Table I. Partial Pressures of Gaseous Species over the Si–BN System and Heat of the Reaction $Si_2N(g) = 2Si(g) + 0.5N_2(g)$

Temp, °K	Pressure, atm Si	Pressure, atm N_2	Pressure, atm Si_2N	$-4.576 \log K$, cal deg^{-1} mole^{-1}	$-\Delta\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$ cal deg^{-1} mole^{-1}	ΔH°_{298}, kcal mole^{-1}
1846	8.03×10^{-6}	2.82×10^{-4}	2.17×10^{-7}	24.3	(43)	124
1806	4.34×10^{-6}	1.91×10^{-4}	1.08×10^{-7}	25.7	(43)	124
1765	2.30×10^{-6}	1.19×10^{-4}	4.20×10^{-8}	26.8	(43)	123
1742	1.66×10^{-6}	1.05×10^{-4}	2.83×10^{-8}	27.4	(43)	123
						$\Delta H^\circ_{298} = 123.5 \pm 1.0$

nitride has been observed mass spectrometrically,[8] but no attempt was made to establish its stability. Optical spectra have been cited as evidence for gaseous MoN[9] and TiN.[10]

In the course of a mass spectrometric study of the vaporization of silicon from a boron nitride Knudsen cell, the Si_2N molecule has been identified in the gas phase. This species is isoelectronic with the well-established gaseous species C_2N for which both the CCN and CNC isomers are known from optical spectra.[11]

The experiments were performed on a 12-in. radius, 60°-sector mass spectrometer, similar to that described by Chupka and Inghram.[12] The Knudsen cell was machined from a high-purity boron nitride rod and was tightly fitted into a heavy tantalum crucible. The cell was heated by electron bombardment, and the temperature was measured with an optical pyrometer sighted into the blackbody hole in the bottom of a tantalum crucible.

With the cell heated above 1500°K, the main peaks in the mass spectrum were N_2^+ and Si^+, both increasing with temperature. At temperatures above 1700°K, the ions Si_2^+, Si_3^+, and Si_4^+, as well as peaks at m/e 70, 71, and 72, were observed. From the isotopic abundance calculations the peaks at masses 70, 71, and 72 were identified with the Si_2N^+ ion. The appearance potential, determined by the vanishing-current method, using the ionization potential of Si as standard was 9.4 ± 0.3 ev. This value suggests that the Si_2N^+ ion is formed by direct ionization of the Si_2N molecule and not by fragmentation.

It was impossible in these experiments to decide unambiguously whether the molecules Si_2N_2 or Si_2N_4 existed in the vapors, because of interference of Si_3^+ and Si_4^+ ions at the same mass.

The ion intensities of Si^+, N_2^+, and Si_2N^+ were measured at several temperatures in the range 1742–1846°K and were used to calculate the equilibrium constant for the reaction

$$Si_2N(g) = 2Si(g) + 0.5N_2(g) \qquad (1)$$

With the JANAF[13] free-energy functions for Si(g) and N_2(g), values for Si_2N(g), estimated by analogy with Al_2O(g), and equilibrium constants derived from the ion-current data with the aid of a silver calibration, one can derive the heat of reaction 1 by the third-law method. The results are given in Table I.

From the heat of reaction 1 and the heat of sublimation of silicon, $\Delta H_s{}^\circ{}_{298} = 108.4 \pm 3.0$ kcal mole^{-1},[14] one calculates $\Delta H_f{}^\circ[Si_2N(g)] = 93 \pm 5$ kcal mole^{-1}. The heat of atomization of Si_2N(g), as calculated from the heat of reaction 1 and the dissociation energy of N_2, $D_0{}^\circ = 225.0 \pm 2$ kcal mole^{-1},[13] is $\Delta H_a[Si_2N(g)] = 236 \pm 10$ kcal mole^{-1}, close to the atomization energy for Al_2O of 248 kcal mole^{-1}.[15]

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission under Contract AEC No. AT-(40-1)-2907 and by the National Aeronautics and Space Administration.

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(16) On leave from the Boris Kidrich Institute of Nuclear Sciences, Belgrade, Yugoslavia.

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Sulfur Dioxide Insertion. IV. A New Allylic Rearrangement[1]

Sir:

The unusual paucity of data on insertion reactions of σ-bonded allylic complexes of the transition elements[2] prompted us to examine the behavior of several such organometallics toward sulfur dioxide. Reported now are some preliminary results on a new type of rearrangement which accompanies insertion of SO_2 into metal–carbon bonds.

The qualitative observation of one of us (F. A. H.) that allylmanganese pentacarbonyl inserts sulfur dioxide at a rate much faster than do the methyl and benzyl analogs[3] suggested a possibility of mechanistic differences between these reactions. Particularly inviting was a path involving an allylic rearrangement resulting from cleavage of the Mn–C(1) bond and formation of the Mn–S and S–C(3) bonds (eq 1). In order to test for this possibility we have examined the reaction of

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(1) For part III of this series, see J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 4862 (1966).

