

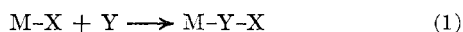
Sulfur Dioxide Insertion Reactions of Transition Metal Alkyls and Related Complexes

ANDREW WOJCICKI

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

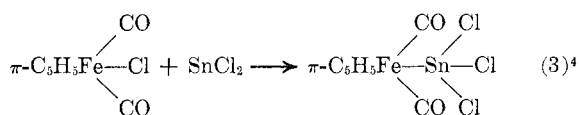
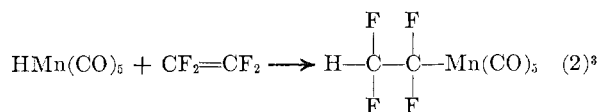
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A number of diverse organometallic processes conform to the general equation

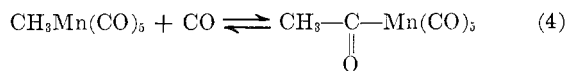


where M is a metal and X and Y are monatomic or polyatomic species (ancillary ligands have been omitted). Such processes are termed insertion reactions. The name has been used in a rather broad context and carries no mechanistic connotations; it merely reflects the overall structural result of cleavage of a metal-element bond (M-X) in a covalent complex by an interposing unsaturated species, Y. M-X linkages which are known to engage in such reactions include metal-hydrogen, metal-alkyl, metal-halogen, metal-metal (same or different), and metal-oxygen, to mention a few. Some of the more common inserting molecules are CO, SO₂, olefins, acetylenes, and organic isocyanides.

Two typical examples (eq 2 and 3) illustrate this type of process. For a comprehensive compilation and discussion of known insertion reactions the reader is referred to two relatively recent reviews.^{1,2}



Historically, the first convincing example of insertion into a metal-alkyl bond dates back to 1957, when Coffield and coworkers⁵ demonstrated the reversible reaction (eq 4) of Mn(CO)₅CH₃ with CO to give Mn-



(CO)₅(COCH₃). In subsequent years the generality of this type of reaction was ascertained and considerable progress was made in the understanding of its mechanism.⁶ More recently, the discovery and studies of sulfur dioxide (1964),⁷ germanium(II) chloride (1968),⁸

tetracyanoethylene (1970),⁹ and alkyl isocyanide (1969)¹⁰ insertions have appeared in the literature. A number of other, diverse types of insertion may be expected further to enrich organometallic chemistry in the near future.

The recent growth of interest in insertion reactions undeniably stems from the emphasis placed on development of homogeneous catalysis as a rational discipline. The realization that reactions such as the hydroformylation¹¹ or the polymerization of olefins¹² and isocyanides¹³ which involve metal complexes proceed by one or more insertion reactions has provided an enormous impetus for investigations of these transformations. The results have already shed light on certain mechanistic aspects of catalytic processes. Additionally, dividends have frequently been obtained through discoveries of new reactions and syntheses of unusual organometallic and organic compounds which cannot be prepared otherwise or are accessible only with difficulty.¹⁴ The research on insertion reactions has helped systematize a large body of previously unrelated facts and opened new areas of chemistry for investigation.

This Account is concerned with insertion reactions of transition metal alkyls and related complexes such as the aryls, alkenyls, and alkynyls. Particular emphasis focuses on the development of the sulfur dioxide insertion,¹⁵ much of which took place in the author's laboratory, though comparison is also made with other inserting species (especially carbon monoxide) which have been studied in several laboratories.¹⁶⁻²¹

(8) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Demisov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1419 (1968).

(9) S. R. Su, J. A. Hanna, and A. Wojcicki, *J. Organometal. Chem.*, **21**, P21 (1970).

(10) Y. Yamamoto, H. Yamazaki, and N. Hagihara, *ibid.*, **18**, 189 (1969).

(11) See, for example, C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, Chapter 6.

(12) P. Cossee in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, pp 241-250.

(13) Y. Yamamoto and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1084 (1966).

(14) Some of these aspects are discussed in a recent review; see R. F. Heck, *Accounts Chem. Res.*, **2**, 10 (1969).

(15) For a recent review of sulfur dioxide insertion reactions see W. Kitching and C. W. Fong, *Organometal. Chem. Rev., Sect. A*, **5**, 281 (1970).

(16) P. J. Craig and M. Green, *J. Chem. Soc. A*, 157 (1969).

(17) S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, **27**, 231 (1971).

(18) I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 2074 (1967).

(19) K. Noack, M. Ruch, and F. Calderazzo, *ibid.*, **7**, 345 (1968), and cited references to Calderazzo's previous papers.

(20) R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 331 (1970), and cited references to Mawby's previous papers.

(21) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 651 (1963), and references cited there.

(1) R. F. Heck, *Advan. Chem. Ser.*, **No. 49**, 181 (1965).

(2) M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5**, 225 (1967).

(3) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

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(5) T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

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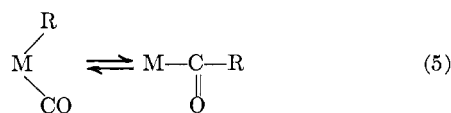
(7) J. P. Bibler and A. Wojcicki, *ibid.*, **86**, 5051 (1964).

Discovery and Development of the Sulfur Dioxide Insertion

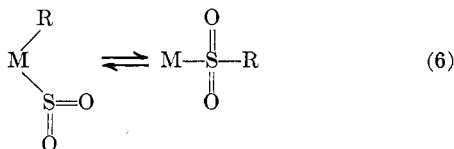
Our research on reactions of SO₂ with transition metal compounds containing M-C σ bonds commenced in 1964, during a period of considerable interest and activity in the investigation of the carbon monoxide insertion. That year reports appeared on the mechanism of reaction of alkylcarbonyl complexes with various nucleophiles⁶ and evidence was presented in support of alkyl migration rather than intramolecular CO insertion.²²

At that time the only other molecules known to undergo insertion into transition metal-carbon bonds were unsaturated hydrocarbons²⁴ and fluorocarbons,²⁵ neither of which had been studied in much detail. We felt that insertion reactions of alkyl complexes are certainly broader in scope and accordingly set out to look for likely candidates to support our generalization.

