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NOTE

SULFUR DIOXIDE INSERTION
X*. STUDIES ON CYCLOPENTADIENYLMOLYBDENUM AND -TUNGSTEN SULFINATO CARBONYL COMPLEXES

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It was demonstrated earlier in these laboratories that cyclopentadienylalkyliron dicarbonyls, $C_5H_5Fe(CO)_2R$, undergo sulfur dioxide insertion reactions yielding the corresponding sulfinates[1]. Since methyl- and ethyl(cyclopentadienyl)molybdenum tricarbonyls, like $C_5H_5Fe(CO)_2R$[2,3], readily react with tertiary phosphines (PR_3) and phosphites ($P(OR)_3$) to give carbon monoxide insertion products, $C_5H_5Mo(CO)_2(PR_3)(COR')$ and $C_5H_5Mo(CO)_2[P(OR)_3](COR')$ ($R'=CH_3$ and C_2H_5)[4-6], respectively, it appeared of interest to examine the reaction of $C_5H_5Mo(CO)_3R$ and of the analogous tungsten alkyls with SO_2. Reported here are the results of our investigation.

The complexes $C_5H_5Mo(CO)_3R$ ($R=CH_3$, C_2H_5, and $CH_2C_6H_5$) react readily with refluxing SO_2 to afford golden and yellow crystalline products analyzing for $C_5H_5Mo(CO)_3R \cdot SO_2$ (Table 1). These derivatives are reasonably stable to air

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR CYCLOPENTADIENYLMOLYBDENUM SULFINATOCARBONYLS

Compound	Color	M.p. (°C)[a]	Analyses, found (calcd.) (%)			
			C	H	S	Mo
$C_5H_5Mo(CO)_3SO_2CH_3$[b]	Golden	138 dec.	33.21 (33.30)	2.69 (2.47)	9.57 (9.88)	29.42 (29.60)
$C_5H_5Mo(CO)_3SO_2C_2H_5$	Yellow	131–134 dec.	35.2 (35.5)	3.18 (2.98)		
$C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$	Yellow	122–125 dec.	44.9 (45.0)	2.97 (3.02)		
$C_5H_5Mo(CO)_2[P(C_6H_5)_3]SO_2CH_3$	Yellow	165	54.9 (55.9)	4.0 (4.1)		

[a] Uncorrected. [b] Mol. wt. found [osmometry, (*ca.* 0.01 *M* $CHCl_3$ solution) with a Mechrolab Model 301-A instrument]: 336; calcd.: 324.

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* For part IX see ref. 17.

TABLE 2

IR AND PMR SPECTRA OF CYCLOPENTADIENYLMOLYBDENUM SULFINATOCARBONYLS

Compound	IR spectrum (cm^{-1})[a]		PMR spectrum[d]		
	CO stretches[b]	SO stretches[c]	Chem. shift (τ)	Rel. intens.	Assignment
$C_5H_5Mo(CO)_3SO_2CH_3$	2058 vs, 1975 vs (br)	1190 s, 1051 s	6.71 s	3	CH_3
			4.06 s	5	C_5H_5
$C_5H_5Mo(CO)_3SO_2C_2H_5$	2056 vs, 1985 vs (br)	1171 s, 1038 s	8.75 t[e]	3	CH_3
			6.88 q[e]	2	CH_2
			4.25 s	5	C_5H_5
$C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$	2056 vs, 1996 vs, 1973 vs	1191 s, 1041 s	5.75 s	2	CH_2
			4.38 s	5	C_5H_5
			2.65 [f]	5	C_6H_5
$C_5H_5Mo(CO)_2[P(C_6H_5)_3]SO_2CH_3$	1982 m, 1901 vs	1170 s, 1042 s	6.78 [g]	3	CH_3
			4.65 [g]	5	C_5H_5
			2.42 [f]	15	C_6H_5

[a] Recorded on a Perkin-Elmer Model 337 spectrophotometer. [b] $CHCl_3$ solution. [c] Nujol mull. [d] Recorded in $CDCl_3$ solution on a Varian Associates A-60 spectrometer using TMS as a reference; s: singlet; t: triplet; q: quartet. [e] $J=7.5$ Hz. [f] Complex pattern. [g] Apparent singlet, insufficient resolution to discern any splitting.

