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ROYAL
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SOLVING INORGANIC SPECTROSCOPIC PROBLEMS

Alan Vincent



ETSG

CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

General Editor:
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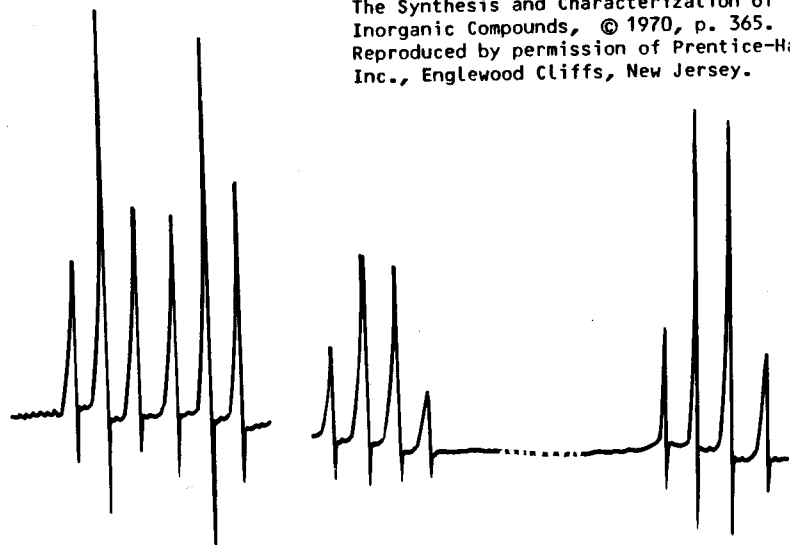
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4

PROBLEM 2

The proton n.m.r. spectrum of GePH_5 is shown below. Deduce the structure of the compound. (Both ^{31}P and ^1H have $I = \frac{1}{2}$ and essentially 100% natural abundance. Coupling constants between P and H are often very large.)

Spectrum reproduced from William L Jolly, *The Synthesis and Characterization of Inorganic Compounds*, © 1970, p. 365. Reproduced by permission of Prentice-Hall Inc., Englewood Cliffs, New Jersey.



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Information obtainable from the ^1H spectrum of GePH_5 :

Quartet - set of protons split by three neighbours
Triplet - set of protons split by two neighbours

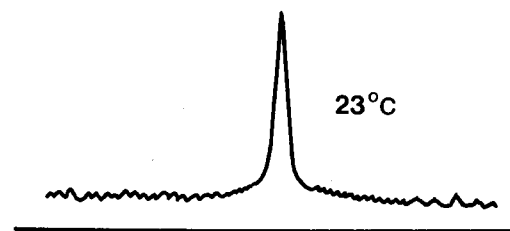
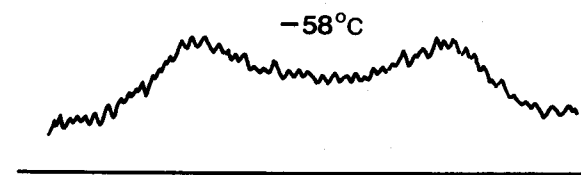
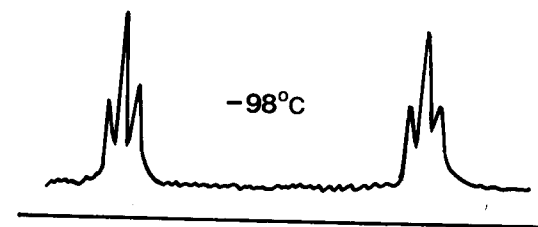
Quartet extensively split by phosphorus
Triplet less extensively split by phosphorus

