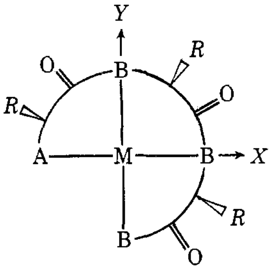
Group	Symmetry	Perturbation
Bridging atoms (β)	C_{2v} (X′)	$\sum_\beta Q_\beta\left[\frac{1}{\sqrt{2}}(X_\beta - Y_\beta)R_\beta^{-3} + (X_\beta Y_\beta)R_\beta^{-5}\right]$
Substituents (γ)	C_2 (X′)	$\sum_\gamma Q_\gamma\left[\frac{1}{\sqrt{2}}(X_\gamma - Y_\gamma)R_\gamma^{-3} + (X_\gamma Y_\gamma)R_\gamma^{-5} + Z_\gamma(X_\gamma^2 - Y_\gamma^2) \times R_\gamma^{-7} + \frac{1}{\sqrt{2}}(X_\gamma Z_\gamma + Y_\gamma Z_\gamma)R_\gamma^{-5}\right]$

Sector rule: $\sum_\alpha\sum_\gamma Q_\alpha Q_\gamma X_\alpha Y_\alpha Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\alpha^{-5}R_\gamma^{-7} + \sum_\beta\sum_\gamma Q_\beta Q_\gamma X_\beta Y_\beta Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\beta^{-5}R_\gamma^{-7}$

4. MAB$_3$



planar chelate rings

Group	Symmetry	Perturbation
MAB$_3$ (α)	C_{2v} (X)	$\sum_\alpha Q_\alpha[X_\alpha R_\alpha^{-3} + (X_\alpha^2 - Y_\alpha^2) \times R_\alpha^{-5} + X_\alpha(Y_\alpha^2 - Z_\alpha^2)R_\alpha^{-7}]$
Bridging atoms (β)	C_s (σ_{xy})	$\sum_\beta Q_\beta[X_\beta R_\beta^{-3} + Y_\beta R_\beta^{-3} + (X_\beta Y_\beta)R_\beta^{-5} + (X_\beta^2 - Y_\beta^2) \times R_\beta^{-5} + X_\beta(Y_\beta^2 - Z_\beta^2)R_\beta^{-7} + Y_\beta(Z_\beta^2 - X_\beta^2)R_\beta^{-7}]$
Substituents (γ)	C_1	All terms in expansion

Sector rule: $\sum_\alpha\sum_\gamma Q_\alpha Q_\gamma[Y_\gamma Z_\gamma X_\alpha(Y_\alpha^2 - Z_\alpha^2)R_\alpha^{-7} \times R_\gamma^{-5} + X_\gamma Y_\gamma Z_\gamma(X_\alpha^2 - Y_\alpha^2)R_\alpha^{-5}R_\gamma^{-7} + X_\alpha Y_\gamma Z_\gamma(Y_\gamma^2 - Z_\gamma^2)R_\alpha^{-3}R_\gamma^{-9}] + \sum_\beta\sum_\gamma[X_\gamma Z_\gamma Y_\beta \times (Z_\beta^2 - X_\beta^2)R_\beta^{-7}R_\gamma^{-5} + Y_\gamma Z_\gamma X_\beta(Y_\beta^2 - Z_\beta^2) \times R_\beta^{-7}R_\gamma^{-6} + X_\gamma Y_\gamma Z_\gamma(X_\beta^2 - Y_\beta^2)R_\beta^{-5}R_\gamma^{-7} + X_\beta Y_\beta Z_\gamma(X_\gamma^2 - Y_\gamma^2)R_\beta^{-5}R_\gamma^{-7} + Y_\beta X_\gamma Z_\gamma \times (Z_\gamma^2 - X_\gamma^2)R_\beta^{-3}R_\gamma^{-9} + X_\beta Y_\gamma Z_\gamma \times (Y_\gamma^2 - Z_\gamma^2)R_\beta^{-3}R_\gamma^{-9}]$

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Sulfur Dioxide Insertion. XV. Transition Metal–Vinyl Complexes Containing a Sultine Ring[1,2]

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Transition metal–2-alkynyl complexes react with liquid sulfur dioxide or with SO_2 in solution to form the corresponding vinyl derivatives containing a sultine ring, $M\overline{C{=}C(R)S(O)OC}H_2$. Prepared in this manner were $Mn(CO)_5(C_3H_2RSO_2)$ (R = H, CH_3), π-$C_5H_5Fe(CO)_2(C_3H_2RSO_2)$ (R = H, CH_3, C_6H_5), π-$C_5H_5Mo(CO)_3(C_3H_2RSO_2)$ (R = H, CH_3, C_6H_5), π-$C_5H_5Mo(CO)_2$-$[P(OC_6H_5)_3](C_4H_5SO_2)$, and the bimetallic π-$C_5H_5M(CO)_x(C_3H_2SO_2)CH_2M(CO)_x(\pi$-$C_5H_5)$ (M = Fe, x = 2; M = Mo, x = 3). The infrared and ^1H nmr spectra of these compounds are presented and compared with those of the organic sultines. The manganese and iron complexes $Mn(CO)_5(C_3H_3SO_2)$ and π-$C_5H_5Fe(CO)_2(C_4H_5SO_2)$ lose SO_2 when heated *in vacuo* or treated with alumina, respectively, and revert to the parent alkynyls. Although 2-alkynyl-*S*-sulfinates are not accessible from the corresponding metal alkynyls and SO_2, one representative of this classs, π-$C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3)$, was synthesized by reaction of π-$C_5H_5Fe(CO)_2^-$ with SO_2, followed by addition of $BrCH_2C{\equiv}CCH_3$. Plausible mechanisms of these and related reactions of SO_2 are considered.

Introduction

Reactions between sulfur dioxide and transition metal–2-alkenyl complexes proceed with the formation of the corresponding *S*-sulfinates which often contain a rearranged allylic moiety[3] (eq 1). In order to ascertain

$$MCH_2CH{=}C(R)(R') + SO_2 \longrightarrow MSO_2C(R)(R')CH{=}CH_2 \quad (1)$$

whether a similar rearrangement to give allenylsulfinato complexes occurs with 2-alkynylmetal derivatives, we examined reactions of the latter with SO_2. Preliminary results of these studies have already been communicated;[4] at that time the products were formulated as possessing an allenyl(oxy)sulfinyl linkage, $MS(O)OC(R){=}C{=}CH_2$. Later, investigations on such reactions were extended to other 2-alkynyls by Roustan and Charrier,[5] who designated the products as allenyl-*O*-sulfinates, $MOS(O)C(R){=}C{=}CH_2$. As our studies on these systems expanded in scope, it became evident

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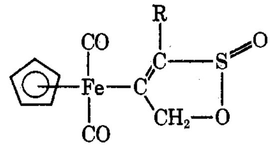
TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF ALKYNYL COMPLEXES

