

SYNTHESIS AND STRUCTURE OF

$[\text{W}_2(\mu\text{-CO})_2\{\mu\text{-HC}(\text{N-3,5-xylyl})_2\}_2\{\text{HC}(\text{N-3,5-xylyl})_2\}\{(\text{N-3,5-xylyl})\text{CH}(\text{N-3,5-xylyl})\text{CH}_2\}]$

W.H. DE ROODE and K. VRIEZE *

Anorganisch Chemisch Laboratorium, Van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam-1004 (The Netherlands)

(Received September 9th, 1977)

Summary

Reaction of $\text{W}(\text{CO})_6$ with *N,N'*-di-3,5-xylylformamidine yielded the title complex I. A crystal structure determination showed that in the solid state the complex contains two tungsten atoms bridged by two carbonyl groups and two formamidino groups. Furthermore one of the tungsten atoms is coordinated by a chelating formamidino group, while the second tungsten is chelated by a formamidino group with a CH_2 group inserted between the metal and the formamidino ligand. The tungsten–tungsten separation is 2.464(3) Å. A similar structure is present in solution, as shown by ^1H and ^{13}C spectroscopy.

Introduction

In a previous paper [1] we reported the reaction of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$) with *N,N'*-diarylformamidines yielding the dimeric complexes $[\text{M}_2\{\text{HC}(\text{NR})_2\}_4]$, containing a quadruple metal to metal bond (Fig. 1). The analogous reaction of tungsten hexacarbonyl with formamidines, however, did not yield this type of complex. From the literature it is known that a similar distinction is found in the reactions of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with acetic acid, which is isoelectronic and isostructural to the formamidines. Thus the complexes $[\text{M}_2(\text{O}_2\text{CCH}_3)_4]$ ($\text{M} = \text{Cr}, \text{Mo}$) are readily accessible, whereas, in spite of many attempts [2–4], the tungsten analogue could not be prepared. Instead the products were formulated either as polymeric $[\text{W}(\text{O}_2\text{CCH}_3)_2]_x$ [4] or as a trinuclear species, possibly $[\text{W}_3(\text{O}_2\text{CCH}_3)_9\text{O}]$ [2,3]. Although for chromium and molybdenum a number of complexes are known with $\text{M}-\text{M}$ bonds with bond orders ranging from three to four, similar tungsten complexes were, until very recently, unknown. During the last few years, however, a series of new tungsten complexes have been

* To whom correspondence should be addressed.

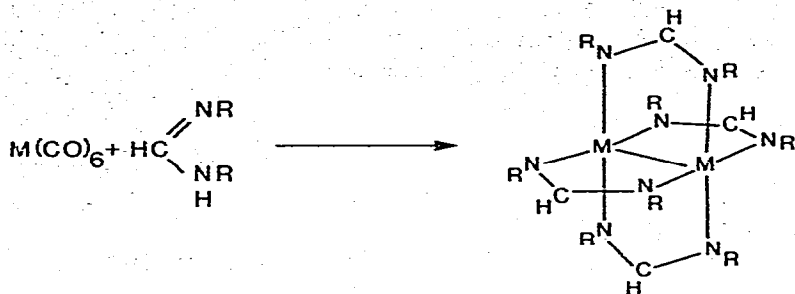


Fig. 1. Reaction of $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}$) with N,N' -diarylformamidines [1].

prepared by Chisholm et al. [6] containing tungsten to tungsten triple bonds. Very recently Collins et al. [7] reported the first crystallographic proof for the existence of a quadruple tungsten—tungsten bond.

In this paper we report the results of a detailed investigation of the reaction of $\text{W}(\text{CO})_6$ with N,N' -di-3,5-xylylformamidine, which yields a novel type of metal—metal bonded tungsten complex.

Results and discussion

Reaction of tungsten hexacarbonyl with N,N' -di-3,5-xylylformamidine in refluxing toluene results in the formation of the purple coloured complex $[\text{W}_2(\mu\text{-CO})_2\{\mu\text{-HC}(\text{N-3,5-xylyl})_2\}_2\{\text{HC}(\text{N-3,5-xylyl})_2\}\{(\text{N-3,5-xylyl})\text{CH}(\text{N-3,5-xylyl})\text{CH}_2\}]$. The complex is air stable in the solid state and in solution. No decarbonylation was observed on irradiation of the complex in benzene with a medium pressure mercury lamp (Hanovia). Complex I was obtained in 24% yield in addition to a very small amount of a dark green unidentified material. The ^1H NMR of this green product in CDCl_3 shows a very complicated spectrum, which differs considerably from that of complex I.

