

bonds are weakened in ${}^4L_1^0$. On the other hand, bond weakening also renders the complex more susceptible to attack by an incoming ligand. While this question remains largely unanswered, we feel that some degree of participation by the incoming solvent molecule in the expulsion of a chloride is at least suggested by the trend in ϕ_{Cl^-} shown by the trans complexes.

The correlation between k_{25° and ϕ_{Cl^-} shown in Figure 4 is unexpected. Seemingly, factors which influence reactivity in the ground state exert a proportional (if not equal) effect in the excited state. One might suppose that similar mechanisms are operative in the thermal and photochemical reactions. The analogy cannot be carried too far, however, since obvious differences exist between the two processes. The thermal aquation of the NH_3 , en, and 2,3,2-tet complexes occurs with retention of configuration, while the opposite is true photochemically. Further, there is a fortuitous similarity in the two types of reaction for $trans-[CrN_4Cl_2]^+$ complexes. No correlation exists for the $[CrN_5X]^{n+}$ series, for

example, since the predominant thermal and photochemical reactions differ. Thus the significance of the correlation is uncertain at present.³⁴

Registry No. *trans*- $[Cr(2,3,2-tet)Cl_2]Cl$, 40813-71-6; *trans*- $[Cr(cyclam)Cl_2]Cl$, 27385-72-4; *cis*- $[Cr(cyclam)Cl_2]Cl$, 27435-95-6; *trans*- $[Cr(NH_3)_4Cl_2]^+$, 22452-49-9; *trans*- $[Cl(en)_2Cl_2]^+$, 14403-88-4; *trans*- $[Cr(cyclam)OH_2Cl]^{2+}$, 41156-37-0; *cis*- $[Cr(2,3,2-tet)OH_2Cl]^{2+}$, 40901-23-3; *cis*- $[Cr(en)_2Cl_2]^+$, 14482-74-7; *cis*- $[Cr(cyclam)OH_2Cl]^{2+}$, 41139-30-4.

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(34) We can suggest one rationalization of the observed behavior; namely, both processes involve a rate-determining attack by a solvent molecule (essentially alternative 4), whose approach is hindered by increasing ring stricture. Subsequent rearrangement (or lack of it) then leads to the difference in product stereochemistries.

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Infrared Spectra of Isotopically Substituted Metal Carbonyls. III. Evidence for Conformational Isomerism in π -Cyclopentadienyldicarbonyl(dialkyl sulfide)manganese(I) Complexes¹

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The *n*-hexane solution ir spectra of the organosulfide complexes $\pi-C_5H_5Mn(CO)_2SR_2$ ($R = Me, Et, n-Pr, n-Bu$) and $\pi-C_5H_5Mn(CO)_2THT$ (THT = tetrahydrothiophene) have been studied under high resolution in the CO stretching region. Each of the complexes exhibits four CO absorptions instead of the two expected. This "CO frequency doubling" is attributed to the first examples of conformational isomerism about the manganese-sulfur bonds. This conclusion is supported by approximate force constant calculations for the CO modes of the two conformers of $\pi-C_5H_5Mn(CO)_2S(n-Bu)_2$ and their $C^{18}O$ -substituted derivatives and by ir data for all of the complexes in the 4000-3700-cm⁻¹ overtone and combination region.

Introduction

Recently, the ir spectra of various π -cyclopentadienylmetal carbonyl complexes in nonpolar solvents have been found to exhibit twice the number of CO stretching frequencies expected. More specifically, these are complexes of iron,²⁻⁴ ruthenium,³ manganese,³ and molybdenum³ containing certain silicon, tin, and phosphorus ligands, e.g., $\pi-C_5H_5Fe(CO)_2-SiCl_2Me$, $\pi-C_5H_5Ru(CO)[P(OMe)_3]I$, and $\pi-MeC_5H_4Mn(CO)_2-[P(OPh)_3]$. This phenomenon has been attributed to conformational isomerism either about the metal-ligand bonds or within the ligands themselves.

