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The anti-syn Equilibria of the Organothio Bridged Derivatives of Iron Carbonyl, $(\mu\text{-RS})_2Fe_2(CO)_6$, and of Their Monosubstitution Products with some Phosphines, $(\mu\text{-RS})_2Fe_2(CO)_5(PR'_3)$ [1]

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The pure anti *and* syn *forms of the compounds* $(\mu\text{-}RS)_2Fe_2(CO)_6$ *(R = CH_3, C_2H_5) isomerize to equilibrium mixtures having the K =* [anti]/[syn] *values of 3.2 and 3.6, respectively. If R = C_6H_5 or C_6F_5 no evidence for "pure" isomers has been found, but anomalies of the IR spectra point to differences in the ring orientations. The new derivative R = C_6Cl_5 has been prepared by photochemical reaction.*

The two isomers of the R = alkyl derivatives react with different rates ($k_{syn} > k_{anti}$) with phosphines to give the monosubstituted derivatives $(\mu\text{-}RS)_2Fe_2(CO)_5\text{-}PR'_3$ (R' = n-Bu, Ph) which have also two distinct isomers. The K = [anti]/[syn] *value changes in favour of the* syn *isomers in the substituted compounds.*

Introduction

The existence of two isomers, *anti* and *syn* (Fig. 1) for some compounds of the type $[Fe(CO)_3SR]_2$ (**I**)[2-5] having non-planar bridging RS– groups[6], has been demonstrated [7-10] and in the case of R = CH_3 (**Ia**),[7,4] C_2H_5(**Ib**),[9] and $C_6H_5CH_2$ (**Ic**)[9] the two isomers could be isolated by chromatography, and characterized by their n.m.r.[7] and i.r. spectra [7,9]. An X-ray study of the *anti* form of **Ib**[11] has been performed.

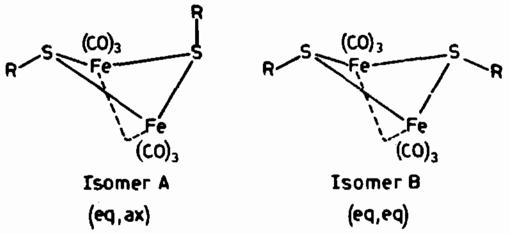

Figure 1. Schematic structures of Forms A and B.

To our knowledge only one quantitative datum on the *anti-syn* ratio in these compounds has been reported in the literature. King and Bisnette[4] have obtained for the R = CH_3 compound a ratio of 80:20 by the integration of the n.m.r. spectra, but apparently they did not perform this measurement on an equilibrium mixture.

There is only a brief qualitative note in the literature on the easy inversion of the methyl groups on the sulphur atom in **Ia**.[12]

The behaviour of the arylthio-bridged analogues has been less thoroughly studied. The only IR spectrum of the R = C_6H_5 (**Id**) compound reported in the literature has a quite low resolution[13] and was taken only to give additional evidence to the dimeric structure of this compound originally formulated[3] as a monomer. More recently the i.r. data of this compound have been used as a basis of approximate force constant calculations[14], but we fear that, even in this case, the resolution was not too good.

No X-ray study has been reported on (**Id**) and not even a 220 Mcps n.m.r. spectrum[14] enabled the detection of the presence of isomers in solution.

With R = C_6F_5 (**Ie**) one paper reports[15] the formation of only one isomer with non-equivalent C_6F_5 groups, i.e. the *anti* form, other workers [16,17], however, have found ^{19}F-n.m.r. evidence for the presence of a smaller amount of the *syn* isomer.

The formation of some monosubstitution products of type **I**, $(CO)_3Fe(\mu\text{-}SR)_2Fe(CO)_2L$ (**II**) with L = Ph_3P, $(PhO)_3P$, etc. was reported,[18,19,16,20] but without mentioning the eventual existence of isomers of the compounds **II**.

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(1) (a) Presented in preliminary form at the 3rd Internat. Symposium of « *Inorganica Chimica Acta* », Sept. 1970, Venice, Proc. E3; (b) This paper is based in part on a dissertation « Tesi di Laurea » of F.G., Department of Chemistry, University of Padua, 1970; (c) Address correspondence to this author.

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We have undertaken a study of the influence of the bridgehead groups R on the *syn-anti* equilibrium of type **I**, and of the modification of these equilibria by the ligands L in compounds **II**. Our studies were mainly based on i.r. spectroscopic evidence, since the combination of the already reported n.m.r.,[7] chromatographic,[7,9] i.r. spectroscopic[7,9] and X-ray[11] results was a sufficient basis for the identification of the obtained products and their isomers.

Experimental Section

All the compounds we dealt with are quite stable to oxidation in the solid state, their solutions however, decompose slowly in the air. For storages over one or two hours they were generally kept under N_2 or CO.

All the solvents used were pure reagent grade. If more careful experimental conditions were to be used, they were distilled from CaH_2.

