

Review

Thiocarbonyl, thiocarbyne and thiocarbene ligands in di- and polynuclear complexes

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This work is a contribution for the special issue dedicated to Prof. Robert J. Angelici on the occasion of his 70th birthday.

Abstract

Thiocarbonyl (CS), homologous to the ubiquitous carbonyl ligand, has interesting and unique properties as ligand. Nevertheless it did not reach the widespread use of CO in the formation of transition metal complexes. This short account, dedicated to professor R.J. Angelici, is focused on the multisite coordination of thiocarbonyl ligand in di- and poly-nuclear transition metal complexes, and to its transformation into thiocarbyne and thiocarbene ligands. These latter, in turn, can be transformed, providing access to a variety of new ligands and functionalities, which are here briefly reviewed.

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1. Introduction

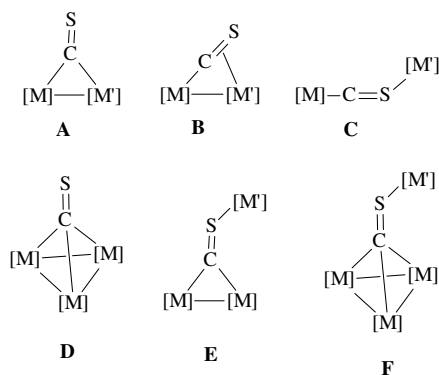
Transition metal bonded thiocarbonyl (CS), homologous to the ubiquitous carbonyl ligand, has always represented a fascinating and challenging topic in organometallic chemistry. This short account, dedicated to professor R.J. Angelici, is focused on the chemistry of the thiocarbonyl ligand and of its congeners: the thiocarbonyl and thiocarbonyl ligands, with particular regards to their coordination to di- and polynuclear metal complexes, and to our contribution in the field.

Since the first thiocarbonyl complex, *trans*- $[\text{RhCl}(\text{PPh}_3)(\text{CS})]$, obtained by Wilkinson et al. [1], the number of CS containing complexes rapidly grew owing to the studies of several excellent research groups. Remarkable contributions from Angelici, Butler, Roper, Broadhurst, Werner, Petz have been reported, among others, in excellent reviews [2]. In spite of these efforts and of superior properties of CS as a ligand compared to CO, the thiocarbonyl complexes are still far from having the widespread use of metal carbonyls. The reason is mainly synthetic and mostly derives from the lack of a direct source of CS and of straight synthetic methods, which is still an open challenge for synthetic chemists.

2. CS coordinated to di- and polynuclear complexes

The synthesis mononuclear thiocarbonyl compounds was soon followed by the development of bridging thiocarbonyl complexes, which exploited the excellent properties of CS to act as ligand capable of coordination to more than a single metal centre. As shown in Scheme 1, a variety of coordination modes have been found: bridging coordination (A), which is the most common; bridging side on (B) [3]; bridging end-to-end (C) [4] and triply bridging (D) [5]. Moreover, since the sulfur atom of these thiocarbonyl complexes maintains relevant coordination ability, an additional metal fragment can be coordinated generating the forms E [6] and F [5a,5b].

Type A complexes can be obtained by coupling of mononuclear thiocarbonyl complexes. As an example, the

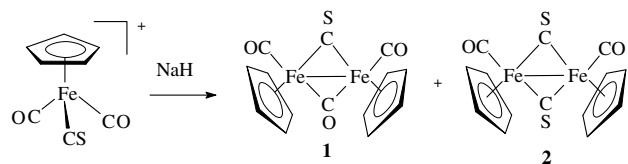


Scheme 1.

reductive coupling of $[\text{Fe}(\text{CO})_2(\text{CS})(\text{Cp})]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) affords a mixture of the mono- and di-thiocarbonyl complexes **1** and **2** (Scheme 2) [7].

Similarly, the homodinuclear μ -thiocarbonyl complexes $[\text{Mn}(\text{CO})(\text{NO})(\text{CS})(\text{Cp})_2]$ [8], $[\text{Ru}_2(\text{CO})_3(\text{CS})(\text{Cp})_2]$ and $[\text{Ru}(\text{CO})(\text{CS})(\text{Cp})_2]$ [9], and the pentamethylcyclopentadienyl (Cp^*) complexes analogue to **1** and **2** [10], have been synthesized by the same route.

Studies on **1** and **2**, as well as on their ruthenium analogues $[\text{Ru}(\text{CO})(\text{CS})\text{Cp}]_2$ and $[\text{Ru}_2(\text{CO})_3(\text{CS})\text{Cp}]_2$, evidenced the preference of CS for bridging over a terminal position in these molecules. This was tentatively explained in terms of the weakness of the $\text{C}\equiv\text{S}$ π -interaction, which loses little π -bond stabilization in moving from a terminal ($\text{C}\equiv\text{S}$) to a bridging ($>\text{C}=\text{S}$) position. These arguments also suggested that CO should have a lower preference for a bridging position than CS [9].



Scheme 2.

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