Compound	Analysis, % C Calcd	C Found	H Calcd	H Found	Mn Calcd	Mn Found	Mol wt Calcd	Mol wt Found	Mp (dec),[a] °C	Color	Yield, %
$Mn(CO)_5CH_2{\equiv}CH$		*b*			23.5	23.4	234	241	*c*	Light yellow	90
$Mn(CO)_5CH_2C{\equiv}CCH_3$		*b*					248	275	~14	Light yellow	55
π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$	57.4	56.6	4.4	4.3					46–48	Yellow	50
π-$C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3$	59.0	58.8	4.9	4.7					*d*	Red	60
π-$C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3$	48.3	48.3	3.4	3.4			298	283	93	Yellow	71
π-$C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_2Mo(CO)_3(\pi$-$C_5H_5)$	44.3	43.8	2.6	2.5					*d*	Yellow	81
π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3$	60.0	59.7	4.6	4.1					104–106	Yellow	60
π-$C_5H_5Mo(CO)_3CH_2CN$	42.1	41.9	2.4	2.3			285	288	109	Yellow	70

[a] Measured in capillaries and uncorrected. [b] Compound too unstable for commercial C and H analyses. [c] Decomposes rapidly at 35°. [d] Not determined.

that neither of the above nor the corresponding alkynyl formulations are entirely compatible with the proton nmr data amassed for a variety of such SO_2-containing complexes. For instance, allenic moieties such as $MS(O)OCH{=}C{=}CH_2$ or $MOS(O)CH{=}C{=}CH_2$ should exhibit a characteristic $J_{\alpha\gamma}$ of 6.1–7.0 Hz,[6] rather than $J = 2.5$ Hz, observed for the compounds in question. The alternative bonding schemes—acetylenic $MS(O)OCH_2C{\equiv}CH$ or $MOS(O)CH_2C{\equiv}CH$—are compatible with the experimental values of J; however, the chemical shifts of the unique proton (τ 3.5–3.6) are significantly lower than those reported for a variety of $-C{\equiv}CH$ species (*ca.* τ 7.5).[7] The above noted inconsistencies prompted an X-ray crystallographic examination of π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3 \cdot SO_2$ which revealed[8] a novel metal–vinyl structure involving a sultine ring (I, R = CH_3). Reported here in detail is our complete investigation on the synthesis and properties of this and other related compounds.



I

Experimental Section

General Procedures and Measurements.—A nitrogen atmosphere was used routinely for reactions of metal carbonyl anions, as well as all other reactions that required temperatures above 25°. All photochemical reactions were carried out with a Hanovia 450-W high-pressure quartz mercury vapor lamp, Model 679 A-36, as described previously.[9] Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer or, wherever specified, on a Beckman Model IR-9 spectrophotometer. Hydrogen-1 nmr spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as a reference. Molecular weight measurements were made on *ca.* 1×10^{-2} *M* $CHCl_3$ solutions with a Mechrolab Model 301-A osmometer. Elemental analyses (except Mn) were by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn. Manganese was determined[10] in this laboratory.

Materials.—Propargyl bromide and chloroacetonitrile were purchased from Aldrich Chemical Co. 1,4-Dichloro-2-butyne was obtained from Farchan Research Laboratories, Willoughby, Ohio. 1-Chloro-2-butyne[11] and 1-bromo-2-butyne[12] were prepared from 2-butyne-1-ol (Farchan) as described in the literature. 1-Phenyl-3-bromo-1-propyne and 5-chloro-2-pentyne were synthesized from the corresponding alcohols (Farchan) by using similar procedures.

Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a P_4O_{10}–$CaCl_2$ column before condensation in a trap at *ca.* −75°. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. All other chemicals and solvents were reagent grade or equivalent. Ventron alumina (neutral, grade III unless otherwise noted) was employed in chromatographic separations and purifications.

The carbonylates $Mn(CO)_5^-$,[13] π-$C_5H_5Fe(CO)_2^-$,[14] π-$C_5H_5Mo(CO)_3^-$,[15] and π-$C_5H_5Mo(CO)_2P(OC_6H_5)_3^-$ [16] were prepared by procedures described in the literature. They were used immediately in subsequent synthetic steps. The organoiron compounds π-$C_5H_5Fe(CO)_2CH{=}C{=}CH_2$,[17,18] π-$C_5H_5Fe(CO_2)CH{=}C{=}CHCH_3$,[19] π-$C_5H_5Fe(CO)_2C{\equiv}CCH_3$,[17] π-$C_5H_5Fe(CO)_2CH{=}CH_2$,[14] and π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\pi$-$C_5H_5)$[20] were prepared according to the literature methods.

Preparation of Alkynyl Complexes.—Two representative examples are described below. Analytical data and physical properties of new complexes are given in Table I.

(a) **$Mn(CO)_5CH_2C{\equiv}CH$.**—A solution of $NaMn(CO)_5$ in 75 ml of THF, prepared from 2 g (0.005 mol) of $Mn_2(CO)_{10}$ and excess sodium amalgam, was added dropwise and with stirring to 1.5 g (0.013 mol) of propargyl bromide in 15 ml of THF at 0°. Following the addition, the mixture was stirred for 1 hr (1.5 hr total) and the solvent was removed under reduced pressure (~10 mm) at 0°. The residue was then sublimed at 25° (0.1 mm) onto a probe cooled to −78° to yield 2.26 g (90%) of a light yellow, crystalline solid. The product is quite unstable at room temperature and decomposes rapidly at 35°. However, it can be stored almost indefinitely at −78° and appears to be unaffected by air.

The rate of addition of $NaMn(CO)_5$ to $BrCH_2C{\equiv}CH$ is very critical; if it is added all at once, only $Mn_2(CO)_{10}$ can be isolated from the reaction mixture. Further, the reverse of the above addition, *i.e.*, $BrCH_2C{\equiv}CH$ to $NaMn(CO)_5$, also results in the formation of $Mn_2(CO)_{10}$ instead of $Mn(CO)_5CH_2C{\equiv}CH$.

$Mn(CO)_5CH_2C{\equiv}CCH_3$ was synthesized by a similar procedure.

(b) **π-$C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3$.**—1-Bromo-2-butyne (1.2 g, 0.0090 mol) in 15 ml of THF was treated dropwise with a solution of $Na[\pi$-$C_5H_5Mo(CO)_3]$, prepared from 2.0 g of $[\pi$-$C_5H_5Mo(CO)_3]_2$ and 1% sodium amalgam in 75 ml of THF. The mixture was stirred for 3.5 hr and then filtered through a 3 × 5 cm column of Zeolite, and the solvent was removed *in vacuo* (20 mm) at 25°. The yellow-orange residue was extracted into 100 ml of pentane and the resulting solution was filtered. Concentration to 50 ml and cooling to −78° afforded 1.7 g (71%) of

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TABLE II

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF SO_2-CONTAINING COMPLEXES OF THE TYPES