We now report the first examples of π -cyclopentadienylmetal carbonyl complexes containing organosulfide ligands displaying this type of "CO frequency doubling." In particular, the ir spectra of $\pi-C_5H_5Mn(CO)_2SR_2$ ($R = Me, Et, n-Pr,$

$n-Bu$) and $\pi-C_5H_5Mn(CO)_2THT$ (THT = tetrahydrothiophene) in *n*-hexane solution exhibit four CO stretching frequencies instead of the two expected. We attribute this to conformational isomerism about the manganese-sulfur bonds. This conclusion is supported by approximate force constant calculations for the CO stretching modes of $\pi-C_5H_5Mn(CO)_2-S(n-Bu)_2$ and its $C^{18}O$ -substituted derivatives and by ir data for all of the organosulfide complexes in the 4000-3700-cm⁻¹ overtone and combination region. To the best of our knowledge, conformational isomerism about metal-sulfur bonds has not been reported previously.

Experimental Section

The organosulfide complexes, $\pi-C_5H_5Mn(CO)_2SEt_2$ and $\pi-C_5H_5Mn(CO)_2THT$, were prepared photochemically from $\pi-C_5H_5Mn(CO)_3$ (a gift from Ethyl Corp.) by the literature methods.⁵ Similar methods were used to prepare the previously unknown $\pi-C_5H_5Mn(CO)_2SR_2$ complexes; these new complexes were fully characterized by elemental analysis and by ir, nmr, and mass spectroscopy.⁶ All the complexes were recrystallized from *n*-hexane solution at -78° immediately prior to use.

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

(6) I. S. Butler and T. Sawai, to be submitted for publication.

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(2) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 89, 2773 (1967).

(3) D. A. Brown, H. J. Lyons, and A. R. Manning, *Inorg. Chim. Acta*, 4, 428 (1970).

(4) W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 10, 843 (1971).

High-resolution ir spectra of spectrograde *n*-hexane (freshly distilled under nitrogen) solutions of the complexes were recorded in the CO stretching and 4000–3700-cm⁻¹ regions on a Perkin-Elmer 521 grating spectrophotometer using a pair of matched 1.0-mm NaCl solution cells. The observed frequencies were calibrated with the 1653.3- and 3744.5-cm⁻¹ bands of water vapor. The precision of the frequencies is ±1 cm⁻¹ (CO stretching region) and ±2 cm⁻¹ (4000–3700-cm⁻¹ region).

The variable-temperature ir spectra (–42 to +25°) of π-C₅H₅Mn(CO)₂S(*n*-Bu)₂ in *n*-hexane solution were also recorded on the Perkin-Elmer 521 spectrophotometer using a variable-temperature ir cell (Research and Industrial Instruments Co. Model VLT-2; 0.1-mm path length, AgCl windows). Acetone–Dry Ice mixtures were used to cool the cell; the precision of the temperature measurements was ±1°, determined by means of a calibrated copper–constantan thermocouple.

¹⁸O-Enriched π-C₅H₅Mn(CO)₂S(*n*-Bu)₂ was prepared by uv light (Rayonet reactor with six lamps emitting at 350 nm) induced exchange at room temperature in Spectrograde *n*-hexane solution with 90% ¹⁸O-enriched CO (Miles Laboratories Inc.). The method used was similar to that described previously⁷ except that the reaction vessel was constructed from quartz and was not blackened. The measurement of the ir-active CO stretching frequencies and the subsequent force constant calculations were also carried out as described previously.⁷

Results and Discussion

The organosulfide complexes π-C₅H₅Mn(CO)₂L (L = SEt₂, SPh₂, THT) have been reported to exhibit only one CO stretching frequency at ~1935 cm⁻¹ in their ir spectra in benzene solution.⁵ However, the Mn(CO)₂ moiety in these complexes possesses C_{2v} local symmetry for which two strong ir-active CO stretching modes (A₁ and B₂) are expected. It was this discrepancy that prompted us initially to investigate the ir spectra of a number of these organosulfide complexes. Moreover, in order to optimize the spectral resolution, *n*-hexane was selected as the solvent for this investigation. However, contrary to our expectations, the ir spectra of all the complexes studied exhibit *four*, not two, CO stretching frequencies (Table I). The spectrum for π-C₅H₅Mn(CO)₂S(*n*-Bu)₂ shown in Figure 1 is typical of the spectra obtained. The data indicate that the spectra consist of two pairs of CO absorptions—the pair at ~1940 and ~1880 cm⁻¹ always being more intense than the pair at ~1950 and ~1885 cm⁻¹. Repeated recrystallization of the complexes does not alter the appearance of the spectra or the relative intensities of the bands. The 60-MHz room-temperature nmr spectra of the complexes do not exhibit any splittings in the expected resonances.⁸