A report by Braye and Hübel²⁶ of the synthesis of two iron carbonyls containing coordinated SO₂ strongly influenced our choice of inserting species. Since both CO and SO₂²⁷ were shown to function as good π-bonding ligands toward low-valent transition metals, we decided to explore what appeared to be an analogy between the two systems. Carbonyl and alkyl groups coordinated to the same metal participate in the carbon monoxide insertion and decarbonylation reactions (eq 5). It was



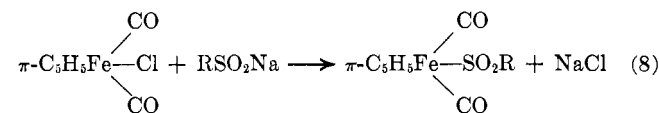
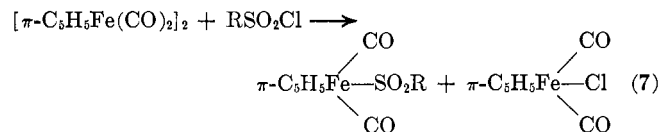
inviting to propose that the corresponding reactions of SO₂, depicted in eq 6, may also occur. Should this



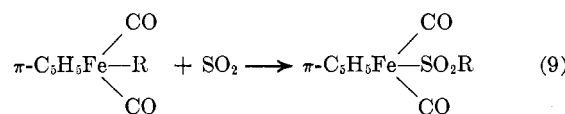
structural analogy become an experimental reality, then a counterpart to the known CO-alkyl-acyl systems of organometallics—SO₂-alkyl-sulfinate—would become available as a synthetic tool for various organosulfur compounds.

It was necessary first to show that the hitherto unknown S-sulfinate can be prepared. Bibler's²⁸ synthesis of π-C₅H₅Fe(CO)₂(SO₂R) via the reactions represented by eq 7 and 8 furnished the needed experimental

support. We then investigated possible SO₂ insertions (also known as sulfonylation).



Our initial reactions were carried out by dissolving π-C₅H₅Fe(CO)₂R in liquid SO₂ and storing the resultant solution for several hours at ca. -40°. Removal of the solvent, followed by alumina chromatography of the residual solid, afforded in excellent yields yellow, crystalline compounds, which were shown to be identical with the corresponding complexes prepared by using RSO₂Cl or RSO₂Na as the source of RSO₂ (eq 7 and 8). Some of these reactions (eq 9) were also conducted by



bubbling SO₂ into a solution of π-C₅H₅Fe(CO)₂R in pentane at 27°. Again the same product was obtained; however, the reactions proceeded much more slowly than in liquid SO₂.

Following the above discovery of Bibler, Hartman³⁰ showed that sulfonylation with Mn(CO)₅R and Re(CO)₅R can be carried out conveniently in SO₂ at reflux (-10°). However, lower temperatures (SO₂ freezes at -75.5°³¹) are frequently more suitable when working with very reactive metal-carbon complexes. Subsequently, investigations on such reactions were extended to π-C₅H₅Mo(CO)₃R,³² π-C₅H₅W(CO)₃R,³² and π-C₅H₅-Cr(NO)₂R³³ in our laboratories and to π-C₅H₅Ni(PR₃)R'³⁴ and a number of different classes of cobalt alkyls elsewhere.³⁵⁻³⁷ In all cases (except π-C₅H₅W(CO)₃R (R = CH₃), which did not react at -10°) 1:1 SO₂ addition complexes, which had infrared and ¹H nmr spectral features very similar to those for π-C₅H₅Fe(CO)₂(SO₂R), were isolated. There was little doubt that all of these products possessed the same type of structure as far as the newly incorporated SO₂ was concerned.

There is no ligand structural ambiguity with CO insertion, since CO and R can combine only to form an

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(30) (a) F. A. Hartman and A. Wojcicki, *ibid.*, **88**, 844 (1966); (b) F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968).

(31) T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1952, p 341.

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

(33) J. A. Hanna, M.S. Thesis, The Ohio State University, 1969.

(34) M. D. Rausch, Y. F. Chang, and H. B. Gordon, *Inorg. Chem.*, **8**, 1355 (1969).

(35) K. Yamamoto, T. Shono, and K. Shinra, *Nippon Kagaku Zasshi*, **88**, 958 (1967).

(36) R. J. Cozens, G. B. Deacon, P. W. Felder, K. S. Murray, and B. O. West, *Aust. J. Chem.*, **23**, 481 (1970).

(37) M. D. Johnson and G. J. Lewis, *J. Chem. Soc. A*, 2153 (1970).

(22) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 5043 (1964); although some data presented therein were later shown to be incorrect and thus invalidated the argument used, the conclusion reached by the authors has been confirmed in a more recent study.²³

(23) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

(24) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3383 (1963).

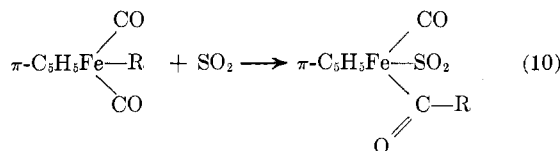
(25) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

(26) E. H. Braye and W. Hübel, *Angew. Chem.*, **75**, 345 (1963).

(27) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **97**, 1871 (1964).

(28) J. P. Bibler, Ph.D. Thesis, The Ohio State University, 1965.

acyl moiety.³⁸ This, however, is not the case for SO₂. First, SO₂ may, at least in theory, function similarly to most other ligands and effect a CO insertion reaction (provided, of course, that CO is present in the parent alkyl), as shown in eq 10. Alternatively, it may itself undergo insertion into the metal-alkyl carbon bond.



The former possibility was ruled out for every SO₂-containing product, since the infrared spectra were incompatible with the presence of the RCO fragment and a reduced number of terminal carbonyl groups. This left for consideration several structures containing SO₂ interposed between the metal and carbon of the original M-C bond. Of these, all but monodentate attachments may be regarded as unsatisfactory, since they would provide the central metal with electrons in excess of those required for an 18-electron configuration.³⁹

The three monodentate types of attachment which merit scrutiny include MS(=O)₂R (I), an *S*-sulfinate; MS(=O)OR (II), an oxysulfinyl; and MOS(=O)R (III), an *O*-sulfinate. Of these, II may be ruled out, since many of the SO₂ insertion products are also accessible by using an appropriate metal complex in conjunction with RSO₂Cl or RSO₂Na (*vide supra*), where an S-R linkage is known to prevail.⁴⁰ Its rearrangement to an S-O-R array during the reaction must be considered extremely unlikely.