For chromatographic separation we used Al_2O_3 of the basic type or silica gel, activated for three hours at 180°C.

$Fe_3(CO)_{12}$ was prepared according to the method described by King and Stone.[21]

$Fe_2(CO)_6(SCH_3)_2$, kindly supplied to us by Dr. P. Braterman, was purified by crystallisation from n-hexane and then separated into the two isomers by chromatography on an alumina column using n-hexane as eluent.

Preparation of Compounds. $Fe_2(CO)_6(SR)_2$ (R = C_2H_5, C_6H_5, C_6Cl_5, C_6F_5). All compounds were prepared photochemically, using sunlight, starting from a solution of $Fe_3(CO)_{12}$ and of the appropriate mercaptane or thiophenol (Fe/RSH = 1:1). The solvents used were either saturated hydrocarbons or benzene. (Benzene had to be used in the case of the pentachloroderivative, because of the extremely low solubility of C_6Cl_5SH in saturated hydrocarbons). After a few hours the solutions turn from green to red while a brown precipitate is formed. The filtered solution is evaporated to dryness and the compounds of interest are separated from the unreacted materials by chromatography.

In the case of R = C_2H_5 (**Ib**) the chromatography was performed on an alumina column, eluent n-hexane.[9] We obtained two red fractions corresponding to the *A* and *B* isomers of $Fe_2(CO)_6(SC_2H_5)_2$, which were crystallized from n-hexane; and a third green fraction of unreacted $Fe_3(CO)_{12}$ (the overall yield of $Fe_2(CO)_6(SC_2H_5)_2$ was ~50% referred to iron).

For R = C_6H_5 (**Id**), we used analogous conditions, but we eluted the column with n-hexane containing ~2% in volume of benzene; we had a unique red fraction containing the only form of $Fe_2(CO)_6(SC_6F_5)_2$ (yield ~60% refered to iron) and the usual green fraction of the unreacted tri-iron dodeca-carbonyl.

$Fe_2(CO)_6(SC_6F_5)_2$ (**Ie**) was obtained by chromatography of the reaction mixture on a silica gel column, eluent n-hexane (alumina was evoided, because it was partly decomposing the perhalo derivative). Also in this case the thio compound comes first, as a red fraction, and then the green band of the $Fe_3(CO)_{12}$. The separation is not complete, and there was a slight overlapping of the two bands. This is the reason why we used n-hexane as eluent although the solubility of $Fe_2(CO)_6(SC_6F_5)_2$ in this solvent is rather low. An enrichment with benzene of the eluting mixture would have increased the overlapping of the two different zones.

$Fe_2(CO)_6(SC_6F_5)_2$ (**Ie**) crystallizes from n-hexane as air stable red needles. It seems to be the most air stable compound of the series; (its solutions do not show any evidence of decomposition even after several hours standing in the atmosphere).

$Fe_2(CO)_6(SC_6Cl_5)_2$ (**If**) was obtained reacting C_6Cl_5SH or $(C_6Cl_5S)_2$ with an excess of $Fe_3(CO)_{12}$ in benzene (Fe/C_6Cl_5SH = 1.3/1 or more), and keeping the solution for a few hours in sunlight. The reaction mixture was filtered, evaporated to dryness, and the solid washed several times to eliminate all the unreacted $Fe_3(CO)_{12}$.

The orange-red residue, obtained in this way, after crystallization from benzene gives the pure perchloro derivative, **If**, (yield: ~40 per cent), which is practically insoluble in saturated hydrocarbons, moderately soluble in benzene and chlorinated solvents. The compound decomposes without a definite melting point: it begins to darken at ~100°C and becomes grey over 160°C).

Preparation of the monosubstituted products. $Fe_2(CO)_5PR'_3(SR)_2$ (PR'_3 = PBu_3^n, PPh_3; R = CH_3, C_2H_5, C_6H_5, C_6F_5).

All the substitution reactions were performed at room temperature with a slight excess of the phosphine in saturated hydrocarbons as solvents. Under these mild conditions only R = alkyl and with R′ = *n*-Bu the reaction goes to completeness within some hours, otherwise, even after one or two days, some unsubstituted compound is still present. We were interested in obtaining the monosubstituted products without the formation of the disubstituted derivative[18,19,20] so we preferred to carry out all the reactions at room temperature and separate then the products from the unreacted hexacarbonyl by chromatography or by fractional crystallization.

Chromatography had to be used in the case of R = CH_3, C_2H_5, R′ = n-Bu, since these derivatives are oily products. We used again an alumina column and saturated hydrocarbons as eluent. The unsubstituted compound is eluted first, then comes the band of the phosphine derivative, which, although it is present in two different isomeric forms, does not separate quantitatively and only the «head» and the «tail» of the unique band contain the pure *A* and *B* isomer, respectively.

