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STEREOCHEMISTRY OF PHOSPHOROUS TRIHALIDE DERIVATIVES OF IRON CARBONYL

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A number of substitution reactions with iron carbonyl and monodentate ligands such as CNR (where R = CH_3, C_2H_5, C_6H_5, $C_6H_4OCH_3$) were carried out by Hieber and Pigenot[1]. Cotton and Parish[2] studied the infrared spectra of compounds, $Fe(CO)_4L$ and $Fe(CO)_3L_2$ (L = Ph_3P, MeNC, EtNC, PhNC, *tert*-BuNC), and Manuel and Stone[3] reported the compound *trans*-$Fe(CO)_3[P(C_6H_5)_3]_2$. Recently, a systematic infrared investigation of several $Fe(CO)_5$ derivatives with mono- and bi-dentate ligands[4] was carried out and for the first time the existence of pure and mixed tri-substituted *cis*-compounds of the type $Fe(CO)_2L_3$, $Fe(CO)_2L_2L'$, $Fe(CO)_2LL'_2$, $Fe(CO)_2L'_3$ has been established.

With all the ligands mentioned above, the symmetry of the complexes is either C_{3v} (L-axial) for mono-substituted, or D_{3h} (L-axial) for di-substituted with monodentate ligands, or C_{2v} (angle between two CO-groups, 120°) for tri-substituted derivatives. However, tetra- and penta-derivatives with these ligands are as yet unknown. On the other hand, using phosphorous trifluoride as ligand, Clark[5] isolated the whole series of compounds $Fe(CO)_{5-n}(PF_3)_n$ ($n = 1–5$) and reported on their infrared spectra. The penta-substituted product was also prepared indirectly by Kruck and Prasch[6] using FeI_2 and PF_3 in the presence of copper powder.

PF_3 is the first known ligand to give with $Fe(CO)_5$ all five substitution products[5]. A comparison of the infrared spectra of mono-, di-, and tri-substituted derivatives of $Fe(CO)_5$ with PR_3 (R = C_2H_5, C_6H_5, OCH_3, etc.) and PX_3 (X = Cl or F) shows many anomalies as pointed out by Clark[5]; the existence of various isomers was suggested but this possibility was not further investigated.

The present investigation is a systematic infrared study of the phosphorous trihalide derivatives of $Fe(CO)_5$ undertaken with a view to assigning the frequencies to the various isomers present. The anticipated symmetry groups, nature and number of CO vibrations related to the isomers of various derivatives are presented in Table 1. The frequencies observed are essentially the same as those reported by Clark[5].

The discussion of the results is not in the order of substitution of the derivatives selected for interpretation as we prefer to start with the tetra-substituted derivative which provides a comparatively simple spectrum because it contains only one CO-group.

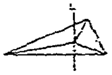
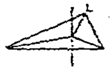
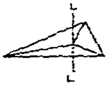
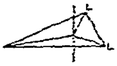
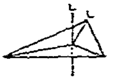
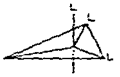
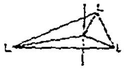
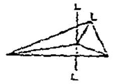
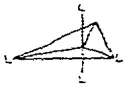
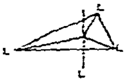
TETRAKIS(TRIFLUOROPHOSPHINE)IRON(0) CARBONYL, $[Fe(CO)(PF_3)_4]$

The tetra-substituted derivative was isolated by repeated fractionation of a mixture containing $Fe(CO)_2(PF_3)_3$, $Fe(CO)(PF_3)_4$ and traces of $Fe(CO)_3(PF_3)_2$.

For all the fractionations carried out on a mixture of the mono-, di-, tri- and

TABLE 1

NUMBER OF C–O IR ACTIVE BANDS OF $Fe(CO)_{5-n}(PF_3)_n$ ISOMERS

Structure	*Symmetry group*	*Symmetry species*	*Number of C–O infrared active modes*
	C_{3v}	$2A_1$ E	3
	C_{2v}	$2A_1$ B_1 B_2	4
	D_{3h}	A'_1 E'	1 (E')
	C_{2v}	$2A_1$ B_2	3
	C_s	$2A'$ A''	3
	C_s	A' A''	2
	D_{3h}	A'_1 A''_2	1 (A''_2)
	C_{2v}	A_1 B_1	2
	C_{2v}	A_1	1
	C_{3v}	A_1	1

tetra-substituted products, the first fraction was always free of $Fe(CO)(PF_3)_4$ indicating clearly that it is the least volatile product in the series $Fe(CO)_{5-n}(PF_3)_n$ ($n=1$–4). On the other hand, the first fraction was rich in $Fe(CO)_2(PF_3)_3$ which is thus the most volatile in this series. Recently, vapour-pressure measurements of the series $Ni(CO)_{4-n}(PF_3)_n$ were reported by Clark and Brim[7] and a regular change in vapour pressure *vs. n* was observed for this series. Several scores of fractionations were performed with different mixtures of all the derivatives of $Fe(CO)_5$ and the same irregularity was always observed. The order of elimination from the mixture was $Fe(CO)_2(PF_3)_3$, $Fe(CO)_3(PF_3)_2$, $Fe(CO)_4(PF_3)$ and $Fe(CO)(PF_3)_4$ which leads us to conclude that the volatility increases with substitution and attains its maximum in the case of the tri-substituted derivative and then suddenly falls with $Fe(CO)(PF_3)_4$, as shown in Fig. 1.

The infrared spectrum of $Fe(CO)(PF_3)_4$ was examined in the region 4200–400 cm^{-1} in n-hexadecane solution and in the vapour state. In the CO-stretching region, in solution, there are two strong bands at 2035.4 and 2007.3 cm^{-1}, accompanied by two satellites at 1989 and 1960.8 cm^{-1}, respectively, the relative intensities of which

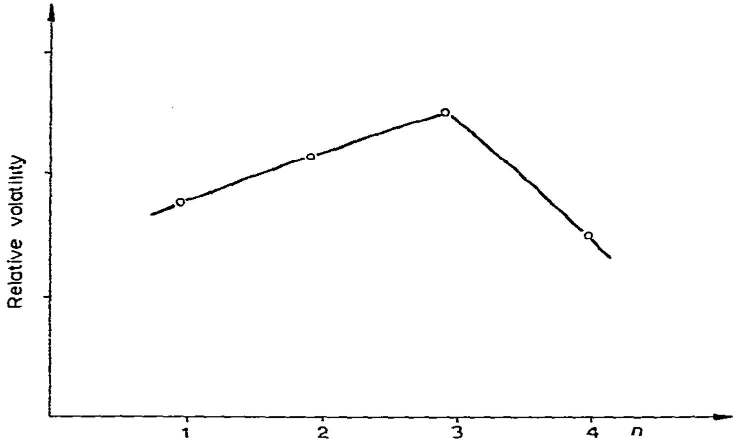


Fig. 1. Relative volatility of the complexes $Fe(CO)_{5-n}(PF_3)_n$.

are approximately equal to those of the principal bands. Analogous results were obtained when the spectrum was recorded in the vapour state (see Table 2). The infrared spectra are presented in Fig. 2.