Coordination of an SR₂ molecule to a metal would be expected to create sp³ hybridization on the sulfur atom with one of the tetrahedrally directed orbitals being occupied by a lone pair of electrons. The single-crystal X-ray structure of PdBr₄(SMe₂)₂ supports this expectation—the angles around the sulfur atoms are approximately tetrahedral.⁹ Moreover, the observed CO stretching frequencies are too high to be due to bridging CO groups. Consequently, we feel that the appearance of more than two CO stretching bands for each of the complexes is due to the presence of conformational isomers. The most likely isomers are the two shown in Newman projection (I and II) in Figure 2 which result from 120° rotation about the manganese–sulfur bond. In isomer I, the two alkyl groups are arranged symmetrically with respect to the mirror plane which bisects the R–S–R angle; the point group for this isomer is C_s and two ir-active CO stretching modes

(7) I. S. Butler and H. K. Spendjian, *J. Organometal. Chem.*, **18**, 145 (1969).

(8) Even at 100 MHz (Varian HA-100 spectrometer), the spectrum of π-C₅H₅Mn(CO)₂SEt₂ in CS₂ was as expected, viz., τ 4.33 (singlet, π-C₅H₅), 2.42 (quartet, CH₂) and 1.23 (triplet, CH₃) relative to TMS (τ 10) as internal standard.

(9) D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc. A*, 1852 (1968).

Table I. ν(CO) (and Relative Intensities) of π-C₅H₅Mn(CO)₂L Complexes in *n*-Hexane Solution and Proposed Vibrational Assignments

L					Isomer and assignment ^a
SMē ₂	SEt ₂	S(<i>n</i> -Pr) ₂	S(<i>n</i> -Bu) ₂	THT	
1951 mw	1951 ms	1949 m	1949 m	1953 mw	I, A' (C _s)
1944 s	1942 s	1941 s	1941 s	1942 s	II, A ⁽¹⁾ (C ₁)
1887 mw	1887 ms	1885 m	1885 m	1889 mw	I, A'' (C _s)
1880 s	1878 s	1877 s	1877 s	1878 s	II, A ⁽²⁾ (C ₁)

^a The superscripts (1) and (2) designate in-phase and out-of-phase CO stretching, respectively.

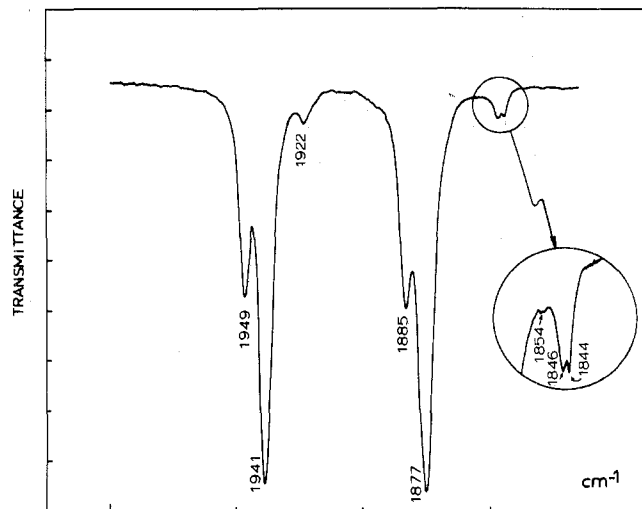


Figure 1. Infrared spectrum of π-C₅H₅Mn(CO)₂S(*n*-Bu)₂ in the CO stretching region (*n*-hexane solution).

