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Photochemical synthesis of the tungsten(II) complex $[WCl_2(CO)_3(bipy)]$

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Abstract

The photochemical oxidation of $W(CO)_6$ to $[W(CO)_4Cl_2]_2$ with CCl_4 has been used to give $[WCl_2(CO)_3(bipy)]$. The same methodology was applied in the synthesis W(II) complexes having the nitrogen ligands acetonitrile, *N,N,N',N'*-tetramethylethylenediamine, pyridine, 1,10-phenathroline, 2,9-dimethyl-1,10-phenathroline, and to make the Mo^{II} and Cr^{II} complexes $[MCl_2(CO)_3(bipy)]$ (M = Mo, Cr).

The source of the divalent group 6 metals for the synthesis of complexes with mixed carbonyl, halide and N-, P-, As or Sb-donor ligands is $[M(CO)_4X_2]_2$, and is obtained by the oxidation of $M(CO)_6$ with halogens X_2 (X = Cl, Br) [1–3].

We previously discovered that the $[W(CO)_4Cl_2]_2$ produced in the photochemical oxidation of $W(CO)_6$ with CCl_4 can be successfully used in the synthesis of W^{II} complexes. The reaction carried out in the presence P-donor ligands permitted us to elaborate a new, high-yield, simple synthesis of the complexes $[WCl_2(CO)_3(PPh_3)]$ and $[WCl_2(CO)_2(dppe)]$ [4].

Although the molybdenum(II) and the tungsten(II) complexes containing nitrogen donor ligands $[MoX_2(CO)_3(L{-}L)]$ (X = Cl, Br; L–L = py_2, 2,2-bipyridyl and 1,10-phenanthroline [3], $[WX_2(CO)_3(py)_2]$ (X = Cl, Br, I) [5] and $[MI_2(CO)_3(L{-}L)]$ (M = Mo, W; L–L = py_2, 2,2'-bipyridyl and 1,10-phenathroline) [6] have been described, to date there have been no reports on the tungsten dichloro complexes $[WCl_2(CO)_3(bipy)]$.

Our goal was to design a photochemical synthesis for W^{II} halocarbonyl complexes having N-donor ligands.

Experimental

General procedures and materials

All operations were carried out by use of standard Schlenk tube techniques under argon previously purified by passage through BTS catalyst. The solvents were dried,

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distilled and deoxygenated before use. $W(CO)_6$, $Mo(CO)_6$, $Cr(CO)_6$, 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (2,9-Me-phen) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), were commercial products and were used without purification.

The photochemical reactions were carried out in a glass reactor with a quartz window. An HBO 200 mercury lamp was used as the light source. Infrared spectra were recorded with Specord 75 and 80 IR instruments. ^1H NMR spectra of the saturated solutions of the complexes were recorded on a Tesla 100 spectrometer. The UV-visible absorption spectra were recorded with a Beckman UV 5240 instrument.

Syntheses

$[WCl_2(CO)_3(bipy)]$ $0.5CH_2Cl_2$. A mixture of $W(CO)_6$ (0.5 g, 1.4 mmol) and 2,2′-bipyridyl (0.2 g, 1.4 mmol) in CCl_4 (150 cm^3) solution was irradiated for 2 h with continuous stirring under a stream of argon. The amorphous, olive-green precipitate that formed was filtered off, washed with 20 cm^3 CCl_4, and four times with 5 cm^3 portions of CH_2Cl_2. The first washing was brown and the last yellow. The compound obtained was recrystallised from CH_2Cl_2/hexane, and dried in vacuo (yield = 0.44 g, 57%).