To distinguish between the isomeric modes of metal-sulfinate bonding (I and III) one may be reasonably confidently guided by empirical infrared spectral criteria.⁴¹ These are based on the observations that the asymmetric and the symmetric $\nu(\text{SO}_2)$ for the organic sulfones, RS(O)₂R', occur at wave numbers considerably higher than for the corresponding sulfinate esters, RS(O)OR'.⁴² The structural relationship among these organic compounds and the metal sulfinate leads to a prediction that the *S*-sulfinate will absorb at higher wave numbers than the *O*-sulfinate. This prediction has been borne out for all compounds whose structures were determined by X-ray crystallography—*fac*-Mn(CO)₃(bipy)(SO₂CH₃)⁴³ (bipy = 2,2'-bipyridine), [$\pi\text{-C}_5(\text{CH}_3)_5\text{Fe}(\text{CO})_2(\text{SO}_2\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5)$]⁴⁴ and *trans*-Cu(H₂O)₄[OS(O)(*p*-C₆H₄CH₃)]₂,⁴⁵ among others—and

now serves as a reliable criterion in making structural inferences.

It is significant that all transition metal sulfinate prepared *via* SO₂ insertion are the *S*-bonded isomers (I). This mode of attachment persists when CO is partially replaced with a more basic ligand, *e.g.*, pyridine (eq 11),⁴⁶ in contrast to the behavior of some thiocyanatocarbonyls which often rearrange from M-SCN to Mn(CO)₅(SO₂CH₃) + 2C₅H₅N \longrightarrow *fac*-Mn(CO)₃(C₅H₅N)₂(SO₂CH₃) + 2CO (11)

M-NCS.⁴⁷ On the other hand, alkyl compounds of representative metals such as Zn⁴⁸ and Sn⁴⁹ afford *O*-sulfinate on treatment with SO₂, in agreement with their reported class "a"⁵⁰ or "hard" acid⁵¹ properties.

A unique situation was encountered by us⁵² and Deacon⁵³ independently for C₆H₅Hg(SO₂C₆H₅) in that both isomeric sulfinate are isolable. The *S*-bonded compound results from the reaction of Hg(C₆H₅)₂ with SO₂ at low temperatures; upon recrystallization it undergoes conversion to an *O*-bonded species, which contains either a monodentate or a bidentate sulfinate. Several other examples of linkage preference among RHg(SO₂R) have been also noted.⁵² Table I contains a number of representative sulfinate complexes prepared by SO₂ insertion, listed together with some of their properties.

Stereochemistry and Mechanism

Most of the information available on sulfur dioxide insertion reactions of transition metal complexes derives from our own kinetic investigation, which is being currently conducted by Jacobson.⁵⁴ The study concerns the system $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ and some structurally analogous compounds. Because of the relatively slow rate of insertion and frequent complications owing to decomposition of these complexes in organic solution, we have employed liquid SO₂ as the solvent. The reactions in this medium are almost invariably quantitative and may be followed conveniently by low-temperature (−70 to −23°) infrared spectroscopy. The obvious drawback is that dependence of the rate on the concentration of SO₂ cannot be determined. We are hoping, however, that the information obtained from this study may help us select suitably constituted

(38) For an X-ray crystallographic study on metal-acyl complexes see, for example, M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

(39) P. R. Mitchell and R. V. Parish, *J. Chem. Educ.*, **46**, 811 (1969).

(40) R. Connor in "Organic Chemistry," H. Gilman, Ed., Wiley, New York, N. Y., 1943, Chapter 10.

(41) Attempts have been made also to apply ¹H nmr spectral criteria in elucidating M-SO₂R bonding, albeit without success.

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(49) C. W. Fong and W. Kitching, *J. Organometal. Chem.*, **22**, 95 (1970).

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(51) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

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(53) G. B. Deacon and P. W. Felder, *Aust. J. Chem.*, **22**, 549 (1969).

(54) (a) S. E. Jacobson and A. Wojcicki, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstracts, No. INOR 112; (b) S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **93**, 2535 (1971).

Table I
Some Representative Sulfinate Complexes Obtained by Reaction of the Corresponding Alkyls with SO₂

Complex	Color	$\nu(\text{SO}_2)$, cm ⁻¹ ^a	Ref
Mn(CO) ₅ (SO ₂ CH ₃)	Pale yellow	1201, 1053	30
Re(CO) ₅ (SO ₂ CH ₃)	White	1192, 1054	30b
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{SO}_2\text{CH}_3)$	Yellow	1194, 1052	29
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3(\text{SO}_2\text{CH}_3)$	Golden	1190, 1051	32
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2(\text{SO}_2\text{CH}_3)$	Dark green	1194, 1053	33
$\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3](\text{SO}_2\text{CH}_3)$	Dark green	Not reported	34
Co(salen)(SO ₂ CH ₃)·3H ₂ O ^b	Olive green	1197, 1063	36
C ₆ H ₅ Hg(SO ₂ C ₆ H ₅) (S-sulfinate)	White	1175, 1048	52, 53
C ₆ H ₅ Hg[OS(O)C ₆ H ₅] (O-sulfinate)	White	1048, 836	52, 53
{(CH ₃) ₃ Sn[OS(O)CH ₃]} _n	White	1000-900	49

^a Nujol mull. ^b salen = *N,N'*-ethylenebis(salicylaldiminato).

Table II
Representative Data for Reactions of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ with Liquid SO₂ at -40°

R	<i>k</i> , sec ⁻¹	Relative <i>k</i> ^a	Taft σ^*	$\nu(\text{CO})$, cm ⁻¹	
				SO ₂ soln	C ₆ H ₁₂ soln
CH ₂ Si(CH ₃) ₃	Very fast ^b		-0.26		2012, 1961
CH ₂ CH=CHCH ₃	Very fast ^b		+0.13		2010, 1959
C ₂ H ₅	1.3 × 10 ⁻³ (-65°)				
	3.2 × 10 ⁻³ ^c	1600	-0.10	<i>d</i> , 1937	2010, 1956
CH ₃	1.1 × 10 ⁻³ (-65°)				
	2.7 × 10 ⁻³ ^c	1400	0.00	<i>d</i> , 1940	2014, 1960
CH ₂ C ₆ H ₅	1.6 × 10 ⁻⁴ ^e	80	+0.22	2004, 1944	2010, 1959
CH ₂ OCH ₃	8.3 × 10 ⁻⁸	4	+0.60	2006, 1947	2017, 1961
CH ₂ SCH ₃	<i>f</i>			2021, 1964	2026, 1970
CH ₂ CN	<i>g</i>		+1.30	2026, 1973	2030, 1981

^a Compared with *k* = 1 for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$. ^b Too fast to measure by low-temperature infrared spectroscopy. ^c Calculated assuming $\Delta H^\ddagger = 2.9$ kcal/mole. ^d Masked by $\nu(\text{CO})$ of the corresponding sulfinate. ^e $\Delta H^\ddagger = 2.9 \pm 0.4$ kcal/mole and $\Delta S^\ddagger = -62 \pm 2$ eu. ^f Reaction 9% complete after 16 hr at 25°. ^g No detectable reaction after 60 hr at 25°.

