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REACTIONS IN $[^2H]_3$-ACETONITRILE BETWEEN TRIMETHYL PHOSPHITE COPPER(I) OR IRON(II) CATIONS AND PHOSPHORUS PENTAFLUORIDE OR TUNGSTEN HEXAFLUORIDE [1]

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SUMMARY

Fluorination of trimethyl phosphite in reactions between phosphorus pentafluoride or tungsten hexafluoride and the cations $Cu[P(OMe)_3]_4^+$ or $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$, n=5 or 4, in $[^2H]_3$-acetonitrile is influenced both by the metal and by the solvent. Mixtures of phosphorus(III and V) and tungsten(VI) fluorides are obtained whose origin can be understood in terms of kinetic control by Cu^I or Fe^{II}, labile and inert towards substitution respectively, and the Lewis base properties of CD_3CN. ^{19}F and ^{31}P n.m.r. spectroscopy was used to study the reactions and the n.m.r. parameters of $PF_5 \cdot P(OMe)_3$ are reported.

INTRODUCTION

Trimethyl phosphite reacts exothermically with phosphorus pentafluoride [2] and tungsten hexafluoride [3], the initial reaction being exchange of F- and MeO-ligands. Several reactions occur subsequently; they involve Michaelis-Arbusov rearrangement of $P(OMe)_3$ and its fluorinated analogues, and salts of the $MeP(OMe)_3^+$ cation have been isolated from both reactions. Boron trifluoride reacts with $P(OMe)_3$ in a similar manner, to give $PF(OMe)_2$,$PF_2(OMe)$ [4], or dimethyl methylphosphonate [5]. The existence of copper(I) and iron(II) cations containing ligated $P(OMe)_3$ [6,7] has enabled the effect of cations with differing electronic configurations, Cu^I, d^{10} labile to substitution, Fe^{II}, low spin d^6 substitutionally inert, on the fluorination reaction to be studied. Fluorophosphite complexes of zerovalent metals, for example Ni^0 and Fe^0, are well known [5,8] and a Cu^I-PF_3 complex has been reported recently [9].

The study has been made using ^{19}F and ^{31}P n.m.r. spectroscopy as the main tool. The solvent chosen, $[^2H]_3$-acetonitrile, contains the necessary ^2H field/frequency lock and is a good solvating agent for Cu^I, Fe^{II}, PF_5, and WF_6.