(2) The only example of such reactions known to the authors is the reversible carbonylation of allylmanganese pentacarbonyl: T. H. Coffield, J. Kozikowski, and R. D. Closson, Lecture to International Conference on Coordination Chemistry, London, England, April 1959; quoted by G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p 280.

(3) F. A. Hartman and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 844 (1966).

Table I. Infrared Carbonyl and Sulfur–Oxygen Stretching Frequencies (cm^{-1}) of the Complexes[a]

Complex[b]	Carbonyl stretches[c]	SO stretches[d]
$Mn(CO)_5SO_2C_3H_5$	2137 (mw), 2088 (w), 2057 (s), 2042 (s), 2025 (m)	1190 (s), 1043 (s)
$Mn(CO)_5SO_2C_4H_7$	2136 (mw), 2089 (w), 2057 (s), 2040 (s), 2024 (m)	1189 (s), 1048 (s)
$Mn(CO)_5SO_2C_5H_9$	2135 (mw), 2088 (w), 2058 (s), 2039 (s), 2020 (m)	1190 (s), 1041 (s)

[a] Recorded on a Beckman Model IR-9 spectrophotometer. Abbreviations: s, strong; m, medium; mw, medium weak; w, weak. [b] Satisfactory carbon, hydrogen, and sulfur analyses and molecular weights were obtained for all complexes reported. [c] CCl_4 solution. [d] Nujol mull.

Table II. Supplementary Information

	Analytical data						Molecular weight	
	Calcd, %			Found, %				
	C	H	S	C	H	S	Calcd	Found
$Mn(CO)_5SO_2C_3H_5$	32.01	1.68	10.68	32.27	1.82	10.68	300	294
$Mn(CO)_5SO_2C_4H_7$	34.41	2.25		34.38	2.28		314	314
$Mn(CO)_5SO_2C_5H_9$	36.59	2.76	9.77	36.74	3.00	9.49	328	326

sulfur dioxide with 2-butenylmanganese pentacarbonyl and with 3-methyl-2-butenylmanganese pentacarbonyl, since structures of the sulfinato products of these reactions should resolve readily the question of occurrence of the postulated rearrangement.

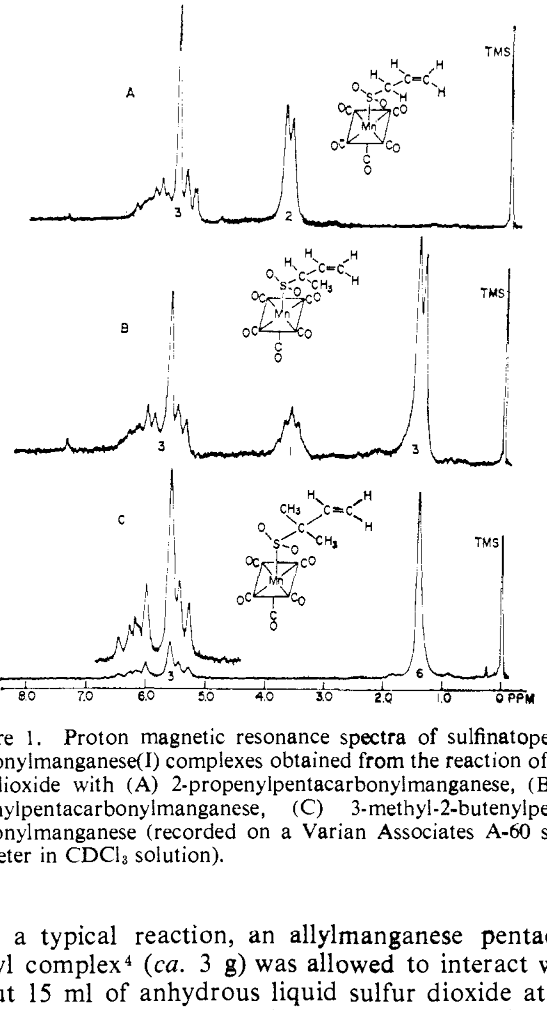
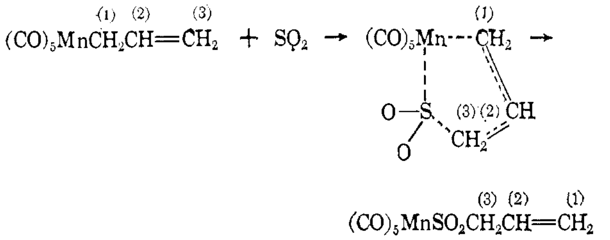


Figure 1. Proton magnetic resonance spectra of sulfinatopentacarbonylmanganese(I) complexes obtained from the reaction of sulfur dioxide with (A) 2-propenylpentacarbonylmanganese, (B) 2-butenylpentacarbonylmanganese, (C) 3-methyl-2-butenylpentacarbonylmanganese (recorded on a Varian Associates A-60 spectrometer in $CDCl_3$ solution).