Quartet - set of two protons
Triplet - set of three protons

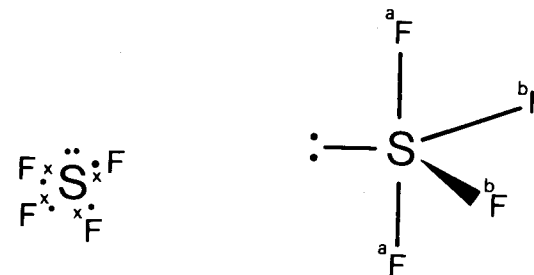
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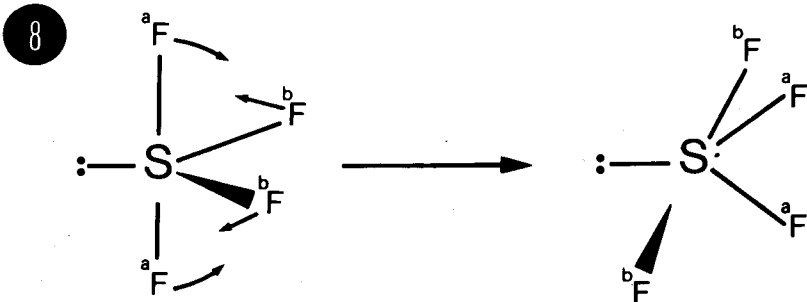
PROBLEM 3

The ^{19}F n.m.r. spectrum of SF_4 varies with temperature as shown. What structure does this suggest at low temperature? Explain the change of spectrum as the temperature is raised.



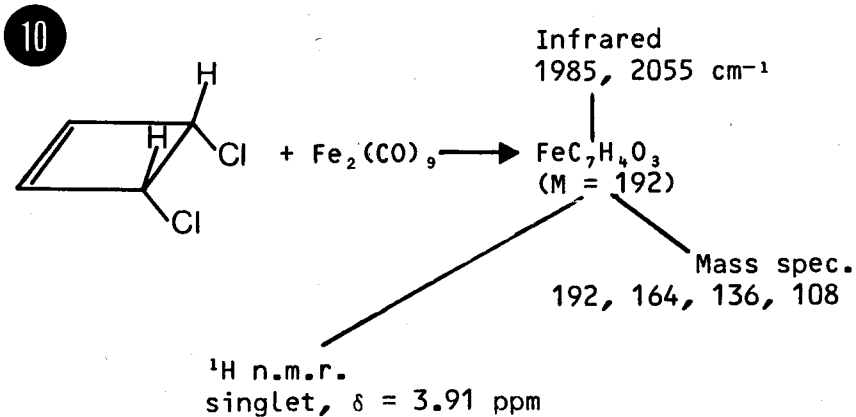
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9 PROBLEM 4

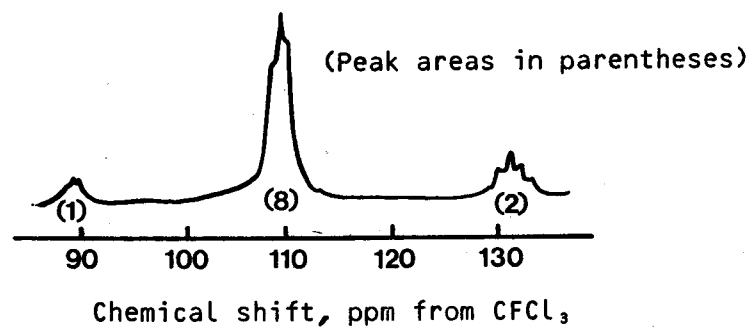
Reaction of *cis*-3,4-dichlorocyclobutene with an excess of $\text{Fe}_2(\text{CO})_9$ in isopentane at 30°C produces a pale yellow compound $\text{FeC}_7\text{H}_4\text{O}_3$. The infrared spectrum shows two strong bands at 1985 and 2055 cm^{-1} and the ^1H n.m.r. spectrum consists of a single sharp line at $\delta = 3.91\text{ ppm}$. The mass spectrum gives peaks at $192, 164, 136$ and 108 . Deduce the structure of the product. [$\text{Fe} = 56, \text{C} = 12, \text{O} = 16, \text{H} = 1$].



11 $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$

12 PROBLEM 5

Caesium fluoride and antimony pentafluoride react exothermically in SO_2 solution to give a soluble product, $\text{CsF} \cdot 2\text{SbF}_5$. This product can be recovered by evaporating the SO_2 . The ^{19}F n.m.r. spectrum of the solution is given below. Deduce the structure of the compound.



