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THE ADDITION OF CARBON MONOXIDE TO CERTAIN BINUCLEAR ORGANOMETALLIC COMPOUNDS OF IRON, MOLYBDENUM AND TUNGSTEN CONTAINING BRIDGING THIOLATE LIGANDS. THE FORMATION OF MONONUCLEAR SPECIES

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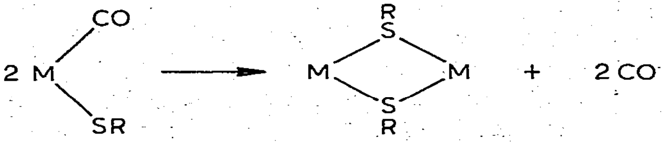
Summary

The reaction of carbon monoxide with $[Fe(CO)(C_5H_5)(RS)]_2$ and $[M(CO)_2(C_5H_5)(RS)]_2$ (where M = Mo or W, and R = p-$CH_3C_6H_4$) in tetrahydrofuran results in (a) the cleavage of the bridging sulfur—metal bond, (b) the uptake of carbon monoxide, and (c) the formation of the mononuclear species; $Fe(CO)_2(C_5H_5)(RS)$ and $M(CO)_3(C_5H_5)(RS)$. The relative stabilities of the two isomers of $[Fe(CO)(C_5H_5)(RS)]_2$ are discussed.

Introduction

The preparation of carbonyl-containing compounds with terminal alkyl- and aryl-thiolates and the subsequent thermal and photochemical loss of carbon monoxide to yield bridging thiolates (eqn. 1) are well documented [1-4]. However, the reverse of this reaction has not been reported, namely the cleavage of the bridging sulfur—metal bond by carbon monoxide.



(1)

Treichel, Morris and Stone [5] reported the formation of $[M(CO)_2(C_5H_5)(CH_3S)]_2$*, where M = Mo or W, by treating dimethyl disulfide with $M(CO)_3(C_5H_5)H$. Havlin and Knox [3] described the preparation of $M(CO)_3(C_5H_5)(RS)$, (M =

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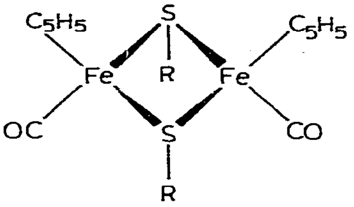
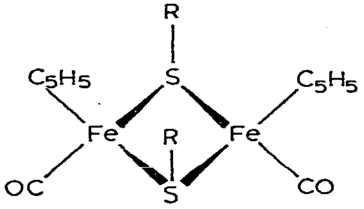
* $C_5H_5 = \eta^5$-C_5H_5, *pentahapto*-cyclopentadienyl.

Mo or W; R = CH_3 or C_6H_5) and their conversion to the corresponding thiolate-bridged compounds, $[M(CO)_2(C_5H_5)(RS)]_2$. Havlin and Knox [3] argued that the tungsten compound previously formulated [5] as $[W(CO)_2(C_5H_5)(CH_3S)]_2$ was actually $W(CO)_3(C_5H_5)(CH_3S)$, although they gave no supporting physical data.

In an extensive series of papers Knox [2,6,7] and coworkers studied the formation of so called stable and unstable isomers of $[Fe(CO)(C_5H_5)(SR)]_2$, where R = CH_3, C_2H_5, p-$CH_3C_6H_4$, etc. The crystal structure of the stable isomer of $[Fe(CO)(C_5H_5)SC_6H_5]_2$ has been determined [8] and is represented by *cis*-I; the C_6H_5 groups are trans to the C_5H_5 groups across the slightly puckered Fe_2S_2 ring. On the other hand, the unstable isomer is proposed [2] to have structure *cis*-II; all C_6H_5 and C_5H_5 groups being mutually *cis*.



(*cis*-I)



(*cis*-II)

We wish to report that carbon monoxide in a polar solvent such as tetrahydrofuran (THF) will cleave bridging thiolate dimers (I) to yield mononuclear species (eqn. 1) in the compounds studied; $[Fe(CO)(C_5H_5)(RS)]_2$ and $[M(CO)_2(C_5H_5)(RS)]_2$ where M = Mo or W, and R = p-$CH_3C_6H_4$).

Experimental

General data. All reactions, work-up and storage of products were carried out in an oxygen-free nitrogen or carbon monoxide atmosphere using standard inert-atmosphere techniques. All solvents were dried, distilled and deoxygenated before use. The percentage of bridged and non-bridged compounds present in mixtures was determined by integrating the methyl protons in proton NMR spectra.

