dimensions for the copper(II) complex would, therefore, question the occurrence of pseudo-rotation alone in these complexes. A closer examination of the process of pseudo-rotation, in the light of these conclusions, confirms that a reduction in the unit cell dimension cannot occur as the movement of the separate ammonia groups is such that at some stage they must separately pass through the position corresponding to a regular octahedral coordination of the copper(II) ion. At this point a general expansion of the interiodide distances must occur for the four iodide ions (which lie in the plane of the ammonia molecule), with a corresponding increase of the unit cell in this plane to 10.92 A, the value applying to a regular octahedral coordination of the copper(II) ion. The only way in which the cubic unit cell could be maintained would be if the expansion in the sheets of iodide ions occurred successively in three planes at right angles and was synchronized to the pseudo-rotation of the hexaamminecopper(II) cations. This situation of coupled pseudo-rotation would produce a slight contraction of the unit cell dimension but is considered less likely than the form of restricted rotation suggested above.

An examination of the effect of temperature on these isotropic esr spectra is in hand in an attempt to resolve these two possible interpretations.

Acknowledgments.—The authors are indebted to Mrs. G. Payne for the reflectance spectra, to Mr. P. A. Dagleish for the electron spin resonance spectra, to the Science Research Council for a grant for special reseach (Beckman spectrophotometer) and for a maintenance grant (H. E.), and to Dr. P. G. Nelson for helpful discussion.

CONTRIBUTION FROM THE MCPHERSON AND EVANS CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Reactions of Cyclopentadienyl(methyl)iron Dicarbonyl with Various Ligands. Cyclopentadienyl(acetyl)iron Carbonyl Phosphine and Phosphite Complexes

BY JANE P. BIBLER AND ANDREW WOJCICKI

Received November 27, 1965

Cyclopentadienyl(methyl)iron dicarbonyl reacts with $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(OC_4H_9)_3$ in refluxing tetrahydrofuran to give almost quantitative yields of the complexes $C_5H_5Fe(CO)(COCH_3)L$ (L = phosphine or phosphite). The properties of these derivatives are listed, and the infrared and nuclear magnetic resonance spectra are briefly discussed. Under similar experimental conditions there is no reaction between $C_5H_5Fe(CO)_2CH_3$ and diethyl sulfide, iodide ion, *p*-toluidine, and *p*-chloroaniline; pyridine affords a noncarbonyl decomposition product. Furthermore, in contrast to its behavior in tetrahydrofuran, $C_5H_5Fe(CO)_2CH_3$ does not react with triphenylphosphine in refluxing hexane.

Introduction

Recently we have reported that $C_5H_5Fe(CO)_2CH_3$ reacts rapidly with liquid sulfur dioxide[1] and more slowly with SO_2 in pentane[2] to yield the sulfonyl derivative, $C_5H_5Fe(CO)_2SO_2CH_3$. Mechanistically, this "insertion" most likely involves methyl group migration;[3] therefore, particular interest attaches to the fact that the CH_3 becomes ultimately bonded to the attacking SO_2 rather than to a CO present in the complex. Since formation of an intermediate acetyl, $C_5H_5Fe(CO)(COCH_3)SO_2$, cannot be ruled out from the evidence on hand, studies on reactions of $C_5H_5Fe(CO)_2CH_3$ with nucleophiles onto which the methyl group cannot migrate may provide valuable information concerning the course of the sulfur dioxide "insertion."

Survey of the literature reveals that the only ligand known to react with $C_5H_5Fe(CO)_2CH_3$ to give a cyclopentadienyliron carbonyl acetyl derivative is carbon monoxide.[4] This scarcity of data on $C_5H_5Fe(CO)_2CH_3$ is in contrast to the amount of information available on reactions between $CH_3Mn(CO)_5$ and various nucleophiles. The latter alkyl reacts with carbon monoxide,[5] amines,[6] phosphines, phosphites,[7,8] arsines, stibines,[8] and iodide, cyanide, thiocyanate, and methoxide ions[9] to cause methyl group migration onto a carbonyl ligand.

