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# SULPHUR DIOXIDE INSERTION

## XX*. THE REACTION OF SULFUR DIOXIDE WITH SOME ALKYL COMPLEXES OF CHROMIUM, MANGANESE, MOLYBDENUM, RHENIUM, AND RUTHENIUM. A COMPARATIVE STUDY OF REACTIVITY

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## Summary

The rates of the cleavage of the metal—carbon bond in $h^5$-$C_5H_5Cr(NO)_2R$, $h^5$-$C_5H_5Ru(CO)_2R$, $h^5$-$C_5H_5Mo(CO)_3R$, $Mn(CO)_5R$, and $Re(CO)_5R$ have been investigated in neat $SO_2$ at —65 to —18° by infrared and $^1H$ NMR spectroscopy. The pseudo-first-order rate constants, obtained here and elsewhere, decrease in the following orders for various groups R: $h^5$-$C_5H_5Fe(CO)_2CH_3 > Re(CO)_5CH_3 >$ $h^5$-$C_5H_5Ru(CO)_2CH_3 \sim Mn(CO)_5CH_3 \gtrsim$ $h^5$-$C_5H_5Mo(CO)_3CH_3 \gg$ $h^5$-$C_5H_5W(CO)_3CH_3$; $h^5$-$C_5H_5Cr(NO)_2CH_2C_6H_5 \gg$ $h^5$-$C_5H_5Mo(CO)_3CH_2C_6H_5 \gtrsim$ $h^5$-$C_5H_5Fe(CO)_2CH_2C_6H_5 \gtrsim Mn(CO)_5CH_2C_6H_5 >$ $h^5$-$C_5H_5Ru(CO)_2CH_2C_6H_5 \gg$ $h^5$-$C_5H_5W(CO)_3CH_2C_6H_5$; $h^5$-$C_5H_5Fe(CO)_2C_2H_5 >$ $h^5$-$C_5H_5Mo(CO)_3C_2H_5 \gg$ $h^5$-$C_5H_5W(CO)_3C_2H_5$; and $h^5$-$C_5H_5Cr(NO)_2C_6H_5 \gg$ $h^5$-$C_5H_5Fe(CO)_2C_6H_5$. In general, the methyl complexes undergo the cleavage more rapidly than their benzyl counterparts. The foregoing trends are compared with those reported in the literature for the CO insertion and for other electrophilic scission reactions.

## Introduction

This article is the second in a three-part series on the investigation of the kinetics and mechanism of sulfur dioxide insertion in transition metal—alkyl and —aryl complexes. Earlier we have reported in considerable detail [1] on the kinetics and mechanism of the reaction of various ($h^5$-ring)$Fe(CO)_2R$ alkyls and aryls with neat $SO_2$. Communicated here is a comparative study of the reactivity in the insertion of several complexes of the type $h^5$-$C_5H_5Cr(NO)_2R$, $h^5$-$C_5H_5Ru(CO)_2R$, $h^5$-$C_5H_5Mo(CO)_3R$, $Mn(CO)_5R$ and $Re(CO)_5R$. On the whole, these reactions were not studied as thoroughly as those of ($h^5$-ring)$Fe(CO)_2R$ because of a less favorable

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* For part XIX see ref. 14.

stability and/or relative reactivity of the alkylmetals and arylmetals. Furthermore, the present investigation, when compared with the previous one, focused considerably less on mechanistic details of the insertion. Instead, the principal objective was to determine the relative reactivities of the alkyl and aryl complexes as a function of the metal and attendant ligands.

In the final paper of this series we shall report [2] on the kinetics and mechanism of the sulfur dioxide insertion reaction of some $h^5$-$C_5H_5Fe(CO)_2R$ alkyls in various organic solvents.

## Experimental

### General procedure

All preparative and kinetic work was performed under an atmosphere of nitrogen. Ventron alumina, deactivated with distilled water (6—10%), and Florisil (60—100 mesh), from Fisher Scientific Co., were used in chromatographic separations and purifications.

### Physical measurements

Except as noted in Table 1, all infrared measurements were made with a Beckman Model IR-9 spectrophotometer. Solution spectra at 25° were obtained using NaCl sample cells of 0.05, 0.10 and 0.50 mm thickness in conjunction with matched reference cells. Solid state spectra were obtained as Nujol mulls.

