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ALUMINUM CHLORIDE-CATALYZED REACTIONS OF FERROCENE WITH PHOSPHORUS(III) AMIDES. NOVEL COORDINATION OF THE P–N SYSTEM*

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SUMMARY

In aluminum chloride-catalyzed reactions with ferrocene, P^{III} compounds show reactivities in the order, $PCl_3 \ll R_2NPCl_2 > (R_2N)_2PCl > (R_2N)_3P$, revealing that active intermediate species are formed by the coordination of aluminum chloride not to phosphorus but to nitrogen. Evidence is presented which supports this, and indicates that aluminum chloride cleaves the P–N bond via bonding to nitrogen, generating P–Cl. HCl, formed as by-product of the Friedel–Crafts reactions, is not a factor in the cleavage of the P–N bond. Catalysis and inhibition of the reactions are discussed in terms of a mechanism based on the concept of a dimolar aluminum chloride complex of a donor species such as R_2NPCl_2 or R_3N. The reactions are seen to generate $(Fc)_3P$ both by a stepwise electrophilic process and by disproportionation of $(Fc)_2PCl$. The coordination of $AlCl_3$ to nitrogen of P–N is rationalized on the basis of bond energetics and the unavailability of electrons for back-bonding to phosphorus. Several new phosphorus amides of ferrocene are reported.

INTRODUCTION

Ferrocene undergoes trisubstitution on phosphorus in reactions with PCl_3, $RPCl_2$ and R_2PCl under Friedel–Crafts conditions[2,3]. Generally, Grignard and lithium reagents[4,5] and alkylaluminum compounds[6] have been used in reactions with phosphoramidous chlorides [R_2NPCl_2, $(R_2N)_2PCl$] to form P–C bonds. Extension of the Friedel–Crafts process to R_2NPCl_2 and $(R_2N)_2PCl$ thus appeared to offer a simpler, more direct route to phosphorus amides of ferrocene since there would be no need to prepare an intermediate metallic derivative of ferrocene. Amides of ferrocenecarboxylic acid have been synthesized by Friedel–Crafts reactions employing carbamyl chlorides[7].

The synthesis of the first known phosphorus amide of ferrocene from ferrocenylphosphorous dichloride (IV) and piperidine has been described[8]. Diferrocenylphosphinous chloride (II), also useful for the preparation of phosphorus amides of ferrocene via aminolysis, was unknown during the initial stages of the present work, and has

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* A preliminary communication describing a portion of this work has appeared (ref. 1); presented in part at the Second International Symposium on Organometallic Chemistry, University of Wisconsin, Aug. 30–Sept. 3, 1965.

become available together with triferrocenylphosphine (I) as a result of this work. Compounds (I) and (II), as well as (IV), arose unexpectedly in aluminum chloride-catalyzed reactions of ferrocene with R_2NPCl_2, and thus the production of phosphorus amides of ferrocene (III) acquired secondary importance. A study has been made for the purpose of shedding light on the mechanism of formation of compounds (I), (II), and (IV).

RESULTS AND DISCUSSION

Reactions of R_2NPCl_2 in n-heptane were found capable of producing a wide variety of products.

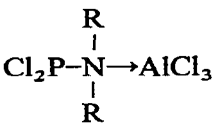
$$R_2NPCl_2 + FcH \xrightarrow{AlCl_3} \left\{ \begin{array}{llll} (Fc)_3P; & (Fc)_2PCl; & (Fc)_2PNR_2; & FcPCl_2; \\ (I) & (II) & (III) & (IV) \\ (Fc)_3PO; & (Fc)_2P(O)H; & (Fc)_2P(O)NR_2; & FcPH(O)OH \\ (Ia) & (IIa) & (IIIa) & (IVa) \\ & & (Fc)_2P(O)OH; & \\ & & (IIIb) & \end{array} \right.$$

($R = CH_3$, C_2H_5; Fc = ferrocenyl)

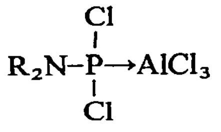
Compounds (I)–(IV) were formed by cleavage of P–Cl and/or P–N bonds; all other products resulted from oxidation and/or hydrolysis occurring during work-up of the reaction mixtures. It was clear that aluminum chloride was instrumental in bringing about cleavage of the P–Cl bond. The results of two experiments showed that cleavage of the P–N bond by HCl[4,5] (which arose as by-product) did not pertain in these reactions: (1). An atmosphere of HCl, supplied from an external source, hindered the reaction of $(CH_3)_2NPCl_2$, causing a reduction in overall yield of ferrocene compounds from 55% to 29%. PCl_3 was obtained in 86% yield as product of the cleavage of $(CH_3)_2NPCl_2$ by HCl in the absence of ferrocene and $AlCl_3$, and it will be seen later that PCl_3 produces only trace amounts of ferrocene derivatives while R_2NPCl_2 gives high yields of products in $AlCl_3$-catalyzed reactions in n-heptane. (2). With $(CH_3)_2NPCl_2$ as reactant, bubbling nitrogen through the Friedel–Crafts reaction mixture produced no significant change in the yields of $(Fc)_3P$ and $FcPCl_2$. These compounds clearly arose via non-hydrolytic cleavage of the P–N bond, such that if the cleavage were caused by HCl, driving off the gaseous by-product by entrainment with nitrogen should have caused a reduction in the yields.

Coordination of aluminum chloride to nitrogen of the P–N system

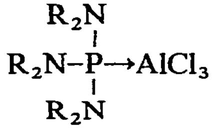
The data in Table 1, both in terms of overall yields and recovered ferrocene, show that the P^{III} amides exhibit reactivities in the order $R_2NPCl_2 > (R_2N)_2PCl > (R_2N)_3P$. As the nucleophilic character of the phosphorus atom increases, reactivity decreases. This order of reactivity is reasonably explained on the basis that active intermediate species are formed by the coordination of aluminum chloride not to phosphorus but to nitrogen. It is envisioned that A occurs rather than B; that C has a greater tendency to form than D and is inactive *per se* under the conditions of this investigation.


$Cl_2P\text{-}\overset{R}{\underset{R}{N}}\rightarrow AlCl_3$

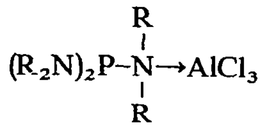
A


$R_2N\text{-}\overset{Cl}{\underset{Cl}{P}}\rightarrow AlCl_3$

B


$R_2N\text{-}\overset{R_2N}{\underset{R_2N}{P}}\rightarrow AlCl_3$

C


$(R_2N)_2P\text{-}\overset{R}{\underset{R}{N}}\rightarrow AlCl_3$

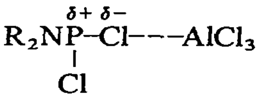
D

It is further evident that *cleavage* of the P–N bond involves prior coordination of aluminum chloride to nitrogen rather than phosphorus, and this is discussed below. There appears to be no previous report of the interaction of aluminum chloride with nitrogen of the P–N system.