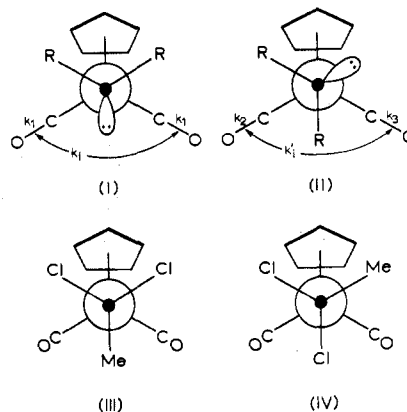


Figure 2. Two rotational conformations for both π-C₅H₅Mn(CO)₂-SR₂ (I and II) and π-C₅H₅Fe(CO)₂SiCl₂Me (III and IV). The views are along the Mn–S and Fe–Si bonds, the large open circles being the metal atoms and the small solid ones the S and Si atoms.

(A' and A'') are expected. On the other hand, isomer II does not possess any symmetry elements and so the point group is C₁; however, again two ir-active CO stretching modes [A⁽¹⁾ and A⁽²⁾] are expected. Furthermore, isomer II is spectroscopically (ir) indistinguishable from its mirror image. Therefore, the probability ratio of isomers I and II is 1:2. In every complex studied in this work, the pair of bands at ~1950 and ~1885 cm⁻¹ is significantly weaker than the other pair. This suggests that provided the extinction coefficients of the four bands are comparable, the two sets can be assigned to isomers I and II, respectively.

The type of conformational isomerism proposed above is not without precedence. For instance, Jetz and Graham have accounted for the two extra CO stretching bands in the ir spectrum of π-C₅H₅Fe(CO)₂SiCl₂Me in cyclohexane solu-

Table II. Assignment of the CO Stretching Frequencies Observed after Reaction of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ with 90% ^{18}O -Enriched CO in *n*-Hexane Solution

Obsd ^a $\nu(\text{CO})$, cm^{-1}	Band designation	Calcd $\nu(\text{CO})$, cm^{-1}	Assignment	
			Molecule	Vib species ^g and local symmetry
2027.7 vvw	a	2028.4 ^b	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$	$A_1 (C_{3v})$
2018.4 vvw	b	2018.1 ^b	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{C}^{18}\text{O})$	$A' (C_s)$
2005.9 vvw	c	2004.7 ^b	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{C}^{18}\text{O})_2$	$A' (C_s)$
1979.1 vvw	d	1979.5 ^c	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{C}^{18}\text{O})_3$	$A_1 (C_{3v})$
1966.2 vvw	e			
1947.4 m ^d	f	1948.4	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ (isomer I)	$A' (C_s)$
1938.3 s ^e	g	1938.9	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ (isomer II)	$A^{(1)} (C_1)$
1932.2 m ^d	h	1932.3	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{C}^{18}\text{O})\text{S}(n\text{-Bu})_2$ (isomer I)	$A^{(1)} (C_1)$
1924.4 ms ^e	i	1924.5	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{C}^{18}\text{O})\text{S}(n\text{-Bu})_2$ (isomer II)	$A^{(1)} (C_1)$
		1922.1		
1915.0 vvw, sh ^f	j	1913.6 ^b	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{C}^{18}\text{O})$	$A' (C_s)$
1904.3 w ^d	k	1901.5	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{C}^{18}\text{O})_2\text{S}(n\text{-Bu})_2$ (isomer I)	$A' (C_s)$
1897.0 m	l	1892.2	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{C}^{18}\text{O})_2\text{S}(n\text{-Bu})_2$ (isomer II)	$A^{(1)} (C_1)$
1883.7 m ^d	m	1882.0	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ (isomer I)	$A'' (C_s)$
1875.8 s ^e	n	1878.1	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ (isomer II)	$A^{(2)} (C_1)$
1856.3 m, sh ^d	o	1852.0	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{C}^{18}\text{O})\text{S}(n\text{-Bu})_2$ (isomer I)	$A^{(2)} (C_1)$
1849.2 ms ^e	p	1848.8	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{C}^{18}\text{O})\text{S}(n\text{-Bu})_2$ (isomer II)	$A^{(2)} (C_1)$
1847.0 s, sh	q	1846.6		
1843.0 w, sh	r	1836.6	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{C}^{18}\text{O})_2\text{S}(n\text{-Bu})_2$ (isomer I)	$A'' (C_s)$
1834.5 m ^e	s	1832.8	$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{C}^{18}\text{O})_2\text{S}(n\text{-Bu})_2$ (isomer II)	$A^{(2)} (C_1)$