$M\overline{C{=}C(R)S(O)OC}H_2$ AND $M'S(O)_2R'$

Compound		Analysis, % C		Analysis, % H		Analysis, % S		Mol wt		Mp (dec),[a] °C	Color	Synthetic procedure[b]	Yield, %
M	R	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found				
$Mn(CO)_5$	H	32.2	32.4	1.2	1.2	10.7	10.6	298	296	c	White	A	93
												B	96
$Mn(CO)_5$	CH_3	34.6	35.0	1.6	1.7	10.2	10.2	312	306	89	White	B	96
$\pi\text{-}C_5H_5Fe(CO)_2$	CH_3	44.9	44.7	3.4	3.5			294	285	136	Yellow	A	80
												B	91
$\pi\text{-}C_5H_5Fe(CO)_2$	C_6H_5	53.9	54.1	3.4	3.5					117–118	Yellow	A	47
$\pi\text{-}C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$	46.0	45.8	3.0	3.0	6.8	6.8			134–135	Yellow	A	52
$\pi\text{-}C_5H_5Mo(CO)_3$	H	37.9	38.4	2.3	2.2			348	361	c	Yellow	C	42
$\pi\text{-}C_5H_5Mo(CO)_3$	CH_3	39.8	39.8	2.8	3.0			362	364	151	Yellow	A	91
$\pi\text{-}C_5H_5Mo(CO)_3$	C_6H_5	48.1	48.0	2.8	2.9					118–119	Yellow	A	50
$\pi\text{-}C_5H_5Mo(CO)_3$	$CH_2Mo(CO)_3(\pi\text{-}C_5H_5)$	39.6	39.3	2.3	2.4					c	Yellow	A	40
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3		d							c	Yellow	A	55
M′	R′												
$\pi\text{-}C_5H_5Fe(CO)_2$	$CH_2CH_2C\equiv CCH_3$	46.7	45.8	3.9	3.8					144–145	Orange	B	40
$\pi\text{-}C_5H_5Fe(CO)_2$	$CH_2C\equiv CCH_3$	44.9	43.9	3.4	3.5					c	Yellow	C	17

[a] Measured in capillaries and uncorrected. [b] Procedures: A, alkynyl + SO_2 in solution; B, alkynyl + liquid SO_2; C, special (see Experimental Section). [c] Not determined. [d] Compound too unstable for commercial C and H analyses.

yellow crystals, which were collected on a filter and dried in a stream of nitrogen.

By employing similar procedures $\pi\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CCH_2Mo(CO)_3(\pi\text{-}C_5H_5)$, $\pi\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C\equiv CCH_3$, $\pi\text{-}C_5H_5Mo(CO)_3CH_2CN$, $\pi\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CCH_3$, $\pi\text{-}C_5H_5Fe(CO)_2CH_2CH_2C\equiv CCH_3$, and the previously reported $\pi\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CC_6H_5$[5] and $\pi\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$[19] were prepared. In the synthesis of $\pi\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CCH_2Mo(CO)_3(\pi\text{-}C_5H_5)$, $\pi\text{-}C_5H_5Fe(CO)_2CH_2CH_2C\equiv CCH_3$, $\pi\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$, and $\pi\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CC_6H_5$, the alkynyl halide was added to the metal carbonyl anion. $\pi\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CCH_3$ and $\pi\text{-}C_5H_5Mo(CO)_3CH_2CN$ were purified further by chromatography on alumina.

Reactions of Alkynyl Complexes with SO_2.—Representative methods of preparation of SO_2-containing compounds are described below. Analytical data and physical properties are given in Table II.

(a) **In Liquid SO_2.**—In a typical reaction, liquid SO_2 (10–20 ml) was condensed in a 50-ml round-bottom flask containing 1.0 g (0.0043 mol) of $Mn(CO)_5CH_2C\equiv CH$ and placed in a dewar flask at *ca.* −75°. After approximately 30 min (or longer in some cases) the flask was allowed to warm up to the reflux temperature (−10°) and excess solvent was removed. The residue was dissolved in 5 ml of $CHCl_3$, the solution was filtered, and 20 ml of cold pentane was added to the filtrate to yield 1.20 g (96%) of the product.

When liquid SO_2 at −10° was allowed to come in contact with $Mn(CO)_5CH_2C\equiv CH$, a violent reaction occurred with pyrolysis of most of the starting material. Dissolution of the residue in 5 ml of $CHCl_3$, filtration, and addition of 20 ml of cold pentane to the filtrate afforded (*ca.* 10%) the SO_2-containing product and a brown, oily decomposition material associated with thermolysis of $Mn(CO)_5CH_2C\equiv CH$.

(b) **In Solution.**—Sulfur dioxide was bubbled through a pentane solution (25 ml) of $\pi\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CCH_3$ (0.30 g, 0.0013 mol) at 25°. A yellow precipitate appeared almost immediately. The flow of gas was terminated after 5–30 min, and the solid was collected by filtration. After washing with pentane, 0.3 g (80%) of the product was obtained.

Alternatively, CH_2Cl_2 can be employed in place of pentane as the solvent for this reaction.

(c) ***Preparation of $\pi\text{-}C_5H_5Mo(CO)_3(C_3H_3SO_2)$.***—Because of the relative instability of the compound $\pi\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CH$ which impeded its isolation, the corresponding SO_2-containing product was prepared by the following procedure.

$Na[\pi\text{-}C_5H_5Mo(CO)_3]$, prepared by reduction of 2.0 g (0.0041 mol) of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in 75 ml of THF, was added dropwise to 1.2 g (0.010 mol) of $BrCH_2C\equiv CH$ under nitrogen. After stirring the resulting solution at 25° for 45 min, during which time it changed from dark green to yellow-green, the nitrogen inlet was removed and SO_2 was bubbled directly into the THF solution for 30 min. Excess THF was evaporated at 25° (20 mm) to afford an oily, red residue which was extracted into 10 ml of $CHCl_3$ and purified by chromatography on alumina. Elution with $CHCl_3$ gave a red band of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ followed by a yellow band of $\pi\text{-}C_5H_5Mo(CO)_3(C_3H_3SO_2)$. The solution from the yellow band was concentrated to 10 ml and cold pentane was added to yield 1.2 g (42%) of a crystalline material which decomposes slowly to a green solid even at 0°.

Preparation of $\pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2C\equiv CCH_3)$.—Sulfur dioxide (3 ml of liquid) was allowed to bubble slowly into a solution of $Na[\pi\text{-}C_5H_5Fe(CO)_2]$ (prepared from 5.0 g (0.014 mol) of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ in 75 ml of THF and freed from any excess sodium amalgam and mercury) contained in a three-neck round-bottom flask at −78°. After the addition of SO_2 was complete and the solution acquired a deep red color, 1-bromo-2-butyne (8 g, 0.06 mol) was introduced in one portion and the mixture was stirred magnetically for 1 hr under nitrogen. The contents of the flask were warmed to 25° and stirred for additional 30 min, and the solvent was removed. The residue was extracted with $CHCl_3$ (three 50-ml portions) and the combined extracts were filtered. The volume was reduced to 15 ml and the resultant solution chromatographed on a 5 × 40 cm alumina column. Elution with $CHCl_3$ afforded a red-brown band of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and excess 1-bromo-2-butyne, a narrow brown band which was not characterized, and a yellow band. The volume of the solution from the yellow band was reduced to 20 ml; addition of pentane (150 ml) with stirring yielded 1.4 g (17%) of a fluffy precipitate which was isolated by filtration.

Purification of SO_2-Containing Products.—The manganese complexes $Mn(CO)_5(C_3H_3SO_2)$ and $Mn(CO)_5(C_4H_5SO_2)$ were purified by sublimation at 75° (0.1 mm). The iron and molybdenum compounds can be readily recrystallized from CH_2Cl_2–pentane or $CHCl_3$–pentane. Some molybdenum derivatives, *e.g.*, $\pi\text{-}C_5H_5Mo(CO)_3(C_4H_5SO_2)$, were further purified by chromatography on alumina. However, our subsequent observation that the iron complex $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ desulfonylates on contact with alumina and reverts to the parent 2-alkynyl led to an abandonment of this method of purification.

