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THE INTERACTION OF FeCl_3 WITH PPh_3 IN CHLOROFORM. X-RAY CRYSTAL STRUCTURE OF $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2$

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Abstract—Interaction of FeCl_3 and PPh_3 in CHCl_3 yields complex mixtures containing unstable adducts. The compound $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2 \cdot \text{CHCl}_3$ was isolated from the solution after the decomposed mixture had been allowed to interact with air. Crystal data: triclinic, space group $P\bar{1}$, $a = 11.459(4)$, $b = 12.102(2)$, $c = 18.109(4)$ Å, $\alpha = 105.15(2)$, $\beta = 102.14(2)$, $\gamma = 94.91(2)^\circ$, $V = 2347(2)$ Å³, $Z = 2$, $d_c = 1.49$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 13.49$ cm⁻¹, $R = 0.045$ ($R_w = 0.054$) for 487 parameters and 5256 observed reflections with $F_o^2 > 3\sigma(F_o^2)$.

We have recently studied the interaction of iron(III) chloride with monodentate phosphine ligands and we have obtained the mononuclear $\text{FeCl}_3(\text{PR}_3)_2$ ($R = \text{Ph, Me, Cy}$) derivatives.¹ These compounds exhibit a trigonal bipyramidal geometry with the phosphine ligands occupying the axial positions. We have also conducted an EPR study of the $\text{FeCl}_3\text{-PPh}_3$ interaction in different molar ratios and shown that a reactive four-coordinate $\text{FeCl}_3(\text{PPh}_3)$ compound, presumably with tetrahedral geometry, is formed when a 1:1 ratio is used. This compound decomposes at room temperature in aromatic solvents according to two competitive pathways, the first involving reduction to iron(II) species by the solvent, and the second being a disproportionation to an ionic iron(III) material.¹ We were interested in understanding the relationship between our reactive 1:1 adduct and a reported² yellow crystalline solid, described as $\text{FeCl}_3(\text{PPh}_3)$, that had been obtained from $\text{Fe}_3(\text{CO})_{12}$ and PPh_3 in CHCl_3 . An EPR spectroscopic study of the $\text{FeCl}_3\text{-PPh}_3$ interaction in CHCl_3 shows¹ that the $\text{FeCl}_3(\text{PPh}_3)$ species also forms in this solvent, but it subsequently decomposes according to the same pathways observed in the aromatic solvents. However, while we were trying to crystallize the ionic iron(III) product from the CHCl_3 solution, we obtained evidence that yet another decomposition

path is available in these conditions. The results of this study are reported here.

EXPERIMENTAL

All operations were carried out under an atmosphere of dinitrogen, unless otherwise specified. Solvents were dried by conventional methods and distilled under dinitrogen prior to use. FeCl_3 was dehydrated by treatment in SOCl_2 and PPh_3 was recrystallized from absolute ethanol.

Reaction of FeCl_3 with PPh_3 in CHCl_3 . Synthesis of $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2$

PPh_3 (0.92 g, 3.51 mmol) was added to a suspension of anhydrous FeCl_3 (0.85 g, 5.26 mmol) in 35 cm³ of CHCl_3 and stirred at room temperature for 1 day. The black solution slowly lightened to produce a yellow solution and a greyish white solid. The solid was filtered and the solution allowed to sit for 1 week. At this point, exposure of this solution to air caused yellow crystals to form within several hours. A single crystal for the X-ray analysis was selected from this batch. The air-stable crystals were filtered and dried under vacuum, yielding 0.21 g (11%) of product, which retained one molecule of interstitial crystallization solvent (CHCl_3). Found: C, 43.3; H, 3.0; Cl, 36.7. Calc. for $\text{C}_{38}\text{H}_{33}\text{Cl}_{11}\text{Fe}_2\text{P}_2$: C, 43.3; H, 3.2; Cl, 37.0%. IR (Nujol mull, cm⁻¹): 1585 w, 1435 s, 1110 m, 995 s,

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810 w, 790 m, 760 m, 740 s, 685 m, 510 m, 500 m, 490 m.

