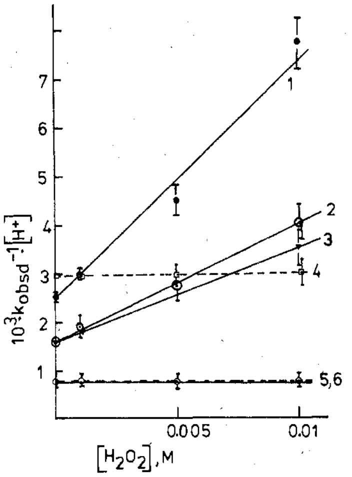


Figure 1. Plot of $k_{obsd}^{-1}[H^+]$ vs. $[H_2O_2]$ for the reaction of $[VO(O_2)_2(L\text{-}L)]^{n-}$ complexes with protons at 25 °C (μ = 1.0 M ($LiClO_4$)). (L-L): 1, phenanthroline; 2, bipyridine; 3, oxalato; 4, tetramethylphenanthroline; 5, picolinato; 6, 1-isoquinolinecarboxylato. Each data point represents the average value of four individual experiments where $[H^+]$ = 0.05, 0.1, 0.2, and 0.3 M.

for c and support the above assumption. An upper limit of b can therefore be estimated, 0.02 s, for the experimentally established H_2O_2 independent reactions.

Discussion

From the kinetic data a simple first-order dependence on $[H^+]$ has been detected for all complexes under investigation. A mechanism where the monoprotonated hydroperoxo ligand, O_2H^-, is the actual leaving group leads to rate law eq 5 which

$$[VO(O_2)_2L]^{n-} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [VO(O_2)L]^{(n-2)-} + HO_2^-$$

$$H_2O_2 \rightleftarrows HO_2^- + H^+ \qquad K_a$$

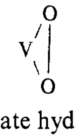
$$[VO(O_2)L]^{(n-2)-} + H_2O \xrightarrow{k_2} [VO(O_2)L(H_2O)]^{(n-2)-}$$

$$\frac{d[VO(O_2)L(H_2O)]}{dt} = \left(\frac{k_1 k_2'}{k_2' + (k_{-1}K_a[H_2O_2]/[H^+])}\right)[H^+][VO(O_2)_2L] \quad (5)$$

$$k_2' = k_2[H_2O]$$

is not consistent with the observed data for the phenanthroline–, oxalato–, and bipyridine–diperoxo complexes. It is noted that for the tetramethylphenanthroline–, picolinato–, and 1-isoquinolinecarboxylato–diperoxo complexes, eq 5 is of the observed form (eq 3) if $k_2' >> (k_{-1}K_a[H_2O_2][H^+]^{-1})$ ($c = k_1$). But it seems highly improbable to us that two different mechanisms should be operative for a series of structurally so similar complexes.

A second mechanism envisages the rapid acid-catalyzed transformation of a one-coordinated peroxo moiety



to a coordinated, monodentate hydroperoxo ligand, V–O–OH. Under our experimental conditions (lowest employed $[H^+]$ = 0.01 M) the entire reactant is believed to be converted to this form. In the rate-determining step the hydroperoxovanadium(V) species undergo an acid-catalyzed substitution reaction—H_2O_2 being the leaving group.

$$[VO(O_2)_2L]^{n-} + H^+ \xrightarrow{\text{rapid}} [VO(O_2)(OOH)L]^{(n-1)-}$$

$$[VO(O_2)(OOH)L]^{(n-1)-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [VO(O_2)L]^{(n-2)-} + H_2O_2$$

$$[VO(O_2)L]^{(n-2)-} + H_2O \xrightarrow{k_4} [VO(O_2)L(H_2O)]^{(n-2)-}$$

A rate law as in eq 6 can be derived which is of the form of eq 2, where $a = 1/k_3$ and $b = k_{-3}/k_3k_4'$ and $k_4' = k_4[H_2O]$.

$$\frac{d[VO(O_2)L(H_2O)]}{dt} = \left(\frac{k_3k_4'}{k_4' + k_{-3}[H_2O_2]}\right)[H^+][VO(O_2)_2L] \quad (6)$$

Thus a in eq 2 represents reciprocal second-order rate constants (c in eq 3 is k_3) for the substitution of a complex-bonded HO_2^- ligand. Values for k_3 for all six complexes are very similar and do not seem to be affected by the electronic properties of the bidentate organic ligand (O,O-, O,N-, and N,N-coordination) or by the steric requirements of the ligand or by the actual overall charge of the diperoxo anion (−1, −2, −3). b in eq 2, on the other hand, is composite, and a more pronounced variation of the values of b within the series of complexes is plausible—leading to relatively small values of b in some cases, producing thereby an H_2O_2-independent experimental rate law.

