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The Organothio-Bridged Derivatives of Iron Carbonyl. II.* The Dynamic Nuclear Magnetic Resonance Study of the *Anti–Syn* Isomerism in Bis(μ-tertiarybutylsulphido)hexacarbonyldiiron and Its Monosubstituted Products with Some Phosphines and Phosphites: an Unusually Fast Interconversion Rate

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The anti–syn *interconversion rate of* $(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$ *is about one thousand times faster than that of the other alkyl and aryl derivatives and becomes fast in the NMR time scale at temperatures above 90 °C. The coalescence temperature of the* Bu^t *signals is lowered by substitution of a carbonyl group with a phosphorus ligand and a single sharp resonance is observed at room temperature with the more basic phosphines. The mechanism of inversion at sulphur is discussed in connection with related systems. Not all monosubstituted products are stable in solution and their tendency to release the coordinated phosphine increases with the bulkiness of the ligand.*

Introduction

In our previous paper [1] we presented a semiquantitative survey of the *anti–syn* equilibria in compounds $(\mu\text{-RS})_2Fe_2(CO)_6$, **I** (with R = CH_3, C_2H_5, C_6H_5 and C_6F_5), and in their monosubstituted products with phosphines $(\mu\text{-RS})_2Fe_2(CO)_5L$, **II** (L = PPh_3 and PBu^n_3). These studies were based upon IR spectral observations and the major conclusions we reached were: (i) the rates of *anti–syn* interconversion in compounds **II** are considerably higher than those of compounds **I**; (ii) in compounds **II** with respect to compounds **I** the composition of the *syn–anti* equilibrium mixture is shifted in favour of the *syn* form.

Meanwhile De Beer, Haines *et al.* published a series of papers [2] having much in common with our studies, although the majority of their data referred to disubstituted complexes: $(\mu\text{-RS})_2Fe_2(CO)_4L_2$. In particular one of these papers [2c] dealt with the Bu^tS-bridged compound, $(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$, especially from the point of view of different types of mono- and poly-substituted products with phosphines.

More recently Ellgen and Gerlach [3] confirmed all of our previous observations and have put on a quantitative basis the kinetics of monosubstitution [reaction(1)] for the methyl-, ethyl-, benzyl-, phenyl-

$$(\mu\text{-RS})_2Fe_2(CO)_6 + L \rightarrow (\mu\text{-RS})_2Fe_2(CO)_5L + CO \quad (1)$$

and *p*-tolyl-thio-bridged compounds (and also for other RS-bridged complexes which cannot give rise to *syn–anti* isomerism). Quantitative isomerization rates for five compounds of type **I** were also reported by these authors; these are the only values of this kind known so far. The equilibrium constant K = [*anti*]/[*syn*] reported for the CH_3S-bridged compound **I**, *i.e.* 3.1 (at 35 °C), is in very good agreement with our previously published value: 3.2 at 40 °C. Ellgen and Gerlach confirmed our suggestion that the bulkier the R group of the bridging RS ligands: (i) the more is the equilibrium shifted in favour of the *anti* isomer, and (ii) the faster is the isomerization rate. For the isomerization rate values between (1–25) × 10^{-5} s^{-1} were given. No data on the Bu^tS-bridged compounds were reported by these authors.

Basato [4] reported a more detailed study on the kinetics of mono- and di-substitution, but only for the PhS-bridged complex.

