The yield of 1-$CH_3B_4H_9$ was 75%. It was stored at −196 °C.

The residue which remained in the reaction vessel after protonation was identified as $[BH_2(NH_3)_2^+][Cl^-]$ by its X-ray powder pattern.[23]

Infrared spectrum of 1-$CH_3B_4H_9$ (cm^{-1}): 2977 (m), 2938 (w), 2856 (w), 2580 (s), 2492 (s), 2278 (w), 2170 (m), 2063 (m), 1505 (w, br), 1438 (w, br), 1386 (w), 1335 (w), 1321 (w), 1278 (w), 1278 (w), 1263 (w), 1145 (m, br), 1050 (m), 972 (m), 939 (m), 855 (w), 765 (m), 751 (s), 496 (w).

The normal boiling point (45 ± 0.6 °C) and heat of vaporization (7.1 ± 0.02 kcal/mol) of 1-$CH_3B_4H_9$ were estimated from an extrapolated plot of log P vs. $1/T$ and the Clausius–Clapeyron equation. The experimental values are as follows: −45.2 °C, 9.3 torr; −22.9 °C, 37.3 torr; 0 °C, 120.0 torr.

A 0.1281-g sample of 1-$CH_3B_4H_9$ exerted a pressure of 111 torr in a 291.39-mL bulb at 0 °C. The calculated molecular weight is 64.5 (theoretical 67.2). The cutoff in the mass spectrum occurs at a mass to charge ratio of 68 as expected for $CH_3{}^{11}B_4H_9$.

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Registry No. 3-$CH_3B_6H_{11}$, 68070-89-3; 3-$CH_3B_5H_{10}$, 68051-06-9; 1-$CH_3B_4H_9$, 68051-07-0; 1-$CH_3B_5H_8$, 23753-74-4; B_2H_6, 19287-45-7; B_6H_{12}, 12008-19-4; B_5H_{11}, 18433-84-6; B_4H_{10}, 18283-93-7.

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A Novel Diphosphorus Zwitterion

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A novel acyclic diphosphorus zwitterion $F_5P^-CH_2P^+F(NMe_2)_2$ (**1**) featuring hexa- and tetracoordinate phosphorus atoms has been synthesized by the action of Me_3SiNMe_2 on methylenebis(tetrafluorophosphorane). Compound **1** was characterized by means of ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy at ambient temperature. The ^1H and ^{19}F resonances were found to collapse at higher temperatures. Possible causes for these spectral changes are discussed. Some unsuccessful attempts to synthesize new F_4PXPF_4 compounds, X = NMe, O, and S, are described.

Introduction

Over the past few years a large number of interesting compounds featuring the difluorophosphino moiety (PF_2) have been reported.[1] By contrast, far less is known about species bearing the tetrafluorophosphoranyl (PF_4) substituent. While several compounds of the type XPF_4, X = H, NR_2, OR, SR, halogen, etc., have been characterized,[2] we are aware of only four materials involving more than one PF_4 group, namely, $F_4PCH_2PF_4$,[3,4] $F_4PCH_2CH_2PF_4$,[4] $F_4PCH{=}CHPF_4$,[4] and $F_4PN(Me)N(Me)PF_4$.[5] Our initial aim was to expand significantly the range of derivatives of this type by incorporating new bridging groups between two or more PF_4 moieties. An aspect of particular interest in structures of this kind is that they represent cases where two or more pentacoordinate geometries are interconnected, thereby raising intriguing questions about the nature of the ligand permutation process(es).

Unfortunately, our attempts to prepare new derivatives of the type F_4PXPF_4 were not successful. However, in the course of exploring the reactivity of $F_4PCH_2PF_4$ toward silyl reagents we discovered that this compound reacts with Me_2NSiMe_3 to afford a novel acyclic zwitterion featuring tetra- and hexacoordinate phosphorus atoms.

Experimental Section

General Procedures. Essentially all the materials described herein are moisture- and/or oxygen-sensitive. Accordingly, volatile compounds were manipulated in a high-vacuum system of conventional design and less volatile materials were handled in a helium-filled drybox. The various reaction vessels were flame-dried several times prior to use.

Materials. The compounds $MeN(PF_2)_2$,[6] $F_2PN(Me)PF_4$,[7] F_2POPF_2,[8] F_2PSPF_2,[9] $F_4PCH_2PF_4$,[3] and Me_3SiNMe_2[10] were prepared and purified according to published procedures. Sulfur tetrafluoride was procured commercially and used as supplied. Xenon difluoride was kindly donated by Mr. Timothy Juhlke of Professor R. J. Lagow's research group.

