

SOME MONONUCLEAR π -CYCLOPENTADIENYLTUNGSTEN DICARBONYL DITHIOCARBAMATES

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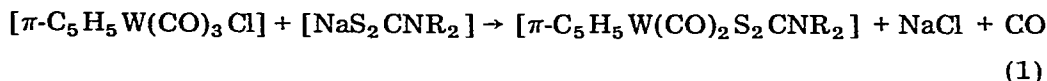
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Summary

Mononuclear tungsten dithiocarbamate complexes π -C₅H₅W(CO)₂S₂CN(CH₃)₂, π -C₅H₅W(CO)₂S₂CN(C₂H₅)₂, and π -C₅H₅W(CO)₂S₂CNC₅H₁₀ (NC₅H₁₀ = piperidiny) have been prepared. ¹H NMR ultraviolet spectra and IR carbonyl stretching spectra are discussed. The dithiocarbamate ligand is bidentate in these diamagnetic complexes, in which tungsten obeys the Effective Atomic Number rule.

Introduction

A dithiocarbamate ligand (DTC) may be either bidentate or chelating with both sulphur atoms bound to a metal, or monodentate with only one metal sulphur bond. We have succeeded in preparing the complexes π -C₅H₅W(CO)₂S₂CN(CH₃)₂, π -C₅H₅W(CO)₂S₂CN(C₂H₅)₂, and π -C₅H₅W(CO)₂S₂CNC₅H₁₀ (NC₅H₁₀ = piperidiny) using a variation of a previous method for iron monodentate dithiocarbamates [1] (eqn. 1).



A few molybdenum bidentate dithiocarbamates have been prepared [2]. Our method is also successful for their preparation, the reaction time being reduced from eighteen to three hours.

Experimental

The method of preparation was virtually identical in all three cases, save for the dithiocarbamate salt. For the dimethyl compound, sodium dimethyl dithiocarbamate dihydrate [3] and cyclopentadieny tungsten tricarbonyl

chloride [4] in a molar ratio of 1/1 were refluxed under nitrogen in 100 ml of 2-methoxyethanol. The reaction was monitored using carbonyl stretching frequencies in the 2100 - 1700 cm^{-1} region. The spectrum changed from one having 3 bands ($\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$) to one having two bands in a period of ca. 3 hours, after which the reaction was taken as complete. The resulting solution was filtered hot under nitrogen and allowed to cool to 0° : purple-red crystals were precipitated. After filtration, the product was washed with pentane, recrystallised from a methylene chloride-heptane mixture, and dried in vacuo. If the initial ratio of starting materials was exactly 1/1, no recrystallisation was needed to obtain analytical purity of the products; a yield of 60% was achieved in all three cases.

The solid and solution state magnetic moments of the complexes were obtained using in the former case a Gouy balance, and in the latter an NMR method [5]. ^1H NMR spectra in deuteriochloroform were run on a Perkin-Elmer R 12 instrument, using tetramethylsilane as internal calibrant.

The carbonyl stretching region was recorded in carbon disulphide solution to $\pm 1 \text{ cm}^{-1}$, using a Perkin-Elmer 337 spectrometer fitted with a Hitachi recorder. CO-M-CO bond angles were calculated from the infrared intensities, using the relationship of Beck et al. [6]. The ultraviolet and visible spectra were recorded on a Perkin-Elmer 402 spectrometer, using benzene vapour and holmium oxide glass as calibrants. Melting points were determined in sealed tubes. The molecular weight of the diethyl complex was determined in benzene using a Perkin-Elmer 119 molecular weight apparatus. All analyses were carried out in the Analytical Laboratory, University College, Dublin.

Results and discussion

The prepared complexes were soluble in most organic solvents except for cyclic aliphatic hydrocarbons (slight solubility) and straight chained hydrocarbons (almost insoluble). They decomposed very slowly in air, and more rapidly in solution.

Analytical data and melting points for the dithiocarbamate complexes are given in Table 1. Since the molecular weight of the complex $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$ obtained in benzene solution was 441 ± 15 (theoretical monomer 453), it is indicated that their general formulation is $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\text{S}_2\text{CNR}_2)$, where R_2 is a dialkyl group.