### Materials

Anhydrous grade $SO_2$, from Matheson, was purified and dried as described previously [3]. $[Ru(CO)_3Cl_2]_2$ was purchased from Strem Chemical Co. Tetrahydrofuran (THF) was distilled from $CaH_2$ under a nitrogen atmosphere immediately before use. Other solvents and chemicals were procured in reagent grade or equivalent quality from various commercial sources and were used as received.

### Alkylmetals, arylmetals and metal S-sulfinates

The alkyls $Mn(CO)_5CH_3$ [4], $Mn(CO)_5CH_2C_6H_5$ [4], $Re(CO)_5CH_3$ [5], $h^5$-$C_5H_5Mo(CO)_3CH_3$ [6], $h^5$-$C_5H_5Mo(CO)_3CH_2C_6H_5$ [7], $h^5$-$C_5H_5Ru(CO)_2CH_3$ [8] and $h^5$-$C_5H_5Cr(NO)_2CH_2C_6H_5$ [9] were prepared by known procedures.

The complex $h^5$-$C_5H_5Ru(CO)_2CH_2C_6H_5$ was synthesized by an adaptation of the method reported for $h^5$-$C_5H_5Ru(CO)_2CH_3$ [8]. The dinuclear $[h^5$-$C_5H_5Ru(CO)_2]_2$ [10] (0.70 g, 1.6 mmoles) in 150 ml of THF was reduced with sodium amalgam and to the resulting solution was added $C_6H_5CH_2Cl$ (0.60 g, 4.7 mmoles). After 21 h of stirring solvent was removed, the residue was extracted with benzene (200 ml), and the extract was filtered through Celite. Benzene and excess $C_6H_5CH_2Cl$ were evaporated; sublimation (60°, 0.1 mm) of the remaining solid afforded 0.04 g of the orange $(h^5$-$C_5H_5)_2Ru$. Extraction of the residue from the sublimation with pentane (100 ml) and chromatography on alumina afforded a small amount (ca. 30 mg) of the desired alkylmetal (as inferred from positions of the infrared $\nu$(CO) bands) contaminated with $(h^5$-$C_5H_5)_2Ru$ and $C_6H_5CH_2Cl$. No attempt was made at further purification of this substance.

The phenyl complex $h^5$-$C_5H_5Cr(NO)_2C_6H_5$ resulted from treatment of $h^5$-$C_5H_5Cr(NO)_2Cl$ [11] (2.0 g, 9.0 mmoles) in THF (20 ml) with 7 ml of 2.14 $M$ $C_6H_5Li$ in 7/3 benzene/ether. The resulting solution was stirred at 0° for 48 h,

TABLE 1

ELEMENTAL ANALYSES AND INFRARED DATA (cm$^{-1}$) FOR NEW ALKYLMETAL AND METAL-$S$-SULFINATO COMPLEXES

| Complex | Analysis found(calcd.) (%) | | $\nu$(CO) or $\nu$(NO)[a] | $\nu$(SO)[b, c] |
|---|---|---|---|---|
| | C | H | | |
| $h^5$-$C_5H_5Ru(CO)_2CH_2C_6H_5$ | | | 2020, 1963 | |
| $h^5$-$C_5H_5Ru(CO)_2S(O)_2CH_3$ | 32.10<br>(31.89) | 2.40<br>(2.68) | 2067, 2014 | 1207, 1069, 1051 |
| $h^5$-$C_5H_5Ru(CO)_2S(O)_2CH_2C_6H_5$ | 44.08<br>(44.56) | 3.11<br>(3.21) | 2068, 2018 | 1213, 1058 |
| $h^5$-$C_5H_5Cr(NO)_2S(O)_2C_6H_5$ | 41.70<br>(41.51) | 3.26<br>(3.16) | 1820, 1710[b] | 1210, 1055 |

[a] Cyclohexane solution of the alkylmetal and $CH_2Cl_2$ solution of the $S$-sulfinate. All absorptions are very strong. [b] Recorded on a Perkin—Elmer Model 337 spectrophotometer. [c] Nujol mull.

solvent was removed, and the residue was extracted with 1/1 THF/ether. After evaporation of the solvent the remaining material was dissolved in 10 ml of pentane and chromatographed on alumina. Pentane was removed from the collected solution to afford 0.21 g (9% yield) of $h^5$-$C_5H_5Cr(NO)_2C_6H_5$ as a green oil. The compound was characterized by conversion to the corresponding $S$-sulfinate.

