Mössbauer Spectra of Square-planar Organometallic Compounds of Iron(II)

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Mössbauer spectra of [Fe(C$_6$Cl$_5$)$_2$L$_2$], L = PEt$_3$ and PEt$_2$Ph have been recorded at different temperatures. The low δ values show a high degree of covalency in the iron–ligand bonds, and the large Δ values are consistent with a planar geometry. The Mössbauer emission spectra of some [^{57}Co(C$_6$Cl$_5$)$_2$-L$_2$] (L = PEt$_3$, PEt$_2$Ph or PEtPh$_2$) show no Mössbauer effect, suggesting the formation of a new iron specimen during the ^{57}Co(EC)^{57}Fe reaction, with an extremely small f-factor.

[Fe(C$_6$Cl$_5$)$_2$L$_2$] compounds have been prepared either from the reaction of C$_6$Cl$_5$MgCl and [FeCl$_2$-L$_2$] or by the addition of the phosphine to a solution of the 'Fe(C$_6$Cl$_5$)$_2$' complex. The stability of these complexes has been studied in different solvents and in the presence of bromine.

Introduction

There are very few Mössbauer studies of Iron(II) in a square-planar environment. These are on complexes with macrocyclic ligands [1] or on the Gillespite, iron(II) in a square-planar arrangement of oxide ions [2], and there are no Mössbauer data of Iron(II) in a strongly covalent square-planar compound. The only compounds of the type [FeR$_2$L$_2$], where R is an aryl group, reported in the literature are [Fe(C$_6$Cl$_5$)$_2$(PEt$_2$Ph)$_2$] [3], [Fe(mesityl)$_2$bipy] [4] and [Fe-Ph$_2$(PEt$_3$)$_2$] [5].

In this paper we report the Mössbauer absorption spectra of two iron compounds: [Fe(C$_6$Cl$_5$)$_2$L$_2$] (L = PEt$_3$ and PEt$_2$Ph) and the emission spectra of the three ^{57}Co compounds [^{57}Co(C$_6$Cl$_5$)$_2$L$_2$] (L = PEt$_3$, PEt$_2$Ph and PEtPh$_2$). The stability of the Iron-(II) compounds has also been studied in order to be compared with the cobalt analogue.

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Results and Discussion

The reaction of the Grignard reagent RMgX (R = C$_6$Cl$_5$, 2,3,5,6-C$_6$HCl$_4$ and 2,4,6-C$_6$H$_2$Cl$_3$) with the complexes [FeCl$_2$L$_2$] (L = PEt$_3$, PEt$_2$Ph, PEtPh$_2$, PPh$_3$ and ½dpe) in THF or benzene solution only leads to isolatable organometallic compounds when R = C$_6$Cl$_5$ and L = PEt$_3$ or PEt$_2$Ph.

When anhydrous FeCl$_2$ is treated with C$_6$Cl$_5$MgCl a deep brown solution is obtained. Although it has not been possible to isolate the complex 'Fe(C$_6$Cl$_5$)$_2$' in the solid state, strong evidence of its existence in solution has been provided by the addition of either PEt$_2$Ph or PEt$_3$ to the solution. In both cases the phosphine complexes [Fe(C$_6$Cl$_5$)$_2$L$_2$] have been obtained. No organometallic complexes have been isolated when other neutral ligands such as PEtPh$_2$, PPh$_3$, dpe or bipy have been added to the solution of the complex 'Fe(C$_6$Cl$_5$)$_2$'.

The golden yellow organometallic complexes prepared slowly decompose on exposure to air, the one containing PEt$_3$ decomposes even under a nitrogen atmosphere. These complexes have been characterized by elemental analysis, IR spectra and magnetic moments. The μ_{eff} of freshly prepared samples, 3.3 B.M. (PEt$_2$Ph) and 3.7 B.M. (PEt$_3$), are consistent with planar iron(II) complexes with two unpaired electrons giving rise to a ground state with S = 1.

Decomposition Reactions

The decomposition of the organometallic compounds [MR$_2$L$_2$], where R is an aryl group in benzene or CCl$_4$, affords a variable mixture of coupling product R–R and reduction product R–H depending on the metal M and on the neutral ligands L. When M = Ni it has been shown that in the thermal decomposition the main product is R–R (~90%). The reductive elimination occurs via a three coordinate intermediate formed by loss of a neutral ligand [6]. For M = Co the yield of coupling product R–R decreases while that of R–H increases [7].