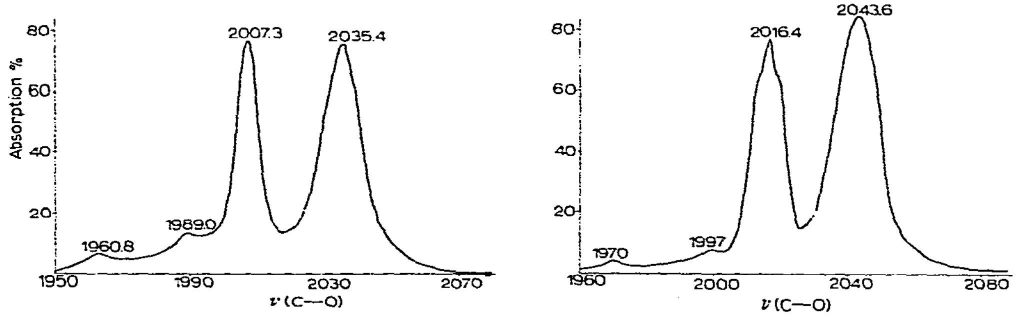


Fig. 2. Spectrum of: (a), $Fe(CO)(PF_3)_4$ in n-hexadecane; (b), $Fe(CO)(PF_3)_4$ in vapour state.

The arguments that favour the existence of two isomers having symmetry C_{3v} and C_{2v} (see Table 1) are as follows:

(1) The existence of two bands in the CO-stretching region.

(2) Of these two bands at 2043.6 and 2016.4 cm^{-1} (Fig. 2b), only the latter presents a structure PQR where the branch Q predominates. This seems to indicate a symmetry C_{3v} for the band at 2016.4 cm^{-1} (CO-axial).

(3) The two CO-stretching frequencies and the satellites are separated by 46.4 and 46.5 cm^{-1} in solution and 46.6 and 46.4 cm^{-1} in the vapour state. A comparison of these differences with the 47.8 cm^{-1} which exists[8] between the CO-stretching frequencies of $Ni(^{12}CO)(PF_3)_3$ and $Ni(^{13}CO)(PF_3)_3$ indicates very clearly that:

(a) The two bands at 2035.4 and 2007.3 cm^{-1} in solution and the corresponding two bands in the vapour state are fundamental bands of CO belonging to the species *A*.

(b) The two satellites are related to ^{13}CO vibrations of the complex studied.

(c) The two CO vibrators of the complex the frequencies of which are

2035.4 and 2007.3 cm^{-1} do not belong to the same molecule; if they were on the same molecule the isotopic substitution $^{12}CO \leftrightarrow ^{13}CO$ would be concerned with only one of the two CO vibrators and *only one satellite* would then be observed. (The concentration of a complex the two CO vibrators of which are ^{13}CO would be only about 1% of the mono-^{13}CO-complex).

The presence of the two satellites demonstrates rigorously that one is concerned with two independent molecules each containing only one CO vibration.

(4) In the region 4000 cm^{-1}, two harmonics of the CO fundamentals with the anharmonicity constants -12.6 and -11.9 cm^{-1}, are observed. No combination band of 2043.6 and 2016.4 cm^{-1} is found. The presence of such a band would indicate that the two CO vibrations belong to the same molecule.

The relative intensity of the bands 4062 and 4009 cm^{-1} (gas) is 2.0 and that of the bands 2043.6 and 2016.4 cm^{-1}, 1.75. However, it is not obligatory that they must be the same, as the anharmonicity constants are not exactly the same. Thus, the spectrum in the 4000 cm^{-1} region provides additional support that the two bands of the 2000 cm^{-1} region belong to two different molecules.

(5) The ratio of intensity of the bands 2043.6 and 2016.4 cm^{-1} (gas) is 1.75 and that of the bands 2035.4 and 2007.3 cm^{-1} (solution), 1.50. It is possible that the composition of the vapour is a little different from that of the liquid. Nevertheless, the two values are near to 3/2 which is to be expected if the CO is arranged statistically at the five positions (three equatorial and two axial).

(6) Although we were unable to discover a physical method for the separation of the two species, it has been possible to eliminate one of the two bands, 2035.4 and 2007.3 cm^{-1}, by a chemical procedure. The treatment of $Fe(CO)(PF_3)_4$ by PMe_3 at 115° for about 20 h provided a mixture which gives the band at 2007.3 cm^{-1} whereas the band at 2035.4 cm^{-1} has almost disappeared. The isolation of the species has not been carried out. The species that disappears (band 2035.4 cm^{-1}) carries its CO in the equatorial position as it is less stable than the other that resists the attack of PMe_3.

This experiment indicates clearly that the two bands, 2035.4 and 2007.3 cm^{-1}, are independent and belong to two different species.

An attempt to change the proportion of the two chemical species was made by varying the temperature of the solution (n-hexane) from $-60°$ to $+30°$ but no change in the optical density of the two bands at 2035.4 and 2007.3 cm^{-1} was observed.

In spite of this last result it is permissible *to conclude that two isomers of* $Fe(CO)(PF_3)_4$ *exist*, one has the CO in the axial position (2007.3 cm^{-1}) and the other in the equatorial position (2035.4 cm^{-1}). This conclusion is based primarily on results 2,3 and 6 although results 1,4 and 5 are in agreement with the conclusion. The result of the infrared spectra recorded at various temperatures is not contrary to the conclusion.

Although result 5 suggests that there is always an equilibrium of isomerisation corresponding to a statistical distribution of CO at all five positions, result 6 is not in accord with this conclusion. The proportion of isomers observed depends mainly on the conditions of their formation.