The NMR (^1H and ^{13}C) study of only two complexes of type **I** has been published recently by Adams *et al.* [5] (for R = CH_3 and C_2H_5). Unfortunately, however, these authors have chosen for their studies two compounds which have been shown previously to isomerize at 35 °C with $t_{1/2}$ of 17.5 and 9.6 hr, respectively, so that it was *a priori* hopeless to expect a fast equatorial–axial R group exchange on the NMR time scale. Hence no wonder that these authors have found these compounds to "show no evidence of axial–equatorial R group exchange prior to the onset of irreversible thermolysis" [5]. (The reported value of 1.5 for the [*anti*]/[*syn*] ratio in the methylthio-bridged compound, instead of 3.1 previously reported [1, 3], might be due to non well equilibrated samples.)†

†*(See overleaf).*

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Thus the survey of the work published so far on these systems shows that in this field there are problems, raised in earlier studies, which are still unresolved. We were especially interested in the Bu^tS-bridged compounds for which: (i) the room-temperature IR spectrum is such as to suggest the presence of only one (probably the asymmetric) isomer [7]; (ii) any effort to separate the isomers by chromatography and fractional crystallization was unsuccessful [7, 8]; (iii) reports of ^1H NMR spectral studies on the Bu^tS-bridged compound I were apparently in conflict: King and Bisnette [8] observed two methyl signals of 'roughly' equal intensity (at τ = 8.62 and 8.72) and suggested thus the presence of only the *anti* isomer; De Beer and Haines [9], more recently, observed three signals (at τ 8.50, 8.53 and 8.62) and they estimated the ratio of the two isomers to be: [*anti*]/[*syn*] = 9. (iv) ^1H NMR spectra (at 38 °C) of the $(\mu\text{-}Bu^tS)_2Fe_2(CO)_5L$ compounds indicated the presence of the *syn* (symmetrical) isomer alone when L = PPh_3, but both isomers were observed when L = $P(OMe)_3$ and $P(OPh)_3$. No quantitative data concerning the isomeric ratio in the latter cases were given [2c]. (v) No variable temperature NMR studies with the Bu^tS-bridged compounds seem to exist.

In this paper the first NMR study at variable temperature of $(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$ and some of its monosubstituted products is reported. We argued that the bulkiness of the R group could be responsible for the 'anomalies' mentioned above, and we thought that in this case (ter-butyl complexes) there was a chance of obtaining important additional information on factors affecting the rate of *anti–syn* interconversion and possibly on the mechanism of isomerization.

Experimental

Materials

$Fe(CO)_5$, Bu^tSH, $P(OMe)_3$, PPh_3, PBu^n_3 and PCy_3 were commercially available and were purified according to standard procedures, all other reagents and solvents used were reagent grade products. $Fe_3(CO)_{12}$ was prepared from $Fe(CO)_5$ according to the method described by King and Stone [10].

Preparations

$(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$ was prepared from triirondodecacarbonyl and tertiarybutylsulphide in stoicheiometric ratio by exposing their benzene solution to sunlight for some hours. The reaction mixture was then filtered and the solution taken to dryness; the solid residue, dissolved in light petroleum (b.p. 40–60 °C), was loaded onto a silica gel column; elution with the same solvent gave a deep red band of the desired compound as the major reaction product. The small zone following the main product contained a few $[(\mu\text{-}Bu^tS)Fe_2(CO)_6]_2S$ identified by its infrared spectrum. This photochemical procedure, unlike the thermal one [9], resulted in a cleaner reaction and no formation of $Fe_3(CO)_9S_2$, which is difficult to remove by chromatography, was observed. *Anal.* Calcd. for $(Bu^tS)_2Fe_2(CO)_6$: C, 36.7; H, 3.9; S, 14.0. Found: C, 36,6; H, 3.9; S, 13.8%.