in the solid; however, their solutions in organic solvents show signs of decomposition after storage for *ca.* 1 h. On the basis of the observed positions of the CO and SO IR stretching frequencies and the ^1H NMR signals, listed in Table 2, and their similarity to the corresponding absorptions in the spectra of $C_5H_5Fe(CO)_2SO_2R$[1], these complexes are assigned *S*-sulfinato structures. No reaction was observed between $C_5H_5Mo(CO)_3CF_3$ and liquid sulfur dioxide; this behavior is consistent with lack of reactivity of other perfluoroalkyl and -aryl compounds toward SO_2, reported earlier[1,7].

Methyl- and benzylcyclopentadienyltungsten tricarbonyls are substantially less reactive toward SO_2 than their molybdenum counterparts. The methyl compound afforded after 6 h at −10° only a trace quantity of what is undoubtedly (from the IR spectral data) $C_5H_5W(CO)_3SO_2CH_3$; the benzyl compound did not yield any detectable sulfinate after 48 h at −10°. These results therefore parallel a much lower reactivity of $C_5H_5W(CO)_3CH_3$ compared to $C_5H_5Mo(CO)_3CH_3$ toward $P(C_6H_5)_3$[5].

Several other synthetic approaches to $C_5H_5Mo(CO)_3SO_2CH_3$ proved unsuccessful. The reactions of $Na[C_5H_5Mo(CO)_3]$ with CH_3SO_2Cl and with CH_3SO_2F yielded $C_5H_5Mo(CO)_3Cl$ and $[C_5H_5Mo(CO)_3]_2$, respectively, but none of the desired sulfinate. There was no detectable reaction between $[C_5H_5Mo(CO)_3]_2$ and CH_3SO_2Cl. The interaction between $C_5H_5Mo(CO)_3H$ and CH_3SO_2Cl afforded mainly $C_5H_5Mo(CO)_3Cl$ and only a trace of $C_5H_5Mo(CO)_3SO_2CH_3$, rendering this method highly impractical for synthesis of the sulfinates.

Treichel and coworkers have reported that $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$[3], but not the molybdenum analog $C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$[5], undergoes carbon monoxide insertion in solution. Since studies in these laboratories have shown that the iron complex inserts also SO_2 to give $C_5H_5Fe(CO)[P(C_6H_5)_3]SO_2CH_3$[8], it appeared of interest to ascertain whether lack of reactivity toward CO of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$ extends also to SO_2 insertion.

The reaction of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$ with liquid sulfur dioxide and with chloroform solutions of SO_2 affords good yields of the corresponding sulfinate. The rate of insertion in $CHCl_3$ is particularly striking, the formation of the product being virtually complete in 10 min at 27°. This stands out in sharp contrast to the failure of the complex to undergo reaction with CO in refluxing tetrahydrofuran in 48 h[5]. It is of further interest that the NMR spectra of the parent methyl compound and of the resulting sulfinate each showed only one cyclopentadienyl proton signal. On the basis of the data presented in the literature[9-11] it is inferred that a single isomer prevails exclusively or almost exclusively for both of the dicarbonyls. The relative intensities of the two IR carbonyl stretching bands (which are time-independent) suggest that the species present have a *trans* configuration of $P(C_6H_5)_3$ and CH_3 or SO_2CH_3[10]. Although such *trans* stereoisomers have been reported to exhibit resonances due to the cyclopentadienyl protons as 1/1 doublets ($J=1$–2 Hz)[9-11], our resolution may have been insufficient to separate the two peaks.

No successful desulfurylation of $C_5H_5Fe(CO)_2SO_2R$ has yet been reported. Inasmuch as $C_5H_5Mo(CO)_3(COR)$ can be decarbonylated much more readily than the corresponding $C_5H_5Fe(CO)_2(COR)$ derivatives[12], we set out to examine the possibility of a photolytic desulfurylation of cyclopentadienylsulfinatomolybdenum tricarbonyls.