X-ray crystallography for $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2 \cdot \text{CHCl}_3$

A single crystal was glued on the tip of a glass fibre and mounted on the diffractometer. The cell constant determination, data collection and reduction were routine. A semi-empirical absorption correction was applied according to the method described by North *et al.*³ Crystal data are assembled in Table 1. The structure was solved by direct methods and refined by alternating cycles of full-matrix least-squares and difference Fourier maps. Hydrogen atoms were included at calculated positions and used for structure factor calculations, but not refined. An interstitial chloroform molecule was also found. This had the carbon atom disordered among two equally populated positions,

above and below the plane containing the three chlorine atoms.

Oxidation state, ionic charge, and synthetic methodology considerations led us to believe initially that the atom bridging the two phosphine moieties in the cation was an oxygen atom. Refinement with all the non-hydrogen atoms, including those of the interstitial chloroform molecule, treated anisotropically, converged to an agreement factor $R = 0.049$ ($R_w = 0.058$). The equivalent isotropic thermal parameter for the bridging atom was $7.5(2) \text{ \AA}^2$, much larger than those of the neighbouring atoms (around 3.00 \AA^2), but still acceptable. However, the results of the elemental analysis, together with this high thermal parameter for the bridging atom, convinced us that we did not have an oxygen atom but rather a carbon atom of a methylene functionality holding together the two PPh_3 moieties. Refinement on the appropriately modified model converged to a lower agreement factor

Table 1. Crystal data for $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2 \cdot \text{CHCl}_3$

Formula	$\text{C}_{38}\text{H}_{33}\text{Cl}_{11}\text{Fe}_2\text{P}_2$
f_w	1053.30
Space group	$P\bar{1}$
Systematic absences	none
a (Å)	11.459(4)
b (Å)	12.102(2)
c (Å)	18.109(4)
α (°)	105.15(2)
β (°)	102.14(2)
γ (°)	94.91(2)
V (Å ³)	2347(2)
Z	2
d_{calc} (g cm ⁻³)	1.49
Crystal size (mm)	$0.5 \times 0.4 \times 0.3$
$\mu(\text{Mo-K}\alpha)$ (cm ⁻¹)	13.49
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)
Orientation reflections: number; range (2θ) (°)	25, 20–30
Temperature (°C)	20
Scan method	$\omega-2\theta$
Data collection range (2θ) (°)	4–50
Number of unique data, total observed	8353, 5256
Number of parameters refined	487
Transmission factors: max, min	1.000, 0.8612
R^a	0.045
R_w^b	0.054
Quality-of-fit indicator ^c	2.04
Largest shift/ESD, final cycle	0.25
Largest peak (e Å ⁻³)	0.574

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

^c Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$.

Table 2. Selected intramolecular distances (Å) and angles (°) for [Ph₃POPPh₃][FeCl₄]₂·CHCl₃