The $S$-sulfinates $Mn(CO)_5S(O)_2CH_3$ [12], $Mn(CO)_5S(O)_2CH_2C_6H_5$ [12], $Re(CO)_5S(O)_2CH_3$ [12], $h^5$-$C_5H_5Mo(CO)_3S(O)_2CH_3$ [13], $h^5$-$C_5H_5Mo(CO)_3S(O)_2C_2H_5$ [13], $h^5$-$C_5H_5Mo(CO)_3S(O)_2CH_2C_6H_5$ [13], and $h^5$-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$ [9] were prepared by literature methods. $h^5$-$C_5H_5Ru(CO)_2S(O)_2CH_3$ and $h^5$-$C_5H_5Ru(CO)_2S(O)_2CH_2C_6H_5$ were synthesized by treatment of the corresponding alkyl complexes with liquid $SO_2$ at —10° for 3 h followed by removal of the solvent. $h^5$-$C_5H_5Cr(NO)_2S(O)_2C_6H_5$ was obtained similarly from $h^5$-$C_5H_5Cr(NO)_2C_6H_5$ and $SO_2$ at —65°. All three $S$-sulfinato complexes were characterized by elemental analyses (Galbraith Laboratories) and infrared spectroscopy in the $\nu$(CO) or $\nu$(NO) and $\nu$(SO) stretching regions, These data, as well as the infrared spectrum of $h^5$-$C_5H_5Ru$-$(CO)_2CH_2C_6H_5$, are presented in Table 1.

### *Kinetic measurements*

Insertion reactions in neat $SO_2$ were followed by infrared or $^1$H NMR spectroscopy. For infrared work, a Beckman Model IR-9 spectrophotometer was employed in conjunction with a VLT-2 variable low-temperature cell unit manufactured by Research and Industrial Instruments Co., London, England (available in the U.S. from Beckman Instruments Co., Fullerton, Calif.). It incorporated a 0.5-mm AgCl sample cell. Suitable adaptations in the cell unit for work with liquid $SO_2$ were described previously [1].

Kinetic runs were made at temperatures between —65 and —28° as reported in detail earlier [1]. All reactions were followed for about two half-lives in the low-temperature infrared cell. Concentrations of the alkyl or aryl complex ranged from $3.5 \times 10^{-3}\,M$ to ca. $7 \times 10^{-3}\,M$.

The rates of the insertion reaction were determined by observing the rate of disappearance of the lower frequency, $\nu_{as}$(CO) of the alkyl or aryl complex. Beer's law was earlier found [1] to hold for the $\nu_{as}$(CO) absorption of $h^5$-$C_5H_5$-$Fe(CO)_2CH_2C_6H_5$ in the concentration range $1 \times 10^{-3}\,M$ to $9 \times 10^{-3}\,M$; it was assumed also to be valid for the complexes investigated herein. For $h^5$-$C_5H_5Cr(NO)_2R$ (R = $CH_2C_6H_5$ or $C_6H_5$), the lower frequency, $\nu_{as}$(NO) band is masked by absorptions of the $SO_2$ solvent; therefore, the higher frequency, $\nu_s$(NO) of the sulfinato product was followed. The treatment of the kinetic data to obtain pseudo-first-order rate constants, $k_{obs}$, was the same as that described earlier [1]. The results are reproducible to ± 10% for $h^5$-$C_5H_5Mo(CO)_3CH_3$ and to ± 15% for the other complexes examined.

The complexes $M(CO)_5R$ (M = Mn, R = $CH_3$ and $CH_2C_6H_5$; M = Re, R = $CH_3$) were investigated by $^1H$ NMR spectroscopy because of an extensive overlap between their infrared $\nu$(CO) absorptions and the $\nu$(CO) bands of the resultant sulfinates. The instrument used was a Varian A-60A spectrometer equipped with low-temperature accessories. Sulfur dioxide was condensed (1—2 ml) onto 50—60 mg of the alkyl complex in an NMR tube which was then sealed under vacuum at —196°. Kinetic measurements were made at —18 ± 2°. The reactions of Mn(CO) (R = $CH_3$ and $CH_2C_6H_5$) were followed for two half-lives whereas that of $Re(CO)_5CH_3$ was monitored only over its last 25% because of a rapid rate. The kinetic data are reproducible to ± 30%.

## Results

The alkylmetals and arylmetals investigated herein react with $SO_2$ to afford the corresponding *S*-sulfinates as the final, isolable products. Recently, several of these same complexes, viz. $h^5$-$C_5H_5Mo(CO)_3CH_2C_6H_5$, $Mn(CO)_5CH_3$, $Mn(CO)_5CH_2C_6H_5$, and $Re(CO)_5CH_3$, have been shown spectroscopically to yield the *O*-sulfinates initially upon the insertion [3]. Their subsequent rearrangement to the *S*-bonded isomers completes the insertion.