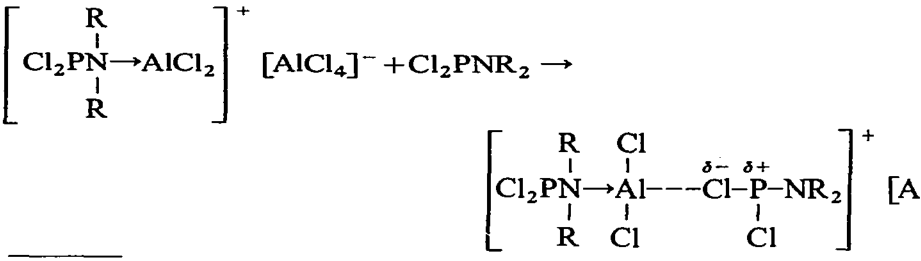
Although phosphorous triamides are known to be powerful nucleophiles via the phosphorus atom[9], the results suggest that the capacity of the nitrogen atom to serve as donor center for aluminum chloride increases as strongly inductive chlorine atoms are introduced into the molecule*. This viewpoint is supported by the fact that PCl_3 gives products in trace amounts while R_2NPCl_2 gives products in excellent yields in identically performed reactions (Table 2). This lack of reactivity on the part of PCl_3 is in accord with the electrophilic character of PX_3[11].

Mechanism of the formation of phosphorus electrophiles

The suggestion that $AlCl_3$ bonds to nitrogen of R_2NPCl_2 is supported by the fact that an equivalent of triethylamine inhibits the Friedel–Crafts reaction of the dichloride with ferrocene, while promoting the analogous reaction of PCl_3 (Table 2). It is evident that the amine does not function as an acceptor for HCl. The high reactivity of R_2NPCl_2 in the absence of the amine, moreover, cannot be due to the generation of an electrophilic species as follows.


$$R_2N\underset{Cl}{\overset{\delta+}{P}}\text{-}\overset{\delta-}{Cl}\text{---}AlCl_3$$

This seemingly anomalous behavior is understandable in the light of the fact that in the presence of a tertiary amine, greater than an equivalent amount of $AlCl_3$ is necessary for the catalysis of aromatic alkylation[12]. A dimolar aluminum chloride complex of the amine has been proposed as an intermediate, and this concept can be extended to the present results. It is evident [eqn. (1)] how inhibition of the reaction of R_2NPCl_2 would be the result of a deficiency in $AlCl_3$ due to its coordination by the added amine.


$$\left[Cl_2P\overset{R}{\underset{R}{N}}\rightarrow AlCl_2\right]^+[AlCl_4]^- + Cl_2PNR_2 \rightarrow \left[Cl_2P\overset{R}{\underset{R}{N}}\rightarrow \overset{Cl}{\underset{Cl}{Al}}\text{---}\overset{\delta-}{Cl}\text{-}\underset{Cl}{\overset{\delta+}{P}}\text{-}NR_2\right]^+[AlCl_4]^- \quad (1)$$

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* The P–Cl bond shows little or no π character (ref. 10).

(*continued* p. 148)

TABLE 1

REACTIVITY OF P^{III} AMIDES IN ALUMINUM CHLORIDE-CATALYZED REACTIONS WITH FERROCENE

P^{III} amide	Molar ratio, FcH/P^{III} amide/$AlCl_3$	Reflux time (h)[a]	Product yields (%)[b]								Additional product (%)[c]	Recovered FcH (%)
			$(Fc)_3P$	$(Fc)_3PO$	$(Fc)_2PCl$	$(Fc)_2P(O)H$	$(Fc)_2P(O)NR_2$	$(Fc)_2P(O)OH$	$FcPCl_2$	Total		
$(C_2H_5)_2NPCl_2$	2/1/1	20		57[d]		7		7	3[e]	74	2	0
$[(C_2H_5)_2N]_2PCl$	2/1/1	20	11			4	2			17	20	40
$(CH_3)_2NPCl_2$	2/1/1	20	16	29	12		5	2		64	4	8
$[(CH_3)_2N]_2PCl$	2/1/1	20	17	13			10			40	<1	42
$(C_2H_5)_2NPCl_2$	3/1/2	20	23	47		1				71	9	14
$[(C_2H_5)_2N]_3P$	3/1/2[f]	20	3	3						6	4	90
$(CH_3)_2NPCl_2$	1/1/1	3	1	11			30	22	11	75	11	0
$[(CH_3)_2N]_3P$	1/1/1	20	5			1		1		7	11	74
$(C_6H_5)_2NPCl_2$	2/1/1	20	28				22[g]			50	11	3

[a] Solvent: n-heptane. [b] All yields are based on ferrocene. [c] Approximate yield based on ferrocene. (Solids were isolated consisting of approximately 50% ferrocenyl, which appeared to be a monoferrocenylated phosphoro-aluminum derivative. They were not characterized further.) [d] Column chromatography[1] was not employed; hence $(Fc)_3P$ was isolated only as the oxide. [e] Isolated as $FcPH(O)OH$. [f] Yields on increasing $AlCl_3$ to 4 equivalents: $(Fc)_3P$, 45%; $(Fc)_3PO$, 5%; $(Fc)_2P(O)OH$, 2%; additional product, 13%; recovered FcH, 14%. [g] Includes 3% isolated as the trivalent amide.

TABLE 2

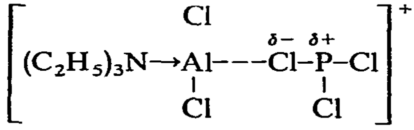
EFFECT OF ADDED DONOR ON THE ALUMINUM CHLORIDE-CATALYZED REACTIONS OF P^{III} CHLORIDES WITH FERROCENE

P^{III} chloride	Added donor	Molar ratio FcH/P^{III} chloride/$AlCl_3$/donor	Reflux time (h)[a]	Product yields (%)[b]									Additional product (%)[c]	Recovered FcH (%)
				$(Fc)_3P$	$(Fc)_3PO$	$(Fc)_2PCl$	$(Fc)_2$-P(O)H	$(Fc)_2$-$P(O)NR_2$	$(Fc)_2$-P(O)OH	$FcPCl_2$	FcPH-(O)OH	Total		
$(CH_3)_2NPCl_2$		3/1/1/0	20	33	10	15	2				1	61	4	29
$(CH_3)_2NPCl_2$	$(C_2H_5)_3N$	3/1/1/1	20	6	2						9[d]	17	5	60
$(CH_3)_2NPCl_2$		2/1/1/0	20	16	29	12		5	2			64	4	8
$(CH_3)_2NPCl_2$	$(C_2H_5)_3N$	2/1/1/1	20	5	4				1		10[d]	20	4	66
$(CH_3)_2NPCl_2$		1/1/1/0	3	1	11			30	22	11		75	11	0
$(CH_3)_2NPCl_2$	$(C_2H_5)_3N$	1/1/1/1	3	4	3		4		4		32[d]	47	10	40
PCl_3		3/1/1/0	20		<1							<1	0	90
PCl_3		1/1/1/0	20		1				<1			<2	0	69
PCl_3	$(C_2H_5)_3N$	1/1/1/0.5	20	3	34		1		26		2	66	14	9
PCl_3	$(C_2H_5)_3N$	1/1/1/1	20		25				2	25		52	23	0
PCl_3	$(C_2H_5)_3N$	1/1/1/2	20		2		1				1	4	7	68
$(C_2H_5)_2NPCl_2$		1/1/1/0	20		53	9		13	15	5		95	5	0
$(C_2H_5)_2NPCl_2$	$(C_2H_5)_2NPCl_2$	1/1/1/2	20		16			18				34	35	4

[a] Solvent: n-heptane. [b] All yields are based on ferrocene. [c] Approximate yields based on ferrocene; *cf.* footnote *c* Table 1. [d] Capable of isolation as $FcPCl_2$.