The PPh_3 derivatives of the alkyl compounds were again purified by chromatography on Al_2O_3. We eluted first the unreacted starting compound with n-hexane and then the monosubstituted product with a mixture of n-hexane +3% (in volume) of benzene. Even in this case we could not separate quantitatively the two isomers present, but we collected a «head» fraction of pure *A* and the final part of the same band containing the pure *B* form.

The two phosphine derivatives of $Fe_2(CO)_6(SC_6H_5)_2$ and $Fe_2(CO)_5PBu_3(SC_6F_5)_2$ were obtained by fractional crystallization of the reaction mixture. They are present only in one form. They do not stand the

Table I. Analysis of Compounds.

Compounds		C	H	S	F	Cl
$[Fe(CO)_3SC_2H_5]_2$	calcd. %	29.95	2.49	15.90		
	found %	29.83	2.51	15.75		
$[Fe(CO)_3SC_6H_5]_2$	calcd. %	43.35	2.01	12.85		
	found %	43.48	2.18	12.65		
$[Fe(CO)_3SC_6F_5]_2$	calcd. %	32.00		9.45	28.20	
	found %	32.16		9.25	28.40	
$[Fe(CO)_3SC_6Cl_5]_2$	calcd. %	25.60		7.60		42.10
	found %	25.43		7.30		42.40
$(CO)_3Fe(\mu\text{-}CH_3S)_2Fe(CO)_2P(C_6H_5)_3$	calcd. %	49.33	3.45	10.54		
	found %	49.14	3.37	10.46		
$(CO)_3Fe(\mu\text{-}C_6H_5S)_2Fe(CO)_2P(C_6H_5)_3$	calcd. %	51.00	3.93	10.07		
	found %	50.85	4.00	9.82		
$(CO)_3Fe(\mu\text{-}C_6H_5S)_2Fe(CO)_2P(C_4H_9)_3$	calcd. %	51.77	5.50	9.53		
	found %	51.82	5.45	9.75		
$(CO)_3Fe(\mu\text{-}C_6H_5S)_2Fe(CO)_2P(C_6H_5)_3$	calcd. %	57.36	3.41	8.75		
	found %	57.50	3.45	8.50		
$(CO)_3Fe(\mu\text{-}C_6F_5S)_2Fe(CO)_2P(C_4H_9)_3$	calcd. %	40.90	3.17	7.54		
	found %	40.80	3.25	7.59		

Table II. C—O stretching frequencies of the $[(\mu\text{-}SR)Fe(CO)_3]_2$ compounds investigated (hexane or heptane solution, ± 1 cm^{-1}).

R	isomer	wavenumbers					
CH_3	A	2073m	2037vs	2002s	1992s		
	B	2071mw	2037vs	1998ms	1990ms		
C_6H_5	—	2075ms	2039vs	2007s	1998s	1991sh	1986w
C_6F_5	?	2089ms	2062vs	2027s	2013s		
				2024sh	2010sh		
C_6Cl_5 [a]		2080m	2051vs	2015s	2007s		

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder. [a] CCl_4 solution.

Table III. C—O stretching frequencies of the $(CO)_3Fe(\mu\text{-}SR)_2Fe(CO)_2PR'_3$ compounds investigated (hexane or heptane solution, ± 1 cm^{-1}).

R	R′	isomer	wavenumbers				
CH_3	C_4H_9	A	2044s	1984vs	1975mv	1965mw	1932w
		B	2041s	1981vs	1967m	1960sh	1924w
	C_6H_5	A	2046s	1989vs	1979mw	1968mw	1936w
		B	2044s	1987vs	1972mw	1965sh	1930w
C_2H_5	C_4H_9	A	2042s	1982vs	1976? [a]	? [a]	1930w
		B	2040s	1982vs	1966ms	1961sh	1923w
	C_6H_5	A	2045s	1988s	1979m	1966mw	1935w
		B	2042s	1986s	1970m	1963sh	1923w
C_6H_5	C_4H_9	—	2048sh 2041m	1988s	1970ms	1930mw	
	C_6H_5	—	2052s	1991s	1975w	1944w	
C_6F_5	C_4H_9	—	2058m	2009s	1992ms	1976mw	1944w
	C_6H_5	—	2068ms 2060s	2017s 2012s	2000s	1985msh 1983ms	1956w 1950w?

vs = very strong; s = strong; ms = medium strong; m = medium; w = weak; sh = shoulder. [a] These frequencies are somewhat uncertain due to the fast isomerization and overlap with the bands of the other isomer.

chromatography on Al_2O_3. Crystallization was the easiest method to obtain them in a pure state.

Elemental analytical data of some representative compounds are given in Table I. The compounds not included in the table were identified on the basis of the analogy of their i.r. spectra.

Infrared spectra were recorded on a Perkin Elmer 621 spectrophotometer with expanded linear wavenumber scale (1 cm = 10 cm^{-1}) and with slit program 700.