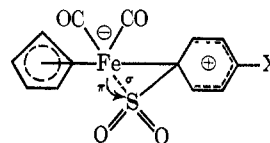
alkyls for which a similar investigation in organic solvents will be feasible.

Listed in Table II are the alkyls $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ in descending order of reactivity toward SO₂. The relative pseudo-first-order rate constants, *k*, decrease as the Taft polar substituent constant,⁵⁵ σ^* , for the group R becomes more positive. The only apparent exception occurs with R = CH₂CH=CHCH₃; as will be seen later, this is due to a different mechanism of insertion for certain σ -allyl complexes. Approximately paralleling the increase in σ^* is a progressive shift to higher frequencies of $\nu(\text{CO})$ for the parent alkyls. This latter trend may be attributed to a decreasing electron charge density at the metal and the consequent reduction of M=CO π bonding.

The foregoing data clearly indicate that R exerts a profound influence through its inductive effect on the rate of insertion of the alkyl complex with SO₂. Since ligands R with strong electron-releasing properties (negative σ^*) react more rapidly than those with electron-withdrawing properties (positive σ^*), we conclude that the interaction of SO₂ with M-C bonds is principally electrophilic in nature.

Additional support for the above proposal is furnished by the data on reactions of the aryls $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Ar}$ with SO₂, given in Table III. The relative rate con-

stants for para- and meta-substituted phenyl complexes correlate with Hammett σ^+ values, which measure the ability of the substituents to stabilize positive charge on the Ar ring.⁵⁶ Thus, these results can be also successfully accommodated in the general framework of electrophilic interactions of SO₂ with M-C linkages. It is of interest that there seems to be practically no variation in $\nu(\text{CO})$ for the substituted aryl complexes examined even though the *k*'s cover a range of 720. This may indicate that the degree of stabilization of the transition state by SO₂, e.g.



rather than the relative energy of the ground state of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Ar}$ is of prime significance, a proposal consistent with the observed relationship between *k* and σ^+ .

There exists further evidence, albeit of a more qualitative nature, in support of an electrophilic interaction of SO₂ with M-C bonds. For instance, whereas $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$ undergoes the insertion at a measurable rate in liquid SO₂ at -40° (Table II), the isoelectronic $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_2\text{C}_6\text{H}_5$ interacts too rapidly

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(56) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

Table III
Representative Data for Reactions of π -C₅H₅Fe(CO)₂Ar with Liquid SO₂ at -40°

Ar	<i>k</i> , sec ⁻¹	Relative <i>k</i> ^a	Hammett σ^+	$\nu(\text{CO}), \text{cm}^{-1}$	
				SO ₂ soln	C ₆ H ₁₂ soln
<i>p</i> -C ₆ H ₄ OCH ₃	3.8×10^{-4} ^b	720	-0.78	c, 1958	2027, 1971
<i>p</i> -C ₆ H ₄ CH ₃	6.6×10^{-5} ^d	33	-0.31	2016, 1960	2027, 1971
<i>m</i> -C ₆ H ₄ CH ₃	1.9×10^{-5} (-23°)				
	1.4×10^{-6} ^e	~1	-0.07	2013, 1957	2027, 1970
C ₆ H ₅	2.0×10^{-6} ^f	1	0.00	2018, 1960	2023, 1972

^a Compared with *k* = 1 for π -C₅H₅Fe(CO)₂C₆H₅. ^b $\Delta H^\ddagger = 3.5 \pm 0.5$ kcal/mole and $\Delta S^\ddagger = -55 \pm 2$ eu. ^c Masked by $\nu(\text{CO})$ of the corresponding sulfinate. ^d $\Delta H^\ddagger = 7.8 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -43 \pm 2$ eu. ^e Calculated assuming $\Delta H^\ddagger = 7.3$ kcal/mole. ^f $\Delta H^\ddagger = 7.3 \pm 0.5$ kcal/mole and $\Delta S^\ddagger = -52 \pm 2$ eu.

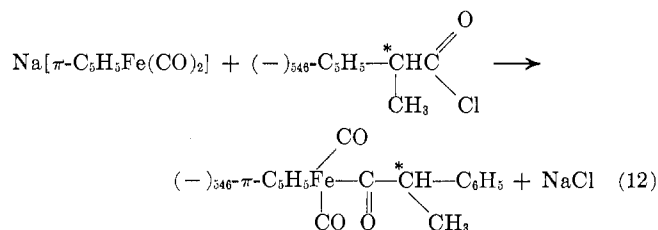
for the reaction to be followed at -65°. Although this difference may be rationalized in more than one way, it is certainly consistent with the lower formal oxidation state of Cr(0) as compared with Fe(II). Finally, Graziani⁵⁷ has shown that the reactivity of π -C₅H₅Fe(CO)(L)CH₃ toward SO₂ in chloroform solution increases as a function of L in the order L = CO \ll P(C₆H₅)₃ < P(*n*-C₄H₉)₃. The last compound undergoes insertion with gaseous SO₂ even in the solid. Thus, the more basic the ligand L, the faster is the reaction of its complex with SO₂.

The activation parameters for the reaction of several π -C₅H₅Fe(CO)₂R and π -C₅H₅Fe(CO)₂Ar with liquid SO₂ are given in Tables II and III. The values of ΔH^\ddagger are 3-8 kcal/mole, whereas ΔS^\ddagger ranges from -43 to -62 eu. Both were calculated by using pseudo-first-order rate constants. The large negative entropies of activation are particularly striking and surprising. Solvent-assisted carbon monoxide insertion reactions usually have ΔS^\ddagger values of -20 to -30 eu,⁵⁸ and oxidative addition reactions of some square-planar Rh(I) and Ir(I) complexes are known to proceed with $\Delta S^\ddagger = -40$ to -50 eu.^{59,60} The extremely high and negative ΔS^\ddagger for SO₂ insertions may result from two factors: (i) loss of entropy by the solvent and (ii) a constrained structure of the activated complex.