We have studied the decomposition reactions of the organoiron(II) complexes in CCl_4, in benzene and in benzene either with bromine or PEt_3. The complexes are refluxed for 2 h and then hydrolyzed with 10% hydrochloric acid. The organic layer is dried and analyzed by GLC. The results are collected in Table I.

The obtained organoiron compounds decompose after 2 h in refluxing benzene, while the similar organocobalt compounds can be refluxed in benzene for 6 h without decomposition [7].

The obtained results in these reactions (Table I) may be interpreted in terms of two pathways as is shown in the scheme:

$$[FeR_2P_2] \left< \begin{array}{l} \nearrow R{-}H \\ \searrow `FeR_2P' + P \rightarrow R{-}R \end{array} \right.$$
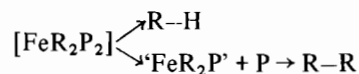
The reactions of formation of C_6HCl_5 and $C_{12}Cl_{10}$ are accompanied by a loss of halogen atoms.

The formation of RH arises from homolytic cleavage of the Fe–C bond and hydrogen abstraction from the solvent or the neutral ligand.

The coupling products, R–R, are formed through the three-coordinate intermediate as is shown by free phosphine addition experiments (Table I). A part of R–H may be formed from the three-coordinate intermediate as reported for the decomposition of $[Co(C_6Cl_5)_2(PEtPh_2)_2]$.

When bromine is added to the benzene solution, RBr is formed and an increase in the coupling products is observed. This result agrees with that obtained in the decomposition of the nickel and cobalt compounds under oxidizing conditions [6–8].

Mössbauer Spectra

The Mössbauer parameters for the complexes are listed in Table II. Each spectrum consists of a single quadrupole doublet with some evidence of iron contaminants in the PEt_3 complex due to the slow decomposition of the organometallic (Fig. 1, 2). Previous Mössbauer studies on square-planar iron(II) complexes having the S = 1 ground state have been found to have I.S. values in the range 0.24–0.45 mm/sec with respect to metallic iron. The values obtained

in this work fall outside this range, even though the compounds have the same spin state. It may be assumed that these differences arise from the higher degree of covalency which can be expected in the organometallic complexes studied, therefore the assumption of an ^3A ground state would explain the obtained values both of the magnetic moment and the IS [9].

The isomer shift value, δ, is dependent upon the s-electron density at the iron nucleus, with increasing s-electron density causing a decrease in the isomer shift. Taking covalence effects into consideration, increasing the σ-donor strength and/or increasing the π-acceptor ability of the coordinated ligands will result in lower isomer shift values. Therefore the covalent σ-bonding between the iron and the pentachlorophenyl group added to the σ-donor plus π-acceptor character of the phosphines accounts for the low δ values observed. The synergetic effect of the phosphine can be responsible for the same isomer shift obtained for both complexes. The temperature variation of δ should be due to the SOD shift.

It has been put forward that the lattice contribution of a square-planar environment of ligands to the quadrupole splitting is very large and positive [10]; *i.e.* in the Gillespite it has been shown that this contribution is as large as 4.1 mm/sec [5]. It has also been claimed [11] that strong σ-donor ligands in the xy plane led to a positive contribution to the quadrupole splitting. Hence, the large quadrupole splitting observed in our studies will arise from the addition of the lattice contribution and covalent σ-bonding in the plane of the complex contribution. Finally, the little variation of the Δ value with temperature suggests the existence of a relatively large energy gap between the ground and the first excited level.

It had not been possible to obtain other organometallic iron(II) complexes, and analogous organocobalt compounds doped with ^{57}Co were prepared in order to get more information on the iron ones. The cobalt complexes $[Co(C_6Cl_5)_2L_2]$, L = PEt_3, PEt_2Ph, $PEtPh_2$, have been synthesized introducing ppm of radioactive ^{57}Co, and used as sources against

TABLE I. Thermal Decomposition of $[Fe(C_6Cl_5)_2L_2]$.[a]