The C–O stretching frequencies of the compounds, we dealt with are reported in Table II and III.

U.V.-visible spectra were recorded on a Beckman DK-2A spectrophotometer.

Results and Discussion

A. *Methyl- and ethylthio-bridged Compounds.*

(a) *Isomeric Equilibria.* The C–O stretching frequencies of the *anti* (King's isomer *A*[7]) and *syn* (King's *B*) form is **Ia** are reported in Table II. They differ considerably from the previous data.[7] The relative intensities and frequencies are very close to those of the isomers of **Ib** (see Figure 1 in Ref. 9).

The n-hexane solutions of either the pure *anti* or *syn* isomer, obtained bv chromatographic separation from the commercial product, transformed into the equilibrium mixture within 2-3 days at 40°C. The isomerization occurs even at room temperature, but slowly enough to enable the chromatographic separation of isomers, and the subsequent study of their reactions.

The equilibrium concentration ratio of the two forms was determined by three independent methods: from u.v.-visible spectra, from i.r. spectra, and by weight after chromatographic separation. All three methods resulted in the same value of equilibrium constant (at 40°C): $K = [A]/[B] = 3.2\ (\pm 0.2)$.

With the ethylthio-compound **Ib** a slightly higher K value has been found, i.e. 3.6. Thus it seems that the growing size of the alkylic goup on the RS-bridge shifts the equilibrium in favour of the *anti* isomer, and, as a matter of fact, it has been reported previously[9] that in the case of the R = *tert.*-C_4H_9 derivative practically *only* the anti (A) isomer could be obtained after chromatography of the product of the reaction between $Fe_3(CO)_{12}$ and Bu^tSSBu^t.

It seems therefore that the repulsion between the organic R groups and the four «basal» CO ligands is the driving force in the equilibria rather than the repulsion between the two R-groups. This repulsion would act into the direction of the formation of a «bis-axial» isomer (form «b» in Figure 4 of Ref. 11), which, however, seems to be handicapped by the mutual repulsion of the organic goups. Thus the predominance of the axial-equatorial form (isomer A) results from a compromise from these two types of repulsion, from which the R–CO repulsions seem to predominate.

(b) *Monosubstitution Products.* Two phosphines were used in the study of the substitution reactions, Ph_3P and Bu_3^nP. All of the tributylphosphine derivatives are new compounds.

The following observations were made:

(i) The monosubstitution products (**II**) exist in *two isomeric forms.* (Starting from the pure isomers the corresponding substituted derivatives are obtained with both phosphines). The two isomers of compounds **II** have characteristically different i.r. spectra in the C–O stretching region (Table III). However, repeated scans of the spectra indicate rapid equilibration, proving that the $anti \leftrightarrows syn$ interconversion is much faster after the substitution, as compared with the parent compounds.

We have no direct (e.g. nuclear magnetic resonance) evidence on the identities of the substituted isomers, which we referred to as forms A and B. This type of study was hindered by the fast isomerization. But starting from a pure isomer of the compounds **I** we could follow the formation of the direct substitution product (through i.r. spectroscopy) followed by the secondary process, i.e. the isomerization. Thus we knew wich were the C–O stretching bands belonging to each isomer, and consequently we could identify the chromatographic fractions. The elution sequence (i.e. that isomer A is eluted before B) observed first by King[7] is maintained also after substitution.

The quantitative separation by chromatography of isomers of type **II** is virtually impossible, it can be improved cooling the chromatographic column but it is never complete.

Apparently the phosphinic substituent changes not only the electronic situation of the Fe–C–O bonds in the well known way, reflected by the low-energy shift of the C–O stretching frequencies, but also the different energy levels of the bridging sulphur atoms are influenced. It is likely that the energy levels of the stable sp^3 and the transitional sp^2 states come closer to each other, and thus the energy barrier of the *inversion* is much lower than in the unsubstituted case. We did not perform kinetic measurements to determine this difference quantitatively.

(ii) Starting from the equilibrium mixture of the isomers of **Ia** or **Ib**, and following the reaction by the change of its i.r. spectra, it could be observed that the *syn* (B) isomer reacted much faster with the phosphines than the *anti* (A) form.

The rate of the monosubstitution reaction with Bu_3^nP is quite high even at room temperature. E.g. the reaction with **Ia** (B-isomer $+ Bu_3^nP$, ratio 1/1.3) is complete within one and a half hours. The same reaction with the A-isomer is complete within some hours.

With the ethylthio-bridged compound **Ib** the reaction rates with Bu_3P seemed to be somewhat lower.

Thiphenylphosphine reacted at much lower rate and the reaction of the isomeric mixture of **Ia** in the ratio 1:2 was after 20 hours far from being complete.

We explain these findings on the following way.