The PCl_3 amine case may be represented as in eqn. (2), and as expected, this reaction was inhibited when the molar ratio of amine to $AlCl_3$ was two (Table 2).

$$[(C_2H_5)_3N\rightarrow AlCl_2]^+[AlCl_4]^- + PCl_3 \rightarrow$$

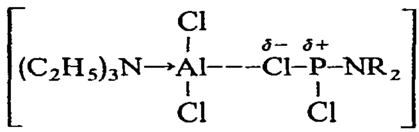


$$\left[(C_2H_5)_3N\rightarrow \overset{Cl}{\underset{Cl}{Al}}---\overset{\delta-}{Cl}-\overset{\delta+}{\underset{Cl}{P}}-Cl\right]^+[AlCl_4]^- \qquad (2)$$

When the ratio was one, however, the inhibition expected on the basis of equation (2) was almost non-existent (*cf.* ratio of one-half, Table 2), possibly due to a competitive interaction between the amine and PCl_3[11]. In comparing the over-all yields listed in Table 2, solids isolated but not fully characterized should be taken into account as product (see Table). The solids, consisting of approximately 50% ferrocenyl, were obtained in insignificant-to-appreciable amount from most of the reactions examined in this work, and appeared to be a monoferrocenylated phosphoro–aluminum derivative, possibly polymeric in nature.

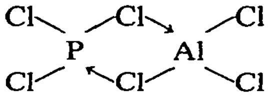
As expected, R_2NPCl_2 used in excess not only produced less tertiary product, but also served to inhibit its own reaction with ferrocene (Table 2) in terms of over-all yield. The amide, however, being a weaker donor than triethylamine, was not as effective an inhibitor as the amine (compare PCl_3/amine case, Table 2). In performing the reactions of R_2NPCl_2 in the presence of the amine (Table 2), R_2NPCl_2 was added dropwise to the mixtures already containing the amine and $AlCl_3$, and this is reflected in eqn. (3) where amine in excess of the indicated stoichiometry would serve to inhibit the reactions.

$$[(C_2H_5)_3N\rightarrow AlCl_2]^+[AlCl_4]^- + Cl_2PNR_2 \rightarrow$$



$$\left[(C_2H_5)_3N\rightarrow \overset{Cl}{\underset{Cl}{Al}}---\overset{\delta-}{Cl}-\overset{\delta+}{\underset{Cl}{P}}-NR_2\right]^+[AlCl_4]^- \qquad (3)$$

The low reactivity of PCl_3 in the absence of the amine (Table 2) was possibly the result of the high acceptor strength of both PCl_3 and $AlCl_3$ giving rise to associated species such as E or higher order, in a non-polar solvent such as n-heptane.



E

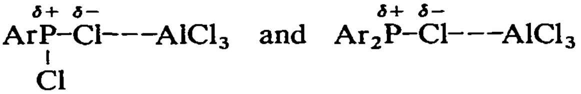
The fact that a trace of ferrocene derivatives *did* form may be due to *some* contribution from species of the type,

$$Cl_2\overset{\delta+}{P}-\overset{\delta-}{Cl}---AlCl_3$$

which may be present in greater amount when excess PCl_3 is used as the solvent[2].

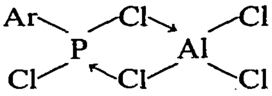
When the solvent was methylene chloride, only a trace amount of product was isolated and identified[1].

Ferrocene derivatives are obtained in high yields[3] from $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$ probably due to the fact that they are weaker acceptors than PCl_3[11]. Contrary to the case of PCl_3, phosphorus electrophiles of the type,

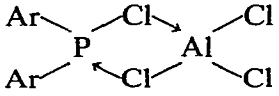


$$\underset{\text{Cl}}{\text{Ar}\overset{\delta+}{\text{P}}}-\overset{\delta-}{\text{Cl}}\text{---AlCl}_3 \quad \text{and} \quad \text{Ar}_2\overset{\delta+}{\text{P}}-\overset{\delta-}{\text{Cl}}\text{---AlCl}_3$$

should have a greater tendency to form than associated species such as F and G.



F



G

It is important to note that in accounting for results obtained in the present and earlier work[3], it is unnecessary to formulate as an intermediate a 3/1 complex between any P^{III} species and $AlCl_3$. This is contrary to the case of reactions of benzene and its derivatives[13]. For the most part, reactions of ferrocene with R_2NPCl_2 gave products in good-to-excellent over-all yields although the ratio of phosphorus compound to $AlCl_3$ was unity (Tables 1 and 2). Yields were found to suffer markedly when the ratio was 3.

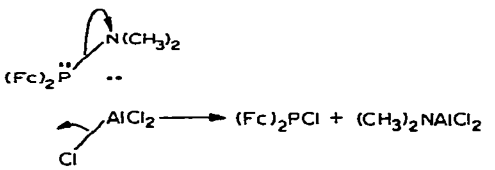
Cleavage of the P–N bond by aluminum chloride with P–Cl bond formation

The concept of "too much donor—too little aluminum chloride" was indeed applicable to $(R_2N)_3P$. When the aluminum chloride was increased from two to four equivalents in the reaction of three equivalents of ferrocene with $[(C_2H_5)_2N]_3P$, yields of identified products increased from 6% to 52% (Table 1), the result directly attributable to cleavage of P–N bonds by aluminum chloride via coordination to nitrogen. Cleavage of P–N by aluminum chloride is not considered to generate a phosphorus electrophilic species directly, but rather to result in the formation of a P–Cl bond from which the electrophile arises by interaction with the amine–$AlCl_3$ complex. Thus a reaction of equivalent amounts of ferrocene, anhydrous aluminum chloride, and *N,N*-dimethyldiferrocenylphosphinous amide (V), the latter prepared in 94% yield by the aminolysis of $(Fc)_2PCl$ with dimethylamine, produced (II) in 19% yield in addition to (IIa), 13%, and tertiary products (I) and (Ia) in a combined yield of 31% [eqn. (4)].

$$\underset{\text{(V)}}{(\text{Fc})_2\text{PN}(\text{CH}_3)_2} \xrightarrow[\text{AlCl}_3]{\text{FcH}} \underset{\text{(I)}}{(\text{Fc})_3\text{P}} + \underset{\text{(Ia)}}{(\text{Fc})_3\text{PO}} + \underset{\text{(II)}}{(\text{Fc})_2\text{PCl}} + \underset{\text{(IIa)}}{(\text{Fc})_2\text{P(O)H}} \tag{4}$$

Formation of (II) in this reaction is best explained on the basis that P–N cleavage involves the bonding of aluminum chloride to nitrogen. This view is supported by results obtained on refluxing $(CH_3)_2NPCl_2$ and $[(C_2H_5)_2N]_3P$ with equivalent amounts of $AlCl_3$ in the absence of ferrocene. In the former case P–N bond cleavage occurred and PCl_3 was obtained in 26% yield. In the latter case, an undistillable oil was formed, most likely the P→Al complex. That PCl_3 in the former case did not arise by disproportionation was apparent when treatment of the undistillable portion of the reaction products with pyridine—to complex the aluminum chloride—failed to produce $[(CH_3)_2N]_2PCl$. This is in accord with the fact that $(C_2H_5)_2NPCl_2$ is formed by recombination between PCl_3 and an equivalent of $[(C_2H_5)_2N]_2PCl$[14].

Both PCl_3 and $(Fc)_2PCl$ are considered to arise by a chloride shift as exemplified by the formation of the latter, eqn. (5).