Our current studies on the mechanism of sulfur dioxide insertion with $C_5H_5Fe(CO)_2CH_3$ prompted us to investigate the reaction of this alkyl complex with several other nucleophiles. It was of particular interest to determine whether, as with $CH_3Mn(CO)_5$, methyl migration is a fairly general reaction and, if so, what properties of a nucleophile are responsible for effecting this process. Reported now are results on reactions of

---

[1] J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **86**, 5051 (1964).

[2] A. Wojcicki and J. P. Bibler, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 36 M.

[3] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

[4] T. H. Coffield, J. Kozikowski, and R. D. Closson, Special Publication No. 13, The Chemical Society, London, 1959, p 126.

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

[6] K. A. Keblys and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

[7] R. J. Mawby, F. Basolo, and R. G. Pearson, *ibid.*, **86**, 3994 (1964).

[8] W. D. Bannister, M. Green, and R. N. Haszeldine, *Chem. Commun.*, 54 (1965).

[9] F. Calderazzo and K. Noack, *J. Organometal. Chem.* (Amsterdam), **4**, 250 (1965).

TABLE I

$C_5H_5Fe(CO)(COCH_3)L$ COMPLEXES

Complex	Color	Mp, °C[a]		Mol wt[b]	Analyses, % C	H	P	Fe
$C_5H_5Fe(CO)(COCH_3)[P(C_6H_5)_3]$[c]	Orange	145	Calcd	454	68.95	5.06	6.82	
			Found	431	69.06	5.00	6.56	
$C_5H_5Fe(CO)(COCH_3)[P(C_4H_9)_3]$	Orange	35–37	Calcd	280	60.90	8.90	7.86	14.20
			Found	305	60.60	9.30	7.83	14.13
$C_5H_5Fe(CO)(COCH_3)[P(OC_6H_5)_3]$	Yellow-orange	65	Calcd	502	62.15	4.58	6.18	
			Found	481	61.94	4.49	6.21	
$C_5H_5Fe(CO)(COCH_3)[P(OC_4H_9)_3]$	Yellow-orange	. . .[d]	Calcd		54.30	7.91	7.01	
			Found		55.13	8.13	6.82	

[a] Determined with a melting-point block and uncorrected. [b] Osmometry (10^{-2} to 2×10^{-2} *M* solutions in $CHCl_3$) with a Mechrolab Model 301-A instrument. [c] Also prepared independently by M. L. H. Green and R. H. Hurley (private communication). [d] Liquid at 25°.

$C_5H_5Fe(CO)_2CH_3$ with several ligands as well as the synthesis and properties of some new complexes $C_5H_5Fe(CO)(COCH_3)L$ where L is a phosphine or a phosphite.

Experimental Section

Materials.—The compound $C_5H_5Fe(CO)_2CH_3$ was prepared by the method of Piper and Wilkinson.[10] Triphenylphosphine, triphenyl phosphite, tri-*n*-butyl phosphite, diethyl sulfide, *p*-chloroaniline, *p*-toluidine, and tetramethylammonium iodide were purchased from Matheson Coleman and Bell and used without further purification. Tri-*n*-butylphosphine was obtained from Metal and Thermit Co.; it was distilled *in vacuo*. Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Chloroform, ether, and pyridine were analytical reagent grade. Technical grade pentane and hexane were used without further purification. Woelm alumina (neutral, activity grade III) was employed for chromatography.

Reaction of $C_5H_5Fe(CO)_2CH_3$ with Phosphines and Phosphites in Tetrahydrofuran. General Procedure for the Synthesis of $C_5H_5Fe(CO)(COCH_3)L$ (L = $P(C_6H_5)_3$, $P(C_4H_9)_3$, $P(OC_6H_5)_3$, $P(OC_4H_9)_3$).—One gram (0.005 mole) of $C_5H_5Fe(CO)_2CH_3$ and *ca.* 0.005 mole of ligand dissolved in 10 ml of freshly distilled tetrahydrofuran were refluxed under dry nitrogen. Progress of the reaction was monitored by infrared spectroscopy. When no more iron alkyl could be detected (*ca.* 48 hr), the mixture was filtered to remove trace amounts of an insoluble brown solid. Solvent was then evaporated under reduced pressure (~20 mm), and the residue was dissolved in *ca.* 10 ml of pentane. Purification was effected by chromatography on an alumina column (5 × 20 cm). In all cases, only one band (orange to yellow-orange) was eluted with pentane (phosphine complexes) or 50:50 (by volume) pentane–chloroform (phosphite complexes). Solvent was removed under reduced pressure (~20 mm) to give 96–99% yield of the acetyl derivative. Elemental analyses and other data on the complexes are given in Table I.