The α-toluenesulfinate, $C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$, loses SO_2 when irradiated in benzene solution to give a 35% yield of $C_5H_5Mo(CO)_3CH_2C_6H_5$; the corresponding methanesulfinate affords only $[C_5H_5Mo(CO)_3]_2$ under comparable conditions. The former compound thus becomes the first transition metal sulfinate which undergoes both SO_2 insertion and desulfurylation, albeit not reversibly. The only cases of reversible reaction of metal alkyl (aryl) compounds with SO_2 have been reported recently by Deacon and Felder[13] for $(C_6H_5)_2Hg$ and $(p\text{-}C_6H_4CH_3)_2Hg$. We can provide no satisfactory explanation for the observed reactivity pattern with respect to desulfurylation at present.

EXPERIMENTAL

Anhydrous grade sulfur dioxide, from Matheson, was passed through concentrated H_2SO_4 and a P_4O_{10}-$CaCl_2$ column before condensation. CH_3SO_2Cl and CH_3SO_2F were purchased from Eastman Organic Chemicals and used as received. Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Technical grade pentane was used without further purification. All other solvents were of reagent grade or equivalent. Ventron alumina (neutral, grade III) and Florisil were employed in chromatography.

Most of the cyclopentadienylmolybdenum and -tungsten tricarbonyl complexes were synthesized by procedures reported in the literature for $[C_5H_5Mo(CO)_3]_2$[14], $Na[C_5H_5Mo(CO)_3]$[14], $C_5H_5Mo(CO)_3H$[15], $C_5H_5Mo(CO)_3CH_3$[15], $C_5H_5Mo(CO)_3C_2H_5$[15], $C_5H_5Mo(CO)_3CH_2C_6H_5$[16], $C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$[5], and $C_5H_5W(CO)_3CH_3$[15]; $C_5H_5Mo(CO)_3CF_3$ was a gift from Professor R. B. King. The hitherto unreported $C_5H_5W(CO)_3CH_2C_6H_5$ was prepared analogously to $C_5H_5W(CO)_3CH_3$; it was characterized by IR spectroscopy (ν(CO) at 2018 vs, 1936 vs, and 1926 vs cm^{-1}, cyclohexane solution).

Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Mr. P. J. Kovi in these laboratories using a Coleman Model 29 analyzer. Sulfur and molybdenum were determined by Galbraith.

Synthesis of sulfinato complexes by SO_2 insertion

The reactions of cyclopentadienylalkylmolybdenum carbonyl complexes with liquid SO_2 were carried out in a manner analogous to that employed previously for other alkyl metal carbonyls[1,7,17]. In general SO_2 solutions of the parent complexes were allowed to reflux for 2–6 h (although reactions may have reached completion in a much shorter time), excess sulfur dioxide was removed, the residue was dissolved in chloroform, and the resulting solution was filtered and chromatographed on alumina or Florisil eluting with chloroform or acetone. Slow addition of pentane to the eluate afforded crystalline products in 72–85% yields.

The sulfinate $C_5H_5Mo(CO)_2[P(C_6H_5)_3]SO_2CH_3$ may be also prepared by bubbling SO_2 into a solution of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$ (~0.5 g) in $CHCl_3$ (50 ml) at 27°. The reaction is virtually complete in 10 min; after chromatography on alumina using $CHCl_3$ eluent, 0.48 g (80%) of the sulfinate is obtained upon addition of pentane to the eluate.

The reaction of $C_5H_5W(CO)_3CH_3$ with refluxing SO_2 for 6 h afforded a trace amount of an orange solid which showed IR CO stretching bands at 2048 vs and 1953 vs (br) cm^{-1} and SO stretching bands at 1190 m and 1056 m cm^{-1} (CH_2Cl_2 solution). Insufficient amount of this material, presumably $C_5H_5W(CO)_3SO_2CH_3$, precluded its complete characterization. No apparent reaction occurred when SO_2 solutions of $C_5H_5W(CO)_3CH_2C_6H_5$ and $C_5H_5Mo(CO)_3CF_3$ were maintained at −10° for 48 h and at −40° for 168 h, respectively.

