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STABLE IMINE COMPLEXES OF TUNGSTEN CARBONYLS

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Summary

Ketimine and aldimine complexes of pentacarbonyltungsten(0) were obtained from a reaction of $(CO)_5W \cdot THF$ with ketoximes and aldoximes respectively. Pentacarbonylacetaldiminetungsten(0) was isolated in the solid state, while the formaldimine complex was detected in solution.

Introduction

Ketimines and aldimines, especially those of ammonia, are unstable species [1]. Transition metal complexation provides a method for their stabilization, isolation and subsequent use in chemical reactions. Thus ketazines, which are obtained by air oxidation of ketimines of ammonia, are useful intermediates in the synthesis of hydrazine [2,3]. However, the synthesis of ketimines of the type $R_2C{=}NH$ is beset with difficulties, and it was Fischer et al. [4], followed by King et al. [5], who first reported the isolation of an acetone ketimine complex, $(CO)_5CrNH{=}C(CH_3)_2$, the lowest molecular weight ketimine which was ever isolated. Aldimine complexes are even rarer [6].

Scheme 1 shows the three main synthesis routes to complexed imines. Carbene complexes serve as the organometallic precursors in the Fischer route. With hydroxylamine, a ketimine type of complex, $(CO)_5CrNH{=}C(OCH_3)CH_3$ was obtained [7]. Later [4], oximes instead of hydroxylamine were employed thus establishing a general method for the synthesis of ketimine and aldimine complexes of chromium (Scheme 1, Fischer).

Amminepentacarbonyl-chromium and -tungsten complexes react with acetone and cyclohexanone to give the corresponding ketimine complexes [3] in good yields (Scheme 1, Sellmann), but aldimine complexes could not be obtained by this method.

The nature of the starting materials and the low yields in King's synthesis [5] (Scheme 1, King) make this route unattractive for the preparation of ketimine complexes and impossible for aldimine complexes.

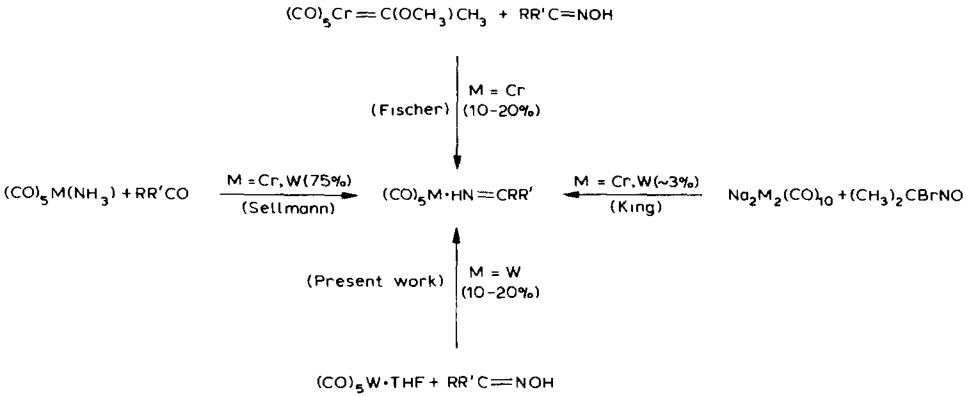
TABLE 1

PROPERTIES OF IMINE AND NITRILE COMPLEXES OF PENTACARBONYLTUNGSTEN(0)