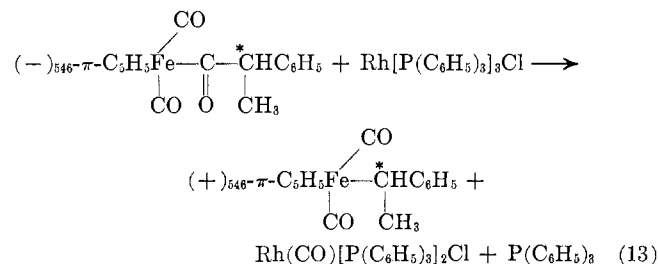
Since the foregoing kinetic study is still incomplete, no mechanistic picture can be constructed at this time. However, the possibility of a free-radical pathway may be ruled out, since the scavenger 2,2-diphenyl-1-picrylhydrazyl has no effect on the rate of reaction between π -C₅H₅Fe(CO)₂CH₂C₆H₅ and SO₂.

To learn more about the nature of the transition state in these reactions we examined stereochemical consequences of insertion of SO₂ into an Fe-C bond. Our approach was to synthesize an optically active alkyl complex with an asymmetric α carbon atom and then to investigate its reaction with SO₂.

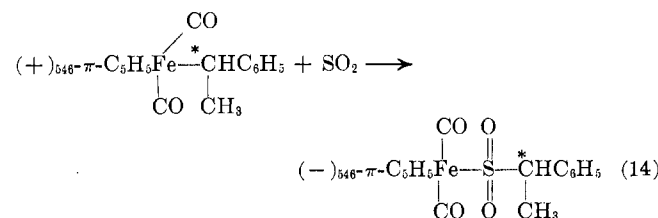
The synthesis of optically active π -C₅H₅Fe(CO)₂[CO-*CH(CH₃)C₆H₅], the acyl precursor of the desired alkyl, was effected⁶¹ by reaction 12. After the initial un-



successful attempts at thermal and photochemical decarbonylation of the acyl, Alexander obtained the optically active alkyl by employing Rh[P(C₆H₅)₃]₃Cl as the decarbonylating reagent⁶² (eq 13). The optically



active alkyl ($[\alpha]_{546}^{27} + 78^\circ$ (CHCl₃)) reacts with SO₂, either in the liquid at -60 to -10° or in pentane solution at 25°, affording the corresponding sulfinate (eq 14)



whose chloroform solutions also exhibit optical activity ($[\alpha]_{546}^{27}$ ranges from -158 (pentane preparation) to -186° (liquid SO₂ at -60° preparation) (CHCl₃)).

It thus appears that the insertion is a substantially stereospecific process both in liquid SO₂ and in pentane solution, although neither the degree nor the nature of the configurational change (inversion or retention) can be ascertained from these data. Very recently, however, Professor Whitesides⁶³ advised us that the reaction

(61) J. J. Alexander and A. Wojcicki in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, New York, N. Y., 1968, pp 383-384.

(62) J. J. Alexander and A. Wojcicki, *J. Organometal. Chem.*, **15**, P23 (1968).

(63) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); we thank Professor Whitesides for sending us this information prior to publication.

(57) M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, **4**, 347 (1970).

(58) A. J. Hart-Davis and R. J. Mawby, *J. Chem. Soc. A*, 2403 (1969).

(59) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968).

(60) P. B. Chock and J. Halpern, *ibid.*, **88**, 3511 (1966).

Table IV
Representative Data for Reactions of σ -Allyl Complexes with SO₂ under Various Conditions

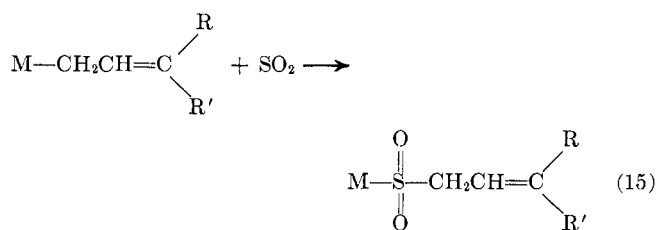
Reaction no.	Complex	Conditions	—Relative % of sulfinate—		Ref
			Rearranged allyl group	Unrearranged allyl group	
I	Mn(CO) ₅ CH ₂ CH=CHCH ₃	SO ₂ at reflux	100		67
II	Mn(CO) ₅ CH ₂ CH=C(CH ₃) ₂	SO ₂ at reflux	100		67
III	Mn(CO) ₅ CH ₂ CH=CHC ₆ H ₅	SO ₂ at reflux or liquid SO ₂ ~ -70°		100	67
IV	Re(CO) ₅ CH ₂ CH=C(CH ₃) ₂	SO ₂ at reflux	100		67
V	π -C ₅ H ₅ Fe(CO) ₂ CH ₂ CH=CHCH ₃	SO ₂ at reflux	100		68
VI	π -C ₅ H ₅ Fe(CO) ₂ CH ₂ CH=C(CH ₃) ₂	SO ₂ at reflux	25	75	68
VII	π -C ₅ H ₅ Fe(CO) ₂ CH ₂ CH=C(CH ₃) ₂	Liquid SO ₂ ~ -60°	85	15	68
VIII	π -C ₅ H ₅ Fe(CO) ₂ CH ₂ CH=C(CH ₃) ₂	Hexane solution, 27°	93	7	68
IX	π -C ₅ H ₅ Fe(CO) ₂ CH ₂ CH=CHC ₆ H ₅	SO ₂ at reflux	20	80	68
X	[π -C ₅ (CH ₃) ₅]Fe(CO) ₂ CH ₂ CH=CHCH ₃	SO ₂ at reflux	100		69
XI	[π -C ₅ (CH ₃) ₅]Fe(CO) ₂ CH ₂ CH=C(CH ₃) ₂	SO ₂ at reflux		100	69
XII	[π -C ₅ (CH ₃) ₅]Fe(CO) ₂ CH ₂ CH=C(CH ₃) ₂	Liquid SO ₂ ~ -50°	40	60	69
XIII	[π -C ₅ (CH ₃) ₅]Fe(CO) ₂ CH ₂ CH=C(CH ₃) ₂	Hexane solution, 27°	10	90	69
XIV	[π -C ₅ (CH ₃) ₅]Fe(CO) ₂ CH ₂ CH=CHC ₆ H ₅	SO ₂ at reflux		100	69
XV	π -C ₅ H ₅ Mo(CO) ₃ CH ₂ CH=CHCH ₃	SO ₂ at reflux	90	10	68
XVI	π -C ₅ H ₅ Mo(CO) ₃ CH ₂ CH=C(CH ₃) ₂	SO ₂ at reflux		100	68

of *threo*- π -C₅H₅Fe(CO)₂CHDCHDC(CH₃)₃ with SO₂ proceeds with inversion of configuration. This unexpected result cannot yet be satisfactorily explained. By contrast, the CO insertion reaction of *threo*- π -C₅H₅Fe(CO)₂CHDCHDC(CH₃)₃ with P(C₆H₅)₃ occurs with retention of configuration.⁶⁴

Rearrangement Reactions of 2-Alkenyl and 2-Alkynyl Complexes

Although the chemistry of π -allyl complexes has been the subject of a number of investigations,⁶⁵ σ -allyl compounds of transition metals have attracted much less attention. In the area of insertion reactions, the only report known to us on σ -allyls prior to 1967 dealt with the reversible carbonylation of Mn(CO)₅CH₂CH=CH₂.⁶⁶

In order to fill this void and to augment our studies on sulfonylation of various transition metal alkyls we have examined SO₂ insertion reactions of a number of metal- σ -allyl complexes.⁶⁷⁻⁶⁹ Two general types of *S*-sulfinate product were isolated: (i) that derived from "direct insertion" of SO₂ into the M-C bond (eq 15),



(64) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).