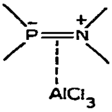


(5)

(II)

Since $(Fc)_2PN(CH_3)_2$ lacks P–Cl—or other means of withdrawing electron density from phosphorus in view of the strong electron-donating character of the ferrocenyl group[15]—the driving force for N-coordination of aluminum chloride may be found in the fact that the combined energies of formation of the P–Cl[16] and Al–N[*] bonds (the latter as in R_2NAlCl_2) are greater than the dissociation energies of the P–N[16] and Al–Cl[*] bonds. It is suggested, moreover, that N-coordination may take precedence over P-coordination partly as a result of the unavailability of electrons on aluminum for back-bonding to phosphorus[**]. The tendency towards *initial* attack on the nitrogen atom would, of course, decrease in the order, $R_2NPX_2 > (R_2N)_2PX > (R_2N)_3P$, and be at a minimum in the case of $(R_2N)_3P$ where the phosphorus atom is the overwhelming nucleophilic center.

The dramatic increase in yield obtained from $[(C_2H_5)_2N]_3P$ and ferrocene on increasing $AlCl_3$ (discussed above) would tend to rule out the possibility in that case at least, that the nitrogen unshared pair may coordinate $AlCl_3$, and be involved at the same time in π-bonding to phosphorus (H)[†].



H

It is envisioned that after the initial attachment of $AlCl_3$ to phosphorus as in C, additional $AlCl_3$ coordinates to nitrogen resulting in cleavage of the first P–N bond as depicted in eqn. (6)[††].

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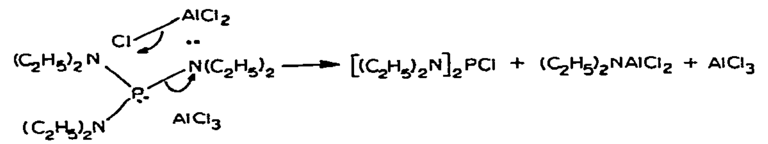
[*] Comparative B–N and B–Cl bond energies are given in ref. 17.

[**] Similar arguments can be posed for the coordination of HCl[4,18], BCl_3 and BF_3[19] to nitrogen of P–N. In addition to $N_{2p} \rightarrow P_{3d}$ π-bonding in P^{III}–N compounds, suggested to account for the P-coordination of such molecules as BH_3 and CH_3I (see refs. cited in ref. 20), bonding to phosphorus may be due in part to transfer of electron density (albeit to a small degree) from these acceptors to the available 3*d* orbitals of phosphorus resulting in a lowering of the energy of the molecule by delocalization effects. NH_2Cl[21], CS_2[22], and certain transition metals[23] would also appear to be acceptors with the capacity to back-bond.

The authors thank Prof. Hans B. Jonassen of Tulane University for this suggestion.

[††] An attempt was made, unsuccessfully, to isolate species containing P–Cl, formed by the interaction of the triamide with four equivalents of $AlCl_3$.



(6)

The bonding of $AlCl_3$ molecules to both the phosphorus and nitrogen atoms of the triamide is very likely grossly related to the situations in which $(CH_3)_2NP(CH_3)_2$ forms a diadduct with two molecules of BH_3[24], and undergoes P–N bond cleavage by the action of a second molecule of $B(CH_3)_3$[19]. Both the phosphorus and nitrogen atoms of this amide, moreover, appear capable of bonding $Al(C_2H_5)_3$[25].

It was found that the P–N bond shows less tendency to cleave when nitrogen is substituted with phenyl groups. *N,N*-Diphenyldiferrocenylphosphinic and -phosphinous amides [(IIIa) and (III), respectively; $R = C_6H_5$] were obtained in a combined yield of 22% while the *N,N*-diethyl- and *N,N*-dimethylphosphinic amides were obtained in zero and 5% yields, respectively, from reactions of the appropriate R_2NPCl_2 under comparable conditions (Table 1). This reduced tendency to cleave is attributed to a steric effect in which the phenyls, in a step analogous to (5), interfere with the chloride shift. The amide, $(Fc)_2PN(C_6H_5)_2$, represents the only trivalent amide isolated from the Friedel–Crafts reaction mixtures.

Triferrocenylphosphine via disproportionation

$(Fc)_3P$ and its oxide were isolated in a combined yield of 10% on refluxing the amide (V) with an equivalent of $AlCl_3$ in the absence of ferrocene. Although the chloride (II) was expected to form as product of the cleavage of P–N by $AlCl_3$, none was isolated. The tertiary products likely arose by the disproportionation of (II) since on substitution of (II) for (V), the phosphinic acid (IVa), the product of the hydrolysis of (IV), was isolated in 11% yield in addition to 23% of the tertiary products. Thus

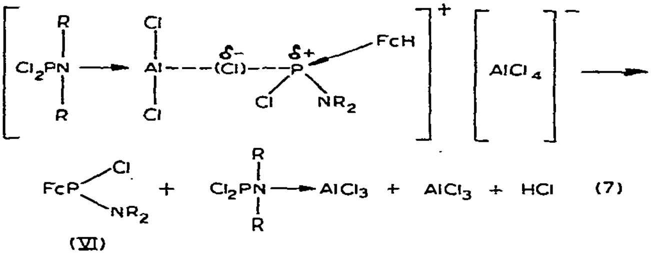
$$\begin{array}{ccccc} 2\,(Fc)_2PN(CH_3)_2 & \xrightarrow{AlCl_3} & 2\,(Fc)_2PCl & \xrightarrow{AlCl_3} & FcPCl_2 + (Fc)_3P \\ (V) & & (II) & & (IV)\quad\ (I) \end{array}$$

An attempt to obtain a complete material balance was not made. No previous example of the disproportionation of R_2PCl in the presence of $AlCl_3$ appears to have been reported. Related types of compounds are known to disproportionate under these[26, 27] and pyrolytic[28, 29] conditions. It was determined that (II) does not undergo disproportionation in refluxing n-heptane without $AlCl_3$.

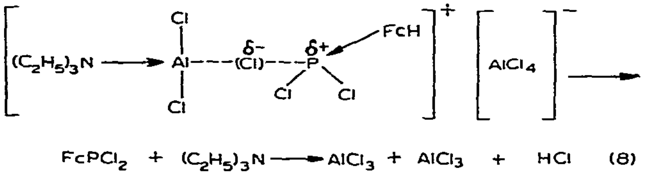
It is now apparent that when $(Fc)_3P$ is prepared under Friedel–Crafts conditions, it arises two ways: by a stepwise electrophilic process[2, 3] *and* by disproportionation. When $(Fc)_2PCl$ and $AlCl_3$ were allowed to interact with an equivalent of ferrocene present, the yield of $(Fc)_3P$ and its oxide rose from 23% to 48%. The increase in yield as a minimum, is attributable to electrophilic substitution. The phenomenon of disproportionation together with the strong nucleophilic character of ferrocene explain the fact that products obtained from reactions of the present and earlier work[2] were largely top-heavy with tertiary compounds. No evidence has been obtained that disproportionation occurs in $AlCl_3$-catalyzed reactions of $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$ with ferrocene[3].

Mechanism of formation of ferrocene derivatives

. Formulations of the transition state such as depicted in eqns. (7) and (8), resembling that proposed for the silylation of ferrocene[30], are suggested for the formation of phosphorus-containing ferrocene derivatives in the presence of donor-complexed aluminum chloride.


(VI)

(7)


(8)

Although the primary site in the ferrocene molecule for interaction with phosphorus (or arsenic) electrophiles has not been established[31], that site is more likely to be the cyclopentadienyl ring π system[30, 32] than the iron atom[33].