Atom	Atom	Distance		Atom	Atom	Distance	
Fe(1)	Cl(1)	2.156(2)		P(1)	C(10)	1.792(4)	
Fe(1)	Cl(2)	2.209(2)		P(1)	C(20)	1.796(4)	
Fe(1)	Cl(3)	2.157(2)		P(1)	C(30)	1.783(4)	
Fe(1)	Cl(4)	2.177(2)		P(1)	C(1)	1.822(4)	
Fe(2)	Cl(5)	2.205(2)		P(2)	C(40)	1.790(4)	
Fe(2)	Cl(6)	2.177(2)		P(2)	C(50)	1.786(4)	
Fe(2)	Cl(7)	2.173(2)		P(2)	C(60)	1.801(4)	
Fe(2)	Cl(8)	2.181(2)		P(2)	C(1)	1.816(4)	
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Cl(1)	Fe(1)	Cl(2)	109.34(7)	C(10)	P(1)	C(30)	112.7(2)
Cl(1)	Fe(1)	Cl(3)	111.17(8)	C(20)	P(1)	C(30)	108.6(2)
Cl(1)	Fe(1)	Cl(4)	109.10(8)	C(10)	P(1)	C(1)	110.3(2)
Cl(2)	Fe(1)	Cl(3)	109.42(7)	C(20)	P(1)	C(1)	106.7(2)
Cl(2)	Fe(1)	Cl(4)	108.88(8)	C(30)	P(1)	C(1)	110.0(2)
Cl(3)	Fe(1)	Cl(4)	108.9(1)	C(40)	P(2)	C(50)	112.1(2)
Cl(5)	Fe(2)	Cl(6)	108.06(7)	C(40)	P(2)	C(60)	107.7(2)
Cl(5)	Fe(2)	Cl(7)	110.22(7)	C(50)	P(2)	C(60)	109.6(2)
Cl(5)	Fe(2)	Cl(8)	108.79(7)	C(40)	P(2)	C(1)	110.8(2)
Cl(6)	Fe(2)	Cl(7)	108.45(7)	C(50)	P(2)	C(1)	110.7(2)
Cl(6)	Fe(2)	Cl(8)	112.48(8)	C(60)	P(2)	C(1)	105.7(2)
Cl(7)	Fe(2)	Cl(8)	108.83(7)	P(2)	C(1)	P(1)	123.4(2)
C(10)	P(1)	C(20)	108.4(2)				

Estimated standard deviations in the least significant figure are given in parentheses.

($R = 0.045$; $R_w = 0.054$) and gave a more reasonable equivalent isotropic thermal parameter for the bridging atom [3.1(1) Å²]. Selected bond lengths and angles are listed in Table 2.*

RESULTS AND DISCUSSION

(a) Chemical studies

The dark brown solutions obtained at low temperature by interacting anhydrous FeCl₃ and PPh₃ in a 1:1 molar ratio, and containing the unstable FeCl₃(PPh₃) species,¹ rapidly changed colour to yellow when warmed to room temperature. We repeatedly tried to work up these solutions under a dinitrogen atmosphere with the hope of crystallizing the yellow decomposition product.

This is believed to be an ionic compound with

* A full list of bond distances and angles, positional parameters, anisotropic displacement parameters and F_o/F_c data have been deposited with the Editor as supplementary material. The atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

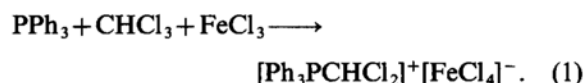
empirical formula FeCl₃(PPh₃)₂,² possibly [FeCl₂(PPh₃)₂]⁺[FeCl₄]⁻. These solutions show high electric conductance, consistent with the production of ionic species. In addition, most of the known derivatives of iron(III) with soft donor ligands, and also a few with hard donor ligands, are ionic. Examples are [Fe(L—L)₂X₂][FeX₄] [X = Cl or Br, L—L = *o*-C₆H₄(AsMe₂)₂;⁴ X = Cl, L—L = methylenebis(diphenylphosphine oxide) or tetramethylenebis(diphenylphosphine oxide)⁵] and [FeCl₂L₄][FeCl₄] (L = N-methylimidazole,⁶ pyridine-N-oxide,⁷ dimethylsulphoxide⁸). Unfortunately all of these materials correspond to the empirical formula FeCl₃L₂ or FeCl₃(L—L). No ionic compound with an empirical formula FeCl₃L, that is with structure [FeCl₂L₂][FeCl₄], seems to have been positively characterized. Four-coordinate tetrahedral iron(III) is common in anionic species, such as [FeX₄]⁻ (X = Cl, Br, SR⁹) and has been suggested for the neutral FeCl₃(THF) compound,¹⁰ but, to the best of our knowledge, never found in cationic complexes.