When the above reaction was carried out using 0.005 mole of $C_5H_5Fe(CO)_2CH_3$ and 0.02 mole of $P(C_4H_9)_3$, the formation of the acetyl complex was virtually complete in 30 hr.

Reaction of $C_5H_5Fe(CO)_2CH_3$ with Phosphines ($P(C_6H_5)_3$, $P(C_4H_9)_3$) in Ether.—One gram (0.005 mole) of $C_5H_5Fe(CO)_2CH_3$ and *ca.* 0.005 mole of phosphine in 10 ml of ether were refluxed for 48 hr under nitrogen. Only a trace amount of an insoluble brown decomposition product resulted. The mixture was treated as described for the tetrahydrofuran reaction. Pentane eluted two bands from the alumina column: unreacted alkyl followed by the product. Yield: 50% with $P(C_6H_5)_3$ and 21% with $P(C_4H_9)_3$.

Reaction of $C_5H_5Fe(CO)_2CH_3$ with Triphenylphosphine in Hexane.—One gram (0.005 mole) of $C_5H_5Fe(CO)_2CH_3$ and 1.31 g (0.005 mole) of triphenylphosphine in 10 ml of hexane were refluxed under dry nitrogen. After 7 days it was determined (infrared spectroscopy) that no reaction had taken place.

Reaction of $C_5H_5Fe(CO)_2CH_3$ with Other Ligands in Tetrahydrofuran. Attempted Synthesis of $C_5H_5Fe(CO)(COCH_3)L$ (L = $(C_2H_5)_2S$, *p*-$CH_3C_6H_4NH_2$, *p*-$ClC_6H_4NH_2$, I^-, C_5H_5N).—One gram (0.005 mole) of $C_5H_5Fe(CO)_2CH_3$ and 0.005 mole of ligand in 10 ml of freshly distilled tetrahydrofuran were refluxed for 48 hr under dry nitrogen. Infrared spectra of the solutions revealed that diethyl sulfide, *p*-toluidine, *p*-chloroaniline, and tetramethylammonium iodide failed to react; pyridine decomposed the carbonyl to an insoluble, black, noncarbonyl material.

Infrared Spectra.—Spectra were recorded on a Beckman Model IR-9 spectrophotometer using a 0.05-mm KBr cell.

Proton Magnetic Resonance Spectra.—The nmr spectra were obtained using a Varian Associates A-60 spectrometer. Tetramethylsilane was employed as an external standard.

Analyses.—Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Reactions of $C_5H_5Fe(CO)_2CH_3$ with Various Ligands.—One of the most interesting observations made in this study concerns the tremendous effect that the nature of solvent exerts upon the rate of reaction of $C_5H_5Fe(CO)_2CH_3$ with triphenylphosphine

$$C_5H_5Fe(CO)_2CH_3 + P(C_6H_5)_3 \longrightarrow C_5H_5Fe(CO)(COCH_3)[P(C_6H_5)_3]$$

In refluxing tetrahydrofuran (65°) the formation of the product is virtually complete in 48 hr; however, in refluxing hexane (68°) no reaction progress can be detected over the same period of time. In boiling ether (34°) the reaction is about 50% complete in 48 hr.