(65) For a review see M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

(66) T. H. Coffield, J. Kozikowski, and R. D. Closson, lecture to International Conference on Coordination Chemistry, London, England, 1959; quoted by G. E. Coates, "Organometallic Compounds," Wiley, New York, N. Y., 1960, pp 280-281.

(67) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 289 (1968).

(68) R. L. Downs, Ph.D. Thesis, The Ohio State University, 1968.

(69) D. A. Ross, Ph.D. Thesis, The Ohio State University, 1970.

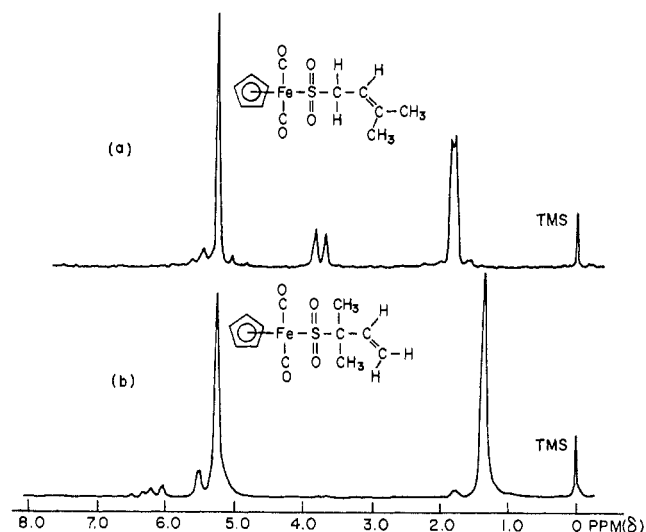
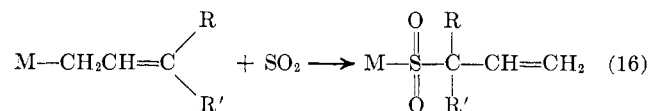


Figure 1. ¹H nmr spectra (60 MHz) of the unrearranged and the rearranged allylic isomers of π -C₅H₅Fe(CO)₂(SO₂C₃H₅) in CDCl₃ solution. The resonance at 1.8 ppm in spectrum b is due to the presence of a small amount (8%) of the unrearranged isomer; see ref 68 for details.

and (ii) that resulting from insertion with rearrangement of the allylic moiety (eq 16). Identification of

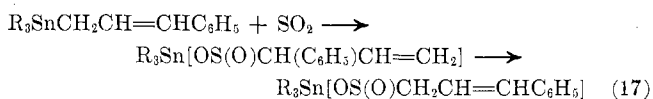


such isomers and determination of their ratios in mixtures have been carried out with the aid of ¹H nmr spectroscopy. Typical spectra—those of the two products derived from π -C₅H₅Fe(CO)₂CH₂CH=C(CH₃)₂—are shown in Figure 1. Table IV contains some representative reactions of allylic complexes along with the relative distribution of the two kinds of sulfinate isomers.

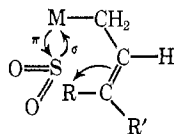
Several generalizations are possible from the data given: (i) the nature of the metal together with its

ancillary ligands plays a major role in determining whether the insertion occurs with or without rearrangement (*e.g.*, reactions II, IV, VI, and XVI in Table IV); (ii) an increasing bulk of substitution at C-3 of the allyl group favors unrearranged sulfinate products (reactions I, II, and III or V, VI, and IX); (iii) electron-releasing substituents on the cyclopentadienyl ring promote formation of "direct insertion" products (reactions XI and VI or IX and XIV); (iv) in liquid SO₂ as the solvent, the relative amounts of the rearranged sulfinate increase as the temperature decreases (reactions VI and VII or XI and XII); (v) an inert solvent such as hexane promotes formation of the rearranged products when compared with liquid SO₂ as the reaction medium (reactions VI and VIII or XI and XIII).

In those cases where both isomers could be isolated, Downs⁶⁸ demonstrated that there is no interconversion between them under the experimental conditions for the insertion. Accordingly, these reactions must proceed by two independent pathways. For those complexes which have been found to yield only one kind of sulfinate (either rearranged or unrearranged), the possibility of isomerization cannot be excluded. A recent report by Kitching⁷⁰ that R₃SnCH₂CH=CHC₆H₅ (R = CH₃ or C₆H₅) inserts SO₂ with rearrangement, followed by isomerization of the initial product (eq 17), dictates caution in interpreting results from the latter reactions.



The incidence of two different pathways for the insertion is probably a direct consequence of the presence of two electron-rich sites in these molecules. Interaction of SO₂ with the M-CH₂ bond, in a manner similar to that for the alkyls, will lead to the formation of the unrearranged sulfinate. By contrast, simultaneous attack of SO₂ at the C=C bond (electrophilic) and the metal (σ , nucleophilic; π , electrophilic) will yield the corresponding rearranged allylic product, as shown below. Although no kinetic studies have yet been carried out on these systems, the latter process must



possess lower E_a than the former. This is based on the observation that whenever mixtures of isomeric sulfinate products result, the relative amount of the rearranged product increases as the temperature of the SO₂ solvent is reduced.

From the data available it appears that the nature of the insertion product often hinges on a delicate balance of several factors. In general, the faster a given alkyl system reacts with SO₂, the greater the tendency for its allyl counterpart to "insert directly." Further,

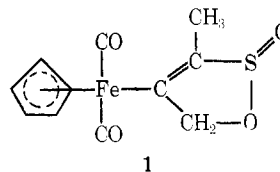
(70) C. W. Fong and W. Kitching, *J. Organometal. Chem.*, **22**, 107 (1970).

whenever direct insertion is disfavored, as, for example, by using hexane solutions, the relative importance of rearrangement increases.