Reaction of $h^5$-$C_5H_5Ru(CO)_2CH_3$ with neat $SO_2$ is accompanied by a diminution of intensity of the $\nu_{as}$(CO) band of the alkylmetal and a simultaneous growth of a sulfinate $\nu_s$(CO) absorption at 2063 $cm^{-1}$. After approximately 40 min at —48° a new band at 2074 $cm^{-1}$ begins to increase in intensity while that at 2063 $cm^{-1}$ remains essentially unchanged. Refluxing the solution for 2 h affords complete conversion to the *S*-sulfinate. It therefore appears that the 2063 $cm^{-1}$ absorption is due to $\nu_s$(CO) of the *O*-sulfinate; that at 2074 $cm^{-1}$ is assigned to $\nu_s$(CO) of the *S*-sulfinate.

The remaining complexes studied herein are structurally very similar to those whose *O*-sulfinates have been observed spectroscopically; accordingly, they are assumed to adopt a similar reaction pathway in the insertion. For the nitrosyl complexes $h^5$-$C_5H_5Cr(NO)_2R$ (R = $CH_2C_6H_5$ and $C_6H_5$) in liquid $SO_2$ at —65°, the first infrared spectra taken revealed the presence of a sulfinate $\nu_s$(NO) band at 1820 $cm^{-1}$. This band did not change intensity on storage of the solution for 2 h, indicating that a very rapid reaction had occurred. We did not ascertain whether the above absorption was due to the *O*-sulfinate or the *S*-sulfinate, or to both.

In this investigation were measured the rates of scission of the M—C$\sigma$ bonds by $SO_2$ to yield the corresponding, detectable sulfinato products. The disappearance of the alkylmetal was found to follow the expression

$$\text{rate} = k_{obs}[\text{alkylmetal}]$$

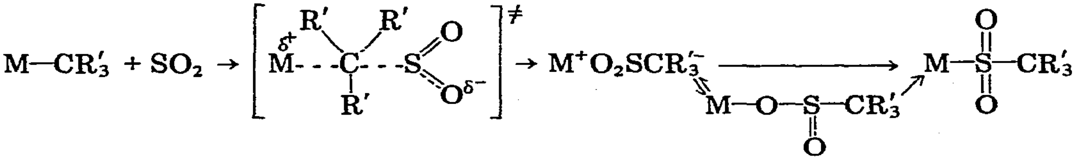
for the complex $h^5$-$C_5H_5Mo(CO)_3CH_3$ whose reaction was studied in considerable detail over the temperature range —58 to —29° (see Table 2). In the above equation $k_{obs}$ contains an indeterminable dependence on the concentration of $SO_2$. The same rate expression was found earlier for the insertion in several alkylirons and arylanions of the formula ($h^5$-ring)$Fe(CO)_2R$ [1]; it is assumed to hold also for the remaining complexes investigated herein.

The reaction of $h^5$-$C_5H_5Mo(CO)_3CH_3$ with $SO_2$ proceeds cleanly, without any sign of decomposition, for two half-lives. In contrast, the insertion in $h^5$-$C_5H_5Mo(CO)_3C_2H_5$ and $h^5$-$C_5H_5Mo(CO)_3CH_2C_6H_5$ is accompanied by a gradual change of color from orange to green and by some deposition of a black, insoluble material. These signs of decomposition become apparent in less than two half-lives. Solutions of other alkylmetals for which values of $k_{obs}$ were determined did not show decomposition in the course of the kinetic measurements.

Rate data obtained in this study are presented in Table 2. Complexes of the formula $h^5$-$C_5H_5Fe(CO)_2R$, which were investigated earlier [1], and $h^5$-$C_5H_5W(CO)_3R$, which were studied qualitatively elsewhere [14], are included for broader comparison. The listing of the various metal—alkyl systems follows descending order of reactivity of their methyl ($R = CH_3$) derivatives toward $SO_2$ at —18°. Rate constants, $k_{obs}$, which could not be measured at —18° were calculated either using known $\Delta H^{\neq}$ or, if $\Delta H^{\neq}$ was not available, assuming it to be 2.9 kcal/mole. This last value was obtained for the insertion in $h^5$-$C_5H_5Fe(CO)_2CH_2C_6H_5$ which proceeds very cleanly and which was studied over a comparatively wide temperature range [1]. Significantly, it compares extremely well with $\Delta H^{\neq}$ 2.7 kcal/mole obtained in this investigation for the insertion reaction of $h^5$-$C_5H_5Mo(CO)_3CH_3$.