On the basis of the different reaction rate of the two parent isomers we suppose that the phosphine occupies one of the axial (or «apical») coordination sites, as shown in Figure 2, which is definitely less shielded in the case of the B form. Our assumption is in accord with an X-ray study of the compound $As_2Co_2(CO)_5PPh_3$[22] which has a basic geometry similar to the sulphur bridged compounds, and where the PPh_3 ligand occupies an axial position.

The higher reaction rate of the more basic trialkylphosphine as compared with that of the Ph_3P is a well known phenomenon in metal carbonyl chemistry.

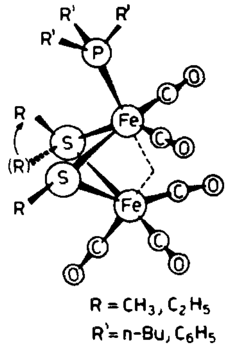

Figure 2. Proposed structures for the monosubstituted compounds $Fe_2(CO)_5(PR'_3)(SR)_2$.

(iii) The equilibrium concentration in the case of monosubstitution is shifted in favour of the *syn* isomer. For R = CH_3 the $K = [anti]/[syn]$ ratio decreases to the value of ~2 if L = PPh_3, and even to ~0.6 in the case of L = PBu_3^n; for R = C_2H_5 we have no quantitative data, but we could observe a similar trend.

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[22] Foust A.S., Foster M.S., and Dahl L.F., *J. Amer. Chem. Soc.*, *91*, 5633 (1969).

This finding confirms that the phosphinic substitution occurs in the «apical» position as indicated in Figure 2. The steric repulsion between the R′ groups of the phosphine and the R groups of the bridges is the third factor that, beside the repulsion R–R and R–CO, governs the equilibrium concentrations. This repulsion is clearly greater than the repulsion between the bridging R groups and the basal CO ligands, and this can account for the shift of the equilibria.

(iv) In the i.r. spectra of the *A* isomers of the $Fe_2(CO)_5L(SR)_2$ compounds there are 5 well resolved bands (see Figure 3).

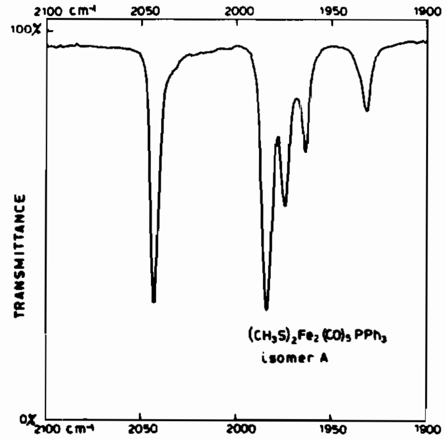

Figure 3. IR spectrum of $(CH_3S)_2Fe_2(CO)_5PPh_3$, isomer A.

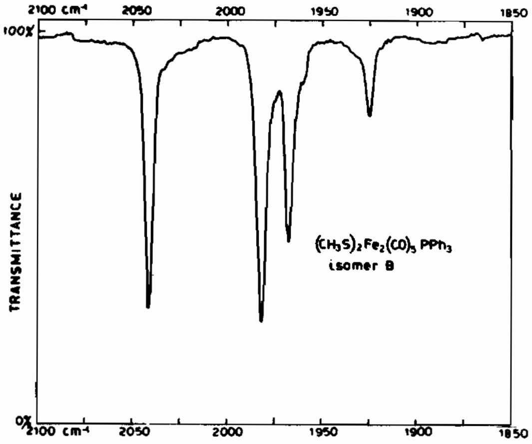

Figure 4. IR spectrum of $(CH_3S)_2Fe(CO)_5PPh_3$, isomer B.

In the spectra of the *B* isomers, however, the fourth (weakest) band from the left appear only as a shoulder, or it is completely overlapped by the close-lying strong band (Figure 4).

Due to the fast isomerization we succeeded only in a few cases to obtain «pure» spectra directly after chromatographic separation, but repeated scans indicated clearly the changes due to the other isomer. In this way we could «substract» the bands due to the increasing concentration of the latter (Figure 5).

The 10-band spectra (including the shoulders) obtained after equilibration (Fig. 6) show frequencies in the regions indicated previosly[18] but apparently the resolution used by this author was not good enough to show the details found by us.

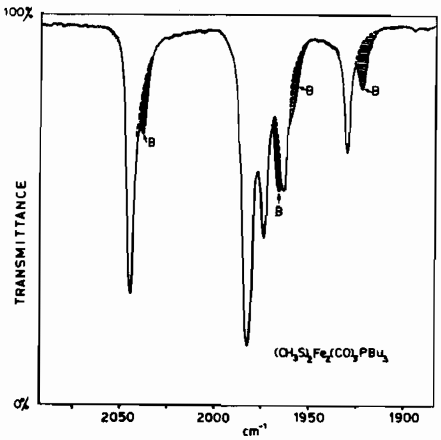

Figure 5. IR spectrum of $(CH_3S)_2Fe_2(CO)_5PBu_3$, isomer A containing some isomer B.