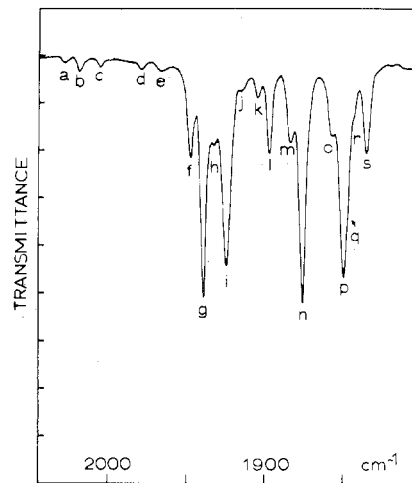
^a After 30 min of uv light induced reaction. ^b Experimentally observed values.¹ ^c Calculated value¹ using 2028.4 and 1947.2 cm^{-1} as the input frequencies for $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$. ^d Input frequencies for the force constant calculation for isomer I; the optimum force constants are k_1 (transoid to *n*-Bu group) = 14.84 and $k_1' = 0.50$ mdyn/Å. ^e Input frequencies for the force constant calculation for isomer II; the optimum force constants are k_2 (transoid to lone pair) = 14.68, k_3 (transoid to *n*-Bu group) = 14.74, and $k_1' = 0.47$ mdyn/Å. ^f The other bands for the various C^{18}O -substituted $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ species are very weak and are buried beneath bands of the other species present. ^g See footnote a in Table I.

tion by the presence of two rotational isomers (III and IV, Figure 2) which differ by rotation through 120° about the Si-Fe bond.² This suggestion has been confirmed by Dalton¹⁰ using a novel method for CO band assignments which will be discussed in more detail shortly. Brown, *et al.*,³ have observed similar CO frequency doubling for a variety of π -cyclopentadienylmetal carbonyl derivatives containing symmetric tertiary phosphine or phosphite ligands such as PPh_3 and $\text{P}(\text{OMe})_3$. Extra CO bands were observed chiefly for tertiary phosphite complexes but not for complexes containing the constrained $\text{P}(\text{OCH}_2)_3\text{CMe}$ ligand. In view of this, Brown, *et al.*, concluded that the extra CO bands arise because of conformational isomerism within the P-O-C groups of the tertiary phosphites rather than rotation about the metal-phosphorus bonds. In the case of the PPh_3 derivatives, the presence of eclipsed and staggered rotamers about the metal-phosphorus bonds was proposed.

In the present work, four strong CO bands are observed for the simplest dialkyl sulfide derivative $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{SMe}_2$, as well as for $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{THT}$ in which, effectively, two ethyl groups are tied together thus restricting rotation about the S-C bonds. These observations support the suggestion that the two extra CO bands in the case of the organosulfide complexes arise because of conformational isomerism about the manganese-sulfur bonds.

It was mentioned above that Dalton¹⁰ has verified the presence of rotamers III and IV for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiCl}_2\text{Me}$. His novel approach made use of the naturally occurring ^{13}CO satellite absorptions of the complex. He pointed out that the ^{13}CO satellite bands for isomer IV should be split whereas those for isomer III should not. On this basis, he successfully assigned the two strong absorptions due to each isomer.

When the ir spectrum of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ shown in Figure 1 is expanded, as in the inset, a small splitting ($2.1 \pm 0.5 \text{ cm}^{-1}$) can be detected in the lowest frequency ^{13}CO satellite band ($\sim 1845 \text{ cm}^{-1}$). Other ^{13}CO satellite bands are

**Figure 3.** Infrared spectrum in the CO stretching region of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ after 30 min of uv light (six 350-nm lamps) induced reaction with 90% ^{18}O -enriched CO (*n*-hexane solution).

observed at 1922 and 1954 cm^{-1} . These observations are unaffected by concentration changes. Similar splittings are apparent in the lowest ^{13}CO satellite bands of the Me_2S and THT derivatives but are not observed for the other complexes presumably because of accidental degeneracy of the bands in question.