## Discussion

On the basis of a recent kinetic study of the sulfur dioxide insertion in ($h^5$-ring)$Fe(CO)_2R$ we have proposed [1] a general reaction mechanism which is depicted below. Very likely, the same mechanism holds also for the alkyl compounds examined herein. This supposition is supported by the observed intermediacy of O-bonded sulfinates in $SO_2$ insertion of alkylmetals, as well as by the large and negative value of $\Delta S^{\neq}$ (—63 ± 2 eu) for the reaction of $SO_2$ with $h^5$-$C_5H_5Mo(CO)_3CH_3$. As indicated earlier in this paper, the reported rate constants, $k_{obs}$, refer to the scission of the M—$CR'_3$ (or M—R) bond by $SO_2$.



Examination of the data in Table 2 reveals that, with the exception of $h^5$-$C_5H_5Cr(NO)_2R$ and $h^5$-$C_5H_5W(CO)_3R$, there generally does not appear to be much of a variation among the rate constants for different metal—alkyl systems having the same group R. The chromium complexes $h^5$-$C_5H_5Cr(NO)_2R$ ($R = CH_2C_6H_5$ and $C_6H_5$) react very rapidly whereas the tungsten complexes $h^5$-$C_5H_5W(CO)_3R$ ($R = CH_3$, $C_2H_5$, and $CH_2C_6H_5$) react immeasurably slowly. Moreover,

TABLE 2

REACTIONS OF $h^5$-$C_5H_5M(CO)_xR$, $M(CO)_5R$, AND $h^5$-$C_5H_5Cr(NO)_2R$ ALKYLS AND ARYLS WITH NEAT SULFUR DIOXIDE[a]

| General formula of complex | R = $CH_3$ | | R = $CH_2C_6H_5$ | | R = $C_2H_5$ | R = $C_6H_5$ |
|---|---|---|---|---|---|---|
| | $k_{obs}$(sec$^{-1}$) | Rel. $k_{obs}$ | $k_{obs}$(sec$^{-1}$) | Rel. $k_{obs}$ | $k_{obs}$(sec$^{-1}$) | $k_{obs}$(sec$^{-1}$) |
| $h^5$-$C_5H_5Cr(NO)_2R$ | | | v. fast at −65°[h] | | | v. fast at −65°[h] |
| $h^5$-$C_5H_5Fe(CO)_2R$[b] | $1.1 \times 10^{-3}$ at −65° | | $1.6 \times 10^{-4}$ at −40° | | v. fast at −65°[h] | $2.0 \times 10^{-6}$ at −40° |
| | $5.0 \times 10^{-3}$[d] | 15 | $3.0 \times 10^{-4}$[f] | <2 | | $8.6 \times 10^{-6}$[f] |
| $Re(CO)_5R$ | $1.3 \times 10^{-3}$ | 4 | | | | |
| $h^5$-$C_5H_5Ru(CO)_2R$ | $3.3 \times 10^{-4}$ at −48° | | slow at −28°[i] | | | |
| | $8.0 \times 10^{-4}$[d] | 2 | | | | |
| $Mn(CO)_5R$ | $7.4 \times 10^{-4}$ | 2 | $1.7 \times 10^{-4}$ | 1 | | |
| $h^5$-$C_5H_5Mo(CO)_3R$ | $1.8 \times 10^{-4}$ at −40°[e] | | $1.6 \times 10^{-4}$ at −48° | | $5.6 \times 10^{-4}$ at −48° | |
| | $3.3 \times 10^{-4}$[f] | 1 | $3.9 \times 10^{-4}$[d] | >2 | $1.4 \times 10^{-3}$[d] | |
| $h^5$-$C_5H_5W(CO)_3R$[c] | v. slow at 50°[g] | | v. slow at 50°[g] | | v. slow at 50°[g] | |