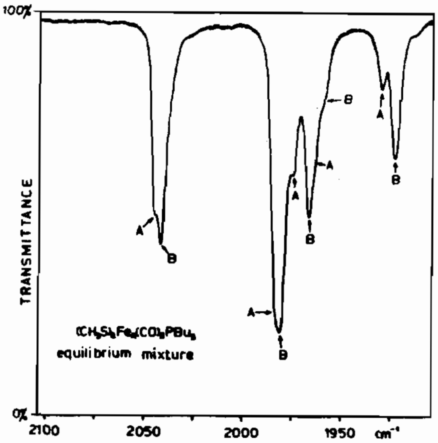

Figure 6. IR spectrum of an equilibrium mixture of $(CH_3S)_2Fe_2(CO)_5PBu_3$.

(v) Also another effect could have contributed to the fact that previously the existence of isomers of the $Fe_2(CO)_5(PPh_3)(SR)_2$ compounds remained unobserved. We noticed that during the slow crystallization of a concentrated equilibrium mixture of the isomers only *one isomer* crystallizes out whereas the mother liquor maintains always the equilibrium composition. In this way, if the spectra are taken on freshly prepared solutions of slowly crystallized samples a relatively pure spectrum of only one isomer is obtained.

Curiously enough the isomer crystallized out from the solution of the triphenylphosphine derivates is the pure *anti* form in the case of the C_2H_5S-bridged compound, but it is the pure *syn* form for the CH_3S–compound. Only crystal lattice effects could account for this behaviour. A quick evaporation of the solvent leaves the equilibrium composition unaltered even in the solid phase.

The tributylphosphine derivatives appeared to be oils and thus this crystallization effect could not have been studied.

B. Phenyl- and Pentahalophenylthio-bridged Compounds. (a) *Isomerism.* In this part we report our observations on the behaviour of the compounds (μ–$C_6X_5S)_2Fe_2(CO)_6$, with X = H (**Id**),[3] F (**Ie**),[15,16] and Cl (**If**). We succeeded in obtaining for the first time the perchlorophenyl derivative in a photochemical way at room temperature, whereas previous attempts to prepare this compound by thermal reaction resulted only in the formation of $S_2Fe_3(CO)_9$.[17]

Compounds **Id**, **Ie**, and **If** do not behave similarly to their alkylthio analogues in the respect that we were unable to separate, even partially, isomeric forms of them, and we cannot even be sure of the existence of their isomers.

We concentrated our efforts on the separation, or at least on the enrichment of the isomers mainly of the pentafluorophenyl compound. For this complex Beck, Tadros, *et al.*[16,17] gave an interpretation of the ^{19}F–NMR spectrum in terms of the presence of two isomers (with the predominance of a form having non-equivalent C_6F_5 rings), whereas Cook *et al.*[15] reported the presence of a single isomer.

Chromatography on a silica gel column of the length of 150 cm, cooled to 0°C, loaded with 65 mgs of the compound and eluted with *n*–hexane gave «fractions» which all showed completely identical IR spectra in the C–O stretching region.

In this respect it is interesting to note that the two «shoulders» observed on the low-energy wings of the two lowest frequency strong C–O stretching bands and indicated by arrows on Figure 7 and which we attributed[1a] to the *syn* isomer on the basis of the ^{19}F–NMR data of Tadros and Beck[16,17] do not show any change in relative intensity, not even in the very first or last chromatographic fraction. Also attempts of separation by fractional crystallization were unsuccessful.

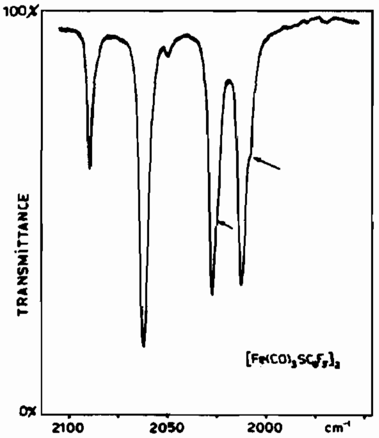

Figure 7. IR spectrum of $[Fe(CO)_3SC_6F_5]_2$.

In spite of these negative results we have obtained additional experimental data which indicate the presence of two different forms of the C_6F_5S–bridged compound. The IR spectrum of its concentrated solutions shows 4 weak bands in the region below 2000 cm^{-1} (Figure 8), whereas 3 bands, could be explained. The two lower ones (at 1970 and 1960 cm^{-1}) might be attributed to isotopic satellites due to natural ^{13}CO substitution, (like the band at 2049 cm^{-1}) and one of the bands at 1996 and 1988 cm^{-1} could be assigned to ν_5^{CO} (b_1) which is usually very weak. A possible explanation for the fourth band could be that it is the ν_3^{CO} (a_2) mode which is forbidden by the selection rules for point group C_{2v} but might have gained some intensity if the molecular geometry deviated considerably from that symmetry.