Other regions

(a) P–F stretching (900 cm^{-1}) and F–P–F deformation (500 cm^{-1}) regions cannot be used for the identification of the isomers as the spectrum is very complex due to the presence of four PF_3-groups.

(b) Fe–C–O deformation vibrations — one band E is expected for the C_{3v} isomer and two bands, B_1 and B_2, for the C_{2v} isomer. We have observed only two bands in solution and in the vapour state. It is very probable that the band E of one species overlaps with B_2 of the C_{2v} isomer. The band at 569.7 cm^{-1} is particularly assigned as E of the species C_{3v} as it is known that the frequencies of the vibrations M–C–O vary in the same sense as the CO-stretching vibrations. B_1 and B_2 are then situated at 584.7 and 569.7 cm^{-1}.

(c) Fe–C stretching region — analogous to CO-stretching vibrations, two bands are observed at 465 and 423 cm^{-1} and are assigned to the species, C_{3v} and C_{2v}, respectively.

TABLE 2

IR FREQUENCIES OF $Fe(CO)(PF_3)_4$

Combination bands

Solution	*Gas*	*Assignment*	*Anharmonicity constant*
4044 m	4062 m	$(A_1)^2\ (C_{2v})$	−12.6
3988 m	4009 m	$(A_1)^2\ (C_{3v})$	−11.9

Solution	*Assignment*	*Gas*	*Assignment*
2603 m	2035.4+569.7	2614 m	2043.6+571.4
2575 m	2007.3+569.7	2584 m	2016.4+571.4
2550 w	2035.4+516	2558 w	2043.6+519
2525 vw	2007.3+516	2535 vw	2016.4+519
2439 vw	2035.4+404		
2410 vw	2007.3+404		
2335 w			
2140 w			

CO-stretching frequencies		*P–F stretching frequencies*	
Solution	*Gas*	*Solution*	*Gas*
2035.4 vs	2043.6 vs $A_1(C_{2v})$	945.2 s	950.2 s
2007.3 vs	2016.4 vs $A_1(C_{3v})$	913.2 vs	920.2 vs
1989.0 w	1997.0 w $A_1(^{13}CO)(C_{2v})$	895.1 s	902.2 s
1960.8 w	1970.0 w $A_1(^{13}CO)(C_{3v})$	884.2 s	894.2 s
		874.3 w	880.4 vw
		860.3 w	870.0 vw
		851.3 vs	860.4 vs

M–C–O region		*F–P–F region*		*M–C region*	
Solution	*Gas*	*Solution*	*Gas*	*Solution*	*Gas*
584.7 s	587.4 s(B_1)	546 m	548 w	465 vw	466 vw $A_1(C_{3v})$
569.7 s	571.4 s$(E+B_2)$	539 m	545 vw	423 vw	423 vw $A_1(C_{2v})$
		532 s	537 m		
		516 vs	519 vs		
		510 w			

(d) Combination bands with CO-stretching vibrations — between 2603 and 2525 cm^{-1}, two pairs separated by nearly 28 cm^{-1} are observed; their assignments are given in Table 2. However, these assignments are correct only if the bands 569.7 and 516 cm^{-1} (solution) belong to the species C_{3v} and C_{2v} at the same time, since two bands of a mixture of two different compounds cannot give combination bands.

It has already been recognised that the band 569.7 cm^{-1} belongs to the two species [see (b) above] and it must be the same for the very strong band at 516 cm^{-1}.

TABLE 3

IR FREQUENCIES OF $Fe(CO)_2(PF_3)_3$

Combination bands

Solution	*Gas*	*Assignment*	*Anharmonicity constant (average)*
4043.4 s	4065.2 s	A_1+B_1	−16
3996.4 m	4015.3 m	$2A''_2$	−11

Solution	*Assignment*	*Gas*	*Assignment*
2620 vw	2008.8+620.9	2657.3 m	2061.7+606.5
2584 vw	2008.8+586.0	2575.2 vw	2061.7+517.8
2557 w	2053.3+514.7	2530.0 vw	2019.9+517.8
2510 vw	2008.8+514.7	2475.3 m	1998.4+487
2465 s		2165.3 m	
2335 m		2112.8 m	
2157 m			

CO-stretching frequencies

Solution	*Gas*	*Assignment*
2053.3 m	2060.5 m	A_1
2035.4 w	2041.5 w	A'
2008.8 vs	2019.5 vs	B_1, A''_2
1985.8 m	1998.4 m	A''
1953.0 vw	1964.0 vw	

P–F stretching frequencies		*F–P–F region*	
Solution	*Gas*	*Solution*	*Gas*
924.4 m	933.2 m	534.2 vw	535.3 vw
906.4 w	916.2 w	528.2 vw	
895.4 m	903.2 s	514.7 vs	517.8 vs
879.1 vs	889.3 vs		
852.6 vs	863.3 vs		

M–C–O region		*M–C region*	
Solution	*Gas*	*Solution*	*Gas*
621.4 m	623.5 s	487 vw	487 vw
601.4 vw	606.5 vw	451 w	452 vw
586.4 m	586.5 m		
570.4 w	571.5 vw		

Conclusion

There is strong evidence that the complex $Fe(CO)(PF_3)_4$ is a mixture of two isomers, C_{3v} and C_{2v}. All the results, whether obtained by chemical reactions or spectroscopic investigations, can be explained by the existence of these isomers, and even the less favourable results are not against their existence.

TRIS(TRIFLUOROPHOSPHINE)IRON(0) DICARBONYL, $[Fe(CO)_2(PF_3)_3]$

The tri-substituted derivative, being the most volatile in the series, was purified comparatively easily by fractional distillation of a mixture containing mainly $Fe(CO)_2(PF_3)_3$ and $Fe(CO)(PF_3)_4$ and only traces of $Fe(CO)_3(PF_3)_2$. The latter derivative was largely eliminated by heating a mixture of $Fe(CO)_{5-n}(PF_3)_n$ ($n = 1$–3) with a large excess of PF_3 at 250° for several days. The CO evolved was occasionally removed from the reaction vessel in order to facilitate higher substitution. The results of the infrared spectra are reported in Table 3.

The infrared spectrum of the derivative shows more bands in the CO-stretching region than expected for any of the species represented in Table 1. We are discussing the spectra on the assumption of the presence of various isomers.