[a] At −18° unless otherwise indicated. [b] Data from ref. 1. [c] Data from ref. 14. [d] Calculated assuming $\Delta H^{\neq} = 2.9$ kcal/mole. [e] $k_{obs} \times 10^4$ (sec$^{-1}$) at various temperatures: 2.90 (−29°), 2.45 (−32°), 2.08 (−37°), 1.83 (−37.5°), 1.63 (−44.5°), 1.91 (−46°), 1.65 (−47°), 1.90 (−48°), 0.90 (−58.5°), 1.01 (−62°). From these, $\Delta H^{\neq} = 2.7 \pm 0.4$ kcal/mole and $\Delta S^{\neq} = -63 \pm 2$ eu. A general least-squares computer program was used to obtain $\Delta H^{\neq}$. Limits of error for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are one standard deviation. [f] Calculated value. [g] 10-27% S-sulfinate isolated after 3 days at 50—55°. [h] Too rapid to measure by this method. [i] Reaction approximately 50% complete after 3 h at −10°.

apart from $h^5$-$C_5H_5Mo(CO)_3CH_3$ which reacts at about the same rate as $h^5$-$C_5H_5$-$Mo(CO)_3CH_2C_6H_5$, methyl complexes undergo the insertion more rapidly than the analogous benzyl complexes. This order $R = CH_3 > CH_2C_6H_5$ is consistent with electrophilic cleavage of the M—R bond by $SO_2$ [1].

Considering now the relative reactivities of analogous compounds of metals belonging to the same triad, it is to be noted that the $SO_2$ insertion, like the CO insertion [15], proceeds much faster in $h^5$-$C_5H_5Mo(CO)_3R$ than in $h^5$-$C_5H_5W$-$(CO)_3R$. Furthermore, the complexes $h^5$-$C_5H_5Fe(CO)_2R$ ($R = CH_3$ and $CH_2C_6H_5$) react with $SO_2$ more rapidly than do their $h^5$-$C_5H_5Ru(CO)_2R$ counterparts. Again, the CO insertion appears to follow a parallel trend [16]. Based on the above comparisons, the observed reactivity order $Re(CO)_5CH_3 > Mn(CO)_5CH_3$ toward $SO_2$ comes as a surprise. It would be desirable to correlate the rates of $SO_2$ insertion with the relative M—R bond strengths; unfortunately, the latter data are not available.

A comparison of the isoelectronic $h^5$-$C_5H_5Fe(CO)_2R$ and $h^5$-$C_5H_5Cr(NO)_2R$ is also noteworthy. When $R = CH_2C_6H_5$ or $C_6H_5$, the latter system inserts $SO_2$ much more rapidly than the former. This may be a result of the lower formal oxidation state of chromium(0) than of iron(II) and is entirely consistent with an electrophilic nature of the insertion.

Although the CO and $SO_2$ insertions both proceed faster in $h^5$-$C_5H_5Mo(CO)_3R$ than in $h^5$-$C_5H_5W(CO)_3R$ and in $h^5$-$C_5H_5Fe(CO)_2R$ than in $h^5$-$C_5H_5Ru(CO)_2R$, this similarity does not extend to all types of compounds examined. For instance, the reactivity of methyl complexes toward the CO insertion follows the orders $Mn(CO)_5CH_3$ (~ 23) > $h^5$-$C_5H_5Mo(CO)_3CH_3$ (1) and $h^5$-$C_5H_5Mo(CO)_3CH_3$ (100) > $h^5$-$C_5H_5Fe(CO)_2CH_3$ (1) in THF at 25 and 51°, respectively [17]. For the $SO_2$ insertion at $-18°$ the sequence is quite different, viz. $h^5$-$C_5H_5Fe(CO)_2CH_3$ (15) > $Mn(CO)_5CH_3$ (2) > $h^5$-$C_5H_5Mo(CO)_3CH_3$ (1), with the spread being much smaller than for the CO insertion. This is really not very surprising when one considers the marked differences in mechanism of the two types of insertion. Only when the strength of a given M—R bond appears to be dominant is there any parallelism between these reactions.

Very limited data are available in the literature which would permit a comparison of relative reactivities toward different electrophiles of complexes of the type discussed in this paper. Johnson [18] has reported that $h^5$-$C_5H_5Fe(CO)_2R$ ($R = 3\text{-}CH_2C_5H_4NH^+$) is cleaved more rapidly ($\lesssim 10$ times) than the corresponding $Mn(CO)_5R$ by all $HgCl_x^{2-x}$ ($x = 0$—$4$) species in aqueous solution. Interestingly, the same order of reactivity has been observed here in the $SO_2$ insertion when $R = CH_3$ or $CH_2C_6H_5$. Whether or not this observation is significant must await further kinetic as well as stereochemical studies on reactions of alkyl-transition metals with various electrophiles.

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