Attempted Reactions of SO_2 with Other Metal–Carbon Bonded Complexes.—Solutions of $\pi\text{-}C_5H_5Fe(CO)_2CH{=}CH_2$, $\pi\text{-}C_5H_5Fe(CO)_2C\equiv CCH_3$, $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CH_2$, $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CHCH_3$, or $\pi\text{-}C_5H_5Mo(CO)_3CH_2CN$ in liquid SO_2 at reflux were stored for 12–48 hr. Evaporation of the solvent revealed (ir spectroscopy) no detectable amount of an SO_2-containing product in the residue of each compound. Reaction between SO_2 and $\pi\text{-}C_5H_5Fe(CO)_2C\equiv CCH_3$, $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CH_2$, or $\pi\text{-}C_5H_5Mo(CO)_3CH_2CN$ was also carried out in a glass pressure bottle at 25–30° for 24–48 hr; again no addition product could be detected. Further, $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CH_2$ did not react with SO_2 in $CHCl_3$ solution during 8 hr at 25°.

Desulfonylation of $Mn(CO)_5(C_3H_3SO_2)$.—Solid $Mn(CO)_5(C_3H_3SO_2)$ (0.5 g, 0.002 mol) in a sublimation apparatus was heated at 115° under vacuum (0.1 mm). After *ca.* 20 min, approximately 10% $Mn(CO)_5CH_2C\equiv CH$ (characterized by ir spectroscopy) along with unreacted $Mn(CO)_5(C_3H_3SO_2)$ collected on a probe cooled to −78°.

TABLE III

INFRARED SPECTRA OF ALKYNYL COMPLEXES IN THE 2000-CM^{-1} REGION

Compound	$\nu(CO)^g$	$\nu(C{\equiv}C)^g$
$Mn(CO)_5CH_2C{\equiv}CH^{a,b}$	2119 m, 2057 sh, 2023 vs, 1994 s	2099 w
$Mn(CO)_5CH_2C{\equiv}CCH_3^{a,b}$	2118 m, 2054 sh, 2035 vs, 1998 s	2216 vw
$\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3^c$	2025 vs, 1975 vs	
$\pi\text{-}C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3^d$	2005 vs, 1955 vs	
$\pi\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3^a$	2022 s, 1944 s, 1936 s	2206 vw
$\pi\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_2Mo(CO)_3(\pi\text{-}C_5H_5)^d$	2010 s, 1960 sh, 1925 vs, br, 1890 s, 1870 sh	
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3^e$	1961 s, 1883 vs	2200 vw
$\pi\text{-}C_5H_5Mo(CO)_3CH_2CN^a$	2046 s, 1963 s, 1952 s	2211 w[f]

[a] Cyclohexane solution. [b] Recorded on a Beckman Model IR-9 spectrophotometer. [c] Hexane solution. [d] Nujol mull. [e] Chloroform solution. [f] ν(CN). [g] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

Desulfonylation of $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$.—A CH_2Cl_2 solution (10 ml) of $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ (0.6 g, 0.002 mol) was introduced onto a 2 × 20 cm alumina (grade IV) column. Elution with CH_2Cl_2 gave a broad yellow band which was collected under nitrogen. Concentration of the solution to 10 ml in a stream of N_2 and addition of pentane yielded 0.3 g (50%) of the starting $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ which was collected on a filter. The filtrate was evaporated to dryness to give 0.2 g (40%) of $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$.

Thermal and Photolytic Treatment of $Mn(CO)_5(C_3H_3SO_2)$ and $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$.—When solutions of $Mn(CO)_5(C_3H_3SO_2)$ (*ca.* 0.5 g) in 50 ml of chlorobenzene, benzene, $CHCl_3$, or THF were heated at reflux for 6 hr, only noncarbonyl decomposition products and, in some cases ($CHCl_3$ and THF solvents), the unreacted material could be isolated. Irradiation for 8 hr at 25° of a benzene solution of $Mn(CO)_5(C_3H_3SO_2)$ with a 450-W Hanovia lamp resulted in recovery of *ca.* 90% starting compound.

Heating $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ solutions in chlorobenzene, THF, or $CHCl_3$ at reflux afforded the unreacted dicarbonyl and some decomposition material. A similar result was obtained by irradiating $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ in benzene. When solid $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ was heated at *ca.* 100° either *in vacuo* or under 1 atm of N_2, it sublimed unchanged.

Attempts at Replacement of CO in $Mn(CO)_5(C_3H_3SO_2)$ with Various Bases.—Irradiation with a 450-W-Hanovia lamp of a benzene solution (75 ml) of $Mn(CO)_5(C_3H_3SO_2)$ (0.5 g, 0.002 mol) and $P(C_6H_5)_3$ (2 g, 0.006 mol), first for 4 hr at 25° and then for 1 hr at 80°, followed by addition of CH_3I to precipitate $P(C_6H_5)_3CH_3{}^+I^-$ and cooling to −78°, resulted in recovery of 0.3 g (60%) of the starting carbonyl.

Similarly, reactions between $Mn(CO)_5(C_3H_3SO_2)$ and pyridine or 2,2′-bipyridine in THF or acetonitrile at reflux for 12–20 hr led to appreciable decomposition and isolation only of some unreacted pentacarbonyl.

Reaction of $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ with HCl.—HCl was bubbled slowly into a solution of $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ (0.2 g) in methanol (25 ml). Within *ca.* 30 min the solution turned dark red. After 4 hr solvent was removed and the resultant red oil dissolved in CH_2Cl_2 and purified by chromatography on alumina. The yield of $\pi\text{-}C_5H_5Fe(CO)_2Cl$, characterized by ir spectroscopy, was 0.03 g.

When HCl was bubbled into a CH_2Cl_2 solution of $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, almost an immediate color change to red was observed. After 30 min, the flow of the gas was discontinued and the reaction mixture was treated as described above. Approximately 45% $\pi\text{-}C_5H_5Fe(CO)_2Cl$ was isolated.

Results

Synthesis and Characterization of 2-Alkynyl Complexes.—All 2-alkynyl complexes employed in this study were synthesized by the reaction between the corresponding 1-halo-2-alkynes and the metal carbonyl anions. The mode of addition of the two reactants was found to be very critical in the preparation of $Mn(CO)_5CH_2C{\equiv}CH$. Introduction of $BrCH_2C{\equiv}CH$ to a solution of $NaMn(CO)_5$, rather than the reverse of this process, afforded $Mn_2(CO)_{10}$ instead of the desired product. It has not been ascertained whether any of the other reactions are also sensitive to the order of mixing of the reactants. Since both modes of addition have been tried successfully for different 2-alkynyl complexes, it is possible that only 2-propynylmetal derivatives, $MCH_2C{\equiv}CH$, are affected by this variation in the experimental procedure because of the presence of acidic hydrogen therein.