The infrared spectra of $Fe(CO)_2(PF_3)_3$ were examined in the region 4200–400 cm^{-1} both in solution and in the gaseous state. In the CO-stretching region four distinct bands were observed at 2053.3, 2035.4, 2008.8, and 1985.8 cm^{-1}, the latter accompanied by a satellite (see Fig. 3).

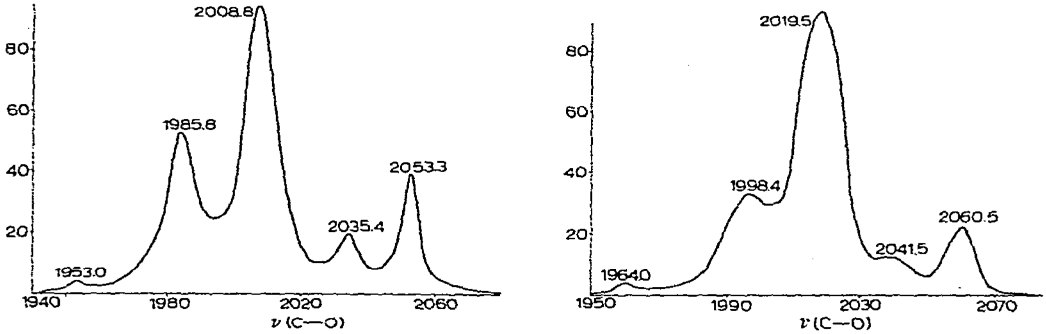


Fig. 3. Spectrum of: (a), $Fe(CO)_2(PF_3)_3$ in n-hexadecane; (b), $Fe(CO)_2(PF_3)_3$ in vapour state.

The arguments that favour the existence of various isomers are as follows:

(1) The existence of more than two bands in the CO-stretching region.

(2) Only one satellite is observed both in solution and in the vapour state. The satellite of the band 2008.8 cm^{-1} is expected at ~1975 cm^{-1} but is very probably merged in the band 1985.8 cm^{-1}. The difference, 32.8 cm^{-1} in solution or 34.4 cm^{-1} in the gaseous state, indicates that the fundamental band at 1985.8 cm^{-1} which produces the satellite at 1953 cm^{-1}, can be assigned either A'' or B_1 or A_2'' of the various species of $Fe(CO)_2(PF_3)_3$.

(3) The harmonics in the region 4000 cm^{-1} show that the bands 2053.3 and 2008.8 cm^{-1} belong to one of the species given in Table 1.

(4) Several unsuccessful attempts were made to separate the various isomers. However, the infrared spectrum of the product obtained by treatment of $Fe(CO)_2(PF_3)_3$ with PMe_3 at 115° for about 16 h, shows a considerable diminution in the

TABLE 4

IR FREQUENCIES OF $Fe(CO)_4(PF_3)$ AND OF $Fe(CO)_4(PCl_3)$

Combination bands

Solution	*Gas*	*Assignment*
4168 vw		$(A_1)^2(C_{3v})$
4159 vw	4186 vw	$(A_1)^2(C_{2v})$
4097 s	4120 s	$A_1+A_1(C_{2v})$
4071 m		$A_1+B_1(C_{2v})$
4025 w	4053 m	$(A_1)^2(C_{2v})$
4007 m	4034 w	$A_1+B_2(C_{2v})$
3982 s	4015 m	$(B_2)^2(C_{2v})$

Solution	*Attribution*	*Gas*	*Attribution*
2585 vw	2018.8+580.2	2653.5 w	2013.7+644.2
2546 w	2001.4+552.2	2621 vw	2013.7+610.3
2500 w	1995.6+520.1	2591 w	2013.7+585.0
2464 m	2001.4+474.3	2554 w	2033.0+523.5
2360 w		2494 m	
2334 w		2472 s	2013.7+474
2320 w		2437 m	2013.7+432
2220 vw		2390 w	
2198 w		2348 vw	
		2300 w	
		2220 m	
		2198 m	

CO-stretching frequencies

PCl_3		*PF_3*		*Assignment*
Solution	*Gas*	*Solution*	*Gas*	
+ 2089.5 m	2085.5 w	2090 m	2100 m	A_1 (eq.)
○ 2078.7 m		2097 m		A_1 (eq.)
○ 2021.5 s	2034.0 s	2023 s	2033 s	A_1 (ax.)
+ 2017.2 vs	2029.0 m	2019 vs	2030 m	A_1 (ax.)
○+ 1997.6 vs	2013 vs	2001.5 vs	2013.7 vs	$E+B_2$ (ax.)
+ 1985.8 s		1996.5 vs		B_1 (eq.)
1963.0 vw	1975 vw	1968.8 vw	1974.8 vw	
1950.5 vw		1963.2 vw		

+ and ○ indicate the frequencies of two species, C_{2v} and C_{3v}, respectively.

P–F and P–Cl regions

P–F		*P–Cl*
Solution	*Gas*	*Solution*
903.8 m	912.1 w	536.3 m
888.0 s	900.0 s	518.1 m
970.9 vs	881.1 vs	

TABLE 4 (*continued*)

M–C–O region		
PF_3		*PCl_3* *Solution*
Solution	*Gas*	
642.5 vs	644.2 vs	641.3 w
634.6 s	637.2 s	633.5 m
618.3 vs	620.2 vs	616.2 m
610.3 s	610.3 s	610.3 w
580.2 vw	585.0 vw	587.3 w

F–P–F region		*M–C region*		
Solution	*Gas*	*PF_3*		*PCl_3* *Solution*
		Solution	*Gas*	
520.1 s	523.5 s	474.3 vw	474 w	492.3 w
		432.3 vw	432 vw	471.0 vw
				434.0 vw

relative intensity of the bands at 2053.3 and 2008.8 cm^{-1} which again indicates clearly that these two bands belong to one species and the remaining two bands at 2035.4 and 1985.8 cm^{-1} to some other species.

(5) The intensity of the band at 2008.8 cm^{-1} is much greater than that of the other bands. This shows that it is A_2'' of *trans*-$Fe(CO)_2(PF_3)_3$ (D_{3h}) and at the same time the antisymmetric band of either of the remaining isomers.

(6) Finally, the ratio of the intensity of the bands 1985.8 and 2035.4 cm^{-1} is definitely much greater than unity, which indicates[4] that the angle between the two CO-groups is greater than 90° and thus these bands belong to *cis*-C_{2v}.