For the reaction of R_2NPCl_2, compounds (I)–(IV) may be depicted as arising analogously to compound (VI) [eqn. (7)], from the appropriate precursors. The latter are capable of forming by a multitude of paths encompassing electrophilic substitution, cleavage of the P–N bond by $AlCl_3$, and disproportionation. Amidic products, (III) and (VI), may serve to coordinate aluminum chloride in the same manner as R_2NPCl_2.

Ferrocene derivatives obtained from the reactions of $(R_2N)_2PCl$ and $(R_2N)_3P$ may be represented as arising in a similar manner after P–N bond cleavage and formation of P–Cl.

That collapse of the activated complexes [*e.g.* eqns. (7) and (8)] may produce uncomplexed ferrocene derivatives, was evident in two cases: $FcPCl_2$ and $(Fc)_2PCl$, in those instances where they could be isolated, were readily obtained from the heptane phase of the reaction mixtures without treatment with water.

EXPERIMENTAL

General

Melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were taken with Nujol mulls (Perkin–Elmer 21 spectrophotometer).

Materials

Ferrocene was obtained from Arapahoe Chemicals, Inc. and was used as received. PCl_3 and n-heptane (both Mallinkrodt, analytical reagent) were used directly, with the exception that the latter was dried over $LiAlH_4$ when indicated below. Anhydrous $AlCl_3$ (Fisher Scientific Co., reagent) was used as obtained. Activated alumina (chromatographic grade; 80–200 mesh) was obtained from Matheson, Coleman and Bell. Triethylamine was dried by refluxing 5 h over barium oxide and was distilled under dry nitrogen.

The P^{III} amides, $(C_2H_5)_2NPCl_2$[34], $(CH_3)_2NPCl_2$[4], $[(C_2H_5)_2N]_2PCl$[35], $[(CH_3)_2N]_2PCl$*, $[(C_2H_5)_2N]_3P$[34], and $[(CH_3)_2N]_3P$[4], were prepared by reactions similar to those described in the literature.

$(C_6H_5)_2NPCl_2$, b.p. 140°/0.7 mm, was prepared in 83% yield from 1.0 mole of diphenylamine and 0.5 mole of PCl_3 in a total of 1 l of dry ether. (Found: C, 53.44; H, 3.86; Cl, 25.42. $C_{12}H_{10}Cl_2NP$ calcd.: C, 53.35; H, 3.73; Cl, 26.25%.)

Aluminum chloride-catalyzed reactions of ferrocene with phosphoramidous dichlorides, phosphorodiamidous chlorides, phosphorus triamides, and phosphorus trichloride

Procedures A and B typify the general method employed for the preparation and isolation of products (Tables 1 and 2).

*A. Triferrocenylphosphine (I), its oxide (Ia), diferrocenylphosphinous chloride (II), diferrocenylphosphine oxide (IIa), and ferrocenylphosphinic acid (IVa)***

A solution of 7.3 g (0.05 mole) of $(CH_3)_2NPCl_2$ in 100 ml of n-heptane was added dropwise during 20 min to 27.9 g (0.15 mole) of ferrocene and 6.7 g (0.05 mole) of $AlCl_3$ in 250 ml of the same solvent with stirring under nitrogen. The mixture was refluxed 20 h with stirring, after which the clear, orange heptane phase was decanted while hot, concentrated to approximately 250 ml and allowed to stand overnight. The red-orange, heptane-insoluble semi-solid phase was hydrolyzed in 300 ml of water with stirring until all solids became pale yellow. The solids were collected on a filter and air-dried†, then extracted with 1 l of boiling benzene in portions leaving 2.3 g of insoluble solids (A). The combined extracts were dried over anhydrous Na_2SO_4, reduced to one-half the volume, then chromatographed on a 100-cm column of activated alumina. Elution with benzene and evaporation of the solvent *in vacuo* afforded pale yellow, hair-like crystals of (I); yield 9.7 g (33%). Crystallization from n-heptane or 95% ethanol gave fine yellow needles with m.p. 271–273° (closed capillary). The compound was infusible and decomposed under normal melting procedure. The melting point was observed by immersion of the sample in the heating bath at 270°. Besides the usual ferrocene absorptions††, the IR spectrum of (I) showed ν_{max} 1202, 1195, 1162 cm^{-1} (all in-plane C–H bending[2,3,8]). The IR spectrum of the methiodide that precipitated from a benzene solution of (I) on treatment with methyl iodide was identical with that of an authentic sample[2]. (Found: C, 61.36; H, 5.33; Fe, 28.14; P, 5.00. $C_{30}H_{27}Fe_3P$ calcd.: C, 61.48; H, 4.64; Fe, 28.59; P, 5.28%.)

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* *Cf.* E. M. Evleth, Jr. *et al.*, ref. 5.

** A reaction yielding only tertiary products [(I) and (Ia)] was described in detail in the preliminary communication[1].

† Hydrolysis under nitrogen, and drying *in vacuo* helped to minimize the oxidation of the phosphine (I) to its oxide (Ia).

†† Phosphorus-containing ferrocene (FcH) derivatives show bands in the following regions[2,3,8]: 3060–3120 (C–H stretching), 1410–1430 (C–C stretching), 1305–1320 (Fc–P), 1105–1112 (asym. ring breathing; monosubstituted FcH), 1015–1045 (Fc–P), 1000–1010 (in-plane C–H bending; monosubstituted FcH), 810–830 cm^{-1} (out-of-plane C–H bending).

The column was eluted next with chloroform, the solvent was evaporated, and the yellow-orange solids extracted with 500 ml of boiling n-heptane in portions leaving 3.0 g (10%) of insoluble (Ia). Recrystallization of (Ia) from benzene/heptane (10/1) or ethylene chloride gave short, infusible, yellow needles. The IR spectrum was identical with that of an authentic sample[2]. Concentration and cooling of the heptane extract produced 0.6 g of (IIa) [3% (2% based on ferrocene)]. Recrystallization from benzene/heptane gave orange needles, slightly soluble in hot water, m.p. 190–193° (decompn.). Immersion of the sample in the heating bath at 193° gave m.p. 194–195° without decomposition. The IR spectrum of (IIa) showed the usual ferrocene absorptions*, also ν_{max} 2350 (P–H stretching), 1222 and 1200 (in-plane C–H bending[2,3,8]), 1189 (P→O stretching), 965 and 953 cm^{-1} (P–H deformation). (Found: C, 57.62; H, 4.55; Fe, 26.86; P, 7.11. $C_{20}H_{19}Fe_2OP$ calcd.: C, 57.46; H, 4.58; Fe, 26.72; P, 7.41%.)

The original heptane phase of the reaction mixture was filtered after standing overnight, affording 4.8 g of (II) [22% (15% based on ferrocene)]; yellow crystals sometimes orange needles from dry n-heptane, m.p. 183–184° (closed capilary). Besides the usual ferrocene absorptions*, the IR spectrum of (II) showed ν_{max} 1198, 1192, 1162 cm^{-1} (all in-plane C–H bending[2,3,8]). (Found: C, 55.42, H, 4.55; Cl, 6.93; Fe, 25.62; P, 6.93. $C_{20}H_{18}ClFe_2P$ calcd.: C, 55.03; H, 4.17; Cl, 8.12; Fe, 25.59; P, 7.10%.) The identity of (II) was confirmed via conversion to diferrocenylphenylphosphine[3] and to (IIa) by treatment with phenylmagnesium bromide and trituration with hot water, respectively. Boiling of (II) with aqueous KOH largely produced (IIa), but also caused some oxidative hydrolysis to (IIIb)[2] which precipitated on acidification of the solution.