These results indicate that coordinating ability of the solvent plays a very important role in effecting conversion of the methyl dicarbonyl complex to the acetyl monocarbonyl derivative. Both ether and tetrahydrofuran may, by entering the coordination sphere of the metal, assist migration of the methyl group in the manner suggested[7] for the reaction of $CH_3Mn(CO)_5$ with a variety of nucleophiles. However, hexane is devoid of coordinating ability, and therefore any assist that the methyl group receives must come from the entering ligand. Since in these reactions the concentration of triphenylphosphine was much lower than that of solvent, the apparent lack of reactivity of $C_5H_5Fe(CO)_2CH_3$ in hexane is not unexpected.

It has been also demonstrated here that the nature of entering ligand is important in effecting the formation of the acetyl monocarbonyl derivatives. Whereas phosphines and phosphites are capable of almost quan-

---

[10] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

TABLE II

INFRARED CO STRETCHING FREQUENCIES AND PROTON MAGNETIC RESONANCE SPECTRA OF $C_5H_5Fe(CO)(COCH_3)L$ COMPLEXES

	CO stretching frequencies, cm^{-1} [a]		Nmr spectrum[b]		
	Terminal	Acetyl	Chem shift, τ	Rel intens	Assignment
$C_5H_5Fe(CO)(COCH_3)[P(C_6H_5)_3]$	1920 vs, br	1598 s	2.41 (multiplet)	15	C_6H_5
			5.38 (singlet)	5	C_5H_5
			7.48 (singlet)	3	CH_3
$C_5H_5Fe(CO)(COCH_3)[P(C_4H_9)_3]$	1916 vs, br	1590 s	5.33 (singlet)	5	C_5H_5
			7.25 (singlet)	3	CH_3
			8.02–9.21 (complex multiplets)	27	C_4H_9
$C_5H_5Fe(CO)(COCH_3)[P(OC_6H_5)_3]$	1950 vs, br	1608 vs	2.54 (multiplet)	15	C_6H_5
			5.68 (singlet)	5	C_5H_5
			7.32 (singlet)	3	CH_3
$C_5H_5Fe(CO)(COCH_3)[P(OC_4H_9)_3]$	1959 vs, br	1625 vs	5.33 (singlet)	5	C_5H_5
			6.03 (quartet)[c]	6	OCH_2
			7.43 (singlet)	3	CH_3
			8.08–9.17 (complex multiplets)	21	$CH_2CH_2CH_3$

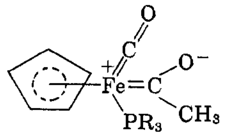
[a] $CHCl_3$ solution. Abbreviations: vs, very strong; s, strong; br, broad. [b] $CDCl_3$ solution. [c] Separation $\sim$6 cps.

titatively reacting with $C_5H_5Fe(CO)_2CH_3$ to give $C_5H_5Fe(CO)(COCH_3)PR_3$ and $C_5H_5Fe(CO)(COCH_3)[P(OR)_3]$, respectively, diethyl sulfide, iodide ion, *p*-toluidine, and *p*-chloroaniline do not react at all under similar experimental conditions. Pyridine, on the other hand, completely decomposes the parent complex to a black, noncarbonyl solid.

Since ligands that do not react are weaker π bonders than phosphines or phosphites, their inability to effect the synthesis of $C_5H_5Fe(CO)(COCH_3)L$ may be due to the insufficient π-bonding capacity of the donor atom. In support of this hypothesis is the fact that $C_5H_5Fe(CO)_2CH_3$ undergoes insertion reactions with CO[4] and SO_2,[1,2] both of which are good π-bonding groups.[11] It therefore appears that the entering nucleophile must have a certain minimum *biphilic*[12] character to react successfully with cyclopentadienyliron carbonyl alkyls. Decomposition which occurs with pyridine may result from a possible instability of the acetyl derivative, $C_5H_5Fe(CO)(COCH_3)(C_5H_5N)$, in the basic pyridine solution. Support for this conjecture is derived from the observation that $C_5H_5Fe(CO)_2CH_3$ forms noncarbonyl decomposition products in solutions containing reagents of basicity comparable to or greater than that of pyridine.[13]

Acetyl Derivatives.—The acetyl derivatives containing triphenylphosphine, tri-*n*-butylphosphine, and triphenyl phosphite are crystalline solids, stable to air; the tri-*n*-butyl phosphite complex is an air-sensitive liquid. Chloroform and benzene solutions of all four compounds decompose rapidly in air to produce brown solids. The derivatives are soluble in pentane, benzene, and dichloromethane but insoluble in methanol and water. The phosphine complexes are deep orange whereas the phosphite compounds are yellow-orange.