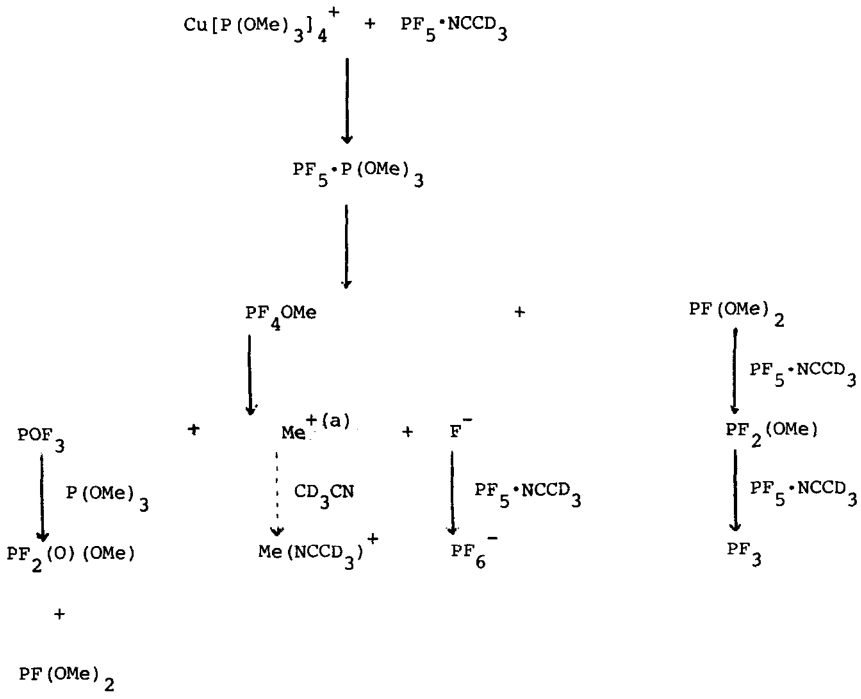
RESULTS

$Cu[P(OMe)_3]_4{}^+MF_6{}^-$, M = P or As, react exothermically with PF_5 or WF_6 in CD_3CN below room temperature, the reactions between $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}][MF_6]_2$, n = 5,4 or 3, and WF_6 are far less vigorous; and that between the Fe^{II} cation, n = 5, and PF_5 is barely detectable at room temperature.

Reaction of $Cu[P(OMe)_3]_4{}^+$ with PF_5

The pathway proposed is summarised in Scheme (1). The first step involves the formation of $PF_5.P(OMe)_3$, which has been mentioned previously [2], although no n.m.r. data were obtained. A P-P bonded structure is clearly indicated from its n.m.r. paramenters, Table 1. $|{}^1J(PP)|$ Values cover a wide range [10] but that reported here appears to be the largest to date. It is significantly greater than that in $PF_5.PMe_3$ [10b], as might be expected on the basis of the usual behavio of $^1J(PX)$ in XPR_3 compounds.

$PF_5.P(OMe)_3$ undergoes a ligand exchange reaction to give PF_4OMe and presumably $PF(OMe)_2$. The latter compound was not observed, possibly due to rapid exchange involving $PF(OMe)_2$ coordinated to Cu^I. Comparison between the spectra of $PF_5.NCCD_3$ and PF_4OMe, Table 1, indicates that the latter is not coordinated by CD_3CN, but even at 243K it is unstable with respect to decomposition to POF_3. MeF is not observed, suggesting that loss of Me^+ and F^- is not concerted. The presence of $PF_6{}^-$ in reactions of the $AsF_6{}^-$ salt suggests that F^- ion reacts with $PF_5.NCCD_3$. The cation $MeP(OMe)_3{}^+$ was observed on



——▶ At least one product identified, see Tables 2-5.

- - -> Products not identified.

(a) $(MeO)_3PMe^+$ observed in one reaction.

SCHEME (1) Proposed pathways for $Cu[P(OMe)_3]_4^+$ + PF_5 in CD_3CN

one occasion but a more important reaction appears to involve Me^+ and the solvent. It is suggested that $[CD_3CNMe]^+$ is formed which initiates polymerisation of the solvent. The cation was not identified, but MeCN is known to behave as a trap for carbocations, for example R_3C^+ reacts with MeCN to give R_3CNCMe^+ which is subsequently hydrolysed to $R_3CN(H)C(O)Me$ [11], and $[MeCNMe^+][O_3SCF_3^-]$ has been isolated from the reaction of $MeOSO_2CF_3$ with MeCN [12].