A crystal structure determination of I [8] (Figure 2) showed that the molecule contains two tungsten atoms at short distance, which are bridged by two formamidino groups and two carbonyl groups. One of the tungsten atoms has a chelating formamidino group, while the other tungsten atom is chelated by a formamidino group with a CH_2 group inserted between the metal and one of the nitrogen atoms. Noteworthy is that the formamidino groups act in this complex as a bridging as well as a chelating group. The same behaviour was also found for the N,N -diethylcarbamato groups in the complex $[\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4]$ [6] in which the groups are bridging as well as chelating. Application of the 18-electron rule reveals that complex I might contain a quadruple tungsten—tungsten bond. However, comparison of the $\text{W}-\text{W}$ distance of 2.464(3) Å in I with the distances found for triple $\text{W}-\text{W}$ bonds (2.29 Å) [6] and single tungsten—tungsten bonds (3.18 Å) [9,10], points to a bond order of two in the present compound.

The presence of a CH_2 group inserted between the metal and the formamidino can be explained by a reaction involving the formation of an intermediate containing a cyclic carbamoyl group " $\overline{\text{WN}(\text{R})\text{CHN}(\text{R})\text{CO}}$ ", followed by reduction of this carbonyl function by the formamidine $\text{N}-\text{H}$ protons. Proof of the

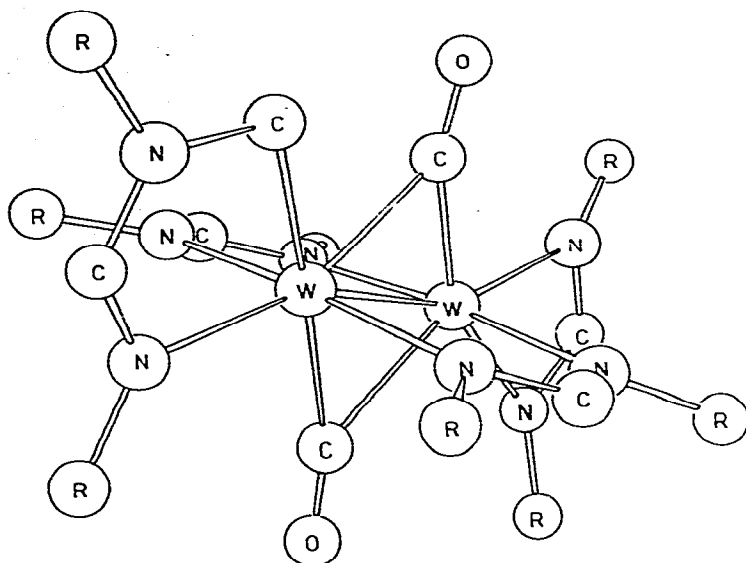


Fig. 2. Crystal structure of complex I (R = 3,5-xylyl).

existence of such a carbamoyl-containing species has recently been provided by us by the isolation of several cyclopentadienyl complexes of chromium, molybdenum and tungsten; for example, the complex $[W(\pi-C_5H_5)\{HC(NMe)N(CO)Me\}(CO)_2]$ [11,12].

The methylene protons could not be located in the crystal structure. However, NMR spectroscopy reveals unambiguous evidence for their presence. The rather broad resonance at 3.26 ppm in the 1H NMR spectrum (Fig. 3) has been assigned to the CH_2 protons. At low temperatures this resonance broadens, while at higher temperatures the CH_2 resonance becomes sharp. This is probably caused by the fact that the chelate ring, $WN(R)CHN(R)CH_2$ is not planar, resulting in inequivalent methylenic protons.

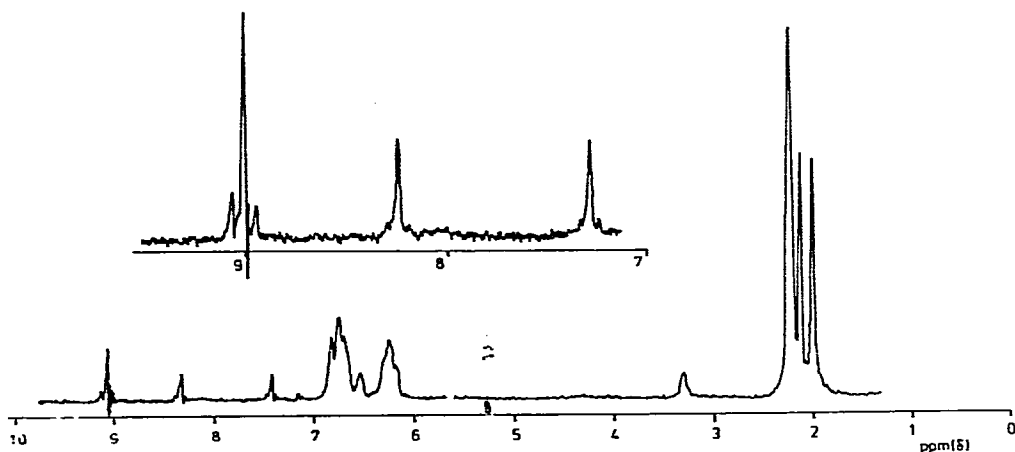


Fig. 3. 1H NMR spectrum of complex I in $CDCl_3$.

