

Reactivity of Tricarbonyl(η^5 -cyclopentadienyl)(dimethyldithiocarbamato)tungsten towards Coordinatively Unsaturated Species

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Abstract

Visible light irradiation of solutions containing $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WSC}(\text{S})\text{NMe}_2]$ (**1**) and $\text{Fe}_2(\text{CO})_9$ or $\text{Mn}_2(\text{CO})_{10}$ leads to a transmetalation type of reaction and formation of $\text{Fe}(\text{S}_2\text{CNMe}_2)_2$ and $\text{Mn}(\text{CO})_4(\text{S}_2\text{CNMe}_2)$ respectively. However, the reaction of **1** with $\text{M}(\text{PPh}_3)_4$, $\text{M} = \text{Pt}$, or Pd , leads to conversion to the dicarbonyl chelate complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}(\text{S}_2\text{CNMe}_2)]$.

Introduction

Lately there has been a considerable interest generated by the chemistry of carbonyl dithiocarbamate complexes [1–4]. Traditionally, complexes of the form $(\text{CO})_n\text{M}(\text{dtc})_m$, where $\text{M} = \text{Mn}$, $n = 4$, $m = 1$; $\text{M} = \text{Fe}$, $n = 2$, $m = 2$; $\text{dtc} = \text{dialkyldithiocarbamate}$, have been prepared by reacting the sodium salts of dialkyldithiocarbamates with metal carbonyl halides or by oxidation of the metal carbonyls with tetraalkylthiocarbamoyl disulfides [5]. The use of trimethyltin thiocarbamates [6], $\text{CS}_2\text{--CO}_2$ exchange on the carbamate derivatives [7] or the reaction of carbamoyl complexes of transition metals with CS_2 [8] are some of the other methods employed for the preparation of dithiocarbamate complexes. Although most syntheses result in the dithiocarbamate ligand acting in a bidentate manner (B), several reports describe complexes containing monodentate dithiocarbamate ligands (A), (Fig. 1). X-ray crystallography has confirmed the monodentate nature of dithiocarbamate ligand in $\text{Pt}(\text{S}_2\text{CN}(\text{i-Bu})_2)_2(\text{PMe}_2\text{Ph})_2$ [9], $\text{Pt}(\text{S}_2\text{CNEt}_2)_2\text{PPh}_3$ [10], $\text{Ru}(\text{S}_2\text{CNEt}_2)_3\text{NO}$ [11], $\text{Au}(\text{S}_2\text{CNEt}_2)_3$ [12], $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WS}_2\text{CNMe}_2$ [1] and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{S}(\text{CNC}_6\text{H}_4\text{S})$ [13]. We have been interested in investigating the reactivity of the uncoordinated sulfur atom in type A complexes towards additional transition metal centers (Scheme 1) and we report here our findings on the reactivity of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WS}_2\text{CNMe}_2$ (**1**) towards coordinatively unsaturated

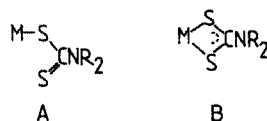
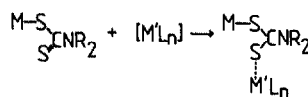
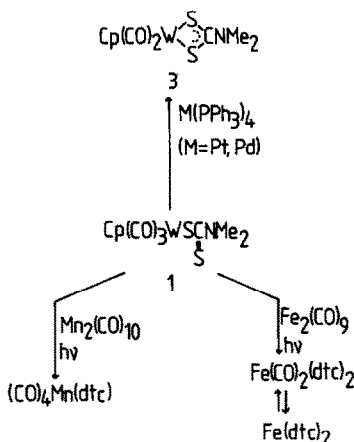


Fig. 1. Bonding modes of dithiocarbamate ligand.



Scheme 1. Reactivity of monodentate dithiocarbamate ligand.



Scheme 2. Some reactions of **1**.

metal fragments (Scheme 2). Part of this work has been the subject of a preliminary communication [14].

