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Preliminary communication

ADDITION OF CS_2 TO THE Mo≡Mo TRIPLE BOND IN $(C_5R_5)_2Mo_2(CO)_4$ (R = H, CH_3): FORMATION OF A NEW BINUCLEAR η^2-CS_2 COMPLEX

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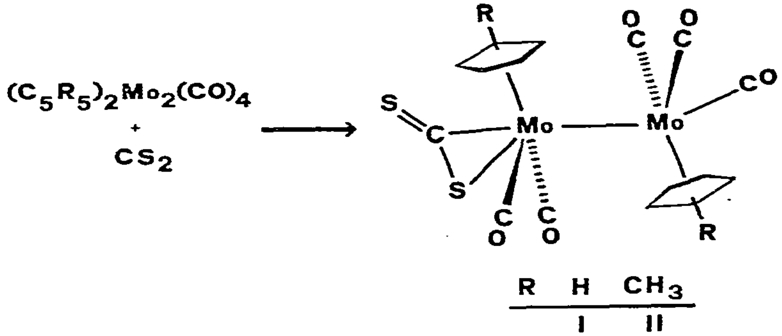
Summary

From the reaction of $(C_5R_5)_2Mo_2(CO)_4$ (R = H, CH_3) with boiling CS_2 the new compounds $C_5R_5(CO)_3Mo$—$Mo(CO)_2(\eta^2\text{-}CS_2)C_5R_5$, I and II, have been isolated. These deep blue products, fully characterised by their IR, ^1H NMR, ^{13}C NMR, and mass spectra, contain as a novel structural feature a non-bridging, terminal η^2-CS_2 ligand.

Binuclear CS_2 complexes, in which the carbon disulfide ligand bridges two metal centers, are well known. For these complexes, including those of Cr, Mn, Fe, Co, Rh, and Pt, however, a number of bonding modes have been observed [1]. Only one binuclear Mo complex of this kind has been described, a dithiocarboxylato compound obtained by a complicated synthesis [2,3].

In order to get direct access to such complexes we choose as starting material $[C_5R_5Mo(CO)_2]_2$ (R = H, CH_3) derivatives, the metal—metal triple bond of which is known to react with various small molecules [4]. In particular, $[C_5H_5Mo(CO)_2]_2$ has been observed to react with aminocyanamides, alkynes, and allenes [4,5], but the analogous chemistry of the pentamethyl dimer has not been reported. The products of these reactions arise from vicinal addition to the metal—metal bond and may be described as "symmetrical" dimers.

After boiling $(C_5R_5)_2Mo_2(CO)_4$ (R = H, CH_3) in CS_2 for one hour the binuclear complexes I and II were isolated as blue crystals in 21 and 28% yield, respectively, by careful column chromatography (silica gel, eluting with pentane/toluene, 1/1), followed by recrystallisation from 1/1 CH_2Cl_2/Et_2O (Scheme 1).



The molecular weight of each complex was confirmed by the field desorption mass spectra (Varian 311 A, emitter voltage 4.2 kV, filament heating 15 mA, acetone solution) both of which exhibit the parent ions, involving two superposed molybdenum isotope patterns.

In accord with the proposed structure, the IR spectra of these compounds show absorptions in the carbonyl region at 2025s, 1970vs, 1930vs, 1840s cm^{-1} (I, KBr) and 2012s, 1968s, 1945vs, 1868s (pentane), respectively. In addition, absorptions characteristic of a η^2-bonded CS_2 ligand were found at 1095s and 680m cm^{-1} for I and at 1065m and 680w cm^{-1} for II. The lower absorption at 680 cm^{-1} is characteristic of the thiometallacycle [6,7].

The chemical nonequivalence of the Mo atoms is evident from the ^1H NMR spectra ($CDCl_3$ solution), which exhibit two cyclopentadienyl resonances in each case; singlets were observed at 5.38 and 5.67 ppm for the C_5H_5 ligands in I and at 1.87 and 1.97 ppm for the pentamethyl groups in II. Further proof was found in the ^{13}C NMR spectrum ($CDCl_3$ solution, internal TMS) of a sample of II containing nearly 25% ^{13}CO enrichment [8]. A pattern of ^{13}CO resonances was observed at 239.2, 245.3, 248.7 ppm (intensities 2:2:1). The signals at 239.2 and 248.7 ppm are assigned to carbonyls in the $C_5R_5Mo(CO)_3$ fragment by analogy with the spectrum of $[C_5H_5Mo(CO)_3]_2$ [9]. As a consequence of the square-pyramidal configuration at the metal center, nonequivalent *cis* and *trans* carbonyls exist. The signal at 245.3 ppm is assigned to the carbonyls on the unique Mo atom bearing the CS_2 ligand. A similar pattern of signals was observed for the related complex $C_5H_5(CO)_3Mo{-}Mo(CO)_2$-$[P(C_6H_5)(OCH_2CH_2)_2NH]C_5H_5$, except that the inner signal from the latter shows phosphorus coupling [10]. The other carbon atoms in II appear at 203.4 ($\mathit{C}S_2$), 108.3 and 106.2 (C_5Me_5), and at 10.7 and 10.6 ppm ($\mathit{C}H_3$).

In contrast to the general bridging potential of the ligand, the heteroallene S=C=S behaves as a "normal" two-electron donor and occupies a terminal coordination site in the complexes I and II. The addition of donor ligands such as phosphines or phosphites, L, to $[C_5H_5Mo(CO)_2]_2$ always occurs in a symmetrical manner to give complexes of the type $[C_5H_5Mo(CO)_2L]_2$. In these reactions a monosubstituted intermediate with one Mo atom in a 16-electron configuration, which rapidly reacts with the second nucleophile, has been postulated [4]. However, stable unsymmetrical addition products such as I or II have never been observed. In the present reaction there is another mechanistic possibility involving the slow substitution of one CO by CS_2 followed by addition of free CO, which is derived from products with a higher degree of substitution. The first example of ligand-induced CO-substitution in $[C_5H_5Mo(CO)_2]_2$ was demonstrated recently [11].

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