Other regions

The spectra in the other regions are too complex to be used in discussing the various species of the derivative, $Fe(CO)_2(PF_3)_3$.

Conclusion

Although the spectrum of $Fe(CO)_2(PF_3)_3$ does not provide definite evidence as does the spectrum of $Fe(CO)(PF_3)_4$, it can be interpreted as a mixture of the three possible isomers (Table 1). The best argument in favour of their existence is the destruction of one of the species by treatment of the derivative with excess PMe_3.

MONO-TRICHLOROPHOSPHINEIRON(0) TETRACARBONYL, [$Fe(CO)_4(PCl_3)$]

$Fe_2(CO)_9$ reacts with PCl_3 at 50° to give a mixture of $Fe(CO)_4PCl_3$ and $Fe(CO)_5$ together with some decomposition products. The desired derivative is isolated in the pure form by repeated distillation of the mixture under vacuum at room temperature.

The infrared spectrum of $Fe(CO)_4(PCl_3)$ was recorded in the region 2000–400 cm^{-1} both in solution and in the vapour state; the results are reported in Table 4.

In the CO-stretching region, in solution, six bands accompanied by two satellites were observed, as shown in Fig. 4.

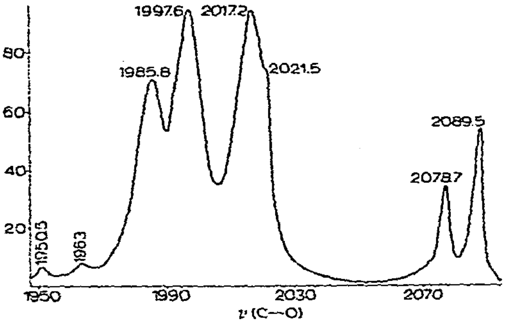


Fig. 4. Spectrum of $Fe(CO)_4(PCl_3)$ in n-hexadecane.

The arguments that favour the existence of two isomers of symmetry C_{3v} and C_{2v} are as follows:

(1) Six bands are observed in the CO-stretching region which is much greater than required by either of the two species represented in Table 1.

(2) The existence of the two satellites at 1963.0 and 1950.5 cm^{-1} corresponding to the fundamentals, 1997.6 and 1985.8 cm^{-1}, in solution, separated by 34.4 and 35.4 cm^{-1}, respectively, indicates clearly that the two fundamental CO vibrations do not belong to the same species and that their symmetry type is either E or B_1 or B_2.

(3) The infrared spectrum of the product obtained by the interaction of $Fe(CO)_4PCl_3$ with PMe_3, shows a large decrease in the intensity of the band at 2089.5 cm^{-1} as compared to that at 2078.7 cm^{-1}, which shows clearly that these two bands do not belong to the same species. Furthermore, there is also a diminution in the intensity of the bands at 2017.2 and 1985.8 cm^{-1}, see Fig. 5. This experimental evidence leads us to conclude that these three bands belong to one species C_{2v}, and the remaining three bands, 2078.7, 2021.5 and 1997.6 cm^{-1} to the species C_{3v}.

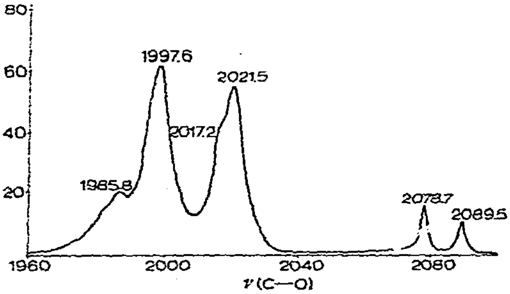


Fig. 5. Spectrum of the product obtained by the reaction of $Fe(CO)_4(PCl_3)$ with PMe_3.

(4) Similar results were obtained by recording the spectrum at low temperatures. The relative integrated intensity of the two bands 2089.5 and 2078.7 cm^{-1} which is 1.8 at +30°, reduced to 1.45 at −40°, which indicates clearly that these two bands belong to two different species.

(5) A single satellite is observed when the spectrum of $Fe(CO)_4PCl_3$ is taken

in the vapour state. Furthermore, the spectrum does not show a band corresponding to 1985.8 cm^{-1} in solution, and there were only four fundamentals in the spectrum of $Fe(CO)_4PCl_3$ (vapour). This is not impossible if there is only one species C_{2v} in the vapour state.

(6) The assignments proposed are based on a consideration of the relative intensities.

MONO-TRIFLUOROPHOSPHINEIRON(0) TETRACARBONYL, $[Fe(CO)_4(PF_3)]$

Although the reaction*,** between $Fe(CO)_5$ and PF_3 starts at 100°, it is necessary to heat the components at 150–160° for about 20 h in order to obtain a mixture rich in the mono-substituted product and free of $Fe(CO)_5$ and it is advisable to use a very large excess of PF_3. The product obtained under such conditions contains a fair amount of the di-substituted product and traces of $Fe(CO)_2(PF_3)_3$. It is purified by fractionation using a special distillation column (see experimental part). However, in order to separate $Fe(CO)_4(PF_3)$ from the mixture the fractionation must be repeated several times.

The infrared spectra of $Fe(CO)_4(PF_3)$ were recorded both in solution and in the vapour state; the results are reported in Table 4. In the CO-stretching region six bands are observed, as shown in Fig. 6.

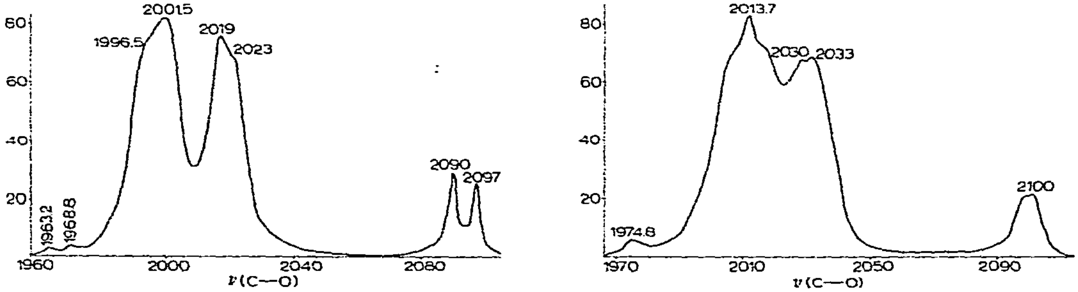


Fig. 6. Spectrum of: (a), $Fe(CO)_4(PF_3)$ in n-hexadecane; (b), $Fe(CO)_4(PF_3)$ in vapour state.