$(\mu\text{-}Bu^tS)_2Fe_2(CO)_5PR'_3$ (R′ = OMe, Ph, Bu^n, or Cy) were prepared by reaction of substitution with a slight excess of phosphine performed at room temperature and using saturated hydrocarbon as solvent. The solution of the reactants was allowed to stand for one or two days and the reaction course was monitored by IR spectroscopy. The derivatives with R′ = OMe, Ph, or Cy were purified by fractional crystallization; in fact the derivative with $P(OMe)_3$ decomposes upon attempted chromatography over silica gel and the products with PPh_3 and PCy_3 are stable in solution only in the presence of excess phosphine. The derivative with R′ = Bu^n was purified by column chromatography over silica gel of the reaction mixture; it is a red oil which was characterized by IR spectroscopy. *Anal.* Calcd. for $(Bu^tS)_2Fe_2(CO)_5P(OMe)_3$: C, 34.7; H, 4.9; S, 11.6. Found: C, 34.5; H, 4.8; S, 11.5%. Calcd. for $(Bu^tS)_2Fe_2(CO)_5PPh_3$: C, 53.8; H, 4.8; S, 9.3. Found: C, 53.7; H, 4.7; S, 9.2%. Calcd. for $(Bu^tS)_2Fe_2(CO)_5PCy_3$: C, 52.4; H, 7.2; S, 9.0. Found: C, 52.3; H, 7.3; S, 9.1%.

Spectroscopic Equipment

The IR spectra were recorded on a Perkin–Elmer 621 grating spectrophotometer. The high temperature IR spectra were run using a RIIC cell equipped with electrical heater and temperature controlling device.

The ^1H NMR spectra were recorded on a Varian NV 14, 60 MHz instrument. Probe temperature was adjusted with a variable temperature probe accessory. Values for the free energy of activation were calculated from variable temperature spectra [11]. The calculated $\Delta G^{\neq}$ values are affected by quite large errors (estimated probable error = 2 kJ mol^{-1}); however their accuracy was adequate for our purposes. The values of $\Delta G^{\neq}$ for the *anti–syn* isomerization process and the proton chemical shift of the Bu^t groups are reported in Table I.

†The low temperature ^{13}C study of the EtS-bridged compound was performed on a sample containing the unsymmetrical (*anti*) isomer alone which crystallizes preferably (the X-ray study of Dahl and Wei [6] was carried out with a crystal of the *anti* isomer) whereas the equilibrated solution of $(\mu\text{-}EtS)_2Fe_2(CO)_6$ shows an [*anti*]/[*syn*] ratio of 3.6 at 40 °C (using hexane as solvent) [1].

TABLE I. Proton Chemical Shift of the Tertiarybutyl Groups (τ Downfield from Me_4Si) of the Complexes $(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$ and $(\mu\text{-}Bu^tS)_2Fe_2(CO)_5L$ [L = $P(OMe)_3$, PPh_3, PBu^n_3 or PCy_3]. Values relative to the two isomers, *syn* and *anti*, are given. The free energy of activation, $\Delta G^{\neq}$, for the *anti–syn* isomerization process is also included.

Complex	θ/°C	Solvent		τ (Bu^t)	$\Delta G^{\neq}$ [a] kJ mol^{-1}
$(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$	+25	$CDCl_3$	*syn*	8.53	77
			anti	8.62, 8.50	
$(\mu\text{-}Bu^tS)_2Fe_2(CO)_5P(OMe)_3$	+25	$CDCl_3$	*syn*	8.61	72
			anti	8.65, 8.70	
$(\mu\text{-}Bu^tS)_2Fe_2(CO)_5PPh_3$	0	$(CD_3)_2CO$	*syn*	8.89	65
			anti	8.70, 8.61	
$(\mu\text{-}Bu^tS)_2Fe_2(CO)_5PBu^n_3$	0	$(CD_3)_2CO$	*syn*	8.63	[c]
			anti	[b]	
$(\mu\text{-}Bu^tS)_2Fe_2(CO)_5PCy_3$	−10	$(CD_3)_2CO$	*syn*	8.51	[c]
			anti	[b]	

[a]Errors are estimated to be *ca.* ± 2 kJ mol^{-1}. [b]The resonances of the *anti* isomer are obscured by those of the phosphine, however the broadening of the signal of the *syn* isomer as the temperature is raised and the appearance in the condition of fast isomerization of a new sharp resonance at slightly different field is an indirect proof of the existence at low temperature of the *anti* isomer in equilibrium with the *syn* one. [c]The $\Delta G^{\neq}$ could not be calculated but it is believed to be lower than 65 kJ mol^{-1}.