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Chemistry: CsF ionises to give F^-
 SbF_5 is a powerful F^- acceptor
 Stoichiometry is $\text{CsF}:2\text{SbF}_5$

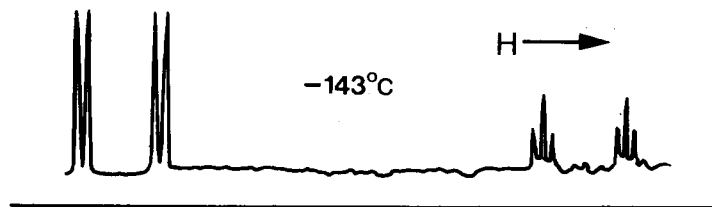
Peak positions: How many types of fluorine?
 Peak areas: How many of each type of fluorine?
 Splitting: How many neighbours?

14

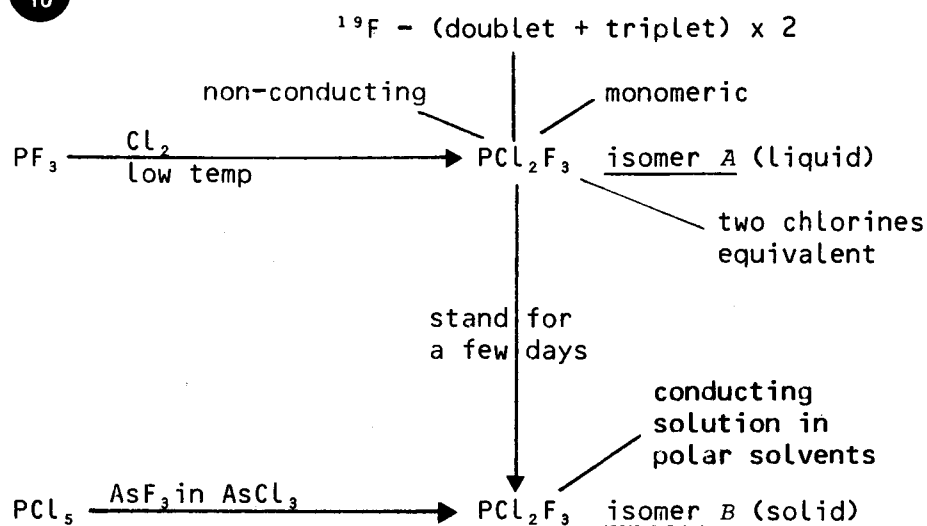
PROBLEM 6

Low temperature chlorination of PF_3 produces a liquid form of PCl_2F_3 (isomer *A*). Treatment of PCl_5 in solution in AsCl_3 with AsF_3 produces a solid form of PCl_2F_3 (isomer *B*). *A* changes to *B* on standing for a few days at room temperature. The ^{19}F n.m.r. spectrum of *A* at -143°C in isopentane is shown below. Cryoscopic measurements in isopentane show it to be monomeric, and the ^{35}Cl nuclear quadrupole resonance spectrum shows the two chlorine atoms to be equivalent. It gives a non-conducting solution in solvents like acetonitrile. The solid form of PCl_2F_3 (isomer *B*) gives a conducting solution in polar solvents.

Suggest structures for *A* and *B*.