Ligand L:	PEt₃				PEt₂Ph		
Solvent[b]	C_6H_6	$C_6H_6(+ PEt_3)$	$C_6H_6(+ Br_2)$	CCl_4	C_6H_6	$C_6H_6(+ Br_2)$	CCl_4
% 1,2,4,5-$C_6H_2Cl_4$	11	11	1	6	6	1	3
% C_6HCl_5	68	80	13	47	61	17	43
% C_6Cl_5Br	–	–	35	–	–	25	–
% $C_{12}H_2Cl_8$[c]	7	1	8	19	4	1	5
% $C_{12}HCl_9$[c]	12	4	18	22	21	19	32
% $C_{12}Cl_{10}$	2	1	23	4	8	37	13

[a]Weight % based on polyhalophenyl and polychlorobiphenyl identified.   [b]Reflux, 2 hr.   [c]Mixture of several isomers.

TABLE II. Mössbauer Parameters for the Iron(II) Complexes.

Compound	Temp. (K)	δ^a (mm/sec)	Δ (mm/sec)	Γ_{exp} (mm/sec)
$[Fe(C_6Cl_5)_2(PEt_3)_2]$	298[c]	0.155 ± 0.003	3.933 ± 0.006	0.26 ± 0.01
	79	0.268 ± 0.003	4.162 ± 0.006	0.59 ± 0.02
$[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$	298[c]	0.136 ± 0.003	3.890 ± 0.006	0.20 ± 0.01
	79	0.253 ± 0.005	4.130 ± 0.01	0.82 ± 0.04[b]

[a]Relative to iron metal.   [b]Some broadening could be due to imperceptible vibrations in the cryostat, set up by boiling of the liquid nitrogen.
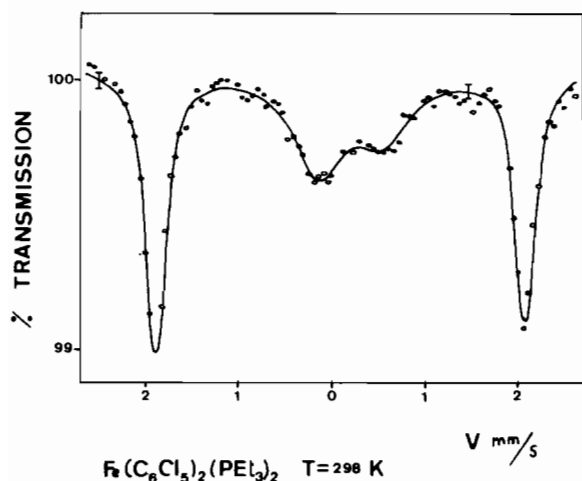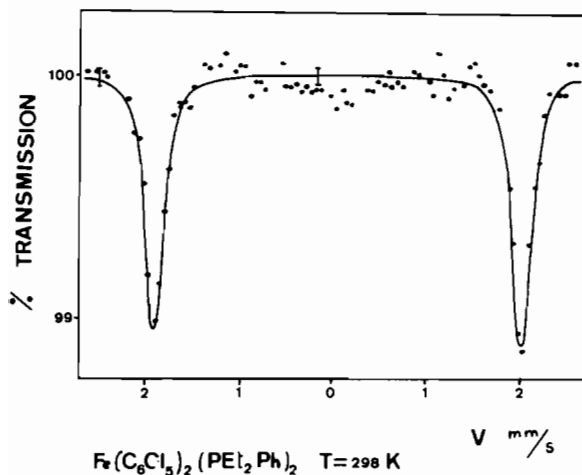

Fig. 1

Fig. 2

stainless steel as a single line absorber in a Mössbauer emission experiment.

In the recorded emission spectra of our complexes no Mössbauer effect has been observed as a consequence of a vanishingly small f factor for the emitting specimen, indicating that some damage to the surrounding of the iron atom has occurred during the nuclear decay. The Auger electron cascade occurring in the iron daughter, after the electronic capture (EC) takes place in the ^{57}Co, gives rise to the appearance of highly ionized iron ions in the solid matrix. The ejected Auger electrons come back to the Mössbauer atom or they are trapped by defects in a time less than 10^{-7} s [12]. Therefore the electrostatic equilibrium is achieved in the time of the Mössbauer life time. Furthermore as a consequence of the EC process a neutrino is emitted, the resulting recoil energy of the iron ion being 3.4 eV.