Results and Discussion

Complex **1** is well suited for investigating the reactivity of uncoordinated sulphur towards coordinatively unsaturated metal fragments because of its convenient synthesis in good yields by the method of Abrahamson *et al.* [1] of irradiating, with visible light, solutions containing $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}]_2$ (**2**) and tetramethylthiuram disulfide, and because the dtc ligand maintains the monodentate

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mode of bonding unless heated strongly or photolysed with UV irradiation. In contrast, we find that visible light irradiation, even at low temperatures, of toluene solutions containing $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{-Mo}]_2$ and tetramethylthiuram disulfide leads to the formation of the dicarbonyl chelate $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MoS}_2\text{CNMe}_2]$.

Reaction of 1 with $\text{Fe}_2(\text{CO})_9$

Visible irradiation of toluene solutions containing 1 and $\text{Fe}_2(\text{CO})_9$ under a nitrogen stream leads to a change in color of the solution from orange-red to dark brown. From the solution two products can be separated by column chromatography and identified as $\text{Fe}(\text{CO})_2(\eta^2\text{-dtc})_2$ and $\text{Fe}(\eta^2\text{-dtc})_2$. There is no observable reaction when toluene solutions of the chelate complex, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{WS}_2\text{CNMe}_2]$ (3) and $\text{Fe}_2(\text{CO})_9$ are irradiated with visible light. The transfer of the dithiocarbamate ligand from the tungsten to the iron complex is in marked contrast to the reaction of 2 with $\text{Fe}(\eta^2\text{-dtc})_3$, which gives compound 1. In our reaction of 1 with $\text{Fe}_2(\text{CO})_9$, even after prolonged photolysis, there is no evidence of any $\text{Fe}(\eta^2\text{-dtc})_3$ in the reaction mixture. Pure $\text{Fe}(\text{CO})_2(\eta^2\text{-dtc})_2$, when photolysed in toluene solution with visible light leads to decarbonylation and formation of $\text{Fe}(\eta^2\text{-dtc})_2$ quantitatively. Thus, in the photolytic reaction of 1 with $\text{Fe}_2(\text{CO})_9$, $\text{Fe}(\text{CO})_2(\eta^2\text{-dtc})_2$ is the initial product which readily loses CO under the reaction conditions to give $\text{Fe}(\eta^2\text{-dtc})_2$.

Reaction of 1 with $\text{Mn}_2(\text{CO})_{10}$

Irradiation with visible light of an oxygen free hexane solution containing 1 and $\text{Mn}_2(\text{CO})_{10}$ results in the formation of $\text{Mn}(\text{CO})_4(\eta^2\text{-dtc})$ in good yield. As in the reaction with $\text{Fe}_2(\text{CO})_9$, here also the fate of the tungsten complex has not been identified, and at present it is not possible to establish with certainty the mechanism of the new type of transmetalation reaction by which the iron and manganese dithiocarbamate complexes are obtained. The ligand exchange is not the result of a simple carbonylation of the tungsten complex by $\text{Fe}_2(\text{CO})_9$ or $\text{Mn}_2(\text{CO})_{10}$ since, neither bubbling CO through a solution of 1, nor the presence of strong donor ligands like phosphines leads to the displacement of the dithiocarbamate ligand from 1. A possible mechanism could involve an initial contact of the incoming metal carbonyl fragment with the uncoordinated sulfur of the dithiocarbamate ligand of 1. The vulnerability of the pendant sulfur towards reactive metal carbonyl fragments has in fact already been demonstrated by the identification of the adduct $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{dtc})\text{-W}(\text{CO})_5]$, formed when 1 is allowed to react with $\text{W}(\text{CO})_5\text{THF}$ [1]. The formation of a similar type of adduct with the iron carbonyl or the manganese carbonyl fragment could be the first step towards

complete transfer of the dithiocarbamate ligand from the tungsten to the iron or manganese metal atoms.