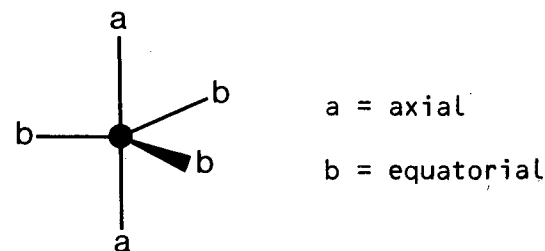
15



16

2 equivalent fluorines - doublet
1 fluorine - triplet } x 2 due to phosphorus

17

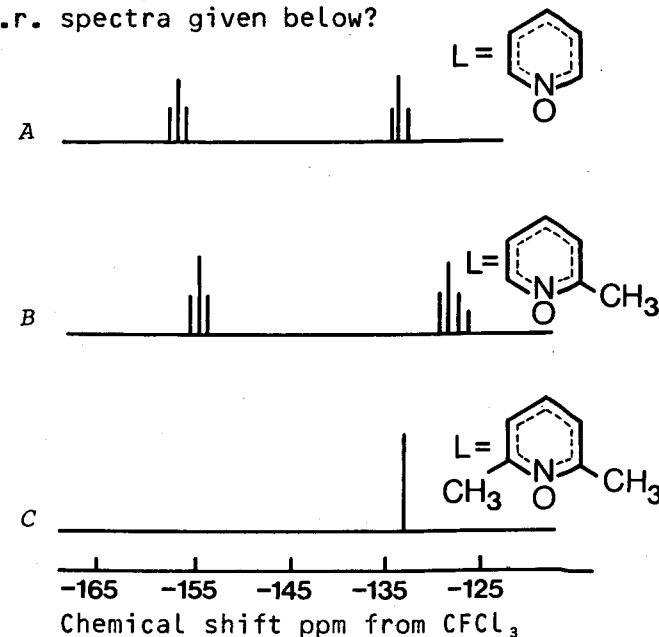


Non-equivalent positions on a trigonal bipyramid.

18

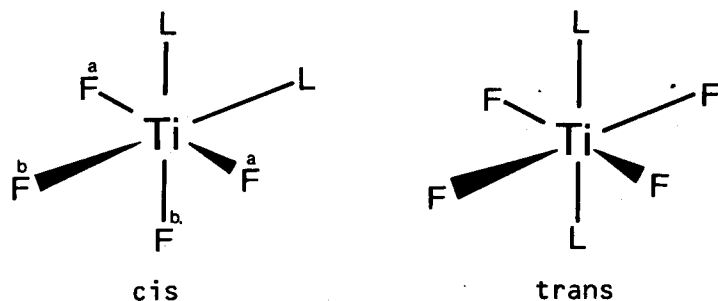
PROBLEM 7

Stable complexes, $\text{TiF}_4 \cdot \text{L}_2$, are formed between TiF_4 and various substituted pyridine-1-oxides (*L*). What information can you deduce about the complexes from the ^{19}F n.m.r. spectra given below?



19

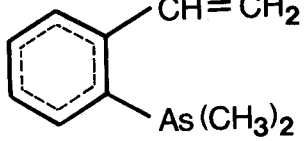
Isomers of an octahedral complex:



20

PROBLEM 8

If anhydrous platinum(II) bromide is suspended in chloroform and treated with *o*-styryldimethyl arsine (*o*-S), three compounds, *A*, *B* and *C* can be isolated. All compounds are monomeric and non-conducting in nitrobenzene. Formulae and infrared data are tabulated below:

<i>o</i> -S		$\bar{\nu}_{\text{C}=\text{C}}/\text{cm}^{-1}$
<i>A</i>	$\text{PtBr}_2(\text{o-S})_2$	1630
<i>B</i>	$\text{PtBr}_2(\text{o-S})_2$	1627
<i>C</i>	$\text{PtBr}_2(\text{o-S})$	1488

Addition of an excess of bromine to *A* or *B* gave an orange complex, *D*, $\text{PtBr}_8(\text{o-S})_2$ in which the bands at 1630/1627 cm^{-1} were absent, but new bands had appeared at 594 and 572 cm^{-1} . Suggest structures for *A*, *B*, *C*, and *D*.

21

Key information from Problem 8:

- (i) Free ligand, *A* and *B* all have >C=C<
- (ii) *A* and *B* are isomers of a Pt(II) complex
- (iii) *C* involves the >C=C< bond
- (iv) *C* only has one ligand per Pt

Brominated product:

- (i) 8 Br atoms but only two As
- (ii) >C=C< bond has gone
- (iii) Are both Pt and ligand brominated?