It has been stated that the Auger electron [13] and the emitted γ and X rays [14] after the ^{57}Co-(EC)^{57}Fe reaction provide an autoradiolysis of the ligands around the site of the decayed nucleus. In the Mössbauer spectrum of an absorbent of $[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$ irradiated with γ photons from a ^{60}Co source (doses 1000 rads) there is no sign of any new species indicating the absence of radiation damage. Accordingly we rule out any radiation damage in the doped complexes due to the emitted X and γ rays. Thus, we suppose that decomposition of the organometallic can take place by three non-self-excluding pathways: radiolysis by Auger electrons, increase in the oxidation number of the ion, and/or local heating of the absorbed recoil energy of the neutrino emission. The result is an emitting specimen with a practically zero f-factor.

Experimental

Anhydrous $FeCl_2$ was prepared by standard methods [15, 16]. PEt_3, PEt_2Ph, $PEtPh_2$ and PPh_3 have been purchased and were used without further treatment. All the solvents were distilled prior to use. All the reactions have been carried out under dry deoxygenated nitrogen. GLC analyses were performed on a Hewlett-Packard 5710A using a 10% SE-30 on Chromosorb Q column coupled to a Hewlett-Packard 3390 integrator.

The Mössbauer spectra were recorded using a constant acceleration spectrometer coupled to a conventional multichannel analyzer working in multiscale mode. The samples were mounted in an Oxford Instruments DN-704 cryostat for low temperature studies. The source used in the case of absorbents was ^{57}Co in Rh while in the case of sources the single line

absorbent was stainless steel. Calibration of the velocity of the instrument was done by use of an iron foil enriched in ^{57}Fe. The spectra were fit to Lorentzian curves by the least squares method.

Preparation of the Iron Complexes

(a) A mixture of anhydrous $FeCl_2$ (0.38 g, 3 mmol) and the appropriate phosphine, PEt_3 or PEt_2Ph (6.5 mmol) in benzene (15 ml) was stirred under reflux for 2 hr. To this solution cooled at -10 °C was added the Grignard reagent C_6Cl_5MgCl prepared from magnesium (0.5 g), hexachlorobenzene (2.85 g) and THF (15 ml). The mixture was then stirred at 0 °C for 2 h and cooled at -20 °C. After 12 h the yellow crystals were collected and repeatedly washed with 1% HCl and methanol. Yields 45–50%.

(b) The Grignard reagent C_6Cl_5MgCl prepared as in the previous method was added to anhydrous $FeCl_2$ (0.25 g, 2 mmol) suspended in THF (5 ml). The reaction was kept at room temperature for 1 h and then the appropriate phosphine (4 mmol) was added. After 2 h the solution was worked up as above. Yields: 35–40%.

Analytical data for the freshly prepared complexes: Found (calculated): $[Fe(C_6Cl_5)_2(PEt_3)_2]$, C: 36.0(36.45), H: 3.8(3.82), Cl: 44.3(44.83). Dec. Temp. 118–125 °C. $\mu_{eff} = 3.7$ B.M. $[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$, C: 43.2(43.34), H: 3.3(3.41), Cl: 40.2-(39.97), Dec. Temp. 142–146 °C. $\mu_{eff} = 3.3$ B.M. previously reported [3].

Preparation of the ^{57}Co Sources

$[^{57}Co(C_6Cl_5)_2P_2]$ (P = PEt_3, PEt_2Ph and $PEtPh_2$) were prepared from the complexes $[^{57}CoCl_2P_2]$ following the reported methods for the undoped complexes [1, 7].

$CoCl_2$ was doped with 4 mCi of carrier-free $^{57}CoCl_2$, dissolved in ethanol and the appropriate phosphine added to the solution. The resulting solution was evaporated to dryness under vacuum.

Elemental analysis, IR spectra and X ray diagrams of undoped complexes were obtained in order to verify the quality of the product.

Decomposition Reactions

0.2 mmol of the iron complexes were refluxed for 2 h in 15 ml of the appropriate solvent. The resultant solution was treated with 10% hydrochloric acid and the organic layer was dried and analyzed by GLC. The reaction with free phosphine was carried out under nitrogen with a 1:4 cobalt:phosphine ratio. In the decomposition in the presence of bromine a Co:Br ratio of 1:5 was used; in this case the solution was also treated with Na_2CO_3 for eliminating the bromine excess.

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