The stability of most of the $\pi\text{-}C_5H_5Fe(CO)_2CH_2{\equiv}CR$ and $\pi\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CR$ complexes is comparable with that of the corresponding alkylcarbonyls. $\pi\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CH$ manifests much lower stability, and no attempt was made at its isolation. The readily sublimable manganese alkynyls $Mn(CO)_5CH_2C{\equiv}CR$ (R = H and CH_3) are unstable thermally, decomposing above room temperature to brown oils whose infrared spectra indicate mixtures of several carbonyl-containing species. Similar materials resulted during an attempted replacement of the carbonyl groups in $Mn(CO)_5CH_2C{\equiv}CH$ with $P(C_6H_5)_3$ under either thermal or photolytic conditions over a reasonably extensive temperature range (0–34°).

Since reactions of metal carbonyl anions (M^-) with 1-halo-2-alkynyls are known to afford either the corresponding alkynyls[4] (eq 2) or the isomeric allenyls[18]

$$M^- + XCH_2C{\equiv}CR \longrightarrow MCH_2C{\equiv}CR + X^- \quad (2)$$

$$M^- + XCH_2C{\equiv}CR \longrightarrow MC(R){=}C{=}CH_2 + X^- \quad (3)$$

(eq 3), it was essential to establish the identity of the isolated products before proceeding with subsequent studies. Such characterization was readily achieved with the combined aid of infrared and ^1H nmr spectroscopy. Monosubstituted ($-C{\equiv}CH$) and disubstituted ($-C{\equiv}C-$) acetylenes display characteristic $\nu(C{\equiv}C)$ peaks at 2140–2100 and 2260–2190 cm^{-1}, respectively, whereas allenes show bands due to $\nu(C{=}C{=}C)$ at 1950 and 1060 cm^{-1}.[21] The infrared spectra of some complexes prepared in this study show weak absorptions attributable to $\nu(C{\equiv}C)$ (Table III); however, in a number of cases no bands were discernible in the above region. Moreover, the possibility of the alternative—allenyl—structure could not be readily ascertained because of the usual interference from the carbonyl stretching peaks around 1950 cm^{-1}.

Evidence for the alkynyl rather than allenyl linkages in those latter situations, as well as further support for such formulations in the former cases, was furnished by the ^1H nmr spectra. For a $-CH_2C{\equiv}CR$ moiety, α hydrogens are reported to absorb at τ 8–9,[7] whereas for a $-C(R){=}C{=}CH_2$ (R = H, alkyl, or aryl) fragment, α and γ hydrogens display signals in the region τ 5–6, with $J_{\alpha\gamma} \approx$ 6.1–7.0 Hz.[6] It may be seen readily from the data in Table IV that the spectra of all new complexes are consistent only with the alkynyl structural assign-

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[21] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 58–62.

TABLE IV

PROTON MAGNETIC RESONANCE SPECTRA OF ALKYNYL COMPLEXES (τ)[a]

Compound	Chem shift,[b] ppm	Rel intens	Assignment
$Mn(CO)_5CH_2C{\equiv}CH$	8.64 d (J = 3 Hz)	2	$-CH_2-$
	7.79 t (J = 3 Hz)	1	$\equiv CH$
$Mn(CO)_5CH_2C{\equiv}CCH_3$	8.64 q (J = 3 Hz)	2	$-CH_2-$
	8.18 t (J = 3 Hz)	3	$-CH_3$
π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$	8.4–8.0 cp	1	$-CH_2-$, $-CH_3$
	5.24 s	1	C_5H_5
π-$C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3$	8.12 s	1	$-CH_2$, $-CH_3$
	4.48 s	1	C_5H_5
π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3$	8.0 cp	1	$-CH_2-$, $-CH_3$
	4.99 d (J = 1.5 Hz)	0.67	C_5H_5
	4.88 s	0.33	
	2.5 cp	3	$-C_6H_5$
π-$C_5H_5Mo(CO)_3CH_2CN$	8.60 s	2	$-CH_2-$
	4.54 s	5	C_5H_5

[a] $CDCl_3$ solution. [b] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; cp, complex pattern.

TABLE V

INFRARED CO AND SO STRETCHING FREQUENCIES (cm^{-1}) OF SO_2-CONTAINING COMPLEXES

OF THE TYPES $M\overline{C{=}C(R)S(O)OC}H_2$ AND $M'S(O)_2R'$[a]

Compound		ν(CO)	ν(SO)
M	R		
$Mn(CO)_5$	H	2130 m, 2068 sh, 2035 vs, 2012 s[b,c]	1111 s, 906 ms[c]
$Mn(CO)_5$	CH_3	2130 m, 2068 sh, 2035 vs, 2014 s[b,c]	1105 s, 902 ms[c]
π-$C_5H_5Fe(CO)_2$	CH_3	2039 vs, 1983 vs	1100 s, br, 903 s
π-$C_5H_5Fe(CO)_2$	C_6H_5	2026 vs, 1972 vs	1108 vs, 899 ms[d]
π-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\pi$-$C_5H_5)$	2036 s, 2014 ms, 1981 s, 1959 ms	1094 s, 900 ms[d]
π-$C_5H_5Mo(CO)_3$	H	2042 s, 1970 s, 1950 s	1105 s, 906 ms
π-$C_5H_5Mo(CO)_3$	CH_3	2040 s, 1973 s, 1949 s	1110 s, 900 ms
π-$C_5H_5Mo(CO)_3$	C_6H_5	2031 s, 1964 s, 1944 s	1115 s, 895 ms[d]
π-$C_5H_5Mo(CO)_3$	$CH_2Mo(CO)_3(\pi$-$C_5H_5)$	2036 s, 2017 s, 1969 s, 1947 s, 1936 sh	1098 s, 893 ms[d]
π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	1977 s, 1900 vs	1100 s, 915–900 s, br
M′	R′		
π-$C_5H_5Fe(CO)_2$	$CH_2CH_2C{\equiv}CCH_3$	2069 vs, 2016 vs	1180 s, 1040 s[d]
π-$C_5H_5Fe(CO)_2$	$CH_2C{\equiv}CCH_3$	2062 vs, 2016 vs	1200 s, 1050 s

[a] ν(CO) and ν(SO) recorded using $CHCl_3$ solutions and KBr pellets, respectively, unless otherwise noted. For abbreviations see Table III. [b] CCl_4 solution. [c] Recorded on a Beckman Model IR-9 spectrophotometer. [d] Nujol mull.

ment. The remaining 2-alkynyl compounds used in this study were synthesized earlier and have all been satisfactorily characterized in a similar fashion.[5,19,20]

Synthesis and Characterization of Metal–Sultine Complexes.—Transition metal–2-alkynyl complexes referred to in the preceding section undergo a very facile reaction with either liquid SO_2 at *ca.* −75° or SO_2 in solution at 25° to yield crystalline materials analyzing as 1:1 compounds of the two reactants. Most of these SO_2-containing derivatives display a high degree of stability. For instance, $Mn(CO)_5(C_3H_2RSO_2)$ (R = H, CH_3) and π-$C_5H_5Fe(CO)_2(C_4H_5SO_2)$ can be sublimed without appreciable decomposition. Further, heating at reflux or irradiation of solutions of $Mn(CO)_5(C_3H_3SO_2)$ or π-$C_5H_5Fe(CO)_2(C_4H_5SO_2)$ in benzene, chlorobenzene, $CHCl_3$, or THF for several hours generally leads to recovery in good yield of the unreacted compound. The only unstable derivatives synthesized are π-$C_5H_5Mo(CO)_3(C_3H_3SO_2)$ and π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3](C_4H_5SO_2)$. The former compound decomposes on storage at 0°. The latter complex is even less stable and could not be characterized through elemental analyses. Its structure was inferred from the infrared spectrum in the CO and SO stretching regions (*vide infra*).