Physical measurements. Infrared spectra were recorded on a Perkin—Elmer Model 621 spectrophotometer. Proton NMR spectra were run on a Varian Associates Model A-60-D spectrometer. Mass spectra were obtained with a Perkin—Elmer Hitachi RMU-6D double focussing spectrometer operating at 20-eV ionizing energy. Molecular weights were taken from the mass spectra and quoted using the average masses of the elements. Correct ratio of isotopes was observed in each case. Melting points were determined in sealed capillary tubes and were uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Syntheses. $[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ was prepared and separated into the stable and unstable isomers by a published procedure [2].

$W(CO)_3(C_5H_5)(CH_3S)$ was prepared by a variation of a published procedure [3]; CH_3SK was treated with $W(CO)_3(C_5H_5)I$. The crude product was placed on an alumina column. Elution with a 1/1 benzene/heptane mixture removed unreacted $W(CO)_3(C_5H_5)I$. An orange band eluted with a 3/1 benzene/heptane mixture. Removal of solvent gave bright orange crystals of $W(CO)_3(C_5H_5)(CH_3S)$ in 75% yield, m.p. 65-66°C. Anal. Found: C, 28.41; H, 2.18; mol. wt., 380. $C_9H_8O_3SW$ calcd.: C, 28.44; H, 2.12%; mol. wt., 380.

$W(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$. To a solution of $W(CO)_3(C_5H_5)I$ (1.00 g, 2.20 mmol) in THF (50 ml) was added $p\text{-}CH_3C_6H_4SK$ (0.36 g, 2.20 mmol). The mixture was stirred for 3 h. Solvent was removed and the crude product was dissolved in benzene and stripped onto 2 g of alumina and placed on an alumina column. Elution with a 3/1 benzene/petroleum ether (b.p. 30-60°C) mixture removed an orange band. Removal of solvent gave bright orange crystals of product in 82% yield, m.p. 118-119°C (dec.). Anal. Found: C, 39.16; H, 2.71; mol. wt., 456. $C_{15}H_{12}O_3SW$ calcd.: C, 39.49; H, 2.95%; mol. wt., 456.

$Mo(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ and $[Mo(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$. $Mo(CO)_3(C_5H_5)I$ (1.00 g, 2.7 mmol) was dissolved in THF (50 ml) and stirred for 7 h with 0.49 g (3.0 mmol) of $p\text{-}CH_3C_6H_4SH$. Solvent was removed, the crude product dissolved in benzene (25 ml) and filtered. Benzene was removed from the filtrate and the crude product chromatographed on an alumina column. Elution with a 1/1 benzene/heptane mixture produced a dark green band containing the dimer followed by an orange band that contained $Mo(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$. The dimer was isolated in 30% yield, m.p. 260°C. Anal. Found: C, 49.08; H, 3.86; mol. wt., 680. $C_{28}H_{24}O_4SMo_2$ calcd.: C, 49.42; H, 3.56%; mol. wt., 680.

$[W(CO)_2(C_5H_5)(CH_3S)]_2$. A solution containing 0.04 g (0.01 mmol) of $W(CO)_3(C_5H_5)(CH_3S)$ in benzene (5 ml) was heated at reflux for 20 min. Solvent was removed to yield a mixture containing a small amount of starting material and what was believed to be the desired product. However, attempted purification by chromatography resulted in extensive decomposition.

$[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$. A solution containing 0.25 g (0.54 mmol) of $W(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ in benzene (25 ml) was heated at reflux for 135 min. Solvent was removed and the crude product chromatographed on an alumina column. Elution with benzene followed by removal of solvent yielded a small amount of a green compound, and the lavander product in 46% yield, m.p. 235°C. Anal. Found: C, 39.54; H, 3.08; W, 43.29. $C_{28}H_{24}O_4S_2W_2$ calcd.: C, 39.27; H, 2.82; W, 42.94%.

Reactions with carbon monoxide. $[Mo(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ (0.01 g, 0.15 mmol) was dissolved in benzene (50 ml) and CO bubbled through the solution for 1 h. Solvent was removed to yield unreacted starting material. When CO was bubbled through a THF solution of the same concentration for 3 h, removal of solvent revealed a mixture of starting material (95%) and $Mo(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ (5%). However, when CO was bubbled through a THF solution heated at reflux for 1 h, removal of solvent revealed mainly $Mo(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ (>95%).