In a typical reaction, an allylmanganese pentacarbonyl complex[4] (*ca.* 3 g) was allowed to interact with about 15 ml of anhydrous liquid sulfur dioxide at *ca.* −40° for approximately 2 hr.[5] The SO_2 was then removed, the orange residue was extracted with 20 ml of absolute ethanol, and 10 ml of ether was added to the extracts. Cooling the resulting solution to −40° for 1 hr caused separation of pale yellow crystals. The product was washed with 20 ml of ether and then recrystallized from chloroform–hexane. The yield ranged from 70 to 80%.



$$(CO)_5Mn\overset{(1)}{C}H_2\overset{(2)}{C}H{=}\overset{(3)}{C}H_2 + SO_2 \rightarrow \cdots \rightarrow (CO)_5MnSO_2\overset{(3)}{C}H_2\overset{(2)}{C}H{=}\overset{(1)}{C}H_2 \quad (1)$$

The infrared carbonyl and sulfur–oxygen stretching frequencies of the products, listed in Table I, are very similar to those reported for the analogous methyl,[3] ethyl,[6] and benzyl[3] derivatives and attest to the S-sulfinatopentacarbonyl formulation of the complexes. Supplementary data are given in Table II.

The question concerning the position of attachment of the allyl moieties to sulfur in $(CO)_5MnSO_2C_4H_7$ and $(CO)_5MnSO_2C_5H_9$ is resolved upon examination of the proton magnetic resonance spectra of these derivatives in conjunction with the spectrum of the 2-propenylpentacarbonyl sulfinate, all shown in Figure 1. The nmr spectrum of $(CO)_5MnSO_2C_3H_5$ consists of a doublet centered at τ 6.25 and of a complex multi-line absorption farther downfield (relative intensities 2:3). The former signal is assigned to the two protons of the methylene group bonded to SO_2, and the latter to the three vinyl hydrogens. The salient features in the spectrum of $(CO)_5MnSO_2C_4H_7$ are presence of a multiplet at τ 6.10–6.38 and of a complex absorption pattern at τ 3.59–4.66 (relative intensities 1:3). No signal is detectable in the τ 5–7 range of the spectrum of $(CO)_5MnSO_2C_5H_9$; the resonances at τ 3.91–4.83 and the sharp line at τ 8.59 (due to the six methyl protons) occur with the intensity ratio of 3:6.

These data are in complete agreement with the structures containing rearranged allylic moieties of the last two derivatives (see Figure 1). Had there been no rearrangement, each spectrum would be expected to ex-

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(4) Prepared from sodium pentacarbonylmanganate(−1) and the organic halide; see W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961). The compound was characterized by nmr spectroscopy.

(5) Actually, these reactions reach completion in much shorter times.

(6) F. A. Hartman, Ph.D. Thesis, The Ohio State University, 1966.

hibit a doublet at τ 5–7 with the relative intensity corresponding to two methylene protons. Furthermore the downfield signals would occur with the relative intensities and multiplicities reflecting the presence of two and one vinyl protons in the C_4H_7 and C_5H_9 sulfinates, respectively.[7]

The generality of the above-described allylic rearrangement is supported by the behavior of the 2-butenyl derivatives of cyclopentadienyliron dicarbonyl, cyclopentadienylmolybdenum tricarbonyl, and cyclopentadienyltungsten tricarbonyl toward sulfur dioxide. The nmr spectra of all of the resulting sulfinates are consistent with the rearranged structure of the hydrocarbon moiety.[9]

We are currently examining insertion reactions between allyl metal complexes and substrates other than sulfur dioxide with a view to elucidating the scope of the rearrangement described herein.

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(7) This argument receives support from the recent isolation of $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ *via* the reaction of $Na[C_5H_5Fe(CO)_2]$ and sulfur dioxide with 1-chloro-3-methyl-2-butene. The proton magnetic resonance spectrum of the sulfinate exhibits doublets at τ 8.08 (CH_3) and 6.17 (CH_2) with the relative intensity ratio of 6:2, a sharp singlet at τ 4.68 (C_5H_5), and a complex signal at τ 4.30–4.95 ($CH{=}C$), in complete accord with the proposed allylic attachment.[8]

(8) R. L. Downs and A. Wojcicki, to be published.