22

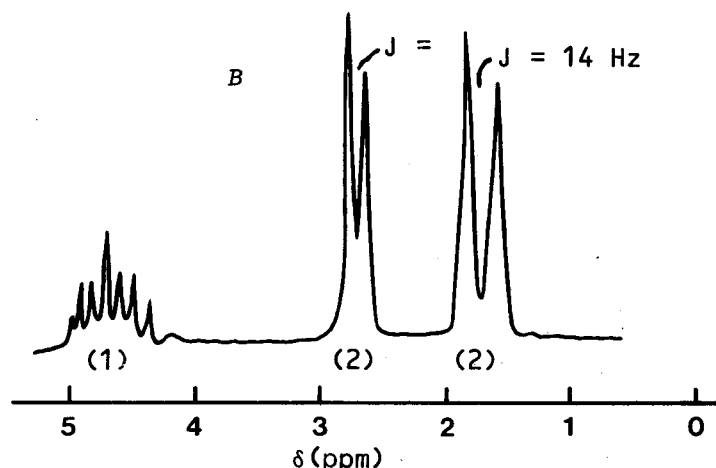
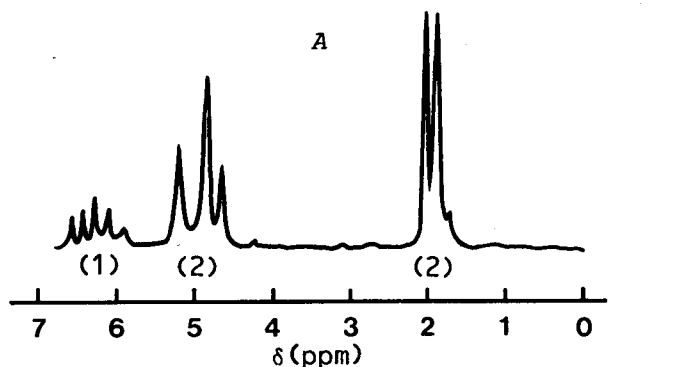
PROBLEM 9

Allyl chloride, $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$, reacts at room temperature with lithium manganese carbonyl, $\text{LiMn}(\text{CO})_5$, to produce a yellow liquid **A** (C: 40.7% H: 2.2% Mn: 23.2%).

On heating **A** to 100°C , one mole of CO is given off per mole of **A**, and a pale yellow solid **B** is formed.

^1H n.m.r. and infrared data on **A** and **B** are given below.

Suggest structures for **A** and **B**. [C = 12, H = 1, O = 16, Mn = 55]



^1H n.m.r. spectra. (Peak areas in parentheses)

Infrared data/ cm^{-1}

A: 3085 3010 2925 2110 2079 2024 2004 1620

1310 985

B: 3080 3030

2110 2060 2049 1950

1505

23

Infrared spectrum (cm^{-1})

n.m.r. spectrum

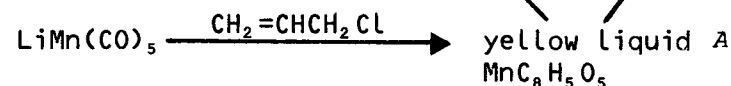
Around 3000 - C-H

2 + 2 + 1 protons

Around 2000 - C=O

extensive splitting

1620 - C=C



100°C

yellow solid **B** + CO
 $\text{MnC}_7\text{H}_5\text{O}_4$

infrared spectrum (cm^{-1})

around 3000 - C-H (but no 2925)

around 2000 - C=O

1505 - modified C=C?

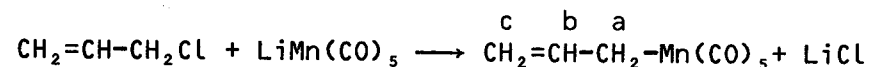
n.m.r. spectrum

2 + 2 + 1 protons

extensive splitting

24

Possible product of reaction:

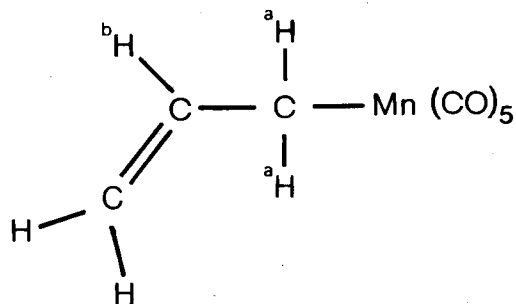


25

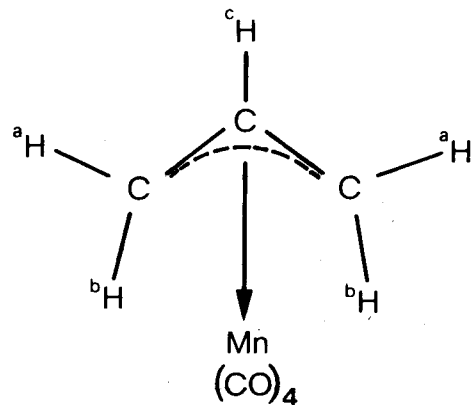
Infrared assignments (cm^{-1})

