W, 25.92. Found: C, 47.41; H, 3.83; P, 9.32; Cl, 10.83; W, 26.32%.

IR (KBr): ν(CO) 1930vs, 1840m. ^1H NMR ($CDCl_3$): δ (ppm) 7.37 (phenyl); 2.20 (CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) 198.89 (CO); 128.41; 130.79; 133.26 (phenyl). The compound is diamagnetic in the range 81–296 °C.

Results and Discussion

Photochemical Reaction between $W(CO)_6$ and CCl_4

Irradiation of $W(CO)_6$ in hexane/CCl_4 (10:1) solution under an inert atmosphere caused the appearance in the IR spectra of new absorption bands at 2100m, 2010s, 1940m characteristic for $[W(CO)_4Cl_2]_2$ [17] and the formation of C_2Cl_4, recombination product of two :CCl_2 [5b].

However, the ESR studies with application of a several spin traps allowed the identification of the $^{\bullet}CCl_3$ radical only [5b, 18]. The produced $[W(CO)_4Cl_2]_2$ is unstable and very oxygen sensitive. The prolonged irradiation of a solution results in the precipitation of products of the complete decarbonylation of $W(CO)_6$.

Photochemical Reaction between $W(CO)_6$ and CCl_4 in the Presence of PPh_3

Irradiation of $W(CO)_6$ in C_6H_{12}/CCl_4 (10:1) in the presence of PPh_3 results in the precipitation of a yellow, amorphous precipitate.

The IR spectrum of the reaction mixture shows the bulk of bands characteristic for $[W(CO)_5PPh_3]$ (2067m, 1940s cm^{-1}), followed by their decay. Neither the bands deriving from $[W(CO)_4Cl_2]_2$ nor from the reaction product are observed. After 2 h of irradiation in solution only trace amounts of nonreacted $W(CO)_6$ are left.

The yellow compound isolated under neutral atmosphere shows three IR absorption bands, ν(CO) 2015s, 1935vs, 1890s (Fig. 1), like the $[WCl_2(CO)_3(PPh_3)_2]$ complex synthesized by Colton *et al.* [19].

The crude product, besides showing bands typical for the coordinated phosphine, shows the additional absorption bands at 1115, 720 and 540 cm^{-1} (Fig. 1), which could be attributed to a $Cl_2C{=}PPh_3$ type compound, possibly formed in the reaction of triphenylphosphine with the *in situ* generated dichlorocarbene [20]. That compound was washed out from the crude product by acetonitrile.

Exposed to the air, that compound was transformed into triphenylphosphine oxide indicated by the IR band at 1185 cm^{-1} (ν(P–O)). The isolated tungsten compound **A** is rather stable in air, as a dry powder. In solution (CH_2Cl_2, $CHCl_3$) it suffers decomposition with liberation of the blue precipitate.

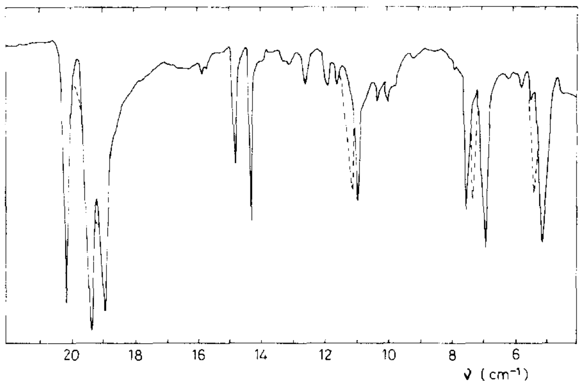

Fig. 1. IR of $[WCl_2(CO)_3(PPh_3)_2]$ in KBr. Dashed line denotes the bands deriving from the $Cl_2C{=}PPh_3$ present as a crude product.

The composition of the compound was confirmed by means of elemental and thermal analysis. The compound is considerably stable thermally; it loses the first CO molecule at 165 °C, the next ones at 185 and 205 °C; two PPh_3 molecules are detached at 320 and 500 °C.

Similar to the other seven-coordinate tungsten compounds, complex **A** is diamagnetic in the whole temperature range (81–296 °C), confirming the low-spin d^4 configuration of tungsten(II).

Compound **A** obtained by that method is a very good catalyst for olefin metathesis reactions [21]).