TABLE 1

N.m.r. data for selected reaction products

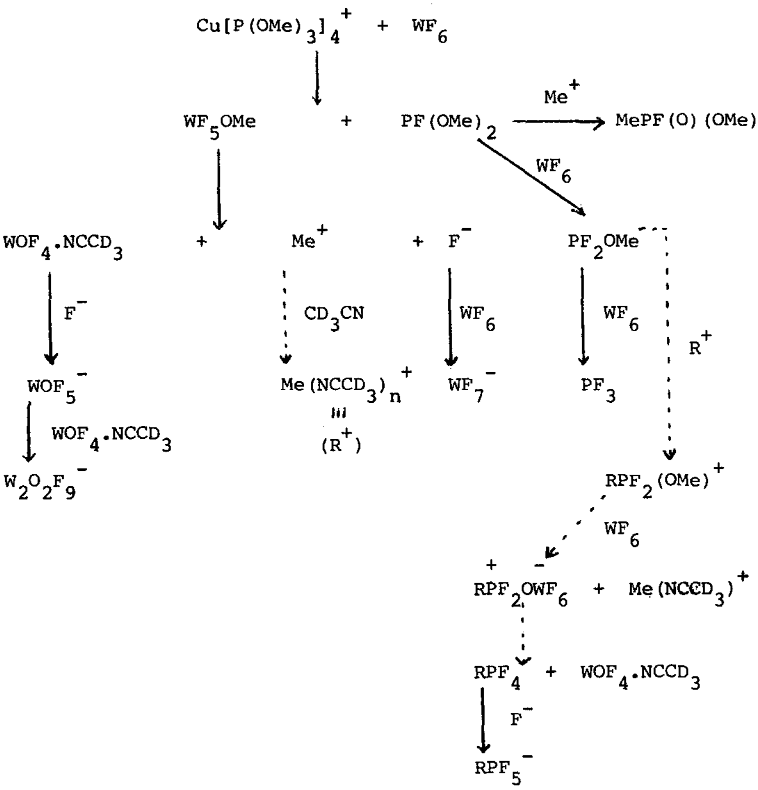
Compound	Chemical shifts (ppm.)[a]		Coupling constants (Hz)
	^{19}F	^{31}P	
$PF_5 \cdot P(OMe)_3$	-48.1 eq	$49.6, P^{III}$	$^1J(F_{eq}P)$ 875, $^1J(F_{ax}P)$ 787
	-79.9 ax	$-145.6, P^{V}$	$^1J(PP)$ 1205, $^2J(F_{eq}P)$ 285, $^2J(F_{ax}P)$ 0, $^2J(F_{ax}F_{eq})$ 57
$PF_5 \cdot NCCD_3$		-144.8	$^1J(FP)$ 770
PF_4OMe	-66.9	-76.7	$^1J(FP)$ 872
RPF_5^- (i)	-61.3 eq	-148.8	$^1J(F_{eq}P)$ 812, $^1J(F_{ax}P)$ 740, $^2J(F_{eq}F_{ax})$ 47.5
(ii)	-62.0 eq	-150.8	$^1J(F_{eq}P)$ 797, $^1J(F_{ax}P)$ 746, $^2J(F_{eq}F_{ax})$ 48
	-73.0 ax		
$MePF_4$	-44.8	-26.6	$^1J(FP)$ 968, $^2J(HP)$ 20, $^3J(HF)$ ~0.5
WF_5OMe	113.6 eq		$^2J(F_{eq}F_{ax})$ 66, $^1J(F_{eq}W)$ 42
	69.3 ax		
$W_2O_2F_9^-$	62.5 eq		$^2J(F_{eq}F_{br})$ 58, $^1J(F_{eq}W)$ 72
	-144.0 br		
$(W_2O_2F_9^-)'$	61.3 eq		$^2J(F_{eq}F_{br})$ 56.5, $^1J(F_{eq}W)$ 72
	-144.4 br		

[a] With respect to CCl_3F and H_3PO_4, positive to low field; ax = axial, eq = equatorial, br = bridging.

Additional fluorination occurs to produce $PF_2(OMe)$ and a small quantity of PF_3. Other, minor products are $PF_2(O)(OMe)$, presumably formed from POF_3 and $P(OMe)_3$, and a six coordinate phosphorus-fluorine species formulated as RPF_5^-. The latter is a major product from the WF_6 reaction and is discussed below.

Reaction of $Cu[P(OMe)_3]_4^+$ with WF_6

The products obtained depend to some extent on the reaction stoicheiometry and the degree to which the very exothermic, initial reaction is controlled. The proposed pathway is summarised in Scheme (2).