Results

$(\mu\text{-}Bu^tS)_2Fe_2(CO)_6$

^1H NMR spectra of this compound were recorded in the range of temperature 25–100 °C in $CDCl_3$ solution (Figure 1). At room temperature we observed three resonances (at 8.50, 8.53 and 8.62 τ) which are in complete accord with the results of De Beer and Haines [9]. On raising the temperature the signals broaden and coalesce in only one peak.

Spectra in the range −60–+30 °C were recorded in $(CD_3)_2CO$ solution (in this solvent the two resonances at lower field overlap and therefore a two-peak spectrum, similar to that reported by King and Bisnette [8], is observed). Quantitative evaluation of the band areas between −60 and +30 °C showed that K = [*anti*]/[*syn*] remains constant (4.4 ± 0.3) within experimental error in this temperature range. This finding shows that the enthalpy difference between the two isomers is very small and the concentration ratio is determined mainly by the entropy difference.

The IR spectrum in the carbonyl stretching region shows the presence of four major bands at 2069ms, 2033vs, 2001s, and 1989s cm^{-1}, with the intensity ratio characteristic of the *anti*-type isomer (this is the reason why initially the *anti*-isomer was thought to be the only existing form [7]. However, the lowest frequency CO stretching band (1989 cm^{-1}) is somewhat broader than in the *anti* form of analogous complexes and has two unresolved shoulders, one at lower and one at higher frequency, that can be indicative of the presence of another isomer (the low frequency shoulder can be also assigned to ν^5, which, owing to its low intensity, is observed as an ill resolved shoulder in the analogous compounds with R = Me, Et [12]). We have also run the IR spectrum varying the temperature from 30 to 100 °C using decaline as solvent, and no change whatsoever has been observed.

$(\mu\text{-}Bu^tS)_2Fe_2(CO)_5L$

We have looked also at the monosubstituted products with different phosphines [L = $P(OMe)_3$, PPh_3, PBu^n_3, and PCy_3]. $(\mu\text{-}Bu^tS)_2Fe_2(CO)_5P(OMe)_3$ was already reported to be present at room temperature in two isomeric forms [9]. We have run the variable temperature NMR spectrum of this compound and found that on raising the temperature the three resonances coalesce in one peak which is sharp at 75 °C (Figure 2).

The NMR spectra of the triphenyl-, tri-n-butyl-, and tricyclohexylphosphine derivatives at 35 °C show the presence of only one resonance peak (at 8.83, 8.61 and 8.53 τ respectively) for the tertiarybutyl groups. This behaviour in the PPh_3 derivative was ascribed by other authors to the presence of only the *syn* isomer in solution [2c].

The variable temperature NMR spectrum of $(\mu\text{-}Bu^tS)Fe_2(CO)_5PPh_3$ is shown in Figure 3. It appears that on lowering the temperature the single signal at 8.83 τ first broadens, then splits into three different resonances. The two signals at lower field have equal intensity and are assigned to the *anti* isomer, the higher field signal is more intense and belongs to the *syn* isomer; the approximate [*syn*]/[*anti*] ratio is 2.3 at 0 °C. It is noteworthy that the two resonances of the *anti* isomer occur both at lower

