

Bonding and Reactivity of Transition Metal Complexes of Carbon Disulfide

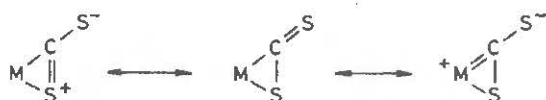
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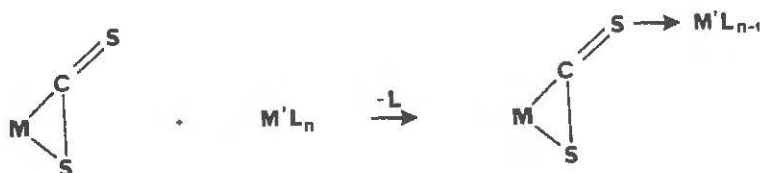
The activation of carbon dioxide by transition metal centers had long been a subject of great interest: if such activation were realized, CO₂ could become an abundant source of reduced C₁ compounds. In spite of intense efforts to induce reactivity, however, CO₂ remains largely inert to transition metals; only a few examples of metal-coordinated CO₂ are known [1]. For this reason, many investigators are now studying the reactions of the more reactive heteroallene carbon disulfide, in the hope that the resulting chemistry might provide some insight into the feasibility of CO₂ activation [2].

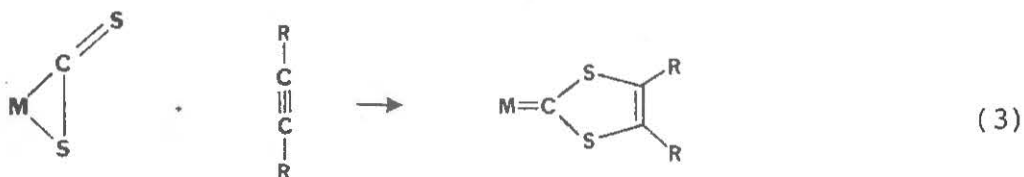
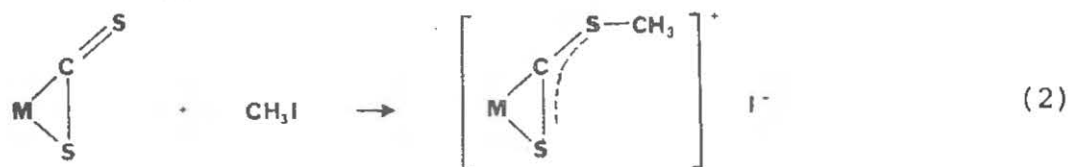
The first transition metal-CS₂ complex was prepared by Wilkinson and Baird in 1966 [3]. An X-ray structural determination [4] showed that the CS₂ fragment was π-bonded in a side-on fashion to the metal as shown below:



This bonding mode is by far the most common in mononuclear metal-CS₂ compounds; analogous complexes of almost every transition metal have been identified [2]. Several of these complexes have been structurally characterized [5], and the structural data indicate substantial electron delocalization over the MCS₂ system as shown above.

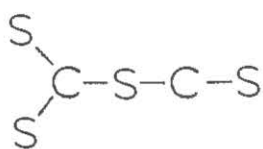
This valence-bond description (and a recent molecular orbital study [6]) indicate that when CS₂ is coordinated to a metal center in this manner, a shift in electron density toward the uncoordinated sulfur atom occurs. The observed reactivity of metal-CS₂ compounds agrees with this description. For example, the exocyclic sulfur can react with another metal center (reaction 1) or with an alkyl halide (reaction 2) to give a heterobinuclear complex or a coordinated dithioester, respectively. The 1,3-dipolar character of the CS₂ moiety is also thought to facilitate cycloadditions with electrophilic alkynes (reaction 3) [7,8,9].



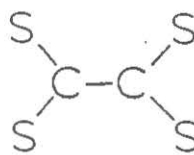


The product of reaction 1 is an example of a CS₂-bridged binuclear compound. In other structurally characterized binuclear complexes, different bridging modes are seen: the μ -CS₂ moiety can donate a total of 2, 4, or 6 electrons to the two metal centers [10, 11, 7b].

One of the more intriguing aspects of metal-CS₂ chemistry is the recently demonstrated ability of some systems to induce CS₂ coupling. Several examples of head-to-tail coupling (A) [12] and head-to-head coupling (B) [13] have been synthesized and characterized by X-ray crystallography.



(A)



(B)

References

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