SCHEME (2) Proposed pathways for $Cu[P(OMe)_3]_4^+ + WF_6$ in CD_3CN

See note for Scheme (1)

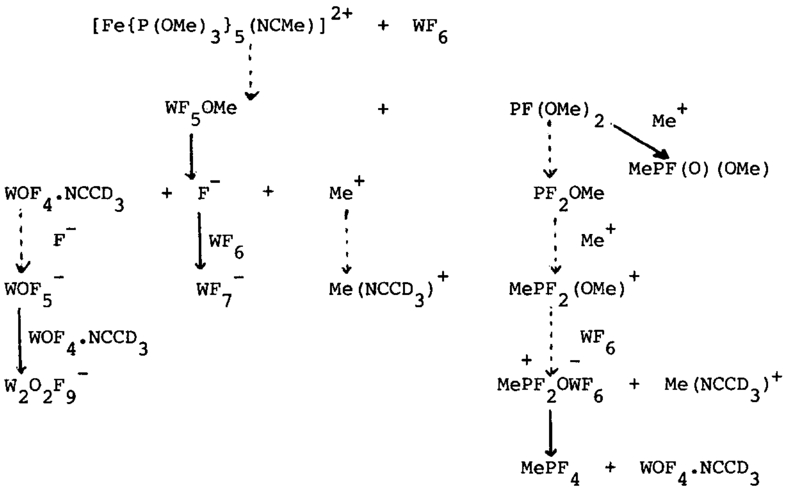
No evidence for $WF_6.P(OMe)_3$ was obtained, although by analogy with the PF_5 reaction and with $WF_6.PMe_3$ [13] a W-P bonded adduct would be expected. The ligand exchange products WF_5OMe and $PF(OMe)_2$ are both observed, and further fluorination produces $PF_2(OMe)$ and PF_3. The ^{19}F n.m.r. spectrum of $PF(OMe)_2$ at 253K is relatively broad, suggesting exchange between free and coordinated species, however $^{63,65}Cu$ spectra are very broad and give no information on this point. The ^{19}F n.m.r. chemical shifts of WF_5OMe, Table 1, are somewhat different from those reported in C_6F_6 [3], in particular the axial ^{19}F resonance is shifted to higher applied field by approximately 20 p.p.m. This implied increase in electron density at $^{19}F_{ax}$ [14] can be accounted for if a specific interaction exists between WF_5OMe and CD_3CN represented by $CD_3CN{-}{-}{-}\overset{\delta+}{Me}OW(F_4)\overset{\delta-}{F}$.

Decomposition of WF_5OMe is rapid at 263K and occurs in a manner similar to that of PF_4OMe. $WOF_4.NCCD_3$ and WF_6 behave as F^- ion acceptors forming WOF_5^-, $W_2O_2F_9^-$, and WF_7^-; the latter undergoes rapid exchange with WF_6 in solution [15]. Formation of $W_2O_2F_9^-$ is favoured when the mole ratio WF_6 : Cu^I salt is relatively small. Although MePF(O)(OMe) is a product, suggesting a Me^+ cation catalysed rearrangement of $PF(OMe)_2$, it is believed that the more important trap for Me^+ is CD_3CN. As the reaction proceeds, its colour changes from pale yellow to dark red and the viscosity of the mixture increases. The major phosphorus-containing species at this point are formulated from their n.m.r. spectra, Table 1, as RPF_5^- anions, by comparison with the spectra of $MePF_5^-$ and HPF_5^- [16]. Two such species, (i) and (ii) in Table 1, are normally observed although their n.m.r. parameters vary slightly depending on the sample's history. The reaction sequence proposed for their formation, Scheme (2), is speculative, but it accounts for the observations made. It is suggested that the final products are $Me[NC(CD_3)]_nNC(CD_3)PF_5^-$ in which n is variable.

Further, indirect evidence for solvent involvement is the observation of two $W_2O_2F_9^-$ species, Table 1, in some reactions. One of these is considered to be a free anion [14], the other, $(W_2O_2F_9^-)'$, is slightly shifted, presumably due to interaction with polymeric $Me(NCCD_3)_n^+$. The reaction between WF_6 and free $P(OMe)_3$ in CD_3CN is very similar to that with $Cu[P(OMe)_3]_4^+$ when the initial reaction is not controlled. The phosphorus-containing products identified are four species of the type RPF_5^-, and PF_6^-.