$[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ (0.10 g, 0.12 mmol) was dissolved in THF (25 ml) and CO bubbled through the solution for 4 h. Unreacted starting material was recovered. However, when the same quantity of starting material was dissolved in THF (150 ml) and CO bubbled through the solution at reflux for 1 h, a 1/1 mixture of starting material and $[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ was obtained. No reaction was observed with CO in benzene, either at room temperature or at 65°C for 1 h.

TABLE 1

CARBONYL STRETCHING FREQUENCIES (cm^{-1})[a] AND PROTON NMR DATA (τ)[b]

Compound	ν(CO)	τ			Reference
		C_5H_5	CH_3S	p-$CH_3C_6H_4$	
$W(CO)_3(C_5H_5)(CH_3S)$	2030vs, 1943vs	5.23	8.44		This work
	(2034s, 1948s)	(4.51)	(8.11		[9]
$W(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$	2033vs, 1948vs	5.17		7.88	This work
		4.29[c]		7.72[c]	This work
$[W(CO)_2(C_5H_5)(CH_3S)]_2$[d]	1955vs, 1930(sh), 1861s, 1852(sh)				
$[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$	1893m, 1848s	4.56[c]		7.70[c]	This work
$Mo(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$	2040vs, 1959vs	5.26		7.88	This work
$[Mo(CO)_2(C_5H_5)(CH_3S)]_2$	1967vs, 1948s, 1940(sh),	4.94	8.05		
	1879s, 1862(sh), 1852(sh)[e]	5.12	8.22		
	(1965s, 1947s, 1877s	(4.53	(8.13,		[5]
	1869, 1952(sh)	4.70)	8.18)		
$[Mo(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$	1964sh, 1954vs, 1873vs	5.01		7.92	This work
$Fe(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)$	2034vs, 1986vs	5.83		7.89	This work
	(2026vs, 1987vs)	(5.21)		(7.79)	[2]
$[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$[f]	1977s	5.42[c]		7.76[c]	This work
	(1973s)	(5.42)		(7.76)	[2]
$[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$[g]	1934s	5.87[c]		7.70[c]	This work
	(1938s)	(5.87)		(7.70)	[2]

[a] CCl_4 solution unless indicated otherwise. Values in parentheses are for previously published data. [b] Relative to Me_4Si. C_6D_6 solution unless indicated otherwise. [c] $CDCl_3$ solution. [d] Impure. [e] Cyclohexane solution. [f] Stable isomer. [g] Unstable isomer.

The unstable isomer of $[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ (0.10 g, 0.18 mmol) was dissolved in THF (50 ml) and CO bubbled through the solution for 3 h. Solvent was removed to give a ca. 1/1 mixture of the stable and unstable isomers, with a trace of $Fe(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)$. When CO was bubbled through a THF (50 ml) solution of the stable isomer (0.25 g, 0.44 mmol) for 6 h, a ca. 3/1 mixture containing the stable and unstable isomers and a trace of $Fe(CO)_2(C_5H_5)$-$(p\text{-}CH_3C_6H_4S)$ was produced. An identical result was observed when the latter reaction was carried out in benzene for 5 h under nitrogen. A 3/1 mixture of the stable and unstable isomer (0.30 g, 0.55 mmol) in THF (50 ml) was heated at reflux for 1 h while CO was bubbled through the solution. Removal of solvent produced a mixture containing ca. 10% unstable and 30% stable isomers, and 60% $Fe(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)$.

Results and discussion

The reaction of $W(CO)_3(C_5H_5)I$ with CH_3SK gave an orange product which we formulate as $W(CO)_3(C_5H_5)(CH_3S)$, in agreement with Havlin and Knox [3]. The infrared spectrum shows two bands due to ν(CO) (2030 and 1943 cm^{-1}) which are slightly lower than the parent iodide (2040 and 1961 cm^{-1}) [9], and very similar to the values reported by Treichel, Morris and Stone [5] (2034 and 1948 cm^{-1}) for $[W(CO)_2(C_5H_5)(CH_3S)]_2$. However the binuclear molybdenum analogue $[Mo(CO)_2(C_5H_5)(CH_3S)]_2$ exhibited ν(CO) absorptions at 1965, 1947, 1877, 1809, and 1852 cm^{-1}. Thus, the infrared spectrum, the parent ion in the mass spectrum at 380 and the elemental analysis strongly support the contention of Havlin and Knox [3] that the compound formulated as $[W(CO)_2(C_5H_5)(CH_3S)]_2$ [5] is actually the non-bridged species $(W(CO)_3(C_5H_5)(CH_3S)$.