The results of the infrared investigation of $Fe(CO)_4PF_3$ are similar to those of $Fe(CO)_4PCl_3$ and the assignments of the various bands are made similarly. However, there is no reaction between $Fe(CO)_4PF_3$ and PMe_3 at room temperature. A slight variation in the intensity of the bands at 2097 and 2090 cm^{-1} was observed when the two components were heated at 115° for about 20 h. The spectrum of $Fe(CO)_4PF_3$ at low temperatures was not recorded.

The vapour pressure of $Fe(CO)_4PF_3$ is sufficient to examine the spectrum in the region 4000 cm^{-1}. All the bands can be attributed to a single species C_{2v}. The structure PQR, where the branch Q (2013.7 cm^{-1}) dominates, cannot be used for the determination of the configuration of the corresponding isomer[9]. We have inter-

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[*] When the reaction was carried out at 200° using excess of $Fe(CO)_5$, there was considerable decomposition but the mixture contained only the mono-substituted derivative and $Fe(CO)_5$.

[**] It was observed also that when $Fe_2(CO)_9$ was suspended in hexane and PF_3 bubbled through at room temperature, the infrared spectrum of the solution showed the bands characteristic for $Fe(CO)_4(PF_3)$ and $Fe(CO)_5$.

changed the order of bands 2097 and 2090 cm^{-1} for the following reasons:

(1) The intensity of the band 2097 cm^{-1} is weaker than that of the band 2090 cm^{-1}.

(2) On treatment with PMe$_3$, it is the band 2090 cm^{-1} the intensity of which diminishes compared to the band 2097 cm^{-1} (see Table 4).

In the CO-stretching region, four bands are observed in the spectrum of Fe(CO)$_4$(PF$_3$) (vapour) analogous to Fe(CO)$_4$(PCl$_3$); they can similarly be attributed to the species C_{2v}. The infrared spectra of Fe(CO)$_4$(PF$_3$) (vapour) in other regions, particularly the P–F stretching vibrations, can be explained in the same way but this has not been verified.

The arguments in favour of the existence of isomers in the mono-substituted derivative are less conclusive than in the case of Fe(CO)(PF$_3$)$_4$. They are based essentially on: the CO-stretching vibrations, the existence of two satellites in solution, the variation in intensity by the interaction of the complex with PMe$_3$ and the investigation of the infrared spectrum at low temperatures. The presence of isomers in the vapour state is doubtful and we have not been able to prove that it contains more than a single species.

BIS(TRIFLUOROPHOSPHINE)IRON(0) TRICARBONYL, [Fe(CO)$_3$(PF$_3$)$_2$]

In order to isolate pure Fe(CO)$_3$(PF$_3$)$_2$, it is necessary to start the fractionation with a mixture of the di- and tri-substituted derivatives. The elimination of Fe(CO)$_4$(PF$_3$) can be easily achieved by heating a mixture of the first 3 derivatives of the series with a large excess of PF$_3$ at 160° for a few days. Under these conditions, traces of Fe(CO)(PF$_3$)$_4$ are also formed but these can be easily removed by fractionation. The infrared spectrum of the pure product, isolated after several fractionations, shows five main CO-stretching vibrations both in solution[5] and in the gaseous state. One band is expected for the species D_{3h} as has been observed in the case of Fe(CO)$_3$(PEt$_3$)$_2$[4] or three bands for either of the species, C_{2v} or C_s, as shown in Table 1.

The infrared spectrum of Fe(CO)$_3$(PF$_3$)$_2$ was examined in the region 4200–400 cm^{-1} both in solution and in vapour state. In the CO-stretching region five bands at 2079.8, 2071.5, 2014.1, 1994.2 and 1988.6 cm^{-1} accompanied by three satellites were observed in solution (see Fig. 7). The same bands were also observed when the spectrum was recorded in vapour state. The results of the infrared spectra are presented in Table 5.

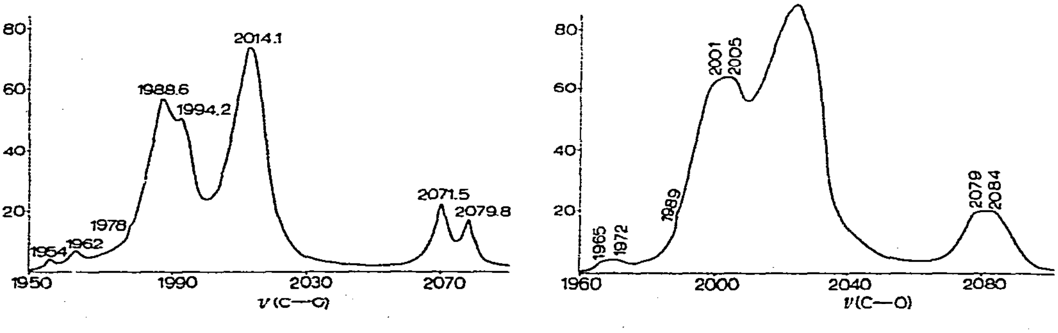


Fig. 7. Spectrum of: (a), Fe(CO)$_3$(PF$_3$)$_2$ in n-hexadecane; (b), Fe(CO)$_3$(PF$_3$)$_2$ in vapour state.