Electronic and steric factors both affect the competition between the two reaction pathways. The allyls with relatively bulky substituents at C-3—cinnamyl and 3-methyl-2-butenyl—exhibit preference for reactions without rearrangement when compared with the sterically less hindered 2-butenyl compounds. Pentamethylcyclopentadienyl complexes of the type $[\pi\text{-C}_5(\text{CH}_3)_5]\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}=\text{C}(\text{R})(\text{R}')$, in which the metal possesses higher electron density than in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}=\text{C}(\text{R})(\text{R}')$, as reflected by the values of $\nu(\text{CO})$, react preferentially *via* "direct insertion."

The foregoing observations on reactions of σ -allyl complexes with SO₂ prompted an extension of the investigation to analogous 2-alkynyl derivatives (MCH₂C≡CR). It had been thought that the products here might be the rearranged allenyl sulfinate (MSO₂C(R)=C=CH₂).

Thomasson⁷¹ discovered that SO₂ exhibits a remarkable affinity for the 2-propynyl (R = H) and 2-butynyl (R = CH₃) complexes of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_2\text{C}\equiv\text{CR}$ and $\text{Mn}(\text{CO})_5\text{CH}_2\text{C}\equiv\text{CR}$, either in the liquid at *ca.* -70° or in pentane solution at 25°, to give stable solids analyzing as 1:1 SO₂ adducts of the parent organometallics. Later it was shown^{69,72,73} that 2-alkynyl derivatives of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CR}$ react analogously. Our initial formulation of these complexes as the allenyl(oxy)sulfinyls, MS(O)OC(R)=C=CH₂, based on limited spectral evidence, as well as their subsequent designation as the allenyl-*O*-sulfinate, MOS(O)-C(R)=C=CH₂, by a French group,⁷² was found later to be incompatible with ¹H magnetic resonance data. Professor Churchill eventually resolved the dilemma by carrying out a three-dimensional X-ray crystallographic study on $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CCH}_3\cdot\text{SO}_2$; the structure proved to be that of a very unusual metal-vinyl complex containing a sultine ring (I).^{74,75} Be-



cause of a close similarity in their infrared and ¹H nmr spectra, all other products derived from transition metal 2-alkynyls and SO₂ no doubt contain the same type of a ring system.

Any proposed mechanism of the preceding reactions

(71) (a) J. E. Thomasson, M.S. Thesis, The Ohio State University, 1968; (b) J. E. Thomasson and A. Wojcicki, *J. Amer. Chem. Soc.*, **90**, 2709 (1968).

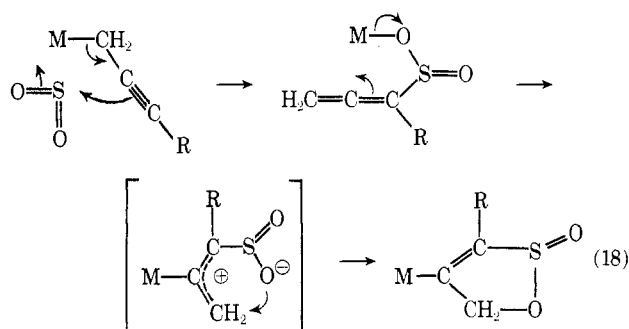
(72) J.-L. Roustan and C. Charrier, *C. R. Acad. Sci., Ser. C*, **268**, 2113 (1969).

(73) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, **10**, 2130 (1971).

(74) M. R. Churchill, J. Wormald, D. A. Ross, J. E. Thomasson, and A. Wojcicki, *J. Amer. Chem. Soc.*, **92**, 1795 (1970).

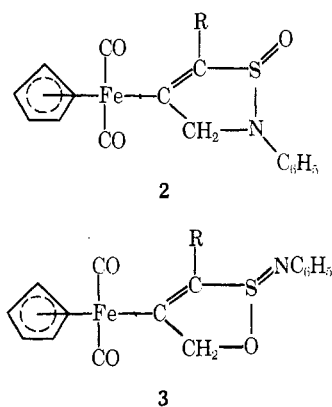
(75) M. R. Churchill and J. Wormald, *ibid.*, **93**, 354 (1971).

must necessarily be conjectural at present. We are, however, inclined to favor pathway 18, principally on



the grounds of partial analogy with the proposed mechanism for the reaction of $(C_6H_5)_3SnCH_2C\equiv CH$ with SO_2 , which gives the stable $(C_6H_5)_3Sn[OS(O)CH=C=CH_2]$.⁷⁰ Note that our suggested intermediate in eq 18 (which has yet to be detected) is also an allenyl-*O*-sulfinate; however, with *M* being now a low-valent transition metal instead of *Sn*, the stability of such a species toward subsequent rearrangement should be considerably reduced. That the anticipated allenyl-*S*-sulfinate does not form in these reactions may be ascribed to the linearity of the 2-alkynyl moiety which prevents simultaneous interaction of the sulfur with the metal and the $C\equiv C$ bond. Other reaction pathways, including a single-step one proposed by Ross⁶⁹ and by Churchill,⁷⁴ are equally plausible.

Structurally similar to SO_2 *N*-thionylamines, $RN=S=O$, present themselves as logical candidates for an extension of the above-described study. Indeed, it has now been ascertained by Robinson⁷⁶ that *N*-thionylaniline reacts with $\pi-C_5H_5Fe(CO)_2CH_2C\equiv CR$ to afford complexes of structure **2** or **3**, with **2** being favored



by infrared spectroscopy and observed chemical properties. Adaptations of these reactions, using other unsaturated molecules, to synthesis of various new ring systems is now being planned in our laboratory. Another related significant problem concerns development of reactions leading to scission of the *M*-*C* bonds and recovery of the cyclic part of the organometallic compound in good yields.

(76) P. W. Robinson and A. Wojcicki, *Chem. Commun.*, 951 (1970).

Extrusion of Sulfur Dioxide from Metal Sulfates

Since the reversibility of carbon monoxide insertion is largely responsible for the salience of this process in catalysis, we sought to determine whether a similar behavior holds for the sulfonylation. Unfortunately, our efforts to date have met with more frustration than success. Of a large variety of sulfates treated by us and others either thermally or photolytically under a wide range of conditions, only $\pi-C_5H_5Fe(CO)_2(SO_2-C_6F_5)$,⁶⁸ $\pi-C_5H_5Mo(CO)_3(SO_2CH_2C_6H_5)$,³² and a few complexes of rhodium,⁷⁷ iridium,^{77,78} and platinum^{79,80} have been found to lose SO_2 . The above-listed molybdenum compound desulfonylates photolytically, and since its parent alkyl inserts SO_2 , this system provides the only known example of insertion-elimination of SO_2 among transition metal-carbon bonds. Among representative metals, arylmercurysulfates of the type $ArHg(SO_2Ar)$, which arise, *inter alia*, via sulfur dioxide insertion, have been reported⁵³ to lose SO_2 , on heating.