3085, 3010	C-H stretch of vinyl group
2925	C-H stretch of $-\text{CH}_2-\text{Mn}$ group
2110, 2079, 2024, 2004	C=O stretch
1620	$>\text{C}=\text{C}<$ stretch
1410	$=\text{CH}_2$ in plane bend
1310	$=\text{CH}$ in plane bend
985	$=\text{CH}$ out of plane bend
925	$=\text{CH}_2$ out of plane bend

26



27

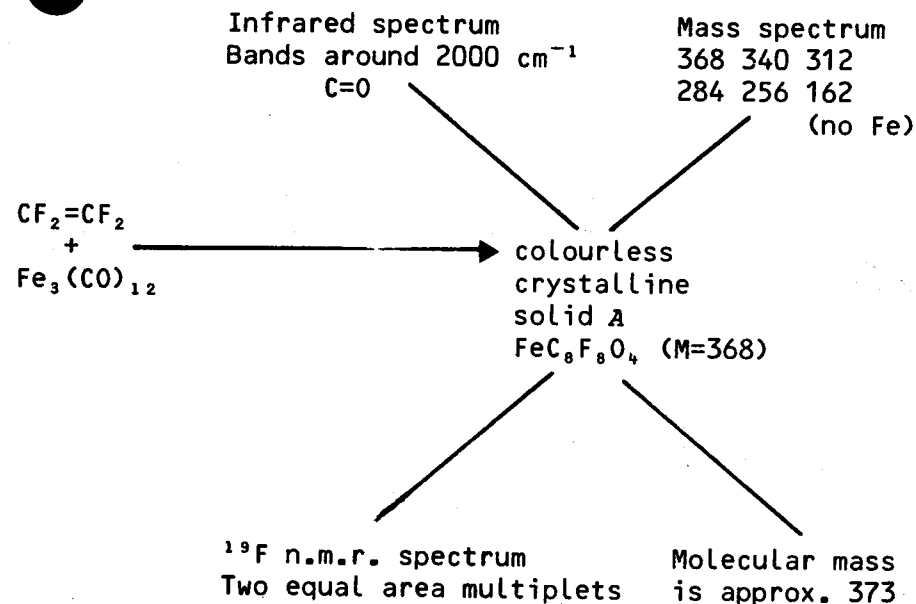


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PROBLEM 10

The reaction of $\text{CF}_2=\text{CF}_2$ with $\text{Fe}_3(\text{CO})_{12}$ gives a colourless crystalline compound A (C: 26.5%, F: 41.7%, Fe: 15.4%). The infrared spectrum of A shows bands at 2160, 2108, 2088 and 2055 cm^{-1} . The mass spectrum includes peaks at m/e values of 368, 340, 312, 284, 256 and 162 (the most intense peak). The first five of these peaks correspond (from the isotope pattern) to iron-containing ions, but the peak at 162 does not contain iron. The ^{19}F n.m.r. spectrum of A consists of two equal-area multiplets at 9.25 and 73.95 ppm upfield of benzotrifluoride. The molecular mass of the compound was estimated from ^{19}F n.m.r. measurements and by X-ray crystallography to be 373. Identify compound A and suggest its structure. [C = 12, F = 19, Fe = 55.8, O = 16. The most abundant isotope of iron has mass 56.]