Reactions of $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$, n=5,4 or 3, with WF_6 or PF_5

The reaction between WF_6 and $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ at room temperature is very slow and is not complete after several weeks even when a large excess of WF_6 is used. Similar behaviour is observed when other cations, n=4 or 3, are used. The extent of solvent involvement in these reactions is far less than with $Cu[P(OMe)_3]_4^+$ and the major product is $MePF_4$, Table 1. This is presumably formed by a route similar to that suggested for RPF_5^-, except that Me^+ rather than $Me(NCCD_3)_n^+$ is involved, Scheme (3).



SCHEME (3) Proposed pathway for $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ + WF_6 in CD_3CN.

See note for Scheme (1)

Significant quantities of MePF(O)(OMe) and $W_2O_2F_9^-$, in addition to $MePF_4$ and $WOF_4.NCCD_3$, are observed only when the concentration of WF_6 is relatively low and under these circumstances Me^+ apparently competes successfully with WF_6 for the intermediate $PF(OMe)_2$. Fluoride ion, produced from the decomposition of the intermediate WF_5OMe, reacts to form $W_2O_2F_9^-$ and WF_7^-. Trace quantities of RPF_5^- and PF_6^-, the latter observed with AsF_6^- salts, are observed after longer reaction times.

The reaction between $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ and PF_5 under similar conditions is even slower, therefore it was not studied in detail. After several weeks $[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$, in addition to unchanged starting material, is observed in its $^{31}P\{^1H\}$ n.m.r. spectrum.

DISCUSSION

There is no evidence that these reactions involve the fluorination of coordinated $P(OMe)_3$, but the metal has a direct effect on the reaction, as it exercises kinetic control on the concentration of free $P(OMe)_3$ in solution. The ^1H n.m.r. spectrum of $Cu[P(OMe)_3]_4^+$ indicates that exchange between free and coordinated $P(OMe)_3$ is rapid on the n.m.r. time-scale at room temperature, as expected for a d^{10} cation. In contrast exchange involving $P(OMe)_3$ in $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$, n=5 or 4, is not observed. As reaction proceeds coordinated $P(OMe)_3$ is replaced by CD_3CN, the latter competing successfully with $PF(OMe)_2$ as a ligand for Cu^I and Fe^{II}. Identical products are obtained whether the counter anion is PF_6^- or AsF_6^-, however the latter salts appear to be less stable thermally, and decomposition occurs when temperature control of the reactions is not complete.

The solvent, CD_3CN, is the second important factor in determining the outcome of these reactions. Its solvation of the ionic reactants is crucial; reactions do not occur in CCl_3F solution, but are initiated by the addition of a small quantity of CD_3CN. The intervention of the solvent as a reactant is seen most obviously in the formation of the RPF_5^- species, and in the decomposition of PF_5OMe and WF_5OMe, for example the latter compound decomposes to give MeF and WF_4O in the absence of solvent, and gives $MeP(OMe)_3^+WF_5O^-$ in the presence of $P(OMe)_3$ alone [3]. The solvent must play a role also in the formation of $MePF_4$ from PF_2OMe.

EXPERIMENTAL

All operations were carried out using a vacuum system ($<10^{-3}$ torr) or an Ar atmosphere glove box ($H_2O<10$p.p.m.). N.m.r. spectra were obtained using Varian 100XL, and Jeol C60HL and FX90Q instruments at 60.0(^1H), 94.15 or 56.4(^{19}F), 40.5(^{31}P), 28.4(^{65}Cu), and 26.5MHz(^{63}Cu). Chemical shifts are reported positive to low field of CCl_3F or 85% H_3PO_4. I.r. and Raman spectra were obtained using P.E.557 and Spex Ramalog instruments using conventional sampling techniques. Analyses were by Malissa and Reuter, F.R.G.