Anal. Found: C, 28.85; H, 1.64; N, 5.34; Cl, 21.15; W, 34.4. $C_{13.5}H_9N_2Cl_3W$ calc.: C, 30.17; H, 1.69; N, 5.21; Cl, 19.79; W, 34.20%. IR (KBr): ν(CO) 2040vs, 1954vs, 1906s; (CH_2Cl_2): ν(CO) 2046s, 1960vs, 1907m. ^1H NMR $\{(CD_3)_2SO\}$ δ (ppm): 9.5(d, 2H), 8.7 (m, 4H), 8.0 (d, 2H); ($CDCl_3$): 5.3(s, 2H, CH_2Cl_2 abs. max. ($CHCl_3$): λ, nm (e, M^{-1} cm^{-1}): 243(11946), 287 (10939), 305(11480), 452(1342), 600(130), 700(84).

Similarly, attempts were made to prepare the complexes $[MCl_2(CO)_3(L–L)]$ (L–L = the various nitrogen ligands mentioned).

Results and discussion

Photochemical reaction between $W(CO)_6$ and CCl_4 in the presence of N-donor ligands

(a) 2,2′-Bipyridyl. Irradiation of a mixture of $W(CO)_6$ and 2,2′-bipyridyl in CCl_4 solution results in the immediate formation of an olive-green precipitate. The IR spectrum of the reaction mixture shows the decay of the band at 1980 cm^{-1}, that is attributable to $W(CO)_6$, and the appearance of a broad band at 1900 cm^{-1}, characteristic of the reaction product $[W(CO)_4(bipy)]$.

The precipitate is a mixture of $[W(CO)_4(bipy)]$ and $[WCl_2(CO)_3(bipy)]$. The former was readily removed from the mixture by washing with CH_2Cl_2. The dark-brown filtrate was found to contain mainly $[W(CO)_4(bipy)]$ as indicated by the bands at 2008m, 1900vs, and 1929 cm^{-1} (Fig. 1). The adduct, $[WCl_2(CO)_3(bipy)] \cdot 0.5\ CH_2Cl_2$ is formed in CH_2Cl_2. The compound is stable as a solid under argon atmosphere; in solution it decomposes to give a blue product.

It is readily soluble in polar solvents such as DMSO, acetonitrile, acetone, but less soluble in CH_2Cl_2, $CHCl_3$, and insoluble in CCl_4 and hydrocarbon solvents.

The composition of the compound was confirmed by elemental and thermal analysis. The compound loses its CH_2Cl_2 molecule at 115 °C. One CO is released between 115–230 °C, and complete decomposition of the compound was achieved

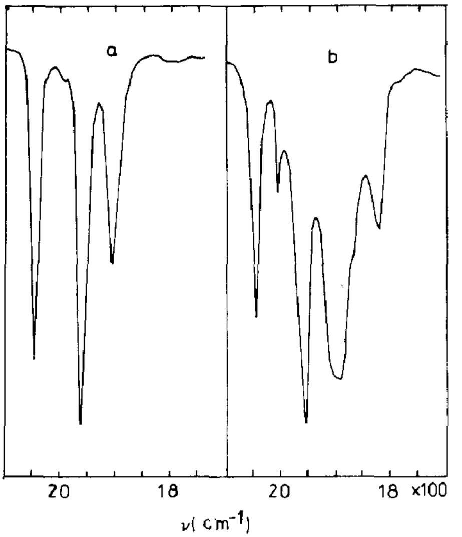

Fig. 1. IR spectrum of $[WCl_2(CO)_3(bipy)]$: (a) pure compound in CH_2Cl_2; (b) CH_2Cl_2 extract of the photochemical reaction product $W(CO)_6$ and bipy in CCl_4.

at 450 °C. The CH_2Cl_2 solvate was confirmed by ^1H NMR spectroscopy (signal at 5.3 ppm) and IR spectroscopy {ν(CCl) 746 cm^{-1}}.

(b) CH_3CN. The photochemical oxidation of $W(CO)_6$ in the mixture CCl_4/CH_3CN gives a blue precipitate, which is partially soluble in CH_2Cl_2, or in THF. However, in the yellow supernatant only $[W(CO)_5(CH_3CN)]$ and $[W(CO)_4(CH_3CN)_2]$ were identified. It is postulated that the W^{II} complex initially formed disproportionates to W^0 and W^{III} as reported by Westland and Muriithi [5].