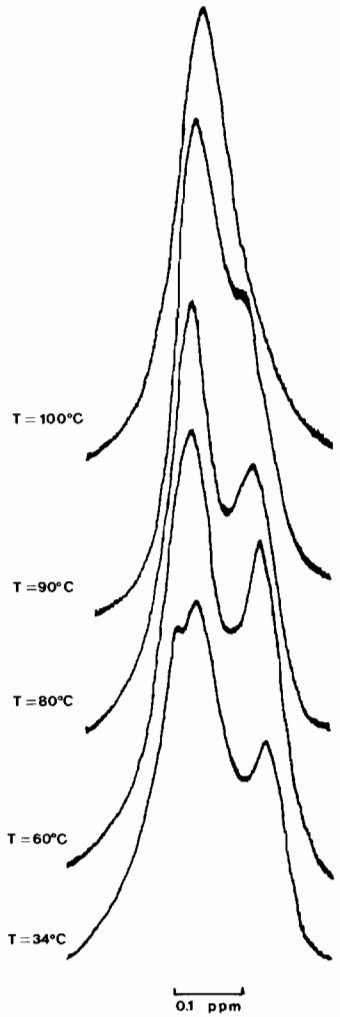

Fig. 1. Variable temperature NMR spectrum of $(\mu\text{-Bu}^t\text{S})_2\text{Fe}_2(\text{CO})_6$ in the region of the tertiarybutyl proton resonances. Solvent $CDCl_3$.

field than that of the *syn* isomer although one could have expected the latter to occur midway in between the former two signals.

In the spectra of the monosubstituted products with PBu^n_3 and PCy_3 the Bu^t signal occurs at the top of a broad resonance due to the phosphinic protons. On lowering the temperature this signal becomes broad and then a sharp resonance at slightly different field appears again. The single resonance observed at low temperature is, most probably, that of the *syn* isomer which would be the more abundant, the resonances of the *anti* isomer being obscured by those of the phosphinic protons.

Discussion

The compounds $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ give rise to two isomers, *syn* and *anti*, which, when R = Me, Et, Bz,

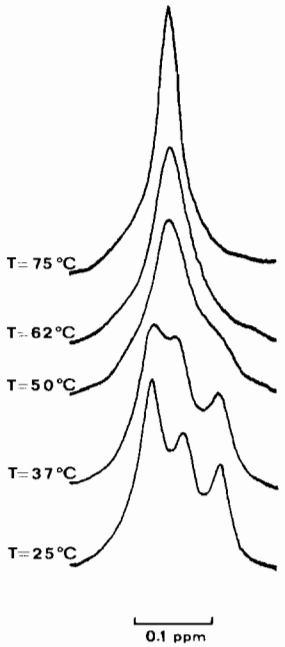

Fig. 2. Variable temperature NMR spectrum of $(\mu\text{-Bu}^t\text{S})_2\text{Fe}_2(\text{CO})_5\text{P(OMe)}_3$ in the region of the tertiarybutyl proton resonances. Solvent $CDCl_3$.

can be separated by column chromatography and fractional crystallization. When R = Ph, *p*-tolyl or Bu^t, however, the conventional physico-chemical methods do not allow separation into isomers. The reason for this can be either a fast interconversion of the two isomers or an overwhelming predominance of one isomer over the other. Kinetic data on the rate of *anti* → *syn* isomerization have shown that this rate in the case of R = Me, Et, or Bz is ten times lower than when R = Ph or *p*-tolyl [3]. In the latter case, however, the rate (*ca.* 2.5×10^{-4} s^{-1}) is not such to preclude the separation of the two isomers by column chromatography, and the fact that all attempted separations have been unsuccessful could have been due to the net predominance of one isomer (*anti*) over the other (IR spectroscopy [12], kinetics of CO substitution by phosphine [11], and X-ray structure of a crystalline compound [13] seemed to confirm this hypothesis.)

Our variable temperature NMR and IR measurements prove that also in the R = Bu^t case there are two distinct isomers in solution, the ratio of which remains practically unchanged in the range of temperature explored. The single resonance observed at high temperature is due to the fast rate of the *anti–syn* interconversion and not to the presence of the *syn* isomer alone.