While our attempts to obtain a crystalline material under dinitrogen were unsuccessful, we sampled an aliquot of the solution for a gas chro-

matographic analysis¹ and observed that a crystalline material was rapidly obtained upon exposure to air. We then decided to expose the rest of the solution to air, and we obtained the product, later proven to be $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2 \cdot \text{CHCl}_3$ by elemental and X-ray structural analysis (*vide infra*), in low yield. The solution had been exposed to air 8 days after the initial $\text{FeCl}_3\text{-PPh}_3$ interaction.

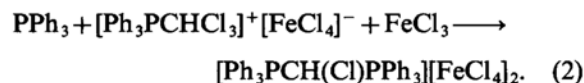
We have repeated the preparation of this crystalline material several times in consistently reproducible low yields. During one of these preparations, the solution was exposed to air shortly after the change of colour to yellow was completed, and *no crystalline product was obtained*.

The presence of a methylene functionality in the cation suggests that interaction with the solvent has occurred. The interaction of PPh_3 with haloforms is documented in the literature. With CHI_3 , an ill-characterized 1:1 adduct was obtained.¹¹ PPh_3 and CHBr_3 do not react at room temperature, but under thermal or photochemical conditions $[\text{Ph}_3\text{PCHBr}_2]^+\text{Br}^-$ is obtained.¹² The reaction of PPh_3 and CHCl_3 has been reported to produce $\text{Ph}_3\text{P}=\text{CCl}_2$ in the presence of a strong base. This reaction has been described as proceeding through the free dichlorocarbene.¹³ From these data, it would appear that the nucleophilic attack of PPh_3 on CHCl_3 is not a facile process. However, the presence of the strong Lewis acid, FeCl_3 , should provide additional driving force by coordinating the chloride leaving group to form the stable FeCl_4^- anion [eq. (1)]:



This type of reactivity has also been described for the $\text{PPh}_3\text{-CCl}_4$ system, where $[\text{Ph}_3\text{PCCl}_3]\text{Cl}$ is obtained without the aid of a Lewis acid.¹⁴

FeCl_3 could as well promote an additional nucleophilic attack to the quaternary carbon, according to eq. (2):



Since this reaction is in large excess of CHCl_3 , this second nucleophilic attack will occur only if reaction 2 is faster than reaction 1.

This reactivity pattern would parallel the one observed for the interaction of PPh_3 with CH_2Br_2 , where $[\text{Ph}_3\text{PCH}_2\text{PPh}_3]\text{Br}_2$ has been obtained.¹⁵ In addition, the reaction¹⁶ of PPh_3 and CCl_4 in a 3:1 ratio, reported to yield $[\text{Ph}_3\text{PC}(\text{Cl})\text{PPh}_3]\text{Cl}$, presumably proceeds through $[\text{Ph}_3\text{PCCl}_2\text{PPh}_3]\text{Cl}_2$.

The product of eq. (2) is the closest compound to the observed product of which we can rationalize

the formation. It is completely obscure to us how the action of oxygen could replace the chlorine atom with a hydrogen atom in $[\text{Ph}_3\text{PCH}(\text{Cl})\text{PPh}_3][\text{FeCl}_4]_2$, assuming that the latter is indeed an intermediate. It initially occurred to us, in view of the synthetic methodology, that the two PPh_3 units might be bridged by an oxygen atom, but this hypothesis has been subsequently ruled out by accurate elemental analysis determinations and by the results of the crystal structure refinement (see Experimental).

We do not have a better explanation as to how the observed product is formed. The only conclusion that can be safely drawn is that the intermediate species upon which oxygen is operating is only slowly produced in the reaction conditions, since no product is obtained when oxygen is introduced promptly after the interaction of FeCl_3 and PPh_3 has occurred. We have not further investigated the mechanism of this curious transformation, nor have we altered the reaction conditions in an attempt to maximize the yield of the product.