(c) TMEDA. The photochemical oxidation reaction of $W(CO)_6$ in the mixture CCl_4/TMEDA is followed by the immediate precipitation of an unidentified product of the oxidative decarbonylation of $W(CO)_6$. The portion that is soluble in CH_2Cl_2 is a mixture of $W(CO)_5$ (TMEDA) and $W(CO)_4$ (TMEDA); it shows the characteristic absorption bands of the two complexes: viz., 2070, 1975, 1917, 1885 cm^{-1} and 2004, 1870, 1855, 1843 cm^{-1}, respectively.

(d) Pyridine. Irradiation of $W(CO)_6$ and pyridine in CCl_4 yields a blue precipitate, from which only small amounts of $[W(CO)_5py]$ and $[W(CO)_4py_2]$ were washed by CH_2Cl_2. Attempts to characterise $[WCl_2(CO)_3py_2]$ failed.

(e) 1,10-Phenanthroline. During irradiation of the $W(CO)_6$ and 1,10-phenanthroline in CCl_4, a dark-brown precipitate settled and the solution turned dark violet. The precipitate was found to be a mixture of predominantly $[W(CO)_4(phen)]$ (IR $\nu(CO)$ = 2005s, 1898vs, 1869sh, 1823s cm^{-1}) and $[WCl_2(CO)_3(phen)]$ (IR $\nu(CO)$ = 2038, 1955, 1920 cm^{-1}) (Fig. 2a).

(f) 2,9-Dimethyl-1,10-phenanthroline. Irradiation of $W(CO)_6$ and 2,9-Me-phen in CCl_4 solution produced a yellow precipitate, containing mainly $[W(CO)_4(2,9\text{-Me-phen})]$ and traces of the oxidised form $[WCl_2(CO)_3(2,9\text{-Me-phen})]$ (Fig. 2b).

Photochemical reaction between $Mo(CO)_6$ and CCl_4 in the presence of 2,2′-bipyridyl

During irradiation of a mixture of $Mo(CO)_6$ and 2,2′-bipyridyl in CCl_4 solution a brown precipitate formed, which was found to be a mixture of $[Mo(CO)_4(bipy)]$ and $[MoCl_2(CO)_3(bipy)]$ (Fig. 3a), but we were unable to separate the complexes.

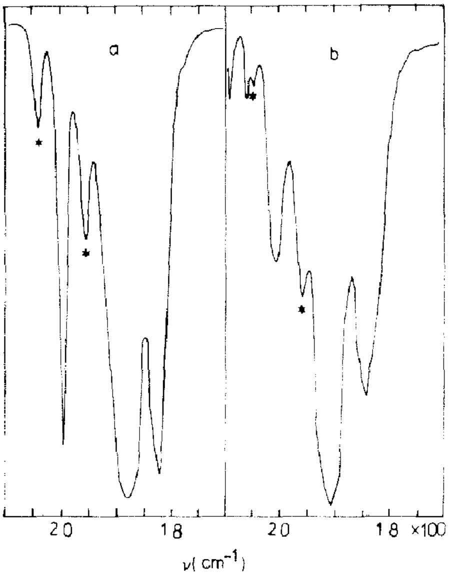

Fig. 2. IR spectra of the photochemical reaction products $W(CO)_6$ with CCl_4 in the presence of : a, 1,10-phenanthroline; b, 2,9-dimethyl-1,10-phenanthroline; denotes bands characteristic for $[WCl_2(CO)_3(L-L)]$.

Photochemical reaction between $Cr(CO)_6$ and CCl_4 in the presence of 2,2′-bipyridyl

The photochemical reaction of $Cr(CO)_6$ with 2,2′-bipyridyl in CCl_4 produced a yellow precipitate, which is a mixture of $[CrCl_2(CO)_3(bipy)]$ and $[CrCl_2(CO)_2(bipy)]$.