The proposed mechanism implies that the basicity of a given peroxo ligand coordinated to V(V) is greatly affected by the total number of peroxo groups coordinated to the same V(V) center. This is qualitatively supported[1] by the fact that the tetraperoxovanadate(V) ion is only stable in strongly alkaline solutions and diperoxovanadium(V) species are stable in neutral solutions, whereas some monoperoxovanadium(V) complexes are known to be stable in 2 M perchloric acid.[3]

Acknowledgment. Financial support of this research from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $K[VO(O_2)_2(Me_4phen)]$, 68782-45-6; $K_2[VO(O_2)_2(pic)]$, 68782-46-7; $(NH_4)_2[VO(O_2)_2(isoquin)]$, 68782-47-8; $[VO(O_2)_2(C_2O_4)]^{3-}$, 68782-48-9; $[VO(O_2)_2(bpy)]^-$, 68832-77-9; $[VO(O_2)_2(phen)]^-$, 68832-78-0; $[VO(O_2)_2(Me_4phen)]^-$, 68782-49-0; $[VO(O_2)_2(pic)]^{2-}$, 68782-50-3; $[VO(O_2)_2(isoquin)]^{2-}$, 68782-51-4; $[VO(O_2)(C_2O_4)OH_2]^-$, 68782-52-5; $[VO(O_2)(bpy)OH_2]^+$, 68782-53-6; $[VO(O_2)(phen)OH_2]^+$, 68782-54-7; $[VO(O_2)(Me_4phen)OH_2]^+$, 68782-55-8; $[VO(O_2)(pic)OH_2]$, 68782-56-9; $[VO(O_2)(isoquin)OH_2]$, 68782-57-0; H_2O_2, 7722-84-1.

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Synthesis of Tris(difluorophosphino)amine and (Trimethylsilyl)bis(difluorophosphino)amine

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A recent publication by Neilson, Lee, and Cowley[1d] prompts us to report on some related studies of ours, concerned with the cleavage of Si–N and Sn–N bonds by phosphorus(III) halides, PF_2X (X = Cl or Br). This method is known to provide a facile means of attaching PF_2 groups to nitrogen.[2] Our interest was, especially, in the synthesis of compounds of type $N(PF_2)_n(SiMe_3)_{3-n}$ ($n = 1, 2$, or 3) which were either unknown or not readily accessible. In such compounds two reactive centers are available, at the PF_2 group[3] and at the Si–N bond which is known to undergo cleavage reactions with various reagents, for $n = 1$ and 3.[4,5]

Experimental Section

Reactions were conducted in an atmosphere of dry, oxygen-free nitrogen, using a standard ground-joint apparatus, or in a vacuum line. Starting materials, such as PF_2Cl,[3,6] PF_2Br,[6] $(Me_3Si)_2NPF_2$,[1] t-$BuN(SiMe_3)PF_2$,[1d] $LiN(SiMe_3)_2$,[7] $Me_3SiN(SnMe_3)_2$,[8] and $N(SnMe_3)_3$,[9] were prepared by the literature methods indicated. Phosphorus trifluoride was used as obtained from Ozark-Mahoning Co.

NMR (^1H, ^{19}F, and ^{31}P) spectra were obtained on a JEOL C-60 HL, and on a Varian XL 100 spectrometer. Trichlorofluoromethane (internal) and 85% H_3PO_4 (external) served as references for ^{19}F and ^{31}P spectra, respectively. Positive signs denote shifts to high field, in both the ^{19}F and ^{31}P NMR spectra. IR spectra (in the gas phase) were recorded on a Beckman IR 20A spectrometer. The mass spectrum of $Me_3SiN(PF_2)_2$ was obtained on an A.E.I. MS 9 instrument, using a direct inlet system; electron energy was 70 eV.

Preparation of $Me_3SiN(PF_2)_2$. (Trimethylsilyl)bis(trimethylstannyl)amine (4.71 g, 11.4 mmol) was placed into a heavy-wall glass tube, fitted with a Teflon stopcock. After addition of 2.50 g (23.9 mmol) of PF_2Cl via a vacuum line at −196 °C, the tube was held at −33 °C for 14 h. Subsequently, products volatile at −63 °C were removed; the residue then remaining was purified by fractional condensation (traps held at −55 and −196 °C). The product (2.20 g; 98%, based on $Me_3SiN(SnMe_3)_2$) was obtained in the −196 °C trap. Vapor pressures were measured in the range 251–294 K by the zero point method, leading to an extrapolated boiling point of 131.7 °C at atmospheric pressure.