The salient features of the infrared and ^1H nmr spectra of all SO_2-containing complexes are presented in Tables V and VI, respectively. Particularly striking are the remarkable similarities among the SO stretching frequencies (Table V), as well as the chemical shifts and coupling constants in the region τ 4–5 (Table VI), in the spectra of the compounds obtained from the metal 2-alkynyls and SO_2. The molecular architecture of one representative of this group—π-$C_5H_5Fe(CO_2(C_4H_5SO_2)$ (I, R = CH_3)—has been recently shown by X-ray crystallography to involve a sultine ring and a metal–vinyl carbon bond.[8] Analogous structures are accordingly assigned to the other members. Included among them is that of the product from the reaction between π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3$ and SO_2. This result is noteworthy because it was observed earlier[22] that replacement of CO with P-donor ligands in transition metal σ-allyls promotes direct insertion of SO_2 at the expense of insertion with rearrangement. Evidently, for the metal 2-alkynyls such a direct insertion into the M–CH_2 bond is energetically much less favored than a process leading to the formation of a sultine complex.

The infrared spectra of the new metal–sultine complexes show SO stretching vibrations at 1115–1094 and 915–893 cm^{-1}. These are to be compared with ν(SO) for the organic sultines at 1149–1120 and *ca.* 940 cm^{-1}.[23,24] Similarly constituted transition metal *S*-sulfinates, on the other hand, display SO stretching bands at considerably higher frequencies—in the re-

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[22] D. A. Ross, Ph.D. Thesis, The Ohio State University, 1970.

[23] R. S. Henion, "Eastman Organic Chemical Bulletin," Vol. 41, No. 3, Eastman Kodak Co., Rochester, N. Y., 1969.

[24] D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969).

TABLE VI

PROTON MAGNETIC RESONANCE SPECTRA OF SO_2-CONTAINING COMPLEXES OF THE TYPES $\overline{MC{=}C(R)S(O)OCH_2}$ AND $M'S(O)_2R'$[a]

Compound		Chemical shift (τ), ppm		
M	R	$-CH_2O$[b-d]	R (R')[b,d]	M (M')
$Mn(CO)_5$	H	4.89, 4.47 (J_{AB} = 15 Hz; $J_{AX} = J_{BX}$ = 2.5 Hz)	H, 3.52 t (J = 2.5 Hz)	. . .
$Mn(CO)_5$	CH_3	4.87, 4.48 (J_{AB} = 15 Hz; $J_{AX} = J_{BX}$ = 2 Hz)	CH_3, 7.80 t (J = 2 Hz)	. . .
π-$C_5H_5Fe(CO)_2$	CH_3	4.81, 4.45 (J_{AB} = 14 Hz; $J_{AX} = J_{BX}$ = 2 Hz)	CH_3, 7.60 t (J = 2 Hz)	C_5H_5, 4.80 s
π-$C_5H_5Fe(CO)_2$	C_6H_5	4.83, 4.45 (J_{AB} = 15 Hz)	C_6H_5, 2.58 s	C_5H_5, 5.25 s
π-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\pi$-$C_5H_5)$	e	$FeCH_2$, 7.84, 7.36[f] (J_{AB} = 11 Hz) C_5H_5, 5.08 s or 5.03 s	C_5H_5, 5.08 s or 5.03 s
π-$C_5H_5Mo(CO)_3$	H	4.90, 4.52 (J_{AB} = 15 Hz; $J_{AX} = J_{BX}$ = 2.5 Hz)	H, 3.58 t (J = 2.5 Hz)	C_5H_5, 4.42 s
π-$C_5H_5Mo(CO)_3$	CH_3	4.94, 4.57 (J_{AB} = 14.5 Hz; $J_{AX} = J_{BX}$ = 2 Hz)	CH_3, 7.95 t (J = 2 Hz)	C_5H_5, 4.42 s
π-$C_5H_5Mo(CO)_3$	C_6H_5	4.76, 4.28 (J_{AB} = 15 Hz)	C_6H_5, 2.52 s	C_5H_5, 4.71 s
π-$C_5H_5Mo(CO)_3$	$CH_2Mo(CO)_3(\pi$-$C_5H_5)$	~4.7[g]	$MoCH_2$, ~8.0[h] C_5H_5, 4.48 s or 4.44 s	C_5H_5, 4.48 s or 4.44 s
M'	R'			
π-$C_5H_5Fe(CO)_2$	$CH_2CH_2C{\equiv}CCH_3$		CH_3, 8.08 t (J = 2.5 Hz) CCH_2C, 7.08 br SCH_2, 6.68 t (J = 8 Hz)	C_5H_5, 4.66 s
π-$C_5H_5Fe(CO)_2$	$CH_2C{\equiv}CCH_3$		CH_3, 8.13 t (J = 2.5 Hz) CH_2, 6.32 br	C_5H_5, 4.84 s

[a] $CDCl_3$ solution. [b] A and B refer to geminal protons. [c] X refers to protons on the α carbon of R. [d] Chemical shifts of nonequivalent CH_2 protons and values of J_{AB} were calculated as in L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Macmillan, New York, N. Y., 1959, pp 89–91. [e] Masked by signals of C_5H_5 protons. [f] A lopsided AB quartet (the two lower field components are broader). [g] Masked in part by signals of C_5H_5 protons. [h] A poorly resolved pattern, perhaps owing to low solubility of the compound in $CDCl_3$. For abbreviations see Table IV.

gions 1210–1170 and 1055–1035 cm^{-1}.[9,25,26] The carbonyl stretching absorptions for the metal–sultine complexes reported here are generally *ca.* 10–35 cm^{-1} lower than those for the corresponding *S*-sulfinates.[9,25,26] This is probably a consequence of considerable M=S π bonding in the latter systems.

A very significant feature in the ^1H nmr spectra of the metal–sultine complexes is magnetic nonequivalence of the $-OCH_2-$ protons. This effect is illustrated for $Mn(CO)_5(C_4H_5SO_2)$, whose nmr spectrum is reproduced in its entirety in Figure 1. A similar phenomenon has been noted for the organic sultines.[23] It may be ascribed to the diamagnetic anisotropy of the S=O bond which deshields the proton cis to the sulfinyl oxygen.[27] The difference in the chemical shift of the two methylene protons of τ 0.36–0.48 for the metal sultines is to be compared with the separation of τ 0.40–0.69 found for the corresponding organic molecules.[23] The geminal coupling constant, J_{AB}, for the former (14–15 Hz) is essentially equal to that found in the spectra of the latter compounds (~14 Hz).[24]

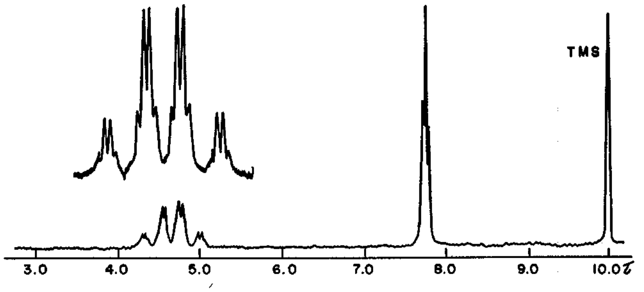
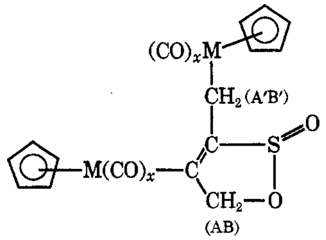


Figure 1.—The ^1H nmr spectrum of $Mn(CO)_5[\overline{C{=}C(CH_3)S(O)OCH_2}]$ in $CDCl_3$.