TABLE 5

IR FREQUENCIES OF $Fe(CO)_3(PF_3)_2$

Combination bands			
Solution	*Assignment*	*Gas*	*Assignment*
4076 m	2079.8+2014.1	4096 m	2084+2026
4037 m	2071.5+1988.6	4060 w	2079+2001
4020 w	2×2014.1	4040 w	2×2026
3998 w	2014.1+1994.2	4019 vw	2026+2005
3968 m	2×1988.6	3992 vw	2×2001
2551 w	2014.1+544.1	2560 vw	2079+489.2
2507 w	1988.6+528.1	2518 vw	2005+519.4
2487 m	1988.6+514.7	2496 m	2084+417.8
2465 s	2071.5+400.0	2475 s	2079+403.5
2427 m	1994.2+445.0	2437 w	2026+417.8
		2400 vw	2001+403.5
2345 vw			
2280 vw		2292 w	
2178 w			

CO–stretching frequencies			*P–F stretching frequencies*	
Solution	*Gas*	*Assignment*	*Solution*	*Gas*
2079.8 m	2084 m	A'	907.2 s	916.2 s
2071.5 m	2079 m	A_1	893.7 s	902.8 vs
2014.1 vs	2026 vs	B_2	874.4 vs	887.7 vs
1994.2 vs	2005 s	E'	852.6 vs	862.8 vs
1988.6 vs	2001 s	A''		
1978 vw	1989 vw			
1962 vw	1972 vw			
1954 vw	1965 vw			

M–C–O region		*F–P–F region*		*M–C region*	
Solution	*Gas*	*Solution*	*Gas*	*Solution*	*Gas*
633.2 m	634.3 w	544.1 vw	550.4 vvw	490.0 w	490.0 vw
624.4 vw		528.1 vw	532.0 vw	469.0 w	469.0 w
619.8 m	623.3 s	519.1 s	519.4 vs	445.0 vw	
601.8 m	605.3 w	514.7 vs		431.5 vw	432.5 vw
587.4 vw					417.8 vw
581.2 m	584.3 m			400.0 w	403.5 w
570.4 vw					

The following arguments favour the existence of various species:

(1) The presence of five bands in the CO-stretching region.

(2) The presence of three satellites both in solution and in the vapour state. The average difference of 34 cm^{-1} in solution and 35 cm^{-1} in gas between the three satellites 1978, 1962, and 1954 cm^{-1} and their respective fundamentals, 2014.1, 1994.2 and 1988.6 cm^{-1}, indicate that these bands are B_2,E',A'' of *the three species* presented in Table 1.

(3) The treatment with excess of PMe_3 at 115° for about 16 h has shown that

there is a change in the relative intensity of the two bands at 2079.8 and 2071.5 cm^{-1}. A diminution in the intensity of the former band compared to the latter, is clearly observed which indicates that these bands do not belong to the same molecule. The formation of several other unidentified products makes it difficult to investigate the influence on other bands.

(4) The assignments of the bands in the CO-stretching region are complicated as only five bands are observed whereas altogether seven bands are expected as shown in Table 1. It appears that several bands overlap because all three species are present. Evidently, the bands 2079.8 and 2071.5 cm^{-1} can be assigned as A' or A_1. B_2 must be situated not far from A_2'' (2022 cm^{-1}) of $Fe(CO)_5$, it is very likely the band at 2014 cm^{-1}. The bands 1994 and 1988 cm^{-1} are attributed as E' and A'' without more exact designation.

Although the spectrum of $Fe(CO)_3(PF_3)_2$ is very complex, the presence of three satellites both in solution and in the vapour state indicates that in this case too we have a mixture of the various species. Our conclusion is further supported by the considerable change in the relative intensity of the two bands at 2079.8 and 2071.5 cm^{-1} when the derivative was treated with PMe_3.

REACTION OF $Fe(CO)_4PR_3$ WITH PF_3

When $Fe(CO)_4PR_3$ (R = Me or Et) is treated with a large excess of PF_3 under pressure, a yellow-coloured liquid is obtained. The reaction between the components is slow at room temperature but rapid at 50°. This liquid is a mixture of three substances (including slight traces of $Fe(CO)_4PEt_3$). The infrared spectrum of the liquid was recorded in the CO-stretching region and the results are given in Table 6.

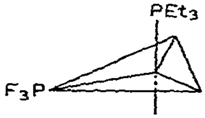
TABLE 6

UNKNOWN PRODUCT

$Fe(CO)_4PEt_3$		X_1	X_2
2048.6	(A_1, CO eq.)		2033 (A', CO eq.)
1974.0	(A_1, CO ax.)		1968 (A', CO ax.)
1934.0	(E, CO eq.)	1931 (E)	1931 (A'', CO eq.)

A mixture of liquids containing X_1 and X_2 was isolated by fractional distillation. If the reaction was carried out at 20°, the mixture was richer in X_2 than when the components were heated at 50°.

It is evident that the product X_1 is the derivative *trans*-$Fe(CO)_3(PEt_3)(PF_3)$, because the substitution of one CO by PF_3 does not appreciably modify the frequencies of the rest of the CO-groups. It would then follow that the product X_2 has the same formula and would be the derivative *cis*-$Fe(CO)_3(PEt_3)(PF_3)$.



Although the two isomers were not separated, we were, nevertheless, able to distinguish the expected CO frequencies. A'(CO eq.) must have a frequency near to

A_1(CO eq.) of the starting material. This may be the band at 2033 cm^{-1}; also A'(ax.) is equivalent to A_1(CO ax.) of Fe(CO)$_4$(PEt$_3$). Finally, A''(CO eq.) must have the same frequency as E of *trans*-Fe(CO)$_3$(PEt$_3$)(PF$_3$). The three frequencies, 2033, 1968 and 1931 cm^{-1}, are in good agreement with the frequencies expected.

Although the separation of the two isomers was not accomplished, our arguments favour their existence. This confirms the results observed with the isomers of the series Fe(CO)$_{5-n}$(PF$_3$)$_n$ (n = 1–4) and indicates that the ligand PF$_3$ has no preference of position.

CONCLUSION

The complexity of the infrared spectra of the derivatives Fe(CO)$_{5-n}$(PF$_3$)$_n$ and Fe(CO)$_4$(PCl$_3$), at least in the region of CO-stretching vibrations, has been resolved, taking into consideration the various isomers possible for a trigonal bipyramidal structure around the iron atom.

The most simple and demonstratable case is that of the tetrasubstituted derivative, Fe(CO)(PF$_3$)$_4$. The existence of two CO-stretching vibrations and the two satellites related to vibrators ^{13}CO, the ratio of the intensity of the two fundamental bands, the disappearance of one of the bands on treatment of the derivative with PMe$_3$ or PEt$_3$ etc., furnish arguments that indicate clearly the presence of two isomers.

Since the tetra-substituted derivative exists in two forms, it is natural to think that other derivatives of the series also occur in various forms and similar arguments were used, therefore, to prove their existence. Although fewer arguments are available in the case of other derivatives, the presence of several satellites separated by nearly 33 cm^{-1} from the fundamentals always provides a very strong argument for the existence of isomers.