Anal. Calcd for $C_3H_9F_4NP_2Si$ (225.16): C, 16.00; H, 4.03; F, 33.75. Found: C, 16.30; H, 4.03; F, 33.0.

Principal IR absorptions (10-cm gas cell; 5-mm pressure; KBr windows): 2970 (m), 2915 (w), 1263 (s), 1040 (w), 933 (vs), 888 (m, sh), 858 (vs), 836 (m, sh), 810 (vs), 758 (m), 692 (m), 530 (vw), 485 (m), 470 (m).

^1H NMR spectrum: δ_{SiMe_3} 0.4 ppm (Me_4Si reference).

Mass spectrum: major fragments observed include m/e 226 (4%, $M + 1$), 225 (<1%, M), 211 (20%, $M + 1 - CH_3$, cf. M^* 197), 162 (trace, $(Me_3Si)_2O$), 147 (20%, $(Me_3Si)_2O - CH_3$), 133 (2%, F_3NP_2), 92 (5%, Me_3SiF), 77 (100%, $Me_3SiF - CH_3$). The mass spectrum is indicative of the compound. The observation of a fragment at m/e $M + 1$ is characteristic of this and other Me_3Si–N–P compounds. The origin of the Me_3SiF could not be established with certainty. The possibility of its formation through thermolysis of $Me_3SiN(PF_2)_2$ cannot be excluded. The other product of this decomposition, "F_3NP_2" (m/e 133), is observed while no evidence for a fragment, derived from its dimer (m/e 266), is obtained. Dimerization of F_3NP_2 under the experimental conditions employed (pressure = 10^{-6} Torr) is, however, considered unlikely.

Preparation of $N(PF_2)_3$. a. Bis(trimethylsilyl)aminodifluorophosphine (2.49 g, 10.9 mmol) was placed into a heavy-wall glass tube which was sealed after 4.06 g (27.3 mmol) of PF_2Br had been added via a vacuum line. After 40 h of heating at 130 °C the tube was opened and the volatile products were separated by fractional condensation (traps held at −65, −85, −126, and −196 °C). The product, $N(PF_2)_3$, was retained in the −126 °C trap; yield 0.2 g (8%, based on $(Me_3Si)_2NPF_2$).

b. Tris(trimethylstannyl)amine (6.80 g, 13.5 mmol) was combined, as described under (a), with 6.30 g (60.3 mmol) of PF_2Cl in a heavy-wall glass tube. The sealed tube was brought to room temperature and was shaken for 0.5 h. After separation as described under (a), the product (1.60 g, 53%, based on $N(SnMe_3)_3$) was obtained from the −126 °C trap. Characterization of $N(PF_2)_3$ was by comparison of its IR spectrum[4] and ^{19}F NMR spectrum[4] to data for the authentic compound.[4]

Results and Discussion

The reaction of trimethylsilyl-substituted amines with PF_3 and phosphorus(III) halofluorides, PF_2X (X = Cl or Br), has been shown to yield mono-PF_2-substituted derivatives of these amines,[2] e.g.

Table I. ^{19}F and ^{31}P NMR Data and Spin–Spin Coupling Constants for Aminobis(difluorophosphines), $RN(PF_2)_2$

R	$^1J_{PF}$, Hz	$^2J_{PP}$, Hz	$^3J_{PF}$, Hz	$^4J_{FF}$, Hz	δ_F	δ_P	lit. ref
Me	−1264	+437	+47	+11.7 +1.7	74.6	−141.5	12
Ph	−1252	371	+40	10.0 4.4	68.2	−132.7	12
H	−1253	154	+21	5.4 5.4	62.0	−144.4	4
GeH_3	−1239	431	+5.8		60.6	−149.8	13
PF_2[a]	1223.9 N[b]	~90	c	c	63.3		this work
	1224 N[b]				62.3	−150.3	4
$SiMe_3$[d]	−1254	346	+57.2	10.6[e] 5.8	59.2	−157.5	this work

[a] 40% in CD_3CN. [b] $N = |^1J_{PF} + 2\,^3J_{PF}|$. [c] Not determined. [d] 40% in toluene. [e] $^2J_{FF}$ assumed to be 50 Hz.