Reaction of $C_5H_5Mo(CO)_3H$ and CH_3SO_2Cl

A solution of $C_5H_5Mo(CO)_3H$ (1 g, 4 mmoles) and CH_3SO_2Cl (0.46 g, 4 mmoles) in 30 ml of tetrahydrofuran was stirred under nitrogen for 30 min at 27°. Solvent was then removed and the residue was dissolved in chloroform; chromatography on alumina eluting with $CHCl_3$ yielded, in the indicated order, 0.01 g of $[C_5H_5Mo(CO)_3]_2$, 0.9 g of $C_5H_5Mo(CO)_3Cl$[15], and 0.01 g (1%) of $C_5H_5Mo(CO)_3$-SO_2CH_3.

Reactions of $Na[C_5H_5Mo(CO)_3]$ with CH_3SO_2X (X=Cl and F)

A tetrahydrofuran solution (60 ml) of $Na[C_5H_5Mo(CO)_3]$, prepared from 4.90 (0.01 mole) of $[C_5H_5Mo(CO)_3]_2$ and excess 1% sodium amalgam, was added dropwise, with stirring, and under nitrogen to 2.30 g (0.02 mole) of CH_3SO_2Cl. Removal of the solvent, dissolution of the residue in $CHCl_3$, and chromatography of the resulting solution on alumina eluting with $CHCl_3$, afforded 3.0 g of $C_5H_5Mo(CO)_3Cl$.

When CH_3SO_2F was substituted for CH_3SO_2Cl, there was considerable effervescence accompanied by deposition of a brown-black noncarbonyl solid. The only carbonyl isolated after filtration and removal of the solvent was $[C_5H_5Mo$-$(CO)_3]_2$.

Attempted reaction of $[C_5H_5Mo(CO)_3]_2$ *with* CH_3SO_2Cl

After 1 g (2 mmoles) of $[C_5H_5Mo(CO)_3]_2$ and 0.23 g (2 mmoles) of CH_3SO_2Cl in 50 ml of tetrahydrofuran had been allowed to react under nitrogen and with stirring for 24 h at 27°, the only carbonyl isolated was unreacted $[C_5H_5Mo(CO)_3]_2$ (0.97 g).

Irradiation of $C_5H_5Mo(CO)_3SO_2R$ ($R{=}CH_2C_6H_5$ *and* CH_3)

A benzene solution (200 ml) of $C_5H_5Mo(CO)_3SO_2CH_2C_6H_5$ (0.6 g) was irradiated at *ca.* 27° for 30 min using photochemical equipment described previously[1]. Solvent was then removed, the residue extracted with CH_2Cl_2, and the extract filtered and evaporated to dryness. The remaining solid was extracted with ether and the insoluble unreacted sulfinate (0.1 g) was collected on a filter. Concentration of the filtrate and cooling at *ca.* −78° afforded 0.15 g (35%) of $C_5H_5Mo(CO)_3CH_2C_6H_5$.

Irradiation of $C_5H_5Mo(CO)_3SO_2CH_3$ under comparable experimental conditions yielded $[C_5H_5Mo(CO)_3]_2$ as the only carbonyl-containing product.

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REFERENCES

1 J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 88 (1966) 4862.
2 J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, 5 (1966) 889.
3 P. M. Treichel, R. L. Schubkin, K. W. Barnett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.
4 I. S. Butler, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 6 (1967) 2074.
5 K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, 6 (1967) 294.
6 P. J. Craig and M. Green, *J. Chem. Soc., A*, (1968) 1978.
7 F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, 7 (1968) 1504.
8 M. Graziani and A. Wojcicki, to be submitted for publication.
9 R. B. King, *Inorg. Chem.*, 2 (1963) 936.
10 A. R. Manning, *J. Chem. Soc., A*, (1967) 1984.
11 R. B. King and K. H. Pannell, *Inorg. Chem.*, 7 (1968) 2356.
12 R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2 (1964) 15.
13 G. B. Deacon and P. W. Felder, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 645.
14 R. G. Hayter, *Inorg. Chem.*, 2 (1963) 1031.
15 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
16 R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, 88 (1966) 709.
17 P. J. Pollick, J. P. Bibler and A. Wojcicki, *J. Organometal. Chem.*, 16 (1969) 201.