No.	Complex	IR(CH_2Cl_2) (cm^{-1})	^1H NMR ($CDCl_3$) δ(ppm)	M.p. (°C)	Yield (%)
1	$(CO)_5WNH{=}CHC_6H_5$	3300w, 2060m, 1930 vs, 1900sh, 1615w	7.56s(5H), 8 70d (J 20 1 Hz, 1H) 9.81d (J 20.1 Hz, 1H)	125	15
2	$(CO)_5WN{\equiv}CC_6H_5$ [8]	2230w, 2070m, 2010w, 1965sh, 1940vs, 1905s	9.98m	100d	10
3	$(CO)_5WNH{=}CHC_6H_4OCH_3$ [4]	3280w, 2060m, 1925vs, 1895sh, 1605w	3.89s (3H), 7.01d (J 8 Hz, 2H), 7.50d (J 8 Hz, 1H), 8.53d (J 22.5 Hz, 1H), 9.34d (J 22.5 Hz, 1H)	135d	10
4	$(CO)_5WN{\equiv}CC_6H_4OCH_3$ [4]	2230w, 2065m, 1975sh, 1940vs, 1905s	3.90s (3H), 7.01d (J 8 Hz, 2H), 7.63d (J 8 Hz, 2H)	115d	22
5	$(CO)_5WNH{=}CHCH_3$	2070w, 1940vs, 1900sh ^{a} 3300br, 1640 ^{b}	2.12d, br (J 5 Hz, 3H), 8.28dq (J 5,22. 1Hz, 1H), 10.61d,br (J 22.1 Hz, 1H) ^{c}	135d	10
6	$(CO)_5WN{\equiv}CC_3H_7$-n	2270w, 2070w, 1935vs 1905sh	1.11t (J 7.1 Hz, 3H), 1.79m (2H), 2.61t (J 7 Hz, 2H)	110d	19
7	$(CO)_5WNH{=}C(CH_3)_2$ [3]	3320w, 2065w, 1925vs 1900sh, 1630w	2.11s (3H), 2.25s (3H)	115d	20
8	$(CO)_5WNH{=}C(CH_3)C_6H_5$	3270w, 2055w, 1925s, 1905sh, 1620w	2.35s (3H), 7.30m (5H) ^{d}	110d	15

[a] Measured in hexane. [b] In KBR. [c] In acetone-d_6. [d] In benzene-d_6.

SCHEME 1



In connection with other work we discovered yet another route to ketimine and aldimine complexes of tungsten which seems to be general and this is described below.

Results and discussion

A THF solution of $(CO)_5W \cdot THF$ reacts with aliphatic or aromatic ketoximes and aldoximes at room temperature to give the corresponding ketimine and aldimine complexes (eq. 1). With aldoximes, the resulting aldimine complexes were accompanied by the corresponding nitrile complexes, $(CO)_5W \cdot N{\equiv}CR$. The mixtures were easily separated by column chromatography. No nitrile complex was obtained on subjecting an aldimine complex to the same reaction conditions. Methyl ethers of ketoximes and aldoximes react with $(CO)_5W \cdot THF$ in the same way as the parent oximes.

$$(CO)_5W \cdot THF + RR'C{=}NOH \xrightarrow[25°C]{THF} (CO)_5W \cdot HN{=}CRR' \qquad (1)$$

(R = alkyl, aryl; R' = H, alkyl)

While the yields of the imine complexes in this study are similar to those obtained by Fischer, the present method circumvents the use of carbene complexes as starting materials. Instead a THF solution of $(CO)_5W \cdot THF$, obtained by irradiation of $W(CO)_6$ in THF, was treated directly with the appropriate oxime at room temperature. In contrast to the method described by Sellman, this new procedure is suitable for the preparation of aldimine complexes.

The ketimine, aldimine and nitrile complexes which were obtained in this study are shown with their physical properties in Table 1. It is noteworthy that acetaldiminpentacarbonyltungsten(0) complex **5**, is reasonably stable; this involves the smallest imine ever stabilized. Preparation of the formaldimine complex from formaldoxime was attempted but isolation led to rapid decomposition. However, the IR spectrum of the reaction mixture exhibits a band (2065 cm^{-1}), indicative of the presence of the formaldimine complex. In the case of **5**, we did not encounter the corresponding acetonitrile complex, while with **6** we isolated only the butyronitrile complex.

TABLE 2

^{13}C NMR DATA (ppm) IN ACETONE-d_6 RELATIVE TO TMS

Compound	
3	198.5, 196.7(CO); 176.9(C=N); 135.7, 130.5, 115.7, 115.0(aromatic C), 55.5(OCH_3).
5	197.4, 192.4(CO); 199.0(C=N); 15.4(CH_3).
7	198.3, 191.3(CO); 187.8(C=N); 27.2, 17.9(CH_3).
4	200.3, 196.7(CO); 135.6, 128.6(aromatic C); 126.1(C≡N); 115.6, 114.5(aromatic C); 55.8(OCH_3).
6	200.1, 196.9(CO); 128.9(C≡N); 20.2, 18.9(CH_2); 12.8(CH_3).