Photochemical Reaction between $[W(CO)_5PPh_3]$ and CCl_4

The photochemical reaction between $[W(CO)_5PPh_3]$ and CCl_4 in cyclohexane is known to also produce $[WCl_2(CO)_3(PPh_3)_2]$. The IR spectrum shows the intensification of the band at 1980 cm^{-1}, deriving from the simultaneously formed $W(CO)_6$.

The yellow–green crude product contains small amounts of $Cl_2C{=}PPh_3$ and an unidentified blue tungsten compound, the product of the complete decarbonylation of the substrate.

Such a composition of products suggests the first reaction stage to be photodissociation of PPh_3, followed by its coordination via the CCl_4 oxygenated tungsten carbonyl.

Photochemical Reaction of $W(CO)_6$ and CCl_4 in the Presence of Bis(diphenylphosphino)ethane (dppe)

The main product of the photochemical reaction of $W(CO)_6$, CCl_4 and dppe in CCl_4 is $[WCl_2(CO)_2(dppe)]$ (**B**), precipitating from the reaction mixture, showing two absorption bands at 1840m and 1930vs cm^{-1}, characteristic for the *cis* coordination of CO groups (Fig. 2). The solution presents bands at 2070w, 1930s and 1945s, which could be attributed

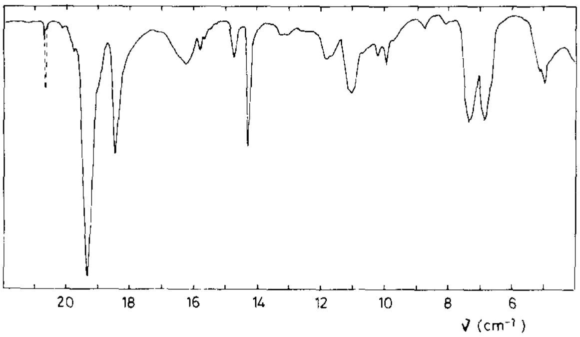

Fig. 2. IR of $[WCl_2(CO)_2(dppe)]$ in KBr. Dashed line denotes the bands deriving from $[W(CO)_5dppe]$ present as a crude product.

to $[W(CO)_5(dppe)]$ settling down simultaneously with the reaction product **B**. It can be removed by repeated recrystallization from $CHCl_3$/hexane solutions.

Mechanism of Formation of the Halocarbonylphosphine Tungsten(II) Complexes in Photochemical Reaction

The up-to-now known synthesis methods of the $[MX_2(CO)_3L_2]$ type complexes (M = W or Mo; X = Cl, Br, J; L = phosphines, arsines, stibines) are based upon two-stage reactions (eqn. (1) [22] and eqn. (2) [19])

$$M(CO)_6 \xrightarrow{2L} [M(CO)_4L_2] \xrightarrow{X_2} [MX_2(CO)_3L_2] \quad (1)$$

$$M(CO)_6 \xrightarrow{X_2} [MX_2(CO)_4] \xrightarrow{2L} [MX_2(CO)_3L_2] \quad (2)$$

In the method elaborated by us advantages was taken of the oxidation of the tungsten hexacarbonyl by CCl_4 to $[W(CO)_4Cl_2]_2$. Thus, $[WCl_2(CO)_3(PPh_3)_2]$ was synthesized in the mono-stage reaction, without isolation of the intermediate product (reaction (3))

$$W(CO)_6 + CCl_4 \xrightarrow{h\nu} [W(CO)_4Cl_2]_2 \xrightarrow{PPh_3} [WCl_2(CO)_3(PPh_3)_2] \quad (3)$$

The reaction is accompanied by the formation of dichlorocarbene, which is trapped by triphenylphosphine to give a co-product of the ylide type ($Cl_2C{=}PPh_3$).

Such a reaction course has found its confirmation in synthesis of **A** using $[W(CO)_5PPh_3]$ as the substrate. The reaction in the first stage is based upon PPh_3 dissociation, followed by W(O) oxidation to W(II), with simultaneous halogenation. In the case of a bidentate ligand such as dppe, $[WCl_2(CO)_2(dppe)]$ was the main reaction product.

This may suggest that $[W(CO)_5dppe]$, produced in the first reaction stage, undergoes oxidation and halogenation by CCl_4.

The synthesis methods of compounds **A** and **B** discussed here are good examples of the use of light for generation of intermediate species which in reaction with appropriate ligands present in the reaction medium produce the stable complexes.

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