The infrared spectra of the derivatives reveal two strong carbonyl stretching absorptions: a terminal one at 1916–1959 cm^{-1} and an acetyl one at 1590–1625 cm^{-1}. These are listed in Table II. It is of interest to note that the above frequencies are lower than those in the parent dicarbonyl compound, $C_5H_5Fe(CO)_2(COCH_3)$. In the latter, the terminal CO groups absorb at 2018 and 1963 cm^{-1}, and the acetyl CO absorbs at 1655 cm^{-1}.[14] The most plausible explanation of these spectral differences is that replacement of CO in $C_5H_5Fe(CO)_2(COCH_3)$ by the more basic and poorer π-acceptor phosphine or phosphite enhances π bonding between the metal and the remaining terminal and acetyl carbonyl groups. This situation arises because now only one terminal CO and the acetyl carbonyl, instead of two terminal CO groups and the acetyl group, make significant demand for iron dπ electrons. Thus, an increased contribution of resonance structure



to the bonding reduces carbon–oxygen bond orders in both the terminal carbonyl and the acetyl moiety and hence lowers the CO stretching frequencies.[15] Also consistent with the above explanation is the observation that phosphines, which π bond less effectively than phosphites,[16] cause larger shifts to lower energy of both carbonyl stretching absorptions.

The proton magnetic resonance spectra of the derivatives, given in Table II, are in complete accord with the proposed structures. Thus, the methyl hydrogen signals occur at τ values (7.25–7.48) which are expected for metal acetyl complexes but which are considerably lower than those reported for transition metal compounds containing $M-CH_3$ bonds.[17] Furthermore, the sharpness of these resonances suggests that the derivatives are diamagnetic. No splitting of the acetyl and cyclopentadienyl hydrogen signals due to interaction of the protons with the phosphorus nucleus was observed in any of the spectra; however, it is conceivable

---

(11) E. H. Braye and W. Hübel, *Angew. Chem.*, **75**, 345 (1963); J. A. Ibers, paper presented at 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5–9, 1965.

(12) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, (1960).

(13) J. P. Bibler and R. L. Downs, unpublished observations.

(14) R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).

(15) Such metal–carbon π bonding in transition metal acyl complexes was first suggested by G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961).

(16) E. A. Magnuson, *Rev. Pure Appl. Chem.*, **7**, 195 (1957).

(17) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

that such splitting can be detected under high resolution.[18]

It is of interest that, in each case, the resonance due to the cyclopentadienyl protons appears at a higher field than the signal reported for the parent $C_5H_5Fe(CO)_2(COCH_3)$. This shift may result from replacement of CO by the more basic phosphines or phosphites which would place higher electron density on the ring. Surprisingly, however, no systematic relationship appears to exist between the basicity of the phosphorus-containing ligand and the chemical shift of the cyclopentadienyl (and acetyl) protons.

The complexes prepared in this study contain four different groups bonded to iron; in this respect they resemble the cyclopentadienylcobalt[19] and -rhodium[20] carbonyl derivatives, $C_5H_5M(CO)(R_F)I$ (M = Co, Rh; $R_F = CF_3, C_2F_5, C_3F_7$), and the methoxycarbonyl compound of manganese, $C_5H_5Mn(CO)(NO)(COOCH_3)$.[21] Since the arrangement of four groups around the metal is in all probability "tetrahedral,"[22] it should be possible to effect resolution of these organometallic racemates into their respective enantiometers. This, however, has not been attempted in our study.

Acknowledgment.—Support of this research by a grant from The Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[18] High-resolution nmr spectra of the isomeric $[C_5H_5Fe\{P(CH_3)_2\}(CO)]_2$ show that the cyclopentadienyl resonances are triplets due to coupling of the cyclopentadienyl protons with the two equivalent phosphorus nuclei; see R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

[19] R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3593 (1961).