^1H NMR spectra presented in Table 2 support this. For example, in the

TABLE 1
MELTING POINTS AND ANALYTICAL DATA FOR THE COMPLEXES $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNR}_2$

	M.p.($^\circ\text{C}$)	Analysis found (calcd.) (%)			
		C	M	N	S
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	275 dec.	28.09 (28.25)	2.86 (2.58)	3.2 (3.3)	15.15 (15.07)
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	149 - 150	31.3 (31.76)	3.4 (3.3)	3.05 (3.09)	14.3 (14.13)
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNC}_5\text{H}_{10}$	264 - 265	33.2 (33.54)	3.48 (3.23)	2.72 (3.01)	13.91 (13.77)

TABLE 2

¹H NMR SPECTRA FOR COMPLEXES $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNR}_2$ USING CDCl_3 AS SOLVENT AND TMS AS INTERNAL CALIBRANT (τ ppm)

Complex	Group $\pi\text{-C}_5\text{H}_5$	$\text{N}(\text{CH}_3)_2$	$\text{N}(\text{CH}_2)_2$	$(\text{CH}_3)_2$	Relative integral
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	4.33 singlet	6.86 singlet			5/6
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	4.36 singlet		6.44 quartet	8.79 triplet	5/4/6
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNC}_5\text{H}_{10}$	4.34 singlet		6.26 complex	8.30 complex	5/4/6

ethyl compound, the proton integration (5/4/6 with increasing τ value) is consistent with one cyclopentadienyl ring and two ethyl groups per molecule. Due to the inductive effect of the nitrogen atom, the cyclopentadienyl protons are more deshielded than protons on carbons α to the nitrogen which are in turn more deshielded than the protons on the β carbons.

The carbonyl stretching region, given in Table 3, is that of a typical *cis* dicarbonyl band configuration. The corresponding molybdenum complexes were prepared using the preparative method given in Experimental section and recorded in carbon disulphide for comparison purposes. The dimethyl and diethyl compounds have previously been prepared [2], but the piperidinyl compound has not been previously reported.

Two points are clear in the comparison. Firstly, the tungsten carbonyls have lower carbonyl stretching frequencies than the corresponding molybdenum complexes. Secondly, the carbonyl stretching frequencies are only very slightly decreased as one progresses from $\text{N}(\text{CH}_3)_2$ to NC_5H_{10} .

The bands are much lower in frequency than those reported for $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{SCH}_3]_2$ at 2034 and 1948 cm^{-1} in CS_2 [7]. This supports the theory that the monomeric effect of the alkyl groups prevents back donation into the sulphur atom, and also agrees with the findings of Cotton and McCleverty [2].

The difference in electron-releasing power of the alkyl groups is shown in the comparison of C—N stretching frequencies which occur at 1514, 1499 and 1490 cm^{-1} ($\pm 2 \text{ cm}^{-1}$) in the Me, Et and C_5H_{10} compounds of tungsten respectively. The C—N bond is adjacent to two alkyl groups and can transmit the total effect to the rest of the molecule. The C—N stretching frequency is decreased as the size of the alkyl group is increased, showing that the combination of inductive and mesomeric effects decreases in the order $\text{CH}_3 > \text{C}_2\text{H}_5 > \text{C}_5\text{H}_{10}$.

TABLE 3

CARBONYL STRETCHING FREQUENCIES^a FOR COMPLEXES $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{S}_2\text{CNR}_2$ (M = Mo, W)

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	1954, 1870
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	1954, 1870
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{S}_2\text{CNC}_5\text{H}_{10}$	1953, 1869
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	1943, 1854
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	1942, 1854
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNC}_5\text{H}_{10}$	1941, 1853

^aValues in cm^{-1} and accurate to $\pm 1 \text{ cm}^{-1}$.