WF_6, PF_5, and AsF_5 (Fluorochem Ltd.) were purified by low temperature trap-to-trap distillation and were stored over predried NaF. MeCN was purified as previously reported [7], and CD_3CN by vacuum distillation and storage over 4A molecular sieves. $P(OMe)_3$ (B.D.H. Ltd.) was distilled at atmospheric pressure, then in vacuo, and stored over 4A sieves.

Preparation of trimethylphosphite-metal-fluoroanion salts

$[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ was prepared by the literature method [7], and the AsF_6^- salt was prepared in a similar manner. Shorter reaction times gave solids in which the predominant cation was cis-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. The products also contained small quantities of fac-and mer-$[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ and $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$. In all cases compounds were identified by their n.m.r. and i.r. spectra.

$[Cu(NCMe)_4][PF_6]$ (0.35mmol), prepared by the literature method [17], reacted with $P(OMe)_3$ (17.0mmol) at room temperature to give a yellow solution and a white solid. Removal of volatile material, identified by ^1H n.m.r. spectroscopy as a mixture of MeCN, unchanged $P(OMe)_3$, and a trace of $MeP(O)(OMe)_2$, gave a white solid identified as tetrakis(trimethylphosphite)copper(I) hexafluorophosphate. Found C, 21.6; H, 5.0; Cu, 8.8; F, 15.9; P, 21.6. $C_{12}H_{36}CuF_6O_{12}P$ requires C, 20.5; H, 5.2; Cu, 9.0; F, 16.2; P, 22.0%. Its i.r. and Raman spectra contained bands assignable to coordinated $P(OMe)_3$ [18] and PF_6^-. Its n.m.r. spectra in CD_3CN consisted of signals assigned to PF_6^-, $^1J(FP)$ 706 Hz, $\delta(^{19}F)$ -71.5, $\delta(^{31}P)$ -144.6p.p.m., and to $Cu[P(OMe)_3]_4^+$, $^1J(P^{63}Cu)$ 1221, $^1J(P^{65}Cu)$ 1311 Hz, $\delta(^{31}P)$ 125.6p.p.m. The ^1H n.m.r. spectrum was a broad singlet at 290K, but fine structure due to the A_9 part of an $[A_9X]_4$ spin system was resolved at 248K. The n.m.r. spectra of the cation were in good agreement with previous work [19], and indicated a tetrahedral structure for the cation. The corresponding AsF_6^- salt was prepared in a similar manner, and identified by its spectra.

Reactions between the phosphite-metal salts and PF_5 or WF_6

Reactions were carried out in Pyrex ampoules fitted with P.T.F.E., glass stop-cocks (Rotaflo) and n.m.r. tubes, enabling the products of a reaction to be examined at various times during its course.

The Cu^{I} or Fe^{II} salts (0.2-0.4g) were dissolved in CD_3CN(2ml) <u>in vacuo</u>, then PF_5 or WF_6 (0.2-2.4g) was added by distillation. Stoicheiometries and conditions used for typical reactions are given in Table 2.

Product identification was made by ^{19}F and ^{31}P n.m.r. spectroscopy by comparison with literature data [2,3,14,15,20], supplemented by i.r. spectra of volatile products. ^{1}H spectra were complex and detailed assignments were not made. The products identified from the reactions listed in Table 2 are given in Tables 3-5.