The filtrate obtained on removal of (II) from the heptane phase of the reaction mixture was evaporated in an air stream, and the orange crystalline residue extracted with boiling petroleum ether (b.p. 36–70°) leaving an insoluble, light yellow solid. Extraction of the latter with boiling n-heptane, filtering, and cooling gave 0.3 g (2%) of (IVa) (1% based on ferrocene) as orange platelets, m.p. 137–138°. Identity was confirmed by mixed melting-point determination and comparison of IR spectrum with that of an authentic sample[2]. The petroleum ether extract was evaporated giving 8.1 g (29%) of unchanged ferrocene.

Solids (A), insoluble or showing only limited solubility in common solvents, were dissolved in 2 *N* sodium ethoxide. The solution was acidified dropwise with concentrated HCl, and the precipitated brownish solids were filtered and discarded. Dilution of the filtrate with water caused pale orange solids to separate; yield 2.0 g (4% based on ferrocene and a molecular content of 50% ferrocenyl). Recrystallization from methanol (CO_2/acetone) produced orange-tan solids showing no melting up to 360°. The IR spectrum showed absorptions characteristic of phosphorus-containing ferrocene derivatives*, in addition to bands at 1180 and 1160 cm^{-1}. (Found: C, 43.76; H, 3.59; Al, 2.27; Fe, 15.57; P, 12.60%.) The solids were not characterized further.

B. Triferrocenylphosphine (I), its oxide (Ia), N,N-dimethyldiferrocenylphosphinic amide (IIIa; R=CH_3), diferrocenylphosphinic acid (IIIb), and ferrocenylphosphonous dichloride (IV)

The reaction of $(CH_3)_2NPCl_2$ (14.6 g; 0.1 mole) with ferrocene (18.6 g; 0.1

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* See footnote, p. 153.

mole) and $AlCl_3$ (13.4 g; 0.1 mole) was performed similarly to the above reaction except that the reflux period was shortened to 3 h. The clear, orange heptane phase was transferred under nitrogen, while hot, to a distillation flask, and the solvent, traces of ferrocene, and unreacted phosphoramidous dichloride were removed under reduced pressure (aspirator) on a steam bath. The remaining red oil, crude (IV), was purified by adding 100 ml of dry heptane and removing the insoluble white solids by filtration in a nitrogen atmosphere, then the solvent under reduced pressure; yield 4.2 g (11%). The IR spectrum of the undistillable red oil was identical with that of an authentic sample of (IV)[8].

Similarly to the work-up of the reaction mixture in Procedure A, the heptane-insoluble, semi-solid phase of the reaction mixture was treated with water (500 ml), and extracted away from 4.5 g of insoluble solids (A) with boiling benzene (800 ml); the extract was dried over anhydrous Na_2SO_4, concentrated to one-half the volume, and chromatographed on activated alumina. Elution with benzene, as in Procedure A, produced (I); yield 0.2 g (1%). Elution next with chloroform followed by evaporation of the solvent and extraction of the solid residue with boiling n-heptane (750 ml), as in Procedure A, gave insoluble (Ia); yield 2.2 g (11%). The IR spectra of both products were identical with those of the samples described under Procedure A. Evaporation of the heptane extract produced 7.0 g (30%) of (IIIa) ($R = CH_3$); pale yellow-orange crystals from n-heptane, m.p. 195–196° (decompn.) when the sample was immersed in the heating bath at 193°. Besides the usual ferrocene absorptions*, the IR spectrum showed ν_{max} 1218, 1200, 1160 (all ferrocene in-plane C–H bending[2,3,8]), 1177 ($P \rightarrow O$ stretching?), 981 [$(CH_3)_2N$–P**], 706 cm^{-1} (P–N stretching). (Found: C, 57.48; H, 5.24; Fe, 23.99; N, 2.77; P, 6.70. $C_{22}H_{24}Fe_2NOP$ calcd.: C, 57.43; H, 5.26; Fe, 24.28; N, 3.04; P, 6.73%.)

Further elution of the column with 5 *N* aqueous NaOH diluted with an equal volume of methanol gave a red-brown taffy on evaporation of the solvents. Extraction with water followed by gravity filtration of the extract and dropwise acidification of the filtrate with concentrated HCl afforded 4.7 g (22%) of (IIIb) as the pale yellow, infusible monohydrate. The IR spectrum was identical with that of an authentic sample[2].

Treatment of solids (A) in the same manner as the solids (A) obtained under Procedure A above, gave the same product; yield 4.1 g (11% based on ferrocene and a molecular content of 50% ferrocenyl). The IR spectrum was identical with that of the sample described above.

C. N,N-Diethyldiferrocenylphosphinic amide [*(IIIa)*; $R = C_2H_5$], *N,N-diphenyldiferrocenylphosphinic amide* [*(IIIa)*; $R = C_6H_5$], *and N,N-diphenyldiferrocenylphosphinous amide* [*(III)*; $R = C_6H_5$]

Starting with the appropriate N-substituted P^{III} amides (Tables 1 and 2), the following amidic products were obtained in the same manner as (IIIa) ($R = CH_3$) in Procedure B, above. Yields are given in Tables 1 and 2.

(IIIa) ($R = C_2H_5$), was isolated as the monohydrate; orange rhombic crystals from n-heptane. Drying 1 h at 100° *in vacuo* gave the anhydrous product, m.p. 134–136.5°. The IR spectra of both the hydrated and anhydrous products showed the

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* See footnote, p. 153.

** *Cf.* E. M. Evleth, Jr *et al.*, ref. 5.

usual ferrocene absorptions★. In addition, the hydrate showed ν_{max} 3470 [bonded O–H (H_2O) stretching], 1220, 1205, 1187 (sh), 1178, 1162 (all ferrocene in-plane C–H bending[2,3,8]), 1153 (H_2O-bonded P→O stretching?), 942 [$(C_2H_5)_2N$–P?], 690 cm^{-1} (P–N stretching). The anhydrous product showed ν_{max} 1220, 1198, 1160 (all ferrocene in plane C–H bending[2,3,8]), 1177 (P→O stretching?), 944 [$(C_2H_5)_2N$–P?], 693 cm^{-1} (P–N stretching). (Found: C, 58.96; H, 5.89; Fe, 22.62; N, 3.13; P, 6.31. $C_{24}H_{28}Fe_2NOP$ calcd.: C, 58.93; H, 5.77; Fe, 22.84; N, 2.86; P, 6.33%.) (Found: H_2O, 3.28 (by wt. loss). $C_{24}H_{28}Fe_2NOP \cdot H_2O$ calcd.: H_2O, 3.55%.)