Reaction of 1 with $\text{M}(\text{PPh}_3)_4$ ($\text{M} = \text{Pt}, \text{Pd}$)

Room temperature stirring of solutions containing 1 and $\text{Pt}(\text{PPh}_3)_4$ or $\text{Pd}(\text{PPh}_3)_4$ results in a clean and almost quantitative conversion of 1 to the bidentate dithiocarbamate complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{WS}_2\text{CNMe}_2]$ (3). Such a conversion could in principle be influenced either by the $\text{M}(\text{PPh}_3)_x$, $x = 2, 3$, species or the presence of free triphenylphosphine liberated into solution by $\text{M}(\text{PPh}_3)_4$. The importance of free triphenylphosphine in influencing the reactivity of coordinated dithiocarbamate ligand has been shown by the conversion of a dithiocarbamate ligand to a thiocarbonylamido ligand in a reaction which produces a dinuclear molybdenum product [15]. In our reactions the triphenylphosphine does not play any role in the conversion of 1 to 3 because even after stirring a toluene solution of 1 and two equivalents of PPh_3 for several hours the bidentate complex 3 is not observed. The initial contact of the reactive $\text{M}(\text{PPh}_3)_3$ or $\text{M}(\text{PPh}_3)_2$ fragments with the uncoordinated sulfur in 1 is probably the first step of the mechanism. Elimination of a carbonyl group from the tungsten creates a vacant site which is taken up by the dithiocarbamate group breaking its contact with the platinum or palladium metals and adopting a bidentate mode of bonding to the tungsten. Alternatively, the Pt^0 and the Pd^0 species may act as CO absorbers, lowering the CO activity in solution. There is however, no observation of known platinum or palladium carbonyl containing species in the reaction mixtures. Though the intermediates involved are very reactive and cannot be isolated, monitoring of the reaction between 1 and $\text{Pd}(\text{PPh}_3)_4$ by infrared spectroscopy does indicate that the conversion of 1 to 3 proceeds through a species having carbonyl stretching frequencies which are not attributable to either 1 or 3, (Fig. 2). When $\text{Pd}(\text{PPh}_3)_4$ is added to a dichloromethane solution of 1 the CO stretching frequencies at 2037, 1957 and 1931 cm^{-1} due to 1 decrease in intensity with time. After 10 min a new frequency appears at 2048 cm^{-1} which reaches maximum intensity after 40 min of reaction. There is an appearance of peaks at 1937 and 1840 cm^{-1} , due to 3, which increase in intensity as the peak at 2048 cm^{-1} gradually decreases in intensity. After 80 min of reaction only the peaks due to the dicarbonyl chelate (3) are observable.

Experimental

General Information

All reactions were routinely performed under an inert atmosphere of argon using standard Schlenk

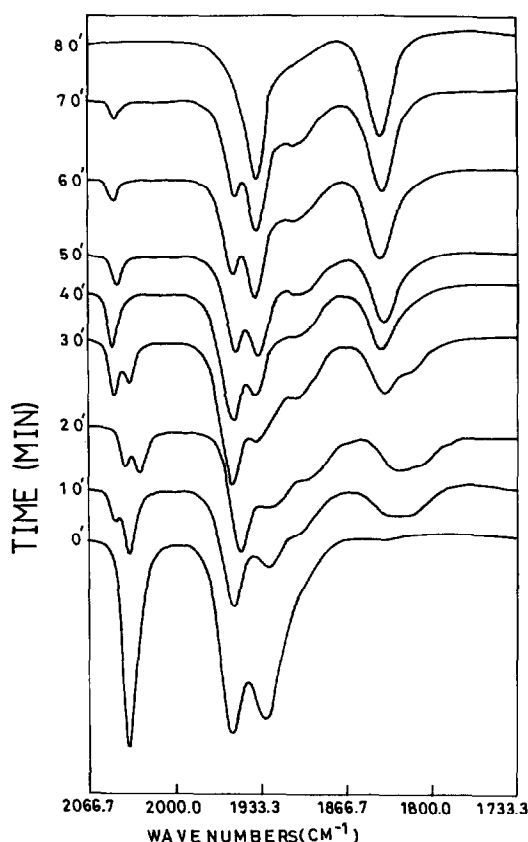


Fig. 2. Infrared spectra in the carbonyl region during reaction of **1** and $\text{Pd}(\text{PPh}_3)_4$ in dichloromethane.

techniques. The solvents were dried and distilled prior to use. Infrared spectra were recorded on a Nicolet 5DXB F.T. spectrometer. NMR spectra were recorded on a Hitachi T-60 spectrometer in CDCl_3 solutions, and UV-Vis spectra on a Shimadzu 260 spectrophotometer. Melting points were obtained on a Ketan melting point apparatus. The metal carbonyls were obtained from Strem Chemicals while $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PPh}_3)_4$ were obtained from Fluka AG and used without further purification. $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{-WSC(S)NMe}_2]$ was prepared as reported in the literature [1].