Finally, we have observed that in the derivatives of Fe(CO)$_5$, when the ligands are comparable to CO from the point of view of their donor–acceptor character, the position of ligands in the molecule is indifferent. The thermodynamical stabilities of the various isomers are very close to one another.

Although there is not much difference in the thermodynamical stabilities of various species, it is not the same with chemical stabilities. It appears that there is a difference in the chemical reactivity of the isomers when they are treated with a phosphine.

The stereochemistry of iron carbonyl derivatives with the ligands, PF$_3$ and PCl$_3$, is exceptional. It is not similar to the PR$_3$ or P(OR)$_3$ complexes of iron carbonyl[4]. The difference in the stability of the isomers with the latter is undoubtedly much greater than with the ligands PX$_3$. One can anticipate the formation of such isomers by allowing the components to react at low temperature.

EXPERIMENTAL

The infrared spectra were measured in n-hexadecane solution and in the gaseous state. The instrument used was an infrared grating spectrophotometer Perkin-Elmer Model 125. Iron carbonyl used for the reaction was purified by distillation and PF$_3$ was prepared by the procedure used by Clark[5]. The compounds were initially prepared as mixtures and then purified by fractionation.

Mono-trifluorophosphineiron(0) *tetracarbonyl*, $Fe(CO)_4(PF_3)$

20 ml of $Fe(CO)_5$ and about 45 ml of freshly prepared PF_3 were distilled into a stainless-steel vessel of capacity 125 ml and were heated at 200° for about 20 h. A mixture of the mono-, di-, and tri-substituted compounds thus obtained was purified by fractionation using a special column fitted with a spiral band 1 m long which was turning at the rate of 4500 c/min. The last fraction thus obtained was free of $Fe(CO)_2$-$(PF_3)_3$ and contained mainly $Fe(CO)_4(PF_3)$ but a fair amount of $Fe(CO)_3(PF_3)_2$. In order to obtain the pure mono-substituted derivative the fractionation was repeated several times. The infrared spectra of the product was taken in the region 4200–400 cm^{-1} both in solution and in gaseous state and the results are given in Table 4.

Bis(*trifluorophosphine*)*iron*(0) *tricarbonyl*, $Fe(CO)_3(PF_3)_2$

25 ml of a mixture of $Fe(CO)_4(PF_3)$, $Fe(CO)_3(PF_3)_2$ and $Fe(CO)_2(PF_3)_3$ was prepared as described above and heated with 30 ml of PF_3 at 160° for about 100 h in a pressure vessel. The CO evolved during the reaction was removed from time to time and the process was repeated thrice in order to obtain a mixture free from $Fe(CO)_4$-(PF_3). The desired product was isolated and purified by repeated fractionation. The results of the infrared spectra are given in Table 5.

Tris- and tetrakis(*trifluorophosphine*) *derivatives*, $Fe(CO)_2(PF_3)_3$ *and* $Fe(CO)(PF_3)_4$

40 ml of a mixture containing mainly the di- and tri-substituted derivatives were treated with 45 ml of PF_3 in a pressure vessel of 250 ml capacity for about 100 h at 250°. The process was repeated three or four times and the mixture thus obtained contained mainly $Fe(CO)_2(PF_3)_3$ and $Fe(CO)(PF_3)_4$ with only traces of $Fe(CO)_3$-$(PF_3)_2$. The desired products were separated by repeated fractionations. The results of the infrared spectra are recorded in Tables 2 and 3.

Mono-trichlorophosphineiron(0) *tetracarbonyl*, $Fe(CO)_4(PCl_3)$

3.75 g (10.3 mmoles) of $Fe_2(CO)_9$ and 7.5 ml (85.9 mmoles) of freshly distilled PCl_3 were heated at 50° with stirring for about 2 h in an atmosphere of N_2. Unreacted PCl_3, and $Fe(CO)_5$ formed during the reaction, were removed under vacuum at room temperature and the product was purified by fractionation under vacuum at 40°. The results of the infrared spectra are presented in Table 4.

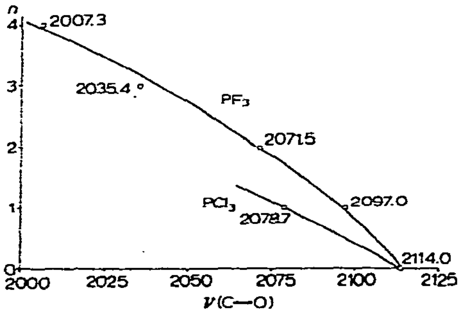


Fig. 8. Frequencies of C–O symmetric vibrations of the most stable isomers.

Reaction with PMe_3

100 mg of $Fe(CO)_4(PCl_3)$ and 1 ml of PMe_3 were sealed in a tube under nitrogen. A solid product was formed immediately. The mixture was stirred at room temperature for about 20–30 h and the excess of PMe_3 removed under reduced pressure. The residue was treated with *n*-hexadecane, filtered and the infrared spectrum recorded.

Unlike $Fe(CO)_4(PCl_3)$, there was no reaction between PMe_3 and $Fe(CO)_{5-n}(PF_3)_n$ ($n = 1$–4) at room temperature and it was necessary to heat the components with excess of PMe_3 at 100–115° for about 20–50 h. The reaction mixture was worked up as described above.

The frequencies the relative intensities of which increase by treatment of the derivatives with PMe_3, are presented graphically in Fig. 8. These are probably the frequencies of those isomers which are chemically more stable.

Reaction of $Fe(CO)_4PEt_3$ with PF_3

1 g of $Fe(CO)_4(PEt_3)$ and about 10 ml of PF_3 were heated at 50° for about 10 h in a 12.5-ml stainless-steel vessel. The yellow liquid thus obtained was purified by distillation at room temperature under high vacuum. The results of the infrared spectrum are recorded in Table 6. The reaction between $Fe(CO)_4(PMe_3)$ and PF_3 was performed by an analogous procedure.

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SUMMARY

The infrared spectra of the derivatives $Fe(CO)_{5-n}(PF_3)_n$ and $Fe(CO)_4(PCl_3)$ have been studied in the region 4200–400 cm^{-1}, particularly from the point of view of satellites due to ^{13}CO-groups. It has been shown that these derivatives contain all the isomers geometrically expected for the trigonal bi-pyramidal structure around the iron atom. The isolation of these isomers was not possible; nevertheless, reaction mixtures containing only one isomer have been prepared.

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