(9) Although we cannot rule out the possibility that the "rearranged" allyl-S-sulfinato complexes result from the initial formation of the corresponding "normal" allyl sulfinates, which then rapidly undergo isomerization, there is evidence against such a sequence of events. The derivative $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ retains its identity after 4 hr of refluxing in liquid SO_2; a 3:1 mixture of the geometric isomers $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ and $C_5H_5Fe(CO)_2SO_2C(CH_3)_2CH{=}CH_2$ becomes *ca.* 8:1 and 14:1 upon refluxing for 4 and 8 hr, respectively, in liquid sulfur dioxide. Thus, at least in this case, isomerization of the sulfinates does occur, *albeit* of the sterically more hindered $C_5H_5Fe(CO)_2SO_2C(CH_3)_2CH{=}CH_2$ to the less crowded $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$.

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Cyclic Polyethers and Their Complexes with Metal Salts

Sir:

Thirty-three cyclic polyethers, derived from aromatic vicinal diols and containing from 9 to 60 atoms including 3–20 oxygen atoms in the ring, have been synthesized. Some of these have been prepared in good yields without the use of a high-dilution technique. Fifteen of the compounds have been catalytically hydrogenated to the corresponding saturated cyclic polyethers.

Many of these cyclic polyethers have the unusual property of forming relatively stable complexes with alkali and alkaline earth metal ions. The more effective ligands are those containing 5–10 oxygen atoms, each separated from the next by 2 carbon atoms. This communication deals primarily with two examples of the six-oxygen compounds which are the most effective and versatile complexing agents: an aromatic compound derived from catechol, 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (I); and its hydrogenation product, a mixture of *cis–trans* isomers, 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]-hexacosane (II).

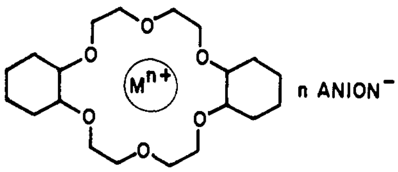

Figure 1. *o*-Benzo or 1,2-cyclohexyl polyethers.

The two cyclic polyethers form stable complexes with ionic compounds of Li, Na, NH_4, RNH_3, K, Rb, Cs, Ag(I), Ca, Sr, Ba, Cd, Hg(I), Hg(II), La(III), Tl(I), Ce(III), and Pb(II). The complexes are thought to be field valency compounds formed by ion–dipole interaction between the cation and the negative dipoles of the oxygen atoms of the polyether ring, as shown in Figure 1; the formation of stable ammonium complexes supports this interpretation. The "hole" in I and II, estimated to be 4 A in diameter, is large enough to accommodate any unsolvated or uncoordinated inorganic cation. The stoichiometry of the complexes is one molecule of polyether per single cation regardless of the valence.

Compound I is prepared by treating 1 mole of catechol, 2 moles of sodium hydroxide, and 1 mole of bis(2-chloroethyl) ether in 1-butanol at reflux temperature (115°) for about 24 hr. The yield is 44–48%, and 1 mole (360 g) of product can be synthesized in a volume of 5 l. White fibrous crystals are obtained by crystallization from benzene; mp 164°; bp *ca.* 380–384° (769 mm). *Anal.* Calcd for $C_{20}H_{24}O_6$: C, 66.6; H, 6.7; mol wt, 360. Found: C, 66.3; H, 6.8; mol wt, 371. Compound I is readily soluble in methylene chloride and chloroform, and very little soluble in methanol and water. Its ultraviolet spectrum in methanol has a peak at 274 mμ (ϵ 5200). Its infrared spectrum shows no OH band but two strong, broad ether bands near 8.1 and 8.5 μ. Its nmr spectrum is consistent with the proposed structure: a multiplet 4.11 ppm downfield from TMS, area ratio 2.2, and a singlet, 6.92 ppm, area ratio 1.00. The good yield of I obtained without resorting to a high-dilution technique is unusual for an 18-membered ring. Possibly the sodium ions promote ring formation by properly orienting the reactants and the intermediate products through ion–dipole interaction.

Compound II is prepared by hydrogenating I in a stainless steel autoclave at 100° and 1600 psig using *p*-dioxane as solvent and ruthenium dioxide as catalyst. The product, free of alcoholic by-products, is obtained by chromatography with acid-washed alumina and *n*-heptane in 67% yield. *Anal.* Calcd for $C_{20}H_{36}O_6$: C, 64.5; H, 9.7; mol wt, 372. Found: C, 64.5; H, 9.6; mol wt, 378. The product is a mixture of isomers, melts between 30 and 56°, and boils at about 344° (769 mm). It is soluble in organic solvents including petroleum ether. Its solubility in water at 26° is 0.036 mole/l. and decreases with rising temperature. Its ultraviolet spectrum shows no significant absorption above 200 μ, and its infrared spectrum shows no OH band but a strong, broad ether band near 9 μ. Its nmr spectrum is consistent with the proposed structure: a multiplet 1.50 ppm downfield from TMS,