Calculations, however, did not confirm these assumptions, and two of the four weak bands, aswell as the two shoulders, indicated by arrows (Figure 7), could not be assigned to one single isomer.[23] Thus, in accord with the ^{19}F–NMR evidence, we are forced to assume the presence of two forms of **Ie**.

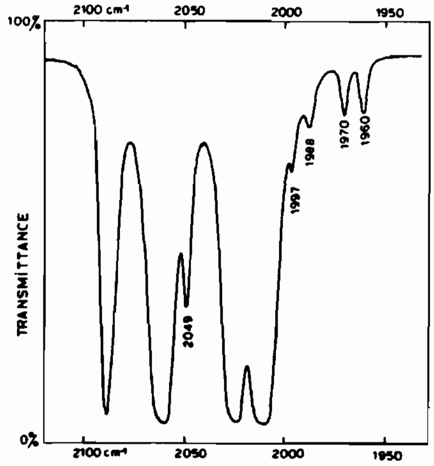

Figure 8. IR spectrum of a very concentrated solution of $[Fe(CO)_3SC_6F_5]_2$.

The unsuccessful atempts of separation could be explained by the too small differences in the physical characteristics of the two isomers. Another explanation might be that instead of a «true» *anti-syn* isomerism only one of the two forms is present but the C_6F_5 rings may have different rotational orientations. The energy barrier between two such *conformers*, however must be very small as compared with that of the sulphur-inversion. Thus the equilibria, if this ring orientational conformers really exist, can be restaured immediately, and no isolation of the different forms is possible.

In the case of the C_6H_5S–compound, **Id**, instead, we have neither NMR- nor IR-spectroscopic evidence of different forms, and also all separation attempts failed. Its IR spectrum, shows 6 ν_{CO} bands (one of them is only a partly resolved weak shoulder; Figure 9). The analysis of the spectrum[23] (with the doublet of the ^{13}CO satellites) proved, however, that in this case all 6 bands fit well into the CO–factored force field i.e.

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(23) A detailed analysis of the infrared spectra together with other compounds of the type $M_2(CO)_6(Bl)_2$ (Bl = bridging ligand) will be published separately; Marcati F., Tesi di Laurea, Univ. of Padova, 1971.

they belong to the same molecule. This observation, in contrast to the C_{2v} selection rules which permit only 5 C–O modes in the IR spectrum, indicates a distorsion of the molecule.

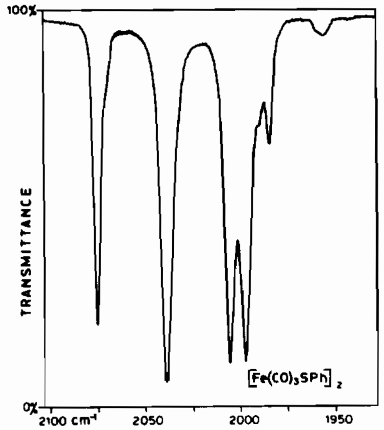

Figure 9. IR spectrum of $[Fe(CO)_3SPh]_2$.

The pentachlorophenylthio compound **If** is soluble only in chlorinated solvents which gave spectra with too broad bands to see the details characteristc of the presence of two forms (Figure 10). Chromatographic working up of this compound was very difficult because its low solubility and consequently did not result in any evidence for isomers.

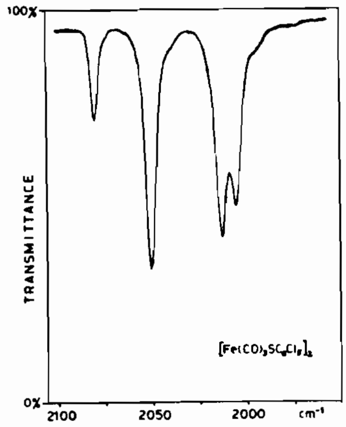

Figure 10. IR spectrum of $[Fe(CO)_3SC_6Cl_5]_2$.

(b) *Monosubstitution products*: $Fe_2(CO)_5(SC_6X_5)_2$-PR_3' (X = H, F; R′ = *n*-Bu, Ph). With the phenyl- and pentafluorophenylthio-bridged compound the formation of the monosubstitution products proceeds under similar smooth conditions like with the alkyl analogues.

(i) *X = H; R′ =* n-*Bu or Ph.* The two compounds do not show any evidence of possible isomers. Their solutions have the same i.r. spectra even after heating for some hours at ~60°C which should have enabled the interconversion between the different forms.