In a similar way $W(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ was prepared and characterized as the non-bridged species by its infrared spectrum, mass spectrum and elemental analysis. However, it was not possible to prepare and isolate a pure sample of $Mo(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ because of its rapid conversion to the binuclear sulfur-bridged compound upon loss of carbon monoxide in solution at room temperature. The latter compound exhibited ν(CO) absorptions at 1964, 1954, and 1873 cm^{-1} and was characterized by elemental analysis and the appearance of a parent ion at 680 in the mass spectrum.

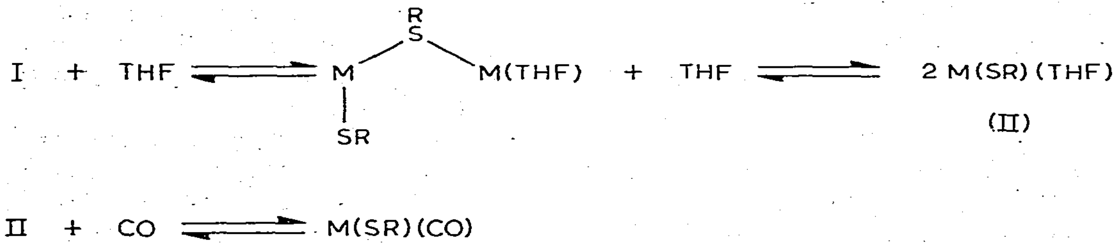
Although $W(CO)_3(C_5H_5)(CH_3S)$ seems to be readily converted to $[W(CO)_2$-$(C_5H_5)(CH_3S)]_2$ by heating in refluxing benzene, attempts to purify the product were unsuccessful. On the other hand $[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$, obtained from $W(CO)_3(C_5H_5)(p\text{-}CH_3C_6H_4S)$ by heating in benzene, was purified by column chromatography and characterized by elemental analysis. The proton NMR spectrum showed only one cyclopentadienyl proton resonance and therefore only one isomer was present. However, the infrared spectrum (ν(CO); 1893m and 1848s cm^{-1}) differed significantly from that for the molybdenum analogue (ν(CO), 1964(sh), 1954vs and 1873vs cm^{-1}) which also only exhibited one cyclopentadienyl proton resonance in the proton NMR spectrum. It therefore appears that the corresponding tungsten and molybdenum compounds exist in different isomeric forms. This is further supported by two facts: (1) the tungsten compound in the solid state decomposes slowly in air while the molybdenum compounds appears to be indefinitely stable in air and (2) $[Mo(CO)_2(C_5H_5)(CH_3S)]_2$ exists as a mixture of stereoisomers [3] (see Table 1). An alternative explanation [3] for the difference may be that the tungsten compound is a trinuclear compound, $[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_3$. Indirect support for this suggestion is forthcoming from more recent work by Haines [10] in which $[Fe(CO)_2(C_5H_5)]_2$ is converted into binuclear and trinuclear compounds upon reaction with dialkyl and diaryl disulfides.

The stable and unstable isomers of $[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ were prepared according to a literature method [2] and separated by column chromatography.

The well characterized binuclear sulfur-bridged compounds $[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$, $[Mo(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ and $[W(CO)_2(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$ all reacted slowly with carbon monoxide at room temperature in THF solvent and much more rapidly when heated at reflux. The molybdenum complex, which is itself formed by the facile loss of carbon monoxide at ambient temperature, showed the greater tendency to dissociated and pick up carbon monoxide to form the mononuclear product (> 95%). Under similar conditions the tungsten compound yielded ca. 50% of the mononuclear product, the remaining material being starting material.

The observed solvent dependence of the above reactions with carbon monoxide may be accounted for by a number of variations of a proposed mechanism that is outlined in Scheme 1. The initial step represents uptake of a THF molecule and concomitant cleavage of one of the sulfur bridges. Since in neither of the iron, molybdenum or tungsten compounds is there a formal metal—metal bond, the second step, the cleavage of the remaining sulfur bridge can be accomplished easily.

SCHEME 1



The reactions of carbon monoxide with the stable, unstable and mixture of stable and unstable isomers of $[Fe(CO)(C_5H_5)(p\text{-}CH_3C_6H_4S)]_2$, respectively (see Experimental Section), clearly indicate that under these conditions the unstable isomer is not unstable in the sense implied by Knox [2] and coworkers, but instead there is an equilibrium between the two isomers in solution. The equilibrium does favor the *cis*-I isomer.

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