It appears that the radical R can greatly influence the rate of isomerization of the $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ compounds. When R = Me, Et, Bz, Ph or *p*-tolyl the rate constant for the *anti–syn* interconversion at 35 °C is: 1.1×10^{-5}, 2×10^{-5}, 4.6×10^{-5}, $2.4 \times$

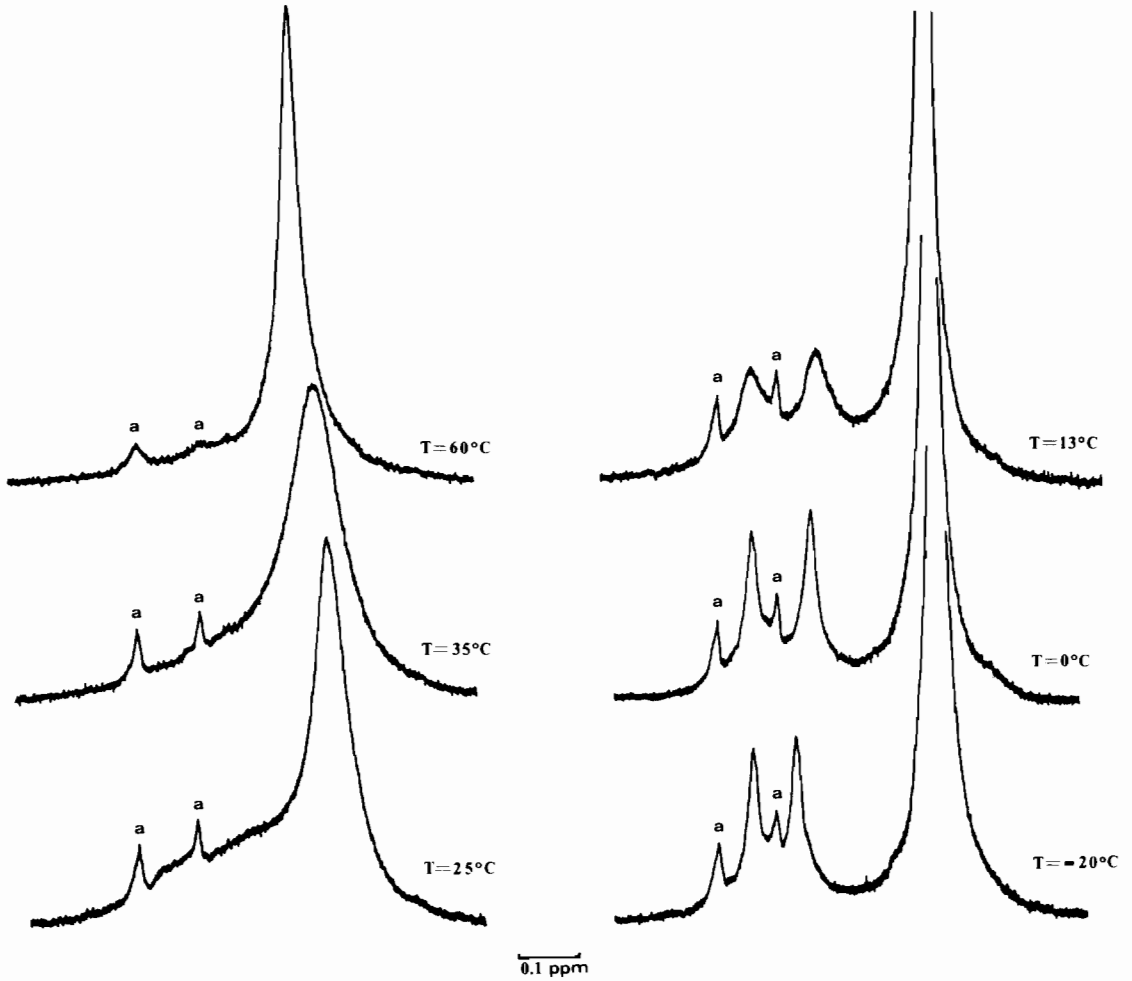

Figure 3. Variable temperature NMR spectrum of $(\mu\text{-Bu}^t\text{-S})_2Fe_2(CO)_5PPh_3$ in the region of the tertiarybutyl proton resonances. Solvent $CDCl_3$. (a) Signal belonging to the unsubstituted product.