The general failure of transition metal sulfates to undergo extrusion of SO_2 may be, at least in part, a consequence of the strong $M=S$ bond therein. A recent X-ray crystallographic study⁴⁴ on $[\pi-C_5(CH_3)_5]Fe(CO)_2(SO_2CH_2CH=CHC_6H_5)$ did reveal an unusually short *M*-*S* distance. Such strong *M*-*S* bonds necessitate vigorous conditions for desulfonylation which may cause decomposition of the resulting alkyl. Indeed, only in those cases where an exceptionally stable *M*-*C* linkage was formed upon extrusion of SO_2 has the reverse of the insertion been observed.

Comparison of the Sulfur Dioxide and Carbon Monoxide Insertions

In the light of the foregoing presentation of our investigations on the sulfonylation reaction it is desirable to compare and contrast the salient features of the two most extensively and intensively studied insertions, those of SO_2 and CO . There exist considerable mechanistic differences between the two processes, resulting largely from the intrinsic electrophilicity of SO_2 .

Carbon monoxide insertion, which has been shown actually to involve alkyl group migration onto a coordinated CO ²³ (see eq 5), is usually effected by nucleophilic reagents such as a coordinating solvent or an incoming Lewis base. There are exceptions, however. The electrophilic tetracyanoethylene, which undergoes insertion into *M*-*C* bonds,⁹ also induces formation of an acyl group in certain alkylcarbonyls (eq 19).⁸¹ Further, it was recently demonstrated that the union of *R* and *CO* attached to the same metal can occur in some cases without any detectable assistance from an external nucleophile.²⁰ Carbon monoxide insertions are not known for metal alkyls lacking a coordinated carbonyl group. There appear to be some exceptions

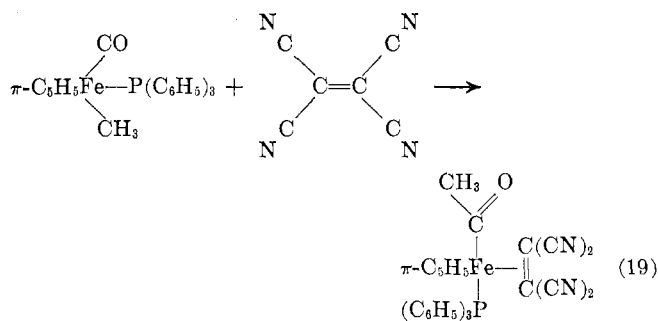
(77) J. Blum and G. Scharf, *J. Org. Chem.*, **35**, 1895 (1970).

(78) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 180 (1966).

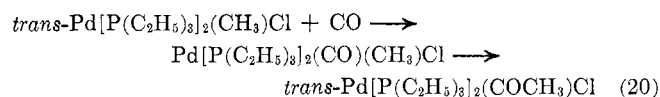
(79) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).

(80) J. Chatt and D. M. P. Mingos, *J. Chem. Soc. A*, 1770 (1969).

(81) S. R. Su and A. Wojcicki, submitted for publication.



to this generalization; in all such cases, however, one can confidently invoke a plausible carbonyl intermediate of higher coordination number as, for example, in eq 20.⁸² The rate of carbonylation is enhanced slightly,



if at all, by accumulation of negative charge at the metal. There has been no systematic study conducted on this problem; however, scattered literature data^{17,57,83} seem to indicate inhibition of insertion on replacement of CO with a P-donor ligand. For example, the rates of reaction of the compounds $\text{CH}_3\text{Co}(\text{CO})_x[\text{P}(\text{OCH}_3)_3]_{4-x}$ with $\text{P}(\text{OCH}_3)_3$ to give $(\text{CH}_3\text{CO})\text{Co}(\text{CO})_{x-1}[\text{P}(\text{OCH}_3)_3]_{5-x}$ decrease as x decreases.⁸³ More work is necessary on this aspect of CO insertion. It is also noteworthy that the carbonylation of unsymmetrical σ -allyl complexes proceeds without rearrangement of the hydrocarbon moiety.¹⁶

Similarities between the two types of insertion are recognizable as well. Both tend to be inhibited by strong metal-carbon bonds. Accordingly, complexes containing $\text{M}-\text{C}_6\text{F}_5$, $\text{M}-\text{CF}_3$, or $\text{M}-\text{CH}_2\text{CN}$ linkages insert neither CO ^{66,84} nor SO_2 .^{29,32,68} Further, within

the chromium triad, complexes $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{R}$ insert CO ⁸⁵ or SO_2 ⁸² much faster than their tungsten counterparts. Whether this relative reactivity extends to the other triads is yet to be determined. Finally, both the CO and SO_2 reactions are stereospecific processes. However, the former proceeds with retention of configuration and the latter with inversion of configuration at the α carbon of R in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$.^{63,64} Whether or not these insertions occur stereospecifically with respect to the metal still remains an unsolved problem. We are working on the synthesis of optically active $\pi\text{-C}_5\text{H}_5^*\text{Fe}(\text{CO})(\text{L})\text{R}$ with a view to elucidating the stereochemistry of insertion reactions in general.

Conclusions

Structural generalizations among reactions of unsaturated molecules with transition metal-carbon bonds led to the discovery of the novel SO_2 insertion. This process has afforded new classes of organometallic compounds with unusual and interesting structures. Significant developments in the reaction chemistry of these sulfonylation products can be expected. Moreover, an extension of the research herein described to other unsaturated electrophiles such as tetracyanoethylene is either under way or forthcoming. The relevance of these findings to the general concept of transition metal basicity should be noteworthy. Applications to homogeneous catalysis are possible but require further studies.

I am indebted to my graduate students and postdoctoral fellows, whose names appear in the bibliography, for their valuable contributions to the research described in this Account. Our work has been generously supported by the National Science Foundation (Grants GP-608, GP-5466, GP-8135, and GP-22544) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2117-A3).

(82) G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).

(83) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 1220 (1963).

(84) R. F. Heck and D. S. Breslow, *ibid.*, **84**, 2499 (1962).

(85) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).