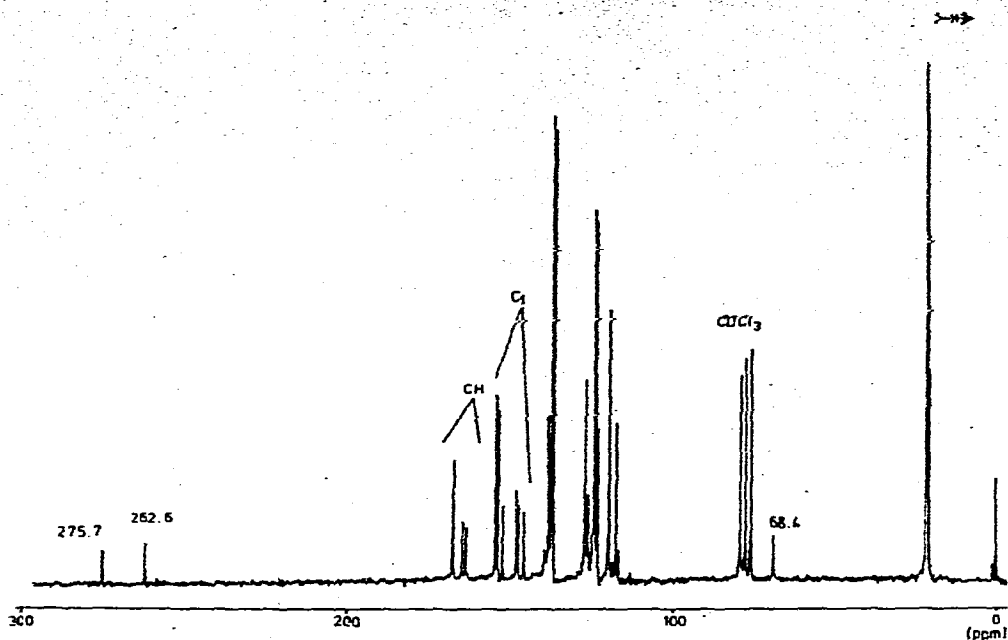


Fig. 4. ^{13}C NMR spectrum of complex I in CDCl_3 .

The ^{13}C resonance of the CH_2 carbon (Fig. 4) appears at 68.4 ppm. An off-resonance decoupled ^{13}C NMR spectrum confirmed this assignment by giving a triplet.

Resonances arising from the methyne protons are found in the ^1H NMR spectrum at 7.38, 8.27 and 9.01 ppm. The resonance at 9.01 ppm assigned, on basis of the relative peak area ratio, to the methyne protons of the two bridging formamidino groups show a $\text{H}-^{183}\text{W}$ coupling of 7.8 Hz. The two other methyne protons show also some $\text{H}-^{183}\text{W}$ coupling, but this is not so clear. This may be due to the asymmetric bonding towards the two tungsten atoms.

The ^{13}C resonances of the two inequivalent carbon-monoxide groups are found at 275.7 and 262.6 ppm, which is about in the same range as has been reported for the bridging carbonyl group in the complex $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ at 275.1 ppm [13].

Experimental

Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. IR spectra were recorded on a Beckman 4250 spectrometer, NMR spectra were recorded on Varian T60A and CFT 20 instruments. The preparation of the *N,N*-di-3,5-xylylformamidine has been described in a previous paper [1]. The reaction was carried out under nitrogen and the solvents were distilled before use.

Preparation of $[\text{W}_2(\mu\text{-CO})_2\{\mu\text{-HC}(\text{N-3,5-xylyl})_2\}_2\{\text{HC}(\text{N-3,5-xylyl})_2\}\{\text{N-3,5-xylyl}\text{CH}(\text{N-3,5-xylyl})\text{CH}_2\}]$ (I)

3.0 g (8.52 mmol) $\text{W}(\text{CO})_6$ and 4.4 g (17.17 mmol) *N,N'*-di-3,5-xylylforma-

midine were refluxed in 100 ml toluene for 3 days. The solvent was then removed in vacuo. Column chromatography of the residue on silicagel (Merck art nr. 7734) with toluene afforded two bands. The first, deep purple band, was collected and the solvent removed. The residue was recrystallised from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ giving 1.5 g (24%) of I. Analyses: Found: C, 59.36; H, 5.68; N, 7.31; W, 24.95; mol. wt.: 1332 (osmometric in benzene). $\text{C}_{71}\text{H}_{78}\text{N}_8\text{O}_2\text{W}_2$ calcd.: C, 59.09; H, 5.45; N, 7.76; W, 25.48%; mol. wt. 1443.2. An IR spectrum (KBr disc) shows in the carbonyl region one band at 1743 cm^{-1} (assigned to the stretching frequency of the bridging carbonyls).

The second, dark green band, gave, after evaporation of the solvent, a tarry unidentified product. Yield < 100 mg (estimated).

Acknowledgement

We thank Dr. G. van Koten for helpful discussion.

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