Both (III) and (IIIa) ($R = C_6H_5$) were obtained by the usual elution of the column with chloroform. The first of two slightly overlapping bands was evaporated under an air stream producing a red oil. Extraction of the oil with ether, filtering and removal of the ether on a steam bath gave oily orange crystals. After washing with cold ether, the pale yellow crystals were collected on a filter. Recrystallization from n-heptane afforded (III) as a yellow powder, m.p. 205–208° (decompn.) on heating 10°/min; infusible under normal melting procedure. The IR spectrum of (III) showed the usual ferrocene absorptions★, except that the band in the region, 1305–1320 (Fc–P) was obscured by a strong band at 1330 cm^{-1}. In addition, the spectrum showed ν_{max} 3420★★ (phenyl C–H stretching), 1600, 1526, 1506 (all phenyl C=C in-plane vibrations), 1193, 1184, 1161 (all ferrocene in-plane C–H bending[2,3,8]), 747 and 699 (phenyl C–H out-of-plane deformations), 638 cm^{-1} (P–N stretching). The product was precipitated immediately on treatment with methyl iodide in benzene; however, the methiodide was not characterized. (Found: C, 67.61; H, 5.77; Fe, 19.02; N, 2.65; P, 5.49. $C_{38}H_{28}Fe_2NP$ calcd.: C, 67.69; H, 4.96; Fe, 19.62; N, 2.46; P, 5.44%.)

Evaporation of the solvent from the eluted second band gave bright yellow solids. Extraction with 500 ml of boiling n-heptane afforded insoluble (IIIa). [Evaporation of the heptane extract produced additional (III).]. Recrystallization of (IIIa) from benzene gave orange crystals, m.p. 255–256° (decompn.) when the sample was immersed in the heating bath at 253°. The IR spectrum showed the usual ferrocene absorptions★, also ν_{max} 3260 and 3170★★ (phenyl C–H stretching), 1596, 1545, 1506 (all phenyl C=C in-plane vibrations), 1198 (sh), 1194, 1145 (all ferrocene in-plane C–H bending[2,3,8]), 1188 (sh) and/or 1177 (P→O stretching?), 757 and 701 (phenyl C–H out-of-plane deformations), 683 cm^{-1} (P–N stretching). No methiodide was obtained on treatment of (IIIa) with methyl iodide in benzene. (Found: C, 65.32; H, 4.87; Fe, 18.89; N, 2.63; P, 5.40. $C_{32}H_{28}Fe_2NOP$ calcd.: C, 65.84; H, 4.82; Fe, 19.08; N, 2.39; P, 5.29%.)

D. Special notes.

Separation of the secondary phosphine oxide (IIa) from the phosphinic amide (IIIa). In those few reactions producing both (IIa) and (IIIa), the column was eluted with chloroform and the solvent evaporated as usual (Procedures A and B, above). Compound (IIIa) was extracted from the residue first with hot n-heptane, then (IIa) with boiling heptane, leaving any tertiary phosphine oxide (Ia) as a heptane-insoluble residue.

Isolation of both phosphinous chloride (II) and phosphonous dichloride (IV). In

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★ See footnote, p. 153.

★★ Drying of compounds (III) and (IIIa) (R = phenyl) *in vacuo* for 3 h at 100° produced no change in the IR spectra.

those few reactions producing appreciable amounts of (IV) in addition to (II), the former, after crystallization of the latter from the heptane phase of the reaction mixture as in Procedure A, was obtained from the filtrate in the manner described for the isolation of (IV) in Procedure B.

Reactions under HCl, and bubbling of nitrogen. Hydrogen chloride was generated by the slow, dropwise addition of concentrated H_2SO_4 to concentrated HCl, and led into the reaction flask to serve as a blanketing atmosphere. The nitrogen inlet extended beneath the surface of the reaction mixture to effect bubbling.

Reactions with added donor. Triethylamine was added to ferrocene and $AlCl_3$ prior to the dropwise addition of the P–Cl reactant species.

Preparation of N,N-dimethyldiferrocenylphosphinous amide (V)

A solution of the phosphinous chloride (II) (10.0 g; 23 mmoles) in benzene (200 ml) with anhydrous dimethylamine (25 ml) was boiled to dryness over a period of 0.5 h on a steam bath, giving yellow solids. Extraction with petroleum ether (b.p. 36–70°), and crystallization, afforded 94% (9.6 g) of (V); golden needles, m.p. 120–121°. (Found: C, 59,89; H, 5.61; N, 3.13. $C_{22}H_{24}Fe_2NP$ calcd.: C, 59.36; H, 5.43; N, 3.15%.)

The IR spectrum showed the usual ferrocene absorptions*, also ν_{max} 1203, 1192, 1159 (all ferrocene in-plane C–H bending[2,3,8]), 983 [$(CH_3)_2N$–P**], 662 cm^{-1} (P–N stretching). The product was precipitated immediately on treatment with methyl iodide in benzene; however, the methiodide was not characterized.

The identity of (V) was confirmed by quantitative oxidation to (IIIa) (above) by refluxing 16 h with a 10-molar excess of activated MnO_2*** in n-heptane.

Aluminum chloride-catalyzed reaction of ferrocene with N,N-dimethyldiferrocenylphosphinous amide (V)

Ferrocene (0.70 g; 3.8 mmoles), $AlCl_3$ (0.50 g; 3.8 mmoles), and (V) (1.67 g; 3.8 mmoles) in dry n-heptane (100 ml) were refluxed 20 h with stirring under nitrogen. Concentration and cooling of the heptane phase gave 0.31 g (19%) of diferrocenylphosphinous chloride (II), and 0.20 g (29%) of unchanged ferrocene. Work-up of the heptane-insoluble semi-solid phase as in Procedure A above produced 0.61 g (27%) of triferrocenylphosphine (I), 0.10 g (4%) of its oxide (Ia), and 0.20 g (13%) of diferrocenylphosphine oxide (IIa). The IR spectra of all products were identical with the spectra of authentic samples (above).

Aluminum chloride-catalyzed reaction of ferrocene with diferrocenylphosphinous chloride (II)

Ferrocene (1.86 g; 10.0 mmoles), $AlCl_3$ (1.33 g; 10.0 mmoles), and (II) (4.37 g; 10.0 mmoles) were refluxed 20 h in dry n-heptane (150 ml) with stirring under nitrogen. Work-up of the reaction mixture as in Procedure A above produced 1.93 g (33%) of triferrocenylphosphine (I), 0.90 g (15%) of its oxide (Ia), 1.07 g (24%) of unchanged phosphinous chloride (II), and 1.11 g (27%) of diferrocenylphosphine oxide (IIa), in addition to 0.65 g (35%) of unchanged ferrocene. The IR spectra of all products were

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* See footnote, p. 153.

** *Cf.* E. M. Evleth, Jr. *et al.*, ref. 5.

*** MnO_2-A was prepared from manganous carbonate as described in ref. 36.

identical with those of authentic samples (above).

Interaction of N,N-dimethyldiferrocenylphosphinous amide (V) with aluminum chloride

A mixture of 3.02 g (6.8 mmoles) of (V) and 0.90 g (6.8 mmoles) of anhydrous $AlCl_3$ was refluxed 20 h in 100 ml of dry n-heptane with stirring under nitrogen. Work-up of the reaction mixture and isolation of products according to procedures described in B and D above, gave 0.18 g (9%) of triferrocenylphosphine (I), 0.02 g (1%) of its oxide (Ia), 1.10 g (39%) of diferrocenylphosphine oxide (IIa), 0.10 g (3%) of *N,N*-dimethyldiferrocenylphosphinic amide (IIIa), and 0.12 g (4%) of diferrocenylphosphinic acid (IIIb). The IR spectra of all compounds were identical with those of authentic samples (above).