Photolysis of **1** and $\text{Fe}_2(\text{CO})_9$

A mixture of **1** (0.25 g, 0.55 mmol) and $\text{Fe}_2(\text{CO})_9$ (0.2 g, 0.55 mmol) in 60 ml of toluene solvent was irradiated with visible light for 2 h. The solvent was removed *in vacuo* and the dark brown residue was put on a silica gel column. Elution with petroleum ether/dichloromethane (50/50) gave a red brown band identified as $\text{Fe}(\eta^2\text{-dtc})_2(\text{CO})_2$, yield = 60%. IR (KBr): $\nu(\text{CO})$ 1970, 2040; $\nu(\text{CN})$ 1535; $\nu(\text{CS})$ 995 cm^{-1} . NMR: δ 3.28, 3.20. UV-Vis ($\text{CH}_2\text{-Cl}_2$): λ_{max} 236, 274, 383 nm. Further elution with neat dichloromethane gave the dark brown $\text{Fe}(\eta^2\text{-$

$\text{dtc})_2$, yield = 30%. IR (KBr): $\nu(\text{CN})$ 1530; $\nu(\text{CS})$ 990 cm^{-1} . NMR: δ 3.60. UV-Vis (CH_2Cl_2): λ_{max} 231, 256, 343 nm.

The photolysis of **1** and $\text{Fe}_3(\text{CO})_{12}$ was carried out similarly to give $\text{Fe}(\text{CO})_2(\eta^2\text{-dtc})_2$ and $\text{Fe}(\eta^2\text{-dtc})_2$ in yields of 60% and 30% respectively. Prolonged photolysis in either reaction resulted in formation of only $\text{Fe}(\eta^2\text{-dtc})_2$, which converted back to $\text{Fe}(\text{CO})_2(\eta^2\text{-dtc})_2$ quantitatively when a toluene solution of $\text{Fe}(\eta^2\text{-dtc})_2$ was bubbled with CO for 1 h.

Photolysis of **1** and $\text{Mn}_2(\text{CO})_{10}$

A mixture of **1** (0.07 g, 0.15 mmol) and $\text{Mn}_2(\text{CO})_{10}$ (0.06, 0.15 mmol) in 100 ml of hexane solvent was irradiated with visible light for 5 h. The solution was filtered over celite and slow evaporation of the hexane precipitated the yellow $\text{Mn}(\text{CO})_4(\eta^2\text{-dtc})$. IR (hexane): $\nu(\text{CO})$ 2087, 2009, 1995 and 1957 cm^{-1} . UV-Vis (hexane): λ_{max} 271, 266 and 226 nm.

Reaction of **1** and $\text{Pd}(\text{PPh}_3)_4$

To a benzene solution (70 ml) containing **1** (0.041 g, 0.09 mmol) was added $\text{Pd}(\text{PPh}_3)_4$ (0.104 g, 0.09 mmol). The mixture was stirred for 1.5 h during which time the color of the solution changed from orange to greenish brown and then to red. Chromatographic work-up on a silica gel column gave the dicarbonyl chelate (**3**) in almost quantitative yield.

Reaction of **1** and $\text{Pt}(\text{PPh}_3)_4$

A mixture of **1** (0.045 g, 0.09 mmol) and $\text{Pt}(\text{PPh}_3)_4$ (0.112 g, 0.09 mmol) in benzene solvent (70 ml) was stirred at room temperature for 6 h. Chromatographic work-up as above gave the dicarbonyl chelate quantitatively.

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