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TABLE 2

Reaction stoicheiometries and conditions

Reaction	Reactants (mmol)[a]	Conditions	Colour of Solution
1	$[CuP_4][PF_6]$ (0.54)+PF_5(5.1)	exothermic reaction $\sim$278K	yellow
2	$[CuP_4][PF_6]$ (0.54)+PF_5(1.9)	$\leqslant$268K	yellow
3	$[CuP_4][AsF_6]$ (0.48)+PF_5(1.9)	exothermic reaction $\sim$273K	yellow → red
4	$[CuP_4][AsF_6]$ (0.48)+PF_5(1.6)	268K	yellow
5	$[CuP_4][PF_6]$ (0.54)+WF_6(4.0)	exothermic reaction $\sim$278K mixture cooled then warmed to 293K	yellow → dark red
6	$[CuP_4][PF_6]$ (0.54)+WF_6(1.8)	exothermic reaction $\sim$278K no temperature control	yellow → dark red
7	$[CuP_4][AsF_6]$ (0.48)+WF_6(1.5)	exothermic reaction $\sim$278K no temperature control	yellow → dark red
8	$[CuP_4][PF_6]$ (0.54)+WF_6(8.0)	273K for 2h then warmed to 298K	dark red
9	$[CuP_4][PF_6]$ (0.54)+WF_6(6.1)	253K then 273K then 295K	pale brown → yellow
10	$[FeP_5N][PF_6]_2$(0.2)+WF_6(3.0)	293K	yellow
11	$[FeP_5N][PF_6]_2$(0.15)+WF_6(1.2)	293K	yellow
12	$[FeP_4N_2][AsF_6]_2$[b] (0.13)+WF_6(1.3)	293K	yellow
13	$P(OMe)_3$(2.6)+WF_6(5.4)	77-273K over 12h	dark red

(a) $P = P(OMe)_3$, N = MeCN. (b) Some fac-$FeP_3N_3{}^{2+}$ and FeP_5N^{2+} also present.

TABLE 3

Products identified from $Cu[P(OMe)_3]_4^+ + PF_5$ reactions

Reaction[a]	Temperature time[b]	Products identified									
		$PF_5.NCCD_3$	$PF_5.P(OMe)_3$	PF_4OMe	POF_3	$PF_2(OMe)$	$PF_2(O)(OMe)$	PF_3	PF_6^-	$MeP(OMe)_3^+$	RPF_5^-
1	278K				✓	✓	✓ (c)	✓ (c)			✓
2	3h 243K	✓	✓	✓	✓						
3	273K				✓	✓			✓		
4	268K	✓ (c)		✓	✓				✓	✓	

[a] Numbers correspond to those in Table 2. [b] Where no time is stated, spectra were recorded immediately after the initial reaction. h = hour, d = day [c] Trace quantity.

TABLE 4

Products identified from $Cu[P(OMe)_3]_4^+ + WF_6$ reactions

Reaction(a)	Temperature (b) time	Products identified										
		WF_5OMe	$WOF_4 \cdot NCCD_3$	WOF_5^-	$W_2O_2F_9^-$	WF_7^-/WF_6	$PF(OMe)_2$	MePF(O)(OMe)	PF_2OMe	PF_3	RPF_5^-	$MePF_4$
5	293K											
	0.5h		√		√	√						
	24h		√ (c)		√					√		
	20d				√			√	√ (c)	√(d)		
6	293K											
	0.5h			√(c)	√	√	√					
	2d			√	√(d)		√			√(d)		
	10d			√	√(d)		√	√		√(d)		
7	293K											
	0.5h			√	√		√					
	4d			√	√(d)		√			√(d)		
8	273K		√		√(c)	√						
	2h											
	293K		√ (c)		√					√		
	2d											
	7d		√ (c)		√			√	√(c)	√(d)		√
9	253K	√	√			√	√					
	273K	√	√		√	√	√					
	295K	√	√		√	√	√	√	√ (c)			

(a)-(c) As Table 3. (d) Two species observed

TABLE 5

Products identified from $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$ or $P(OMe)_3$ with WF_6.

Reaction(a)	Temperature (b) time	Products identified						
		$WOF_4.NCCD_3$	$W_2O_2F_9^-$	WF_7^-/WF_6	MePF(O)(OMe)	$MePF_4$	RPF_5^-	PF_6^-
10	293K							
	1h	✓		✓				
	20d	✓		✓		✓	✓(c)	
11	293K							
	24h	✓	✓	✓				
	5d	✓	✓	✓	✓	✓	✓(c)	
12	293K							
	14d	✓	✓	✓		✓	✓(d)	✓
13	293K							
	12h	✓ (c)	✓	✓(c)			✓(e)	✓

(a)-(d) As Tables 3 and 4. (e) Four species observed.

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