It is now quite well established that the CO stretching frequencies of identical ^{13}CO - and C^{18}O -substituted metal carbonyl complexes differ by only about 1 cm^{-1} .^{1,11} Consequently, ^{18}O -enriched CO can also be used to verify experimentally, through exchange, the assignments proposed for ^{13}CO satellite absorptions. To this end, the uv light induced exchange of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$ with 90% ^{18}O -enriched CO in *n*-hexane solution was investigated. The ir spectrum of the reaction mixture in the CO stretching region after 30 min of exchange is shown in Figure 3. The actual frequencies

Table III. CO Binary Combination Frequencies (and Relative Intensities) of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ Complexes in *n*-Hexane Solution and Proposed Vibrational Assignments

L = SMe ₂		L = SEt ₂		L = S(<i>n</i> -Pr) ₂		L = S(<i>n</i> -Bu) ₂		L = THT		Band designation ^a	Assignment ^b
Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd		
3945 w		3936 w		3945 m		3943 mw		3935 w		a	} Unassigned
3934 w		3923 w		3933 w		3932 m		3927 w		b	
3908 vw	3902	3902 vw	3902	3906 vw	3898	3904 vw	3898	3903 vw	3906	c	2 A'
3889 w	3895	3881 w	3893	3880 mw	3890	3882 m	3890	3888 vw	3895	d	A' + A ⁽¹⁾
3877 m	3888	3862 ms	3884	3868 s	3882	3867 s	3882	3867 ms	3884	e	2 A ⁽¹⁾
3835 vw	3838	3830 vw	3838	3829 vw	3834	3838 w	3834	3837 vw	3842	f	A' + A''
3812 w	3831	3802 w	3829	3805 m	3826	3806 m	3826	3813 w	3831	g	A' + A ⁽²⁾ , A'' + A ⁽¹⁾
3796 s	3824	3786 s	3820	3792 s	3818	3791 s	3818	3790 s	3820	h	A ⁽¹⁾ + A ⁽²⁾
	3774		3774		3770		3770		3778		2 A''
3759 w	3767	3750 w	3765	3747 m	3762	3752 m	3762	3751 w	3767	i	A'' + A ⁽²⁾
3743 m	3760	3734 ms	3756	3740 ms	3754	3739 ms	3754	3737 m	3756	j	2 A ⁽²⁾

^a Figure 4. ^b See footnote ^a in Table I.

and the assignments proposed on the basis of CO force constant calculations for isomers I and II are presented in Table II. The force constants involved are defined in Figure 2.

A number of results are apparent from the C¹⁸O study. First, that the original four bands in the CO stretching region are fundamentals is amply verified by the appearance of a number of bands attributable to C¹⁸O-substituted derivatives of both isomers of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(\textit{n}\text{-Bu})_2$. The calculated frequencies for the various C¹⁸O-substituted derivatives are in good agreement (usually <5 cm⁻¹) with those observed experimentally. The discrepancies are of the order commonly found when using frequencies uncorrected for anharmonicity,¹² and the CO-factored force field.^{1,7,13} Second, the assignment of the bands at 1922, 1854, and ~1845 cm⁻¹ to ¹³CO satellite bands is substantiated by the exchange with C¹⁸O. All three of these bands are greatly enhanced (bands i, o, and p) during the exchange. Furthermore, although neither band i nor band p is actually split, as predicted by the calculation, there is a distinct shoulder (band q) on the latter while the former is somewhat broader than the other absorptions in this region. These results establish the existence of conformational isomers for $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(\textit{n}\text{-Bu})_2$ and also confirm the assignments proposed for the CO stretching vibrations. Moreover, in view of the similarity of the spectra of the other organosulfide complexes to that for the S(*n*-Bu)₂ complex, it seems reasonable to assume that conformational isomerism also exists in these complexes.

It should be mentioned in passing that $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ and its C¹⁸O-substituted derivatives are also formed in the reaction of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(\textit{n}\text{-Bu})_2$ with ¹⁸O-enriched CO. This is not unexpected owing to the known lability of the S(*n*-Bu)₂ ligand. However, it is particularly significant that the A₁ vibration of the all-C¹⁸O-substituted species $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{C}^{18}\text{O})_3$ is directly observable (band d). Previous attempts¹ to prepare this species by uv irradiation of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ in the presence of C¹⁸O resulted only in the formation of the mono- and di-C¹⁸O-substituted species. Furthermore, the experimentally observed frequency (1979.1 cm⁻¹) is in excellent agreement with the predicted value, despite the fact that the calculation only employs a CO-factored force field. This observation lends further support to the use of this force field to predict accurately the vibrational frequencies of ¹³CO- and C¹⁸O-substituted metal carbonyl complexes.