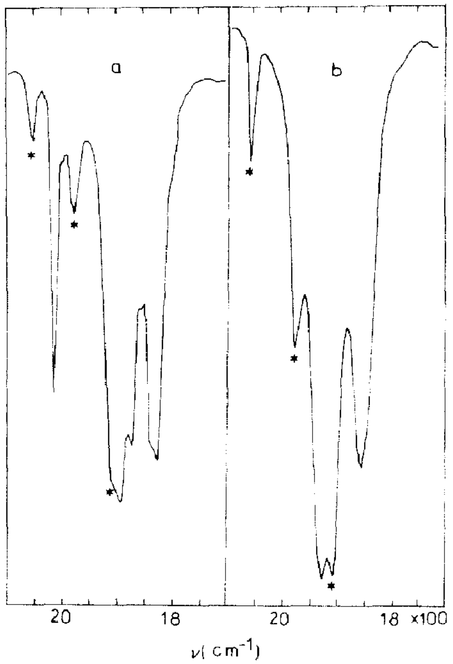

Fig. 3. IR spectra of the products of the photochemical reaction of $M(CO)_6$, bipy, and CCl_4: a, M = Mo; b, M = Cr; * denotes bands attributable to $[MCl_2(CO)_3(bipy)]$.

In CH_2Cl_2 solution the former compound was transformed into the latter, also a yellow compound. This was revealed by the decay of the bands characteristic of $[CrCl_2(CO)_3(bipy)]$ $\{\nu(CO)$ 2060, 1978, 1914 $cm^{-1}\}$ and by an increase in intensity of the bands at 1930 and 1854 cm^{-1}, of the two CO groups in $[CrCl_2(CO)_2(bipy)]$ (Fig. 3b). The lack of absorption at about 2000 cm^{-1} rules out the formation of the complex $[Cr(CO)_4(bipy)]$, characteristic bands of which are found at 2001m, 1874vs, 1850sh, 1816s cm^{-1} [7]. The elemental analysis data indicate that the compound is an adduct with half a CCl_4 molecule. Anal. Found: C, 35.8, H, 1.93, N, 6.85, Cl, 32.97. $C_{13.5}H_8O_3N_2Cl_4Cr$ calc.: C, 36.85, H, 1.83, N, 6.37, Cl, 32.23%. The presence of CCl_4 was also confirmed by IR spectroscopy ($\nu(CCl)$ 768 cm^{-1}).

Concluding remarks

The oxidation of the metal to oxidation states of more than two in the presence of an excess of halogens is the main difficulty encountered in the synthesis of seven-coordinate, group 6-metal complexes of the type $[MX_2(CO)_3(L–L)]$ ($X = Cl$, Br, I; $L =$ ligand containing N, P, As or Sb as donor atom) [1–3,5,8].

The stability of such complexes decreases in the order $I > Br > Cl$, hence the dichloride complexes are seldom obtained. Of the group 6 metals only a few Cr^{II} $[MX_2(CO)_3(L–L)]$ complexes are known [9], because their stability decreases in the order $W > Mo > Cr$.

In the synthesis designed by us, photogenerated W^{II} reacts in situ with ligands present in the solution to give insoluble and inert precipitates [4].

When we applied the procedure to the synthesis of compounds having nitrogen ligands allowed we obtained the previously unknown $[WCl_2(CO)_3(bipy)]$ complex in good yield. The unknown Cr^{II} complex, which can be obtained by the same procedure, is very unstable even in the solid and at the room temperature it is a mixture of complexes that have either two or three CO groups.

Attempts to isolate the W^{II} complexes with acetonitrile, TMEDA and pyridine from the series of the nitrogen ligands, by the photo-oxidation were unsuccessful. The nitrogen ligands, are weak π-acceptors, and in the reaction with W^{II} halocarbonyl gives the complexes that immediately disproportionate to W^0 and W^{III}.

The photochemical reaction of $W(CO)_6$ with phenanthroline in CCl_4 gives the substitution product $[W(CO)_4(phen)]$, which absorbs strongly in the visible region and there acts as an internal filter which prevents the photochemical oxidation of W^0.

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