10^{-4}, and 2.5×10^{-4} s^{-1} respectively [3]. In the Bu^t case we can estimate a rate constant at 35 °C of *ca.* 0.6 s^{-1}. The earlier observation that the isomerization rate increases as the size of the mercapto substituents increases [3] seems to be confirmed.

In the case of the monosubstituted products, $(\mu\text{-Bu}^tS)_2Fe_2(CO)_5L$, neither IR spectroscopy, nor attempted physico-chemical separations gave clear evidence for the presence of two isomers (it is to be noted that if the two isomers have close C–O stretching frequencies, or one isomer predominates, the IR data cannot be diagnostic in this respect). However the variable temperature NMR spectra gave unequivocal evidence for the existence of two isomers also in these compounds.

From the $\Delta G^{\neq}$ values (Table I) it appears that the rate of isomerization of the monosubstituted product with $P(OMe)_3$ is intermediate between that of the unsubstituted product and those of the derivatives with more basic and bulky phosphines as PPh_3, PBu^n_3, and PCy_3. These data are in accord with either the basicity or the steric hindrance of the phosphine being important in determining the isomerization rate.

Whether the steric or the electronic properties of the organic radicals (R and R′) are predominant in determining the rate of *anti–syn* interconversion of the $(\mu\text{-RS})_2Fe_2(CO)_5(CO, PR'_3)$ complexes depend on the mechanism of isomerization. In fact if the isomerization occurs through a planar transition state at the sulphur atom (as generally observed in the inversion of sulphoxides [14]) the steric factors are more important (on going from the original tetrahedral situation to the planar transition state only the steric interactions are significantly decreased). On the contrary, if in the isomerization process the sulphur retains the tetrahedral configuration and the metal atom forms its bond alternately with the two sulphur lone pairs (as proposed for the inversion at

sulphur in *cis*- and *trans*-$PtCl_2(RR'S)_2$ [15]) the electronic factors become important (all groups with electron releasing capability, bonded either to sulphur or to the metal, having the effect of expanding the electronic orbitals of these atoms, will stabilize the transition state in which both sulphur unshared pairs of electrons are involved in multiple bond with the metal).

The mechanism which operates in our complexes is probably the second one. In fact our values of $\Delta G^{\neq}$ are close to those found in the platinum complexes with mercaptans [15], moreover this mechanism has been postulated in the isomerization of dimeric complexes analogous to those presently investigated [4, 16]. If so the increase in rate of isomerization observed when R = Bu^t is not due exclusively to the bulkiness of this group but also to its inductive effect. Similarly the increased isomerization rate observed when a CO is substituted by a phosphine should be related also with the greater basicity of the phosphorus ligand.

Stability of Complexes

We have observed (see Experimental) that the monosubstituted products with PPh_3 and PCy_3 (but not with $P(OMe)_3$ and PBu^n_3) are stable in solution only if an excess of free phosphine is present; otherwise they decompose losing the phosphorus ligand and giving back the unsubstituted product accompanied by partial decomposition. It appears that the observed instability trend parallels the bulkiness of the phosphorus ligands (PCy_3, PPh_3, PBu^n_3 and $P(OMe)_3$ have cone angles of 172 ± 10°, 145 ± 2°, 130 ± 4°, and 107 ± 2° respectively [17]) independently from their donating ability (the basicity sequence is $PCy_3 > PBu^n_3 > PPh_3 > P(OMe)_3$). Since an instability of the monosubstituted products has been observed only in the tertiarybutylmercapto-bridged derivatives, it follows that in addition to the bulkiness of the phosphine that of Bu^t is also important.

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