The monosubstituted products should have 5 bands in the CO stretching region. The PBu_3 derivative shows 4 bands plus a quite strong shoulder on the high-energy wing of the highest frequency absorption (Figure 11). We would suggest, keeping in mind the band distributions in the case of the alkyl analogues, that the fifth band is obscured by some stronger ab-

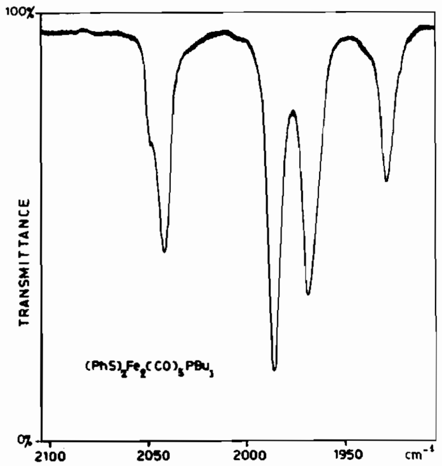

Figure 11. IR spectrum of $(PhS)_2Fe_2(CO)_5PBu_3$.

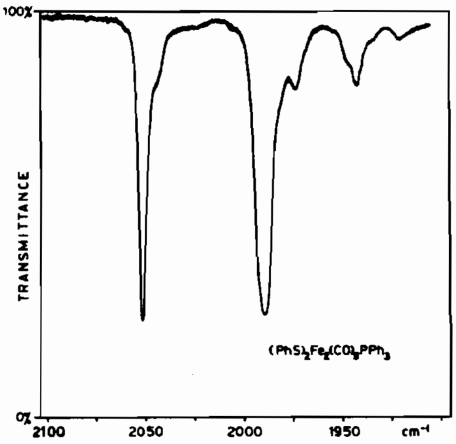

Figure 12. IR spectrum of $(PhS)_2Fe_2(CO)_5PPh_3$.

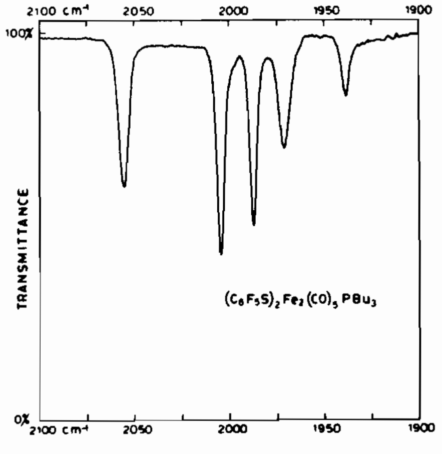

Figure 13. IR spectrum of $(C_6F_5S)_2Fe_2(CO)_5PBu_3$.

sorption bands, probably by the second or the third from the left, while the first shoulder can be due to different orientation of phenyl rings in the molecule.

The i.r. spectrum of the triphenylphosphine derivatives shows again 4 bands in the CO stretching region (Figure 12), however the strongest absorption (at 1991 cm^{-1}) is broad and it seems that two close bands had merged together.

These findings are in accord with the observations on the parent compound, and point to the presence of only one form.

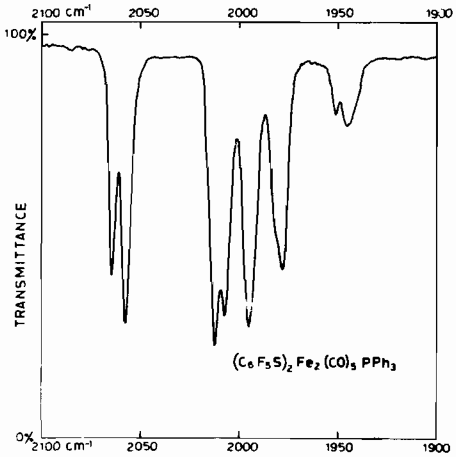

Figure 14. IR spectrum of $(C_6F_5S)_2Fe_2(CO)_5PPh_3$.

(ii) $X = F$, $R' =$ n-*Bu*. This new compound shows clearly 5 C–O stretching bands (Figure 13) and no sign of the presence of isomers could have been found.

(iii) $X = F$, $R' =$ Ph. In contrast to the above mentioned tributylphosphine derivative, this compound shows 10 C–O stretching bands in its i.r. spectrum (Figure 14). The spectrum was identical when the compound was prepared at room temperature and in *n*–hexane solution, or in boiling ethanol, as reported previously.[17]

Neither chromatography, nor crystallisation resulted in any change in the spectrum of the compound. Sublimation resulted in partial decomposition and the ivory coloured deposit on the cool finger was identified as $Fe(CO)_4PPh_3$. Hence we suppose that, like the unsubstituted compound, this Ph_3P-derivative has two (or more) forms which, however, either have nearly identical physical characteristics and thus their separation is impossible, or they are not «true» isomers, but conformers which differ only in the rotational orientation of the C_6F_5-rings, and are thus again inseparable.

(iv) *Attempts to Prepare* $Fe_2(CO)_5L(SC_6Cl_5)_2$ *Compounds.* All efforts to prepare substitution products of the new pentachlorophenylthio compound **If** were unsuccessful, and we ended up always with a complete decomposition of the compound.