There is one unexplained band (e) which is probably due to a combination mode, as it is also present prior to the C¹⁸O exchange.

The overtone and combination spectra in the 4000-3700-

(12) L. H. Jones, *Inorg. Chem.*, **6**, 1269 (1967).

(13) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 2851 (1967).

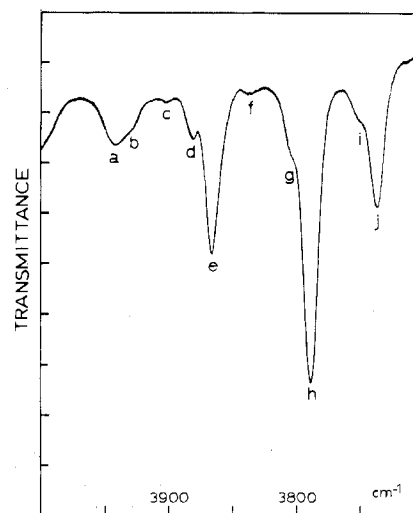


Figure 4. Infrared spectrum of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(\textit{n}\text{-Bu})_2$ in the 4000-3700-cm⁻¹ overtone and combination region (*n*-hexane solution).

cm⁻¹ region (Table III and Figure 4) are virtually identical and are in complete accord with the assignment of the four CO stretching vibrations observed for each complex as fundamentals. With the exception of the 2 A'' overtone, all of the expected binary combinations are observed experimentally. Furthermore, as might be expected, the most intense combination bands (e, h, and j in Figure 4) result from combinations of the two most intense $\nu(\text{CO})$'s [A⁽¹⁾ and A⁽²⁾] whereas the weakest combinations derive from the weakest $\nu(\text{CO})$'s (A' and A''). Consequently, the 2 A'' overtone would be expected to be weak in any case and is most probably buried beneath the wings of neighboring bands. The two unassigned bands (a and b) observed in the range 3945-3920 cm⁻¹ presumably arise from ternary combinations of the $\nu(\text{CO})$'s and some of the very low frequency vibrations.

Recently, Dalton¹⁴ has estimated the energy barrier for rotation about the Fe-Si bond in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiCl}_2\text{Me}$ from a variable-temperature ir study (-78 to +25°) to be about 0.8 kcal mol⁻¹ in favor of the symmetric rotamer (Figure 2, isomer III). With this in mind, the ir spectrum of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(\textit{n}\text{-Bu})_2$ in *n*-hexane solution was recorded at various temperatures between -42 and +25°. Over this temperature range, only a slight variation in the relative intensities of the two sets of CO stretching frequencies belonging to isomers I and II was observed. For this reason, it proved impossible to evaluate the energy barrier for rotation

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about the Mn-S band. Presumably, however, this barrier is less than $0.8 \text{ kcal mol}^{-1}$ or else the preferred isomer should have been "frozen out" sufficiently for some intensity change to be detected spectroscopically. Why the barrier for rotation about an Mn-S band is lower than that about an Fe-Si band may result from the lower steric interaction between the groups attached to the S atom than in the case of the Si atom.

Registry No. $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{SMe}_2$, 40674-63-3; $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{SEt}_2$, 40674-64-4; $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Pr})_2$, 40674-65-5; $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{S}(n\text{-Bu})_2$, 40674-66-6; $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{THT}$, 40674-67-7.