The IR spectra of the imine and nitrile complexes are in general agreement with those reported [7]. The imine stretching band is clearly visible in the 1600 cm^{-1} region. It shifts from 1605 cm^{-1} in **3** to 1640 cm^{-1} in **5**, in accordance with the relative electron-release capacity of the double bond substituents. This electron release also affects the ^{13}C resonance of the imine carbon atom, which shifts from 199.0 ppm in **5** to 176.9 ppm in **3** (Table 2). Concomitant with the above changes is a shift of the infrared CO *E*-stretching band (middle frequency band) from 1925 cm^{-1} in **3** to 1940 cm^{-1} in **5**. This change reflects the effectiveness of ligand-to-metal-to-CO electron transfer, which in turn implies a stronger imine-to-metal bond with electron releasing substituents on the C=N bond. Indeed, the moderate stability of **5** and the instability of the formaldimine complex (vide supra) with respect to **3** are explicable on these grounds.

The NMR spectra of the aldimine complexes (Table 1) are characterized by a large (ca. 20 Hz) spin coupling in the NH=CH system, indicative of an *E* configuration of the double bond. In no case could we detect the presence of the *Z*-isomer. The NH resonance is clearly visible in the 9–10 ppm region. The multiple ^{13}CO NMR resonances (Table 2) are indicative of the conformational stability of an octahedral molecular structure of the aldimine complexes at room temperature.

The mechanism of the reaction is unclear. A balanced reaction of $(CO)_5W \cdot THF$ and an oxime requires oxygen as a product. This could be accomodated for by assuming oxidation of CO to CO_2. However, as previously mentioned, oxime ethers react just as well, thus ruling out CO oxidation, at least in this case. Furthermore, the source of the H atom in an imine complex which is generated from an oxime ether is obscure. Further mechanistic study is clearly necessary but the method provides a simple route to imine complexes, and especially aldimine complexes.

Experimental

IR spectra were recorded on a Perkin–Elmer Grating Infrared Spectrophotometer Model 177 and NMR spectra were measured with Bruker WH-90 spectrometer. Yields, m.p. IR and NMR data are given in Tables 1 and 2.

General procedure for the preparation of aldimine and ketimine pentacarbonyltungsten(0) complexes

A solution of hexacarbonyltungsten (1 g; 2.8 mmol) in THF (dried over K/benzophenone) was irradiated at 360 nm under argon until 46 ml (2 mmol) of CO were

evolved and 2.0 mmol of the appropriate oxime were then added. The mixture was kept overnight at room temperature, the solvent was removed in vacuo, and the residue chromatographed on Silica 60. Good separations were obtained with the following solvent systems:
toluene/petroleum ether (1/1), toluene, toluene/ethyl ether (1/1) and ethyl ether. Hexacarbonyltungsten emerges with petroleum ether followed by nitrile-pentacarbonyltungsten, traces of free nitrile, imine-pentacarbonyltungsten and finally the unreacted oxime. The same products were obtained starting with the methyl ethers of the oximes using the above procedure. Analysis. Found: C, 34.33; H, 2.18; N, 3.02. $(4\text{-MeOC}_6H_4CH{=}NH)(CO)_5W$, $C_{13}H_9NO_6W$ calcd.: C, 34.00; H, 1.98; N, 3.05%.

Acetaldiminpentacarbonyltungsten(0)

The procedure described above was carried out with acetaldoxime (2.8 mmol) and $W(CO)_6$. THF was removed under dry nitrogen with intermittent addition of hexane. Finally the hexane solution was filtered to remove unreacted $W(CO)_6$, and chromatographed (Silica 60) with degassed ether/hexane 1/2 mixture, yellow crystals (10%). Analysis Found: C, 23.15; H, 1.45; N, 3.75. $C_7H_5NO_5W$ calcd.: C, 22.90; H, 1.36; N, 3.82%.

Formaldiminpentacarbonyltungsten(0)

The procedure described above for the acetaldimine complex was followed. The hexane solution, after the removal of THF, exhibits an IR stretching band at 2070 cm^{-1} characteristic of an imine complex. All attempts to isolate the pure complex were frustrated by extensive and rapid decomposition of the complex to metallic tungsten.

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