Dimetallic 2-alkynyl complexes of the type π-$C_5H_5M(CO)_xCH_2C{\equiv}CCH_2M(CO)_x(\pi$-$C_5H_5)$ (M = Fe, x = 2; M = Mo, x = 3) also undergo a facile reaction with SO_2 to yield the corresponding 1:1 derivatives. From their infrared and ^1H nmr spectra these products, too, are assigned metal–sultine structures (II, M = Fe, x = 2; M = Mo, x = 3). In addition to the spectral features strictly similar to those displayed by the monometallic sultines, these complexes show two C_5H_5 ^1H nmr signals, as well as magnetic nonequivalence of the other set of CH_2 protons (A'B' in II). The latter effect no doubt originates from the presence of the chiral sulfur in the heterocyclic ring.



II

The dimetallic sultines (II) combine structural features of metal–vinyl and metal–σ-allyl complexes. Since σ-allyls of π-$C_5H_5Mo(CO)_3$ and π-$C_5H_5Fe(CO)_2$ readily undergo SO_2 insertion,[3] it was of interest to ascertain whether the above sultines would behave similarly. However, after an SO_2 solution of II (M = Fe, x = 2) was maintained at reflux for 12 hr and the solvent was removed, only the unreacted compound could be detected by infrared spectroscopy.

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(25) F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968).

(26) M. Graziani, J. P. Bibler, M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 507 (1969).

(27) J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 2105 (1961).

In an attempt to elucidate whether the formation of sultines by SO_2 is limited to 2-alkynyl(transition metal) systems we examined reaction between a 3-alkynyl, $\pi\text{-}C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3$, and liquid SO_2 (eq 4).

$$\pi\text{-}C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3 + SO_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2CH_2C{\equiv}CCH_3) \quad (4)$$

The isolated product was that of direct insertion—an *S*-sulfinate, rather than a sultine. Furthermore, the 1-alkynyl $\pi\text{-}C_5H_5Fe(CO)_2C{\equiv}CCH_3$ failed to react with SO_2 in 24 hr at 25–30°. Finally, by using $\pi\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}N$ rather than the "isoelectronic" $\pi\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CH$ in conjunction with SO_2, no reaction could be effected even at 25–30° under pressure.

Since in no case has a transition metal–2-alkynyl complex reacted with SO_2 to yield a product of direct insertion, we proceeded to synthesize $\pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3)$ by an independent route. It was of interest to establish whether such an *S*-sulfinato complex would display any tendency toward rearrangement to the corresponding sultine.

The preparation of $\pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3)$ was effected utilizing a reaction discovered by Downs[28] (eq 5 and 6). The anion $\pi\text{-}C_5H_5Fe(CO)_2SO_2^-$,

$$\pi\text{-}C_5H_5Fe(CO)_2^- + SO_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2SO_2^- \quad (5)$$

$$\pi\text{-}C_5H_5Fe(CO)_2SO_2^- + BrCH_2C{\equiv}CCH_3 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3) + Br^- \quad (6)$$

characterized indirectly in previous work, was synthesized *in situ* and allowed to react with $BrCH_2C{\equiv}CCH_3$. The *S*-sulfinate was separated from other components of the crude reaction mixture by chromatography and isolated by precipitation and filtration. Refluxing its THF solution for 24 hr under nitrogen led to the recovery of the starting material; no trace of the corresponding sultine nor of any other tractable product could be detected. The reverse of this attempted isomerization, *i.e.*, $\pi\text{-}C_5H_5Fe(CO)_2\overline{C{=}C(CH_3)S(O)OCH_2} \rightarrow \pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3)$, has also been investigated by photolysis in benzene and by using chlorobenzene, THF, or $CHCl_3$ solutions at reflux. In no case was there any evidence for the formation of characterizable carbonyl products. A similar behavior was noted for $Mn(CO)_5\overline{C{=}CHS(O)OCH_2}$. Thus both the iron sultine and its isomeric *S*-sulfinate are thermodynamically stable species, their respective formation being attributable to kinetic factors.

In the context of the above described investigation it was of interest to ascertain whether other related metal–carbon systems undergo reaction with SO_2. Accordingly we examined solutions of the allenyl compounds $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CH_2$ and $\pi\text{-}C_5H_5Fe(CO)_2CH{=}C{=}CHCH_3$ in liquid SO_2 at −10 to +30° for 12–48 hr. No evidence of reaction other than decomposition to intractable solids could be obtained. The vinyl complex $\pi\text{-}C_5H_5Fe(CO)_2CH{=}CH_2$ behaved similarly. This latter unreactivity toward SO_2 is in agreement with the observed inability of the metal–sultine derivatives to undergo additional incorporation of SO_2 into their M—C(vinyl) bonds. In all cases, including that of $\pi\text{-}C_5H_5Fe(CO)_2C{\equiv}CCH_3$, the lack of reactivity may be best ascribed to the relatively strong M—C bonds in these compounds. This most likely results from the metal's participation in π bonding with the unsaturated σ-bonded hydrocarbon ligand.

Reactions of Metal–Sultine Complexes.—Preliminary studies on reactions of the metal–sultine complexes were directed at (a) removal of SO_2, or desulfonylation, and (b) replacement of CO with other ligands. These investigations were conducted on two compounds: $Mn(CO)_5(C_3H_3SO_2)$ and $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$.

When $Mn(CO)_5(C_3H_3SO_2)$ is heated *in vacuo* at 115°, extrusion of SO_2 takes place and the volatile alkynyl $Mn(CO)_5CH_2C{\equiv}CH$ may be collected in *ca.* 10% yield on a probe cooled to −78°. The iron sultine $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ sublimes without loss of SO_2 on heating at *ca.* 100°. However, when its solution in CH_2Cl_2 is passed through a chromatography column packed with neutral alumina (grade IV), considerable (~40%) desulfonylation occurs and both the unreacted material and the resultant $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ can be eluted off. Interestingly, the molybdenum sultines $\pi\text{-}C_5H_5Mo(CO)_3(C_3H_2RSO_2)$ (R = H and CH_3) do not lose SO_2 under these conditions.

Reaction of methanol solutions of $\pi\text{-}C_5H_5Fe(CO)_2(C_4H_5SO_2)$ with gaseous HCl proceeds to yield $\pi\text{-}C_5H_5Fe(CO)_2Cl$ as the only metal carbonyl. Since $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ affords very rapidly $\pi\text{-}C_5H_5Fe(CO)_2Cl$ when allowed to interact with HCl under similar conditions, it is likely that the former transformation involves desulfonylation (eq 7) followed by electrophilic cleavage of the Fe–CH_2 bond by HCl (eq 8).[29] As already noted above, the first step (eq 7)

$$\pi\text{-}C_5H_5Fe(CO)_2\overline{C{=}C(CH_3)S(O)OCH_2} \xrightarrow[\text{(or }Al_2O_3)]{HCl} \pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3 + SO_2 \quad (7)$$

$$\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3 + HCl \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2Cl + C_4H_6 \quad (8)$$

of this sequence is also catalyzed by alumina. However, a stronger acid such as HCl must be employed to effect the subsequent Fe–CH_2 bond scission.