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Polarographic and Magnetic Susceptibility Study of Various Biferrocene Compounds

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Biferrocene, a series of five bridged biferrocenes (bridge = $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$, $-\text{Hg}-$, and $-\text{CH}=\text{CHC}_6\text{H}_4-$, $\text{CH}=\text{CH}-$ (1,4)), and biferrocenylene were studied polarographically using a rotating platinum electrode. The $-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2-$, $-\text{Hg}-$, and $-\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CH}-$ (1,4) bridged biferrocenes exhibited one irreversible two-electron half-wave. The methylene-bridged biferrocene showed two one-electron waves (0.39 and 0.56 V vs. sce), as did biferrocene (0.31 and 0.64 V vs. sce) and biferrocenylene (0.13 and 0.72 V vs. sce). Both of the half-waves for these compounds were found to be quasireversible. Variable-temperature (4.2–290°K) magnetic susceptibility data were presented for the dioxidized hexafluorophosphate salts of the $-\text{CH}_2-$ and $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ bridged biferrocenes. No intramolecular exchange interactions were detected; however, intermolecular exchange interactions were inferred by a comparison with magnetic data for ferri-cenium triiodide and by computer fitting of the data to a theoretical model. Susceptibility data were also presented for the salts resulting from the reaction of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) with cobaltocene, ferrocene, biferrocene, and biferrocenylene. In each case the anion resultant from DDQ is diamagnetic and in the case of $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{C}_5\text{H}_4)_2\text{Fe}^{2+}]_2\text{DDQ}^{2-}$ the Fe(III) complex is diamagnetic. The esr spectrum of monooxidized biferrocenylene and the above results are discussed in relation to the mixed-valence character found in some biferrocenes.

Introduction

Ferrocene has played an important role in developing a knowledge of electronic structure in organometallic chemistry.^{1,2} Interest has been directed recently toward biferrocene (I), the ring-fused ferrocene dimer $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)-(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)$, which was first observed³ as a reaction by-product in 1959. Oxidation of biferrocene either can lead to a monooxidized compound, as first reported by Spilners,⁴ or can lead with a strong oxidizing agent to the dioxidized product. These materials are proving to have interesting properties.

Very recently Cowan, *et al.*,^{5–10} and Mueller-Westerhoff and Eilbracht¹¹ prepared and investigated the physical properties of some biferrocene and biferrocenylene salts. The monooxidized biferrocene salt was formulated as a

mixed-valence $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ compound. The mixed-valence character was established in part by observing, in the 77°K iron Mossbauer spectrum, separate quadrupole-split doublets for the two different iron atoms. The mixed-valence biferrocene compound was also characterized by an electronic transition in the near-ir spectrum; this feature is absent in the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ compounds and was assigned by Cowan as an $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}} \rightarrow \text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ transition.

In this paper we report on polarographic studies of various biferrocenes and biferrocenylene and discuss the results in reference to the compound's potential as mixed-valence compounds. Variable-temperature magnetic susceptibility data for two dioxidized bridged biferrocene compounds and for dioxidized biferrocenylene are also presented and analyzed.

Experimental Section

Compound Preparation. Samples of phenylferrocene, diferrocenylmethane, 1,2-diferrocenyl-1,1,2,2-tetramethylethane, and 1,2-diferrocenylene were generously provided by Professor K. L. Rinehart. Analyses were performed by the University of Illinois School of Chemical Sciences microanalytical laboratory.

Biferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{C}_5\text{H}_4)-(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)$, was prepared as previously reported.¹² *Anal.* Calcd for $\text{C}_{20}\text{H}_{18}\text{Fe}_2$: C, 64.91; H, 4.90. Found: C, 64.73; H, 5.18. Diferrocenylmercury, $[(\text{C}_5\text{H}_5)_2(\text{C}_5\text{H}_4)\text{Fe}]_2\text{Hg}$, was made according to directions given by Rausch, *et al.*¹³ *Anal.* Calcd for $\text{C}_{20}\text{H}_{18}\text{Fe}_2\text{Hg}$: C, 42.10; H, 3.18. Found: C, 42.77; H, 3.13. Biferrocenylene, $(\text{C}_5\text{H}_4)_2\text{Fe}(\text{C}_5\text{H}_4)_2\text{Fe}$, was prepared according to Rausch.¹⁴ *Anal.* Calcd for $\text{C}_{20}\text{H}_{16}\text{Fe}_2$: C, 65.27; H, 4.38. Found: C, 65.12; H, 4.18. A sample of 1,4-bis(β -ferrocenylvinyl)benzene was purchased from Aldrich and recrystallized twice from absolute ethanol.

A sample of $[1,1-(\text{CH}_2)\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{C}_5\text{H}_4)_2](\text{PF}_6)_2$ was prepared

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