Interaction of diferrocenylphosphinous chloride (II) with aluminum chloride

A mixture of 3.05 g (7.0 mmoles) of (II) and 0.93 g (7.0 mmoles) of anhydrous $AlCl_3$ was refluxed 20 h in 100 ml of dry n-heptane with stirring under nitrogen. Work-up of the reaction mixture and isolation of products according to procedures described in A and B above, gave 0.07 g (3%) of triferrocenylphosphine (I), 0.43 g (20%) of its oxide (Ia), 0.56 g (19%) of diferrocenylphosphine oxide (IIa), 0.14 g (5%) of diferrocenylphosphinic acid (IIIb), and 0.20 g (11%) of ferrocenylphosphinic acid (IVa). The IR spectra of all compounds were identical with those of authentic samples (above). Heating of (II) 20 h in refluxing n-heptane in the absence of $AlCl_3$ produced no change in (II).

Interaction of N,N-dimethylphosphoramidous dichloride and hexaethylphosphorus triamide with aluminum chloride

A mixture of 14.6 g (0.1 mole) of the dichloride and 13.4 g (0.1 mole) of anhydrous $AlCl_3$ was refluxed 20 h in 250 ml of dry n-heptane with stirring under nitrogen. Distillation of the heptane phase gave 3.6 g (26%) of PCl_3. Treatment of the heptane-insoluble semi-solid phase of the reaction mixture with 7.9 g (0.1 mole) of pyridine (to complex the $AlCl_3$), followed by extraction with petroleum ether (b.p. 36–70°), and distillation, failed to produce any $[(CH_3)_2N]_2PCl$.

When the triamide was substituted for the dichloride, no species containing P–Cl could be isolated from the heptane phase. An undistillable moisture-sensitive oil was obtained from that phase but was not characterized. Similarly, the interaction of the triamide with four equivalents of $AlCl_3$, followed by treatment of the reaction mixture with four equivalents of pyridine, failed to yield species containing P–Cl.

Interaction of N,N-dimethylphosphoramidous dichloride and hexaethylphosphorus triamide with hydrogen chloride

The dichloride (29.2 g; 0.2 mole) in dry n-heptane (500 ml) was stirred 15 min under an atmosphere of HCl generated as described under D above, causing white solids to separate. The mixture was refluxed 20 h under HCl, after which 23.6 g (86%) of PCl_3 were obtained from the heptane phase by distillation, and 15.2 g (93%) of $(CH_3)_2NH \cdot HCl$ were obtained from the heptane-insoluble phase by extraction with methanol, and crystallization from methanol/ether.

In a similar manner, the triamide (24.7 g; 0.1 mole in 250 ml of n-heptane) gave $(C_2H_5)_2NPCl_2$ (5.0 g; 29%) and $[(C_2H_5)_2N]_2PCl$ (6.1 g; 29%) on distillation of the heptane phase. No PCl_3 was detected.

REFERENCES

1 G. P. Sollott and W. R. Peterson, Jr., *J. Organometal. Chem.*, 5 (1965) 491.
2 G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, 27 (1962) 4034.
3 G. P. Sollott, H. E. Mertwoy, S. Portnoy and J. Snead, *J. Org. Chem.*, 28 (1963) 1090; unpublished results [in part, *Chem. Abstr.*, 63 (1965) 18147a].
4 A. B. Burg and P. J. Slota, Jr., *J. Amer. Chem. Soc.*, 80 (1958) 1107.
5 A. B. Burg and P. J. Slota, Jr., *J. Amer. Chem. Soc.*, 82 (1960) 2148; K. Issleib and W. Seidel, *Chem. Ber.*, 92 (1959) 2681; H. Nöth and H. J. Vetter, *Chem. Ber.*, 96 (1963) 1109; E. M. Evleth, Jr., L. D. Freedman and R. I. Wagner, *J. Org. Chem.*, 27 (1962) 2192.
6 L. Maier, *Helv. Chim. Acta*, 47 (1964) 2129.
7 W. F. Little and R. Eisenthal, *J. Amer. Chem. Soc.*, 82 (1960) 1577.
8 G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, 29 (1964) 2451.
9 V. Mark, *J. Amer. Chem. Soc.*, 85 (1963) 1884.
10 J. R. Van Wazer, *Phosphorus and Its Compounds*, Vol. I, Interscience, New York, 1958, Chap. 2.
11 R. R. Holmes and E. F. Bertaut, *J. Amer. Chem. Soc. (London)*, 80 (1958) 2980, 2983; J. I. G. Cadogan, *Quart. Rev. (London)*, 16 (1962) 208, and references therein; E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw and B. C. Smith, *J. Chem. Soc.*, (1965) 4295, and references therein; W. R. Trost, *Can. J. Chem.*, 32 (1954) 356.
12 F. A. Drahowzal, in G. A. Olah (Ed.), *Friedel–Crafts and Related Reactions*, Vol. II, Part 1, Interscience, London, 1964, pp. 419, 420 and 444; and references therein.
13 G. M. Kosolapoff, in G. A. Olah (Ed.), *Friedel–Crafts and Related Reactions*, Vol. IV, Interscience, London, 1965, pp. 224, 228.
14 J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, 86 (1964) 811.
15 E. M. Arnett and R. D. Bushick, *J. Org. Chem.*, 27 (1962) 111.
16 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, London, 1962, p. 88.
17 H. A. Skinner and N. B. Smith, *Trans. Faraday Soc.*, 51 (1955) 19.
18 J. Singh and A. B. Burg, *J. Amer. Chem. Soc.*, 88 (1966) 718.
19 R. R. Holmes and R. P. Wagner, *J. Amer. Chem. Soc.*, 84 (1962) 357.
20 A. H. Cowley and R. P. Pinnell, *J. Amer. Chem. Soc.*, 87 (1965) 4454.
21 W. H. Hart and H. H. Sisler, *Inorg. Chem.*, 3 (1964) 617.
22 R. H. Cragg and M. F. Lappert, *J. Chem. Soc., A*, (1966) 82.
23 D. S. Payne and A. P. Walker, *J. Chem. Soc., C*, (1966) 498.
24 A. B. Burg and P. J. Slota, Jr., *J. Amer. Chem. Soc.*, 82 (1960) 2145.
25 D. F. Clemens, H. H. Sisler and W. S. Brey, Jr., *Inorg. Chem.*, 5 (1966) 527.
26 G. M. Kosolapoff and W. F. Huber, *J. Amer. Chem. Soc.*, 69 (1947) 2020; A. E. Senear, W. Valient and J. Wirth, *J. Org. Chem.*, 25 (1960) 2001.
27 D. R. Lyon and G. D. Mann, *J. Chem. Soc.*, (1942) 666.
28 G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 50.
29 R. L. Barker, E. Booth, W. E. Jones, A. F. Millidge and F. N. Woodward, *J. Soc. Chem. Ind., (London)*, 68 (1949) 289.
30 G. P. Sollott and W. R. Peterson, Jr., *J. Amer. Chem. Soc.*, 89 (1967) 5054.
31 G. P. Sollott and W. R. Peterson, Jr., *J. Org. Chem.*, 30 (1965) 389.
32 G. P. Sollott and W. R. Peterson, Jr., *J. Amer. Chem. Soc.*, 89 (1967) 6783.
33 M. Rosenblum and F. W. Abbate, *J. Amer. Chem. Soc.*, 88 (1966) 4178.
34 A. Michaelis, *Justus Liebigs Ann. Chem.*, 326 (1903) 129.
35 P. G. Chantrell, C. A. Pearce, C. R. Toyer and R. Twaits, *J. Appl. Chem. (London)*, 14 (1964) 563; *cf. Chem. Abstr.*, 62 (1965) 6505a.
36 M. Harfenist, A. Bavley and W. A. Lazier, *J. Org. Chem.*, 19 (1954) 1608.