[20] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

[21] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), **4**, 256 (1965).

[22] The existence of optical isomers of $C_5H_5Rh(CO)(C_2F_5)I$ has been demonstrated by X-ray crystallography; see M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

CONTRIBUTION[1] FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

Syntheses of Some Cyclopentadienyl Transition Metal Sulfides and the Crystal Structure of $(C_5H_5FeS)_4$

BY R. A. SCHUNN, CHARLES J. FRITCHIE, JR., AND C. T. PREWITT

Received November 1, 1965

From the reactions of $C_5H_5V(CO)_4$ and $[C_5H_5Fe(CO)_2]_2$ with S_8, the cyclopentadienyl metal sulfides $[(C_5H_5)_2V_2S_5]_n$ and $(C_5H_5FeS)_4$, respectively, have been isolated. $[(C_5H_5)_2V_2S_5]_n$ is also obtained from $C_5H_5V(CO)_4$ and cyclohexene sulfide, while $[C_5H_5Mo(CO)_3]_2$ and cyclohexene sulfide produce $[C_5H_5MoS_2C_6H_{11}]_n$. $(C_5H_5FeS)_4$ crystallizes in both an orthorhombic and a monoclinic phase, respectively characterized by: space group Pnam, with a = 17.444 A, b = 10.488 A, c = 11.348 A, Z = 4; and space group C2/c or Cc, with a = 18.787 A, b = 7.676 A, c = 15.073 A, β = 108.94°, Z = 4. The crystal structure of the former phase, refined to R = 5.8%, shows the molecule to consist of an elongated tetrahedron of iron atoms with a sulfur atom above each face and a cyclopentadienyl ring projecting from each corner. The molecular symmetry is exactly m (C_s) or approximately $\bar{4}2m$ (D_{2d}). Two interiron bonds of lengths 2.644 and 2.618 A, four independent Fe–S bonds averaging 2.206 A, and three independent Fe–S bonds averaging 2.256 A are present. Final refinement of the cyclopentadienyl rings by the Lipscomb–King hindered-rotor approximation resulted in an R of 6.9%.

Introduction

The reactions of organic disulfides and mercaptans with metal carbonyl and cyclopentadienyl metal carbonyl compounds have been widely explored. Examples of products isolated from such reactions are $[C_5H_5Fe(SCH_3)(CO)]_2$,[2] $[C_5H_5V(SCH_3)_2]_2$,[3] $[Mn(CO)_4(SR)]_2$,[4] and $[Fe(CO)_3(SR)]_2$.[5] The reactions of elemental sulfur with such metal compounds have been less thoroughly explored; a few metal carbonyl derivatives such as $Co_3(CO)_9S$[6] and $Co_2Fe(CO)_9S$[7] have been prepared *via* reactions involving S_8. The only reported reaction of S_8 with a cyclopentadienyl metal compound is that with $(C_5H_5)_3Mn_2(NO)_3$ to give the unusual product $[C_5H_5Mn(NO)S_2]_6$.[8]

The reactions of several cyclopentadienyl metal carbonyl compounds with sulfur were thus pursued in a search for additional cyclopentadienyl metal sulfide derivatives. Cyclohexene sulfide was also investigated as a potential source of reactive sulfur.

Several of the new compounds doubtless are oligomeric and representative of a general class of polynucleates containing extensive bonding between the constituent nuclei. The crystal structure of one of these materials, $(C_5H_5FeS)_4$, was determined to examine the stereochemical principles displayed by such polynucleates.

[1] Contribution No. 1124.

[2] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

[3] R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

[4] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

[5] R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

[6] L. Marko, G. Bor, and E. Klumpp, *Chem. Ind.* (London), 1491 (1961).

[7] S. A. Khattab, L. Marko, G. Bor, and B. Marko, *J. Organometal. Chem.*, **1**, 373 (1964).

[8] T. S. Piper and G. W. Wilkinson, *J. Am. Chem. Soc.*, **78**, 900 (1956).