All attempts at replacement of CO in $Mn(CO)_5(C_3H_3SO_2)$ with $P(C_6H_5)_3$, pyridine, and 2,2′-bipyridine under thermal or photolytic conditions in several solvents proved unsuccessful. Only the unreacted sultine and intractable decomposition products were obtained.

Discussion

The main point of interest concerns the unusual course of reaction between transition metal 2-alkynyls and SO_2 to give the sultine complexes. The anticipated products, *viz.*, the rearranged allenyl metal sulfinates or the *S*-sulfinates derived from direct insertion into the M–CH_2 bonds, have not been detected. Furthermore, the reaction in question appears to be unique to transition metal–2-alkynyl compounds; the corresponding 3-alkynyl, 2-alkenyl,[3,22] and cyanomethyl complexes, as well as representative metal counterparts to these propargylic systems,[30] either do not react or insert SO_2 into their M–C bonds.

Combined evidence from related studies[30,31] points

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[28] R. L. Downs and A. Wojcicki, to be submitted for publication.

[29] However, the possibility of an initial cleavage of the Fe–C bond by HCl to give $\pi\text{-}C_5H_5Fe(CO)_2Cl$ and $C_4H_6SO_2$, followed by decomposition of the sultine to C_4H_6 and SO_2, cannot be dismissed. Studies continue on this and related reactions.

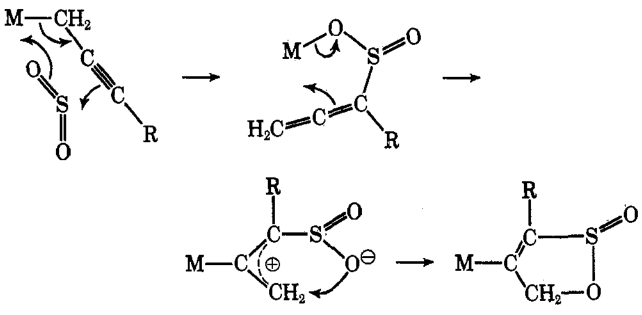
[30] C. W. Fong and W. Kitching, *J. Organometal. Chem.*, **22**, 107 (1970).

[31] M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, **4**, 347 (1970), and references therein.

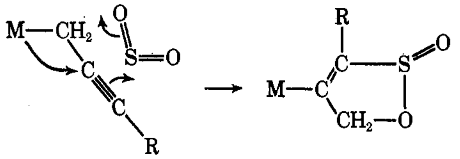
convincingly to an electrophilic interaction of SO_2 with organometallic compounds. In its reactions with transition metal–carbon systems, SO_2 may be best regarded as attacking at the M—C bond site in the alkyls and aryls and either at the M—C or at the C═C linkage in the σ-allyls. Accordingly, with the latter compounds, rearrangement of the allylic moiety often accompanies the insertion.[3]

It appears most reasonable that in the reactions under consideration the site of attack by the electrophilic SO_2 is the electron-rich C≡C bond. Following such an initial interaction, either of the two general pathways given below (Schemes I and II) will lead to the formation of the sultine derivative.

SCHEME I



SCHEME II



Path I receives support from the reaction of $(C_6H_5)_3SnCH_2C{\equiv}CH$ with SO_2 which gives the stable $(C_6H_5)_3Sn[OS(O)CH{=}C{=}CH_2]$.[30] This compound is strictly analogous to the allenyl-*O*-sulfinate intermediate proposed in pathway I. However, unlike its transition metal counterpart, the tin *O*-sulfinate should be very stable toward subsequent rearrangement because of an expected greater strength of its M–O linkage. Path II[22] represents a one-step reaction with rearrangement. It is certainly as plausible as path I, especially in view of the fact that the suggested *O*-sulfinate intermediate has yet to be detected.

Any attempt at differentiation among the two foregoing and other reasonable pathways[32] must be deferred until additional data become available. One may conclude, however, that the formation of the metal sultines from the corresponding 2-alkynyls and SO_2 is a kinetic rather than a thermodynamic effect. This follows from our successful isolation of $\pi\text{-}C_5H_5Fe(CO)_2(SO_2CH_2C{\equiv}CCH_3)$ and demonstration that it does not rearrange to the isomeric sultine. Also worth noting is that allenyl-*S*-sulfinates, $MS(O)_2C(R){=}C{=}CH_2$, do not form in the reactions under consideration as might be expected by analogy with the behavior of the σ-allyls.[3] This may be best attributed to the linearity of the 2-alkynyl moiety which prevents simultaneous interaction of the sulfur with the metal and the C≡C bond (see Scheme I).

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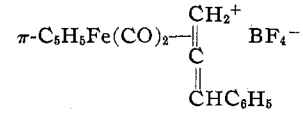
(32) NOTE ADDED IN PROOF.—The recent isolation of



$$\pi\text{-}C_5H_5Fe(CO)_2\text{—}\overset{CH_2^+}{\underset{\underset{CHC_6H_5}{\|}}{\overset{\|}{C}}}\quad BF_4^-$$

from the reaction of $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with HBF_4, as well as the demonstration that $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ and tetracyanoethylene yield the cyclic $\pi\text{-}C_5H_5Fe(CO)_2C{=}C(R)C(CN)_2C(CN)_2CH_2$, suggests that reactions of transition metal–2-alkynyl complexes with various electrophiles may proceed *via* the intermediacy of the corresponding π-allenyls: D. W. Lichtenberg and A. Wojcicki, unpublished results, and S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, in press, respectively.

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The Synthesis and Stereochemistry of Some β-Diketone Derivatives of Titanocene and Zirconocene Dichlorides

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By the interaction of $(C_5H_5)_2MCl_2$ (M = Ti, Zr) (1 mol) and a β-diketone (keH) (2 mol), in the presence of triethylamine (1 mol), in acetonitrile solution at 20°, the compounds $C_5H_5MCl(ke)_2$ were prepared. A similar reaction with tropolone (TH) gave $C_5H_5ZrT_3$. The monomeric nonelectrolytes $C_5H_5MCl(ke)_2$ were investigated by infrared and variable-temperature ^1H nmr spectroscopy, which indicated that these compounds all exist as the cis isomer in solution with the exception of $C_5H_5TiCl(acac)_2$ for which two isomers are observed.

Introduction

As a continuation of our work on the reactions of the group IVa metallocene dihalides with chelating ligands containing a replaceable hydrogen atom,[1] the reactions of $(C_5H_5)_2MCl_2$ (M = Ti, Zr) with some β-diketones (keH) [keH = pentane-2,4-dione (acacH), 1-phenylbutane-1,3-dione (bzacH), 1,3-diphenylpropane-1,3-dione (bzbzH)] and tropolone (TH) have been studied, resulting in the preparation of the compounds $C_5H_5MCl(ke)_2$, the first preparation of compounds of this type with M = Ti. Two reports on related titanium

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[1] J. Charalambous, M. J. Frazer, and W. E. Newton, *J. Chem. Soc. A*, in press.