TABLE 4
ELECTRONIC SPECTRA FROM 200 - 850 nm IN MeOH SOLUTION

	λ^1 max	λ^2 max	λ^3 max	λ^4 max	λ^5 max	λ^6 max	λ^7 max
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	210	231	285	330	343	413	500
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	211	235	290	334	345	414	500
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNC}_5\text{H}_{10}$	210	238	291	335	346	416	500
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$	206	253	318	349	464		

¹H NMR spectra

Table 2 shows that a sharp cyclopentadienyl singlet occurs at τ 4.35 ± 0.02 ppm for the tungsten compounds. The similar tungsten mercaptide, [$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{SCH}_3$] has a cyclopentadienyl resonance [7] at τ 4.51 ppm. Thus an increase in diamagnetic anisotropy, resulting from additional back donation into the cyclopentadienyl ring, occurs in the dithiocarbamate complexes. The hydrogen of the complexed dithiocarbamate ligands gave sharp signals except for the $\text{S}_2\text{CNC}_5\text{H}_{10}$ group, where resonance positions for protons on the carbon atoms α and β to the nitrogen were ill defined, presumably due to ring proton interactions.

Electronic spectra

Table 4 gives electronic spectra (200 - 850 nm) of the prepared dithiocarbamate complexes, together with that of $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ for [4] comparative purposes. The ultraviolet region has been used [8] to indicate the type of bonding between the DTC ligand and metal. Bands at 234 - 265 (Band 1) and 280 - 335 nm (Band 2) are assigned to transitions of the CS_2 group. If the DTC ligand is coordinated to the central metal atom with two nonequivalent C-S bands, band 1 generally has two components. However splitting can also occur because of nonequivalence within the ligand.

Attempts to use this data to distinguish monodentate and bidentate dithiocarbamate groups were unsuccessful due to the degree of band overlapping. It is fortunate that the chelate type bonding is self evident for these complexes, since a carbonyl group is displaced in their preparation.

Magnetic properties

All of the complexes are diamagnetic both in the solid state and in solution. In these cases tungsten obeys the Effective Atomic Number Rule.

Structure

CO-M-C bond angles were calculated from the relation $I_a/I_s = \tan^2(\theta/2)$, where I_s and I_{as} are the integrated intensities of the symmetric and asymmetric bands respectively [6]. The band at higher frequency was assigned to the symmetric stretching frequency yielding the values given in Table 5.

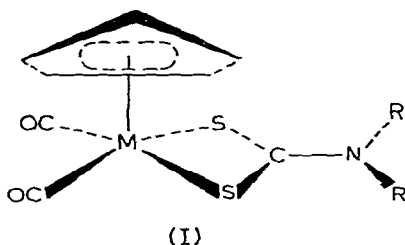
Complexes of the general formula $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{R}_2$ may be regarded formally as 7-coordinate about the metal atom with the cyclopentadienyl ring occupying three coordination positions [9]. A likely structure is that of a trigonal-capped metal atom M at the apex of a square pyramid. That the

TABLE 5

MAGNETIC MOMENTS AND C(O)—W—C(O) BOND ANGLES FOR COMPLEXES $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CNR}_2$

	Magnetic moment	C(O)—W—C(O) Bond angle (°)
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{CH}_3)_2$	Diamagnetic	84
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$	Diamagnetic	86
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{S}_2\text{CN C}_5\text{H}_{10}$	Diamagnetic	87

carbonyl groups and the two sulphur atoms probably have a pseudo square planar type of configuration is supported by the experimental values of the OC—M—CO angle. We propose the structure (I).



We attempted to extend the class of reaction to the Nickel sub-group. Reactions such as that of π -cyclopentadienyltriphenylphosphinenickel chloride with sodium diethyl dithiocarbamate in acetone solution at room temperature, and π -cyclopentadienylnickel carbonyl dimer and nickelocene successively with tetramethyl thiuram disulphide in THF under reflux conditions yielded initial red colourations which immediately changed to green yielding a green bis-(diethyl dithiocarbamate)nickel complex. The expected complex $\pi\text{-C}_5\text{H}_5\text{NiS}_2\text{-CN}(\text{C}_2\text{H}_5)_2$ may be an unstable intermediate.

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