$$MeN(SiMe_3)_2 + PF_2Cl \xrightarrow{90\ °C} MeN(SiMe_3)PF_2 + Me_3SiCl \quad (1)$$

The introduction of a second PF_2 substituent by further reaction with PF_2Cl has not, however, been possible.[2] We have noted in our own work on related systems[3] that multisubstitution by PF_2 groups at nitrogen, based on Si–N precursors, does not occur. Thus, formation of $N(PF_2)_3$ and/or $Me_3SiN(PF_2)_2$ was not observed when a mixture of $(Me_3Si)_2NPF_2$ and PF_2Cl was heated in a sealed tube at 130 °C for 40 h.[3] Similarly, heating a mixture of t-$BuN(PF_2)(SiMe_3)$ and PF_2Cl at 150 °C for 60 h did not produce any t-$BuN(PF_2)_2$, through cleavage of the Si–N bond.[3]

If we used PF_2Br instead of PF_2Cl, however, the trisubstituted product $N(PF_2)_3$ could be obtained in small yield

$$(Me_3Si)_2NPF_2 + 2PF_2Br \xrightarrow{130\ °C\ (40\ h)} N(PF_2)_3 + 2Me_3SiBr \quad (2)$$

The lack of reactivity of the Si–N bond in such systems is, conceivably, due to its partial multiple bond character, originating from p_π–d_π overlap of orbitals at silicon, nitrogen, and phosphorus.

If, however, a trimethylstannyl-substituted amine, instead of a silylated amine, is employed, the reaction proceeds smoothly under mild conditions, furnishing $N(PF_2)_3$ in reasonable yield.

$$N(SnMe_3)_3 + 3PF_2Cl \xrightarrow[\text{temp}]{\text{room}} N(PF_2)_3 + 3SnMe_3Cl \quad (3)$$

Tris(difluorophosphino)amine has previously been obtained only from the reaction of F_2PNH_2 or NH_3 with PF_2Cl,[4] a preparation involving a difficult separation step.

Selective cleavage of the Sn–N bond, in preference to the Si–N bond, with PF_2Cl has been observed for the compound $Me_3SiN(SnMe_3)_2$, viz.

$$Me_3SiN(SnMe_3)_2 + 2PF_2Cl \rightarrow Me_3SiN(PF_2)_2 + 2SnMe_3Cl \quad (4)$$

NMR Spectra. The ^{19}F NMR spectrum of $Me_3SiN(PF_2)_2$ (see Table I) has been analyzed in terms of an $[A[X]_2]_2$ spin system, using the program LAOCOON 1968 of Harris and Stokes.[10] In comparison to alkylbis(difluorophosphino)amines, $RN(PF_2)_2$, both ^{19}F and ^{31}P resonances are markedly shifted toward lower field. The deshielding effect may be caused by a transfer of electron density from nitrogen, phosphorus, and fluorine into silicon d orbitals.

The coupling constants $^1J(PF)$ and $^3J(PF)$ are opposite in sign. The one-bond coupling constant has been shown to be negative.[11] The calculations lead to a $^2J(PP)$ of 346 Hz which is intermediate between the values for $RN(PF_2)_2$ (370–440 Hz) and $HN(PF_2)_2$ (154 Hz). The best agreement between calculated and experimental spectra is obtained when the two long-range coupling constants, $^4J(FF)$, are assumed to have the same sign. The signs of the coupling constants $^2J(PP)$ and $^4J(FF)$ in $MeN(PF_2)_2$ have been shown by Rudolph and Newmark[11] to be positive.

The ^{19}F NMR spectrum of $N(PF_2)_3$ is complicated in appearance; it seems to correspond to an $[A[X]_2]_3$ spin system. The coupling constant $^2J(PP)$ is of the order of 90 Hz. This is in good agreement wih estimates by Arnold and Rankin.[4] The ^{31}P NMR spectrum was found to exhibit very broad lines, due to the quadrupole moment of nitrogen. No attempt was made to determine the δ_P value.

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Registry No. $Me_3SiN(PF_2)_2$, 68738-48-7; $N(PF_2)_3$, 56564-56-8; $Me_3SiN(SnMe_3)_2$, 54123-88-5; $(Me_3Si)_2NPF_2$, 50732-22-4; PF_2Cl, 14335-40-1; PF_2Br, 15597-40-7; $N(SnMe_3)_3$, 1068-70-8.

