Journal of Organometallic Chemistry, 172 (1979) C1—C3

Preliminary communication

ACTIVATION OF SMALL MOLECULES BY TRANSITION METALS. THE REACTION OF CS_2 WITH η^5-$C_5H_5Mo(CO)_3R$ (R = Me, Et)

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(Received March 27th, 1979)

Summary

Reaction of CS_2 with η^5-$C_5H_5Mo(CO)_3R$ (R = Me, Et) yields the η^2-CS_2 complexes η^5-$C_5H_5Mo(CO)_2(\eta^2$-$CS_2)(COR)$ which can reversibly lose CS_2 in refluxing benzene to reform the starting material. Reaction of η^5-$C_5H_5Mo(CO)_2(\eta^2$-$CS_2)(COMe)$ with PPh_3 yields η^5-$C_5H_5Mo(CO)_2(\eta^2$-$CS_2)(PPh_3)(COMe)$.

The ability of transition metals to activate and irreversibly bind the isoelectronic molecules CO_2 [1] and CS_2 [2] is well known. Numerous examples are also known in which a transition metal reversibly binds CO_2 [1] i.e., acts as a "carrier" of CO_2, but the corresponding reaction type for CS_2 has not been studied. A recent report on the complex η^5-$C_5H_5W(CO)_2CS^-$ [3] prompts us to report our findings on the reversible reactions of η^5-$C_5H_5Mo(CO)_3Me$ (I) and η^5-$C_5H_5Mo(CO)_3Et$ (II) with CS_2.

Reactions of I, (I and II were prepared by the literature method [4] with excess CS_2 in refluxing benzene (in the dark) yielded a purple, light sensitive complex, III, in low yield (~ 5%). III was characterized by elemental analysis, IR and NMR (Table 1), and mass spectrometry (parent ion *m/e* 338 and fragments corresponding to loss of COMe and consecutive loss of CO). The

TABLE 1

IR AND ^1H NMR DATA FOR THE η^2-CS_2 COMPLEXES

Complex	IR[a] (cm^{-1})			NMR[b] (ppm)		
	$\nu(CO)$[c]	$\nu(COR)$	$\nu(CS)$	$\delta(C_5H_5)$	$\delta(CH_3)$	$\delta(CH_2)$
III	1983s 1926ms	1667	1223	5.52	2.48	
IV	1980s 1924ms	1664	1165	5.49	1.21[d]	2.89[d]
V	1898	1631	1234			

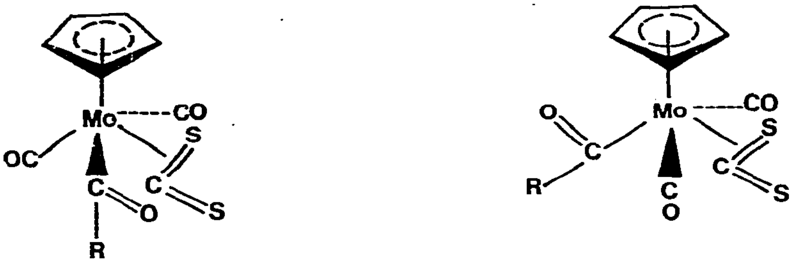
[a] In CS_2 solution. [b] In $CDCl_3$ solution. [c] s = strong, ms = medium strong. [d] J(H—H) = 1.25 Hz.

data indicate that the CS_2 has coordinated to the metal to form η^5-C_5H_5Mo-$(CO)_2(\eta^2$-$CS_2)(COMe)$ as shown in Fig. 1 (R = Me). Complex formation is thus occurring via a "CO insertion" reaction:

$$\eta^5\text{-}C_5H_5Mo(CO)_3Me + CS_2 \rightarrow \eta^5\text{-}C_5H_5Mo(CO)_2(\eta^2\text{-}CS_2)(COMe).$$

and not via a CS_2 insertion into the metal alkyl bond [5].

The NMR spectrum, which contains only one C_5H_5 resonance, and the IR intensity ratios of the two $\nu(CO)$ absorptions [6] suggest that III exists in solution as the *cis*-isomer, Fig. 1(a), rather than the *trans*-isomer, Fig. 1(b), or a mixture of the isomers. This would be the expected product from the insertion reaction if no further rearrangement of ligands took place around the metal atom.



1(a) 1(b)

Fig. 1. Possible structures for the new η^2-CS_2 complexes, (a) *cis*-isomer, (b) *trans*-isomer. η^2-CS_2 is schematically represented as occupying one coordination site.

The use of extended reaction times, different solvents (toluene, tetrahydrofuran and acetonitrile) or light did not increase the yield of III and typically 70—75% unreacted starting material was reclaimed at the end of the reaction. Further, III, in refluxing benzene (in the dark) reverted to starting material, I, plus other unidentified decomposition products.

The complexes I and II are thus inter-related by the equilibrium:

$$III \rightleftharpoons I + CS_2$$

and III thus represents the first example of a CS_2 "carrier" molecule.

Complex II reacted completely with CS_2 in the dark in refluxing benzene to yield a mixture of products as detected by TLC. A purple complex, IV, was isolated in low yield (< 10%) by column chromatography. Elemental analyses, IR and NMR (Table 1) and mass spectrometry (parent ion *m/e* 352) data are in accord with the structure η^5-$C_5H_5Mo(CO)_2(\eta^2$-$CS_2)(COEt)$ as shown in Fig. 1(a) (R = Et). In refluxing benzene (in the dark), IV reverts to starting materials, II, and unidentified decomposition products suggesting that it also acts as a CS_2 "carrier".

Complex III did not react with MeI, either neat or in refluxing benzene [7] but reacted with PPh_3 in benzene to yield the royal blue complex η^5-C_5H_5Mo-

(CO)(η^2-CS_2)(PPh_3)(COMe) (V) in which carbonyl substitution rather than sulfur abstraction to produce a thiocarbonyl complex, has occurred. V was characterized by IR (Table 1) and mass spectrometry (parent ion *m/e* 572).

Acknowledgement

We thank the C.S.I.R. (South Africa) and the University for grants which made this work possible.

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