(b) Crystallographic study

The $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2$ compound crystallizes with one formula unit plus an interstitial CHCl_3 molecule in the asymmetric unit. No significant intermolecular interactions are observed, and the different ions are well separated from each other.

The FeCl_4^- anions display fairly regular tetrahedral geometries, the one containing Fe(2) being slightly more distorted [average Cl—Fe—Cl angles are $109.47 \pm 0.8^\circ$ for Fe(1) and $109.47 \pm 1.6^\circ$ for Fe(2)]. The Fe—Cl distances (average 2.18(2) Å) compare with those found in other FeCl_4^- salts, for instance 2.182(1) Å in the AsPh_4^+ salt, 2.175(5) (av.) Å in the PPh_3Me^+ salt and 2.184(5) (av.) in the $[\text{Fe}(\text{MeCN})_6]^{2+}$ salt.¹⁷

Figure 1 shows a view of the dication. This is arranged in a conformation where the atoms P(1), P(2), C(1), C(20) and C(60) approximately lie in the same plane. This allows the P(1)—C(1)—P(2) angle to close to the observed value of $123.4(2)^\circ$ without major steric repulsions between the phenyl groups on adjacent phosphorus atoms. This angle is smaller than that found in the $[\text{Ph}_3\text{PCHPPH}_3]^+$ cation [$128.2(3)^\circ$],¹⁸ albeit larger than that observed for $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$ [$117.9(6)^\circ$],¹⁸ in agreement with a different hybridization state in the former case and with a decreased steric repulsion and/or with the absence of an electrostatic repulsion in the latter one. The P—C(1) distances (average 1.819(4) Å) are in the expected range for a phos-

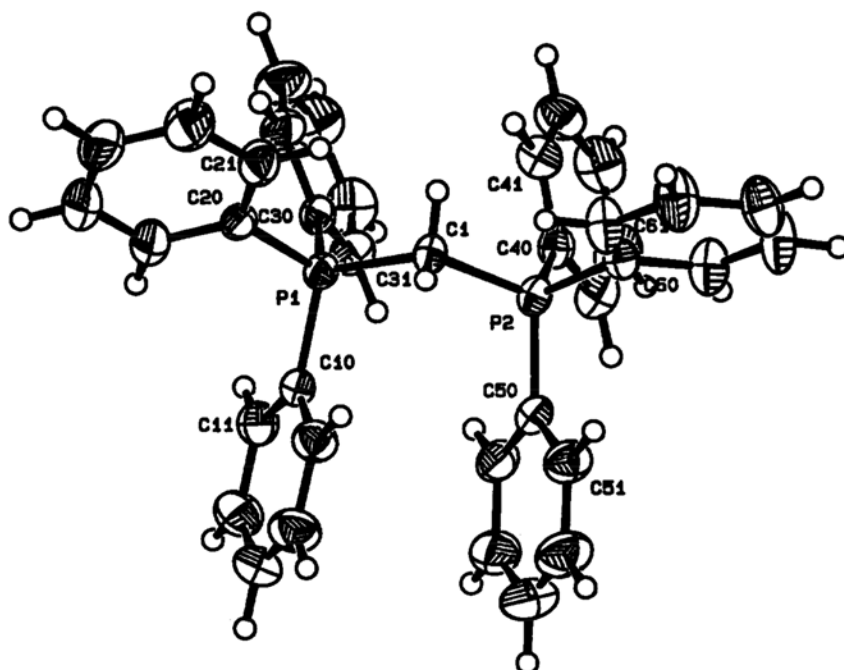


Fig. 1. An ORTEP view of the dication of compound $[\text{Ph}_3\text{PCH}_2\text{PPh}_3][\text{FeCl}_4]_2 \cdot \text{CHCl}_3$. Hydrogen atoms are drawn with arbitrary radii for the sake of clarity.

phorus-carbon (sp^3) single bond, and compare favourably with those observed in $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$ (av. $1.84(1) \text{ \AA}$), the slight decrease being consistent with the presence of positive charges.

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