29

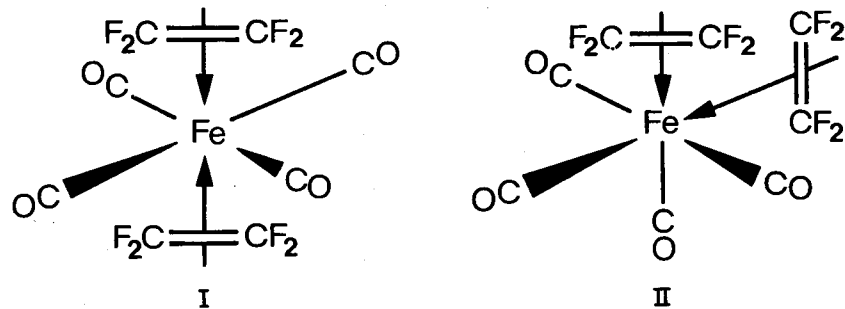


30



31

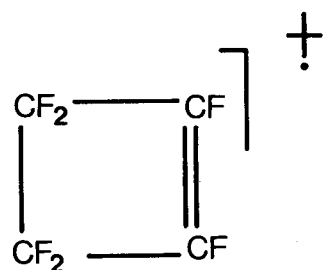
Two unlikely structures:



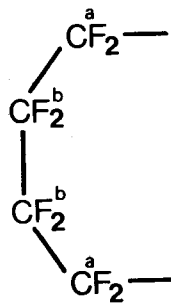
32

$162 = C_4F_6^+$

i.e.

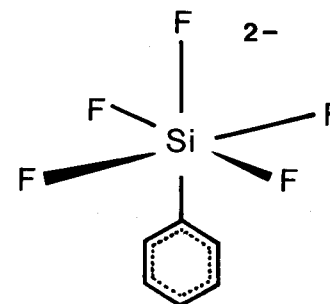


33

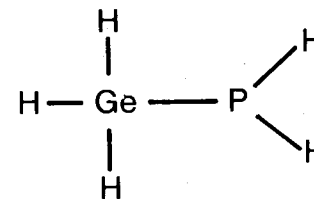


ANSWERS TO PROBLEMS

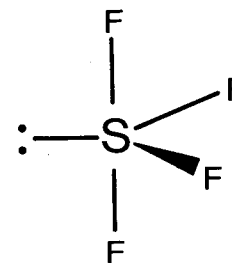
Problem 1



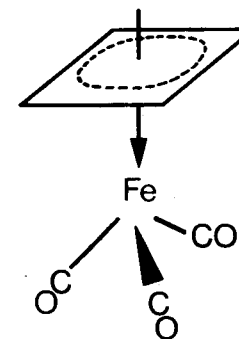
Problem 2



Problem 3

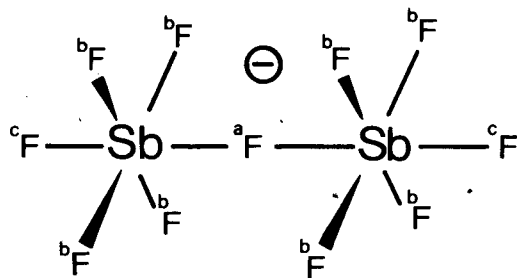


Problem 4



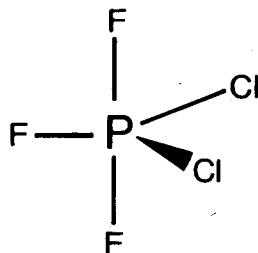
Problem 5

Cs^+



Problem 6

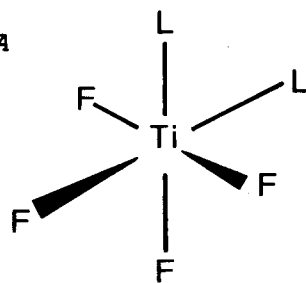
Isomer A:



Isomer B: $[\text{PCL}_4^+][\text{PF}_6^-]$

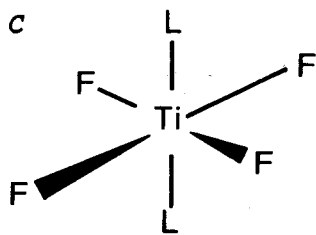
Problem 7

A



cis isomer

C

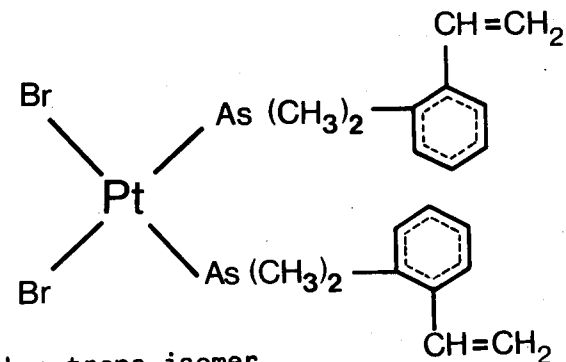


trans isomer

B, Mixture of isomers

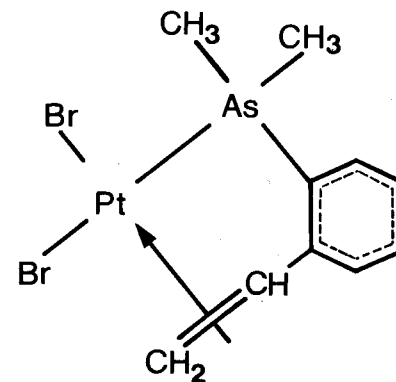
Problem 8

A and B:

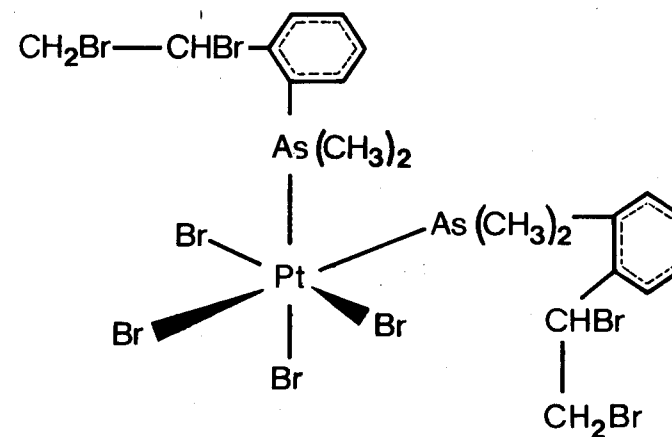


also trans isomer

C:

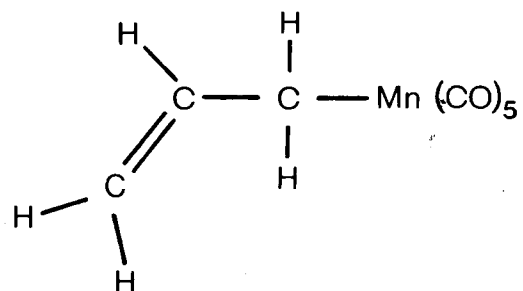


D:

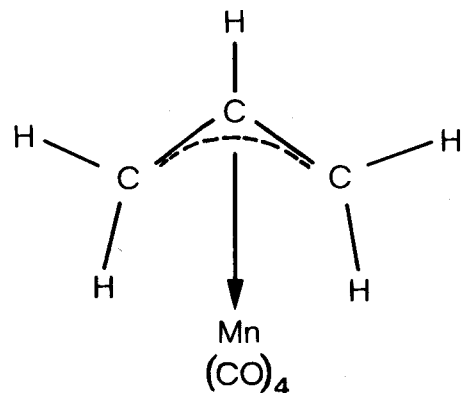


Problem 9

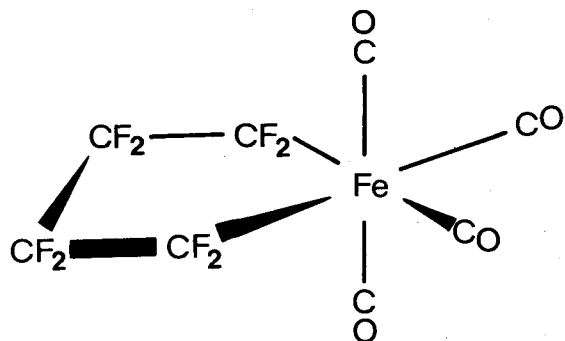
A:



B:



Problem 10



REFERENCES

The original sources of the problems are shown below. In many cases further information on these or related structures can be obtained from these sources. Numbers refer to the problem number.

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- ❖ preparing for examinations

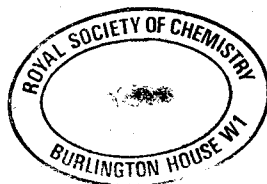
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