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Interaction of Zeise's Dimer, *trans*-μ-Dichloro-bis(ethyleneplatinum chloride), with Polar Olefins

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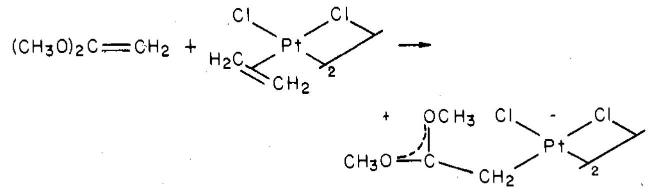
Olefins can potentially coordinate to platinum halides in a η^1 or η^2 fashion, although the π complex is the most frequently observed mode of bonding for olefins and acetylenes.[2]

A particular example of a η^1 complex is the product isolated after treating Zeise's dimer with 1,1-dimethoxyethylene.[3]

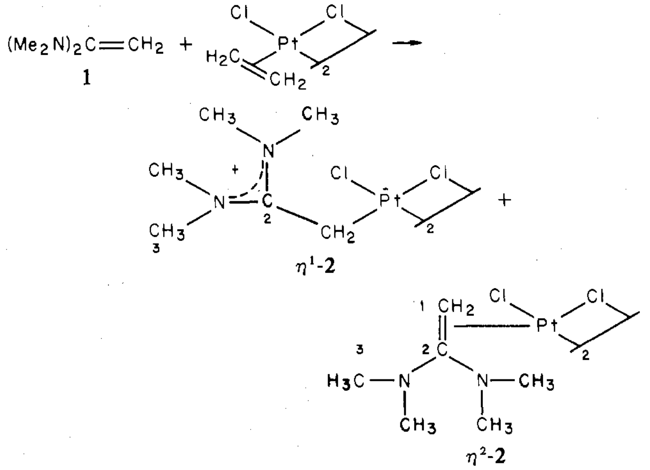


The complex can only be studied in the solid state since the ^1H NMR data show no evidence for ^{195}Pt–H coupling.

In this paper we report our results with 1,1-bis(dimethylamino)ethylene and 1,3-dimethyl-2-methyleneimidazoline with Zeise's dimer.

Results

1,1-Bis(dimethylamino)ethylene and Zeise's Dimer. When a yellow-orange benzene solution of Zeise's dimer $[Pt(C_2H_4)Cl_2]_2$ is treated with 1,1-bis(dimethylamino)ethylene, $[(CH_3)_2N]_2C{=}CH_2$, at 5 °C, the solution becomes deep yellow and ethylene is evolved. A bright yellow solid is obtained after filtering of the solution and sublimation of the excess benzene. A ^1H NMR spectrum of this solid in benzene shows it to be a mixture of two species, η^1-**2** and η^2-**2**.



1

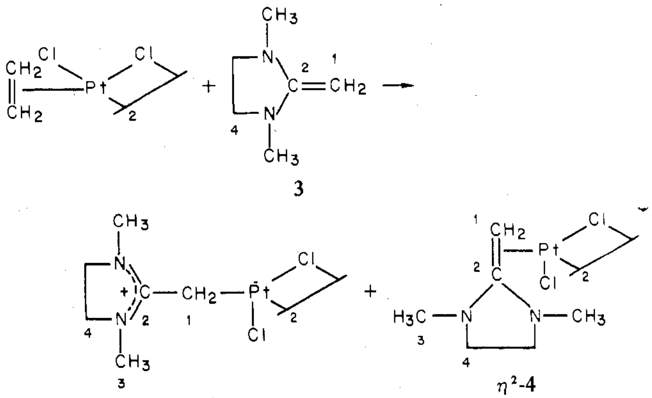
η^1-**2**

η^2-**2**

Structure η^1-**2** represents a η^1 complex where the σ bond to the platinum atom describes the mode of coordination and η^2-**2** represents a η^2 coordination of the olefin.

The molecular weight of the complex in benzene shows it to be dimeric, most likely with chlorine atom bridge bonds. A similar dimeric structure is observed by Paiaro et al.[3] for the olefin 1,1-dimethoxyethylene and its complex with Zeise's dimer.

Similar results are obtained with the olefin 1,3-dimethyl-2-methyleneimidazoline and Zeise's dimer.



3

η^1-**4**

η^2-**4**

Discussion

Zeise's Dimer with 1,1-Bis(dimethylamino)ethylene. Ylides $R_3P^+{-}^-CH_2$ are highly reactive 1,2-dipolar molecules which

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