Reaction of $MeN(PF_2)_2$ with SF_4. In a typical reaction, SF_4 (1.7 mmol) and $MeN(PF_2)_2$ (1.5 mmol) were condensed in a heavy-walled Pyrex tube reactor at −196 °C. The reactor and its contents were allowed to warm to −78 °C and were maintained at this temperature for 2 days. Following this, the reactor was attached to the vacuum system and arranged so that the contents were maintained at −20 °C. The volatile materials which emerged were subjected to fractional vacuum condensation with U-traps held at −78, −90, and −196 °C. The −196 °C trap was found to contain PF_5 (identified by IR spectroscopy[11]), and mass spectral/NMR analysis indicated that the −78 °C trap retained $MeN[P(S)F_2]_2$[12] and trace amounts of $(MeNPF_3)_2$.[13] The same products were observed when reaction

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Table I. Mass Spectral Data for Diphosphorus Zwitterion **1**

m/e	rel abund, %	tentative assignt
259	19.8	$C_5H_{14}N_2P_2F_5^+$
258	7.43	$C_5H_{13}N_2P_2F_5^+$
239	10.40	$C_5H_{13}N_2P_2F_4^+$
234	15.35	$C_3H_8NP_2F_6^+$
214	29.21	$C_3H_7NP_2F_5^+$
198	4.95	$C_2H_3NP_2F_5^+$
187	0.5	$C_4H_{11}N_2P_2F_2^+$
171	3.96	$CH_2P_2F_5^+$
157	11.39	$C_3H_7NP_2F_2^+$ or $C_2H_5N_2P_2F_2^+$
152	7.43	$CH_2P_2F_4^+$ or $C_3H_7N_2P_2F^+$
137	10.89	$C_4H_{11}N_2PF^+$ or $C_3H_6NP_2F^+$
132	37.62	$C_3H_6N_2P_2^+$
128	14.85	$CH_2NP_2F_2^+$
109	19.31	$CH_2NP_2F^+$
107	12.87	PF_4^+
102	4.46	$CH_2PF_3^+$
94	100.0	Me_2NPF^+
83	2.48	$CH_2PF_2^+$
69	3.47	PF_2^+
45	12.87	CH_2P^+
44	26.73	Me_2N^+

temperatures of −50 and −90 °C were employed.

Reaction of $F_2PN(Me)PF_4$ with SF_4. The procedure employed was essentially identical with the one described above. Typically, the reaction mixture comprised 2.5 mmol of SF_4 and 2.0 mmol of $F_2PN(Me)PF_4$, the reaction temperature being maintained between −90 and −98 °C. After 1–2 days, the products were distilled on the vacuum line with U-traps held at −78, −160, and −196 °C. The diazadiphosphetidine $(MeNPF_3)_2$ collected in the −78 °C trap and PF_5 condensed in the −160 °C trap.

Reaction of $MeN(PF_2)_2$ with XeF_2. The reaction vessel for the XeF_2 experiments consisted of a ~60 mL capacity Pyrex tube equipped with a right-angled Teflon stopcock and a 14/20 standard taper joint. A magnetic stirring bar was placed in the bottom of the reactor. Xenon difluoride (2.23 mmol) and $MeN(PF_2)_2$ (1.85 mmol) were condensed into the reaction vessel at −196 °C. The reactor was then detached from the vacuum line and surrounded by a −78 °C bath, and the reaction mixture was stirred magnetically for a period of 1 day. Distillation of the volatiles with U-traps held at −78, −90, and −196 °C revealed that the products were Xe, PF_5, $F_2PN(Me)PF_4$, and traces of unreacted $MeN(PF_2)_2$. The identification of the products was made on the basis of IR and mass spectroscopy. When the amount of XeF_2 was doubled, small amounts of $(MeNPF_3)_2$ were detected along with the other products.

Reaction of $F_2PN(Me)PF_4$ with XeF_2. Using a very similar procedure to that described in the previous section, 2.3 mmol of XeF_2 was allowed to react with 1.4 mmol of $F_2PN(Me)PF_4$. The reaction mixture was monitored by IR spectroscopy each 20 °C as the reaction temperature was allowed to rise over a 6-h period from −130 to −78 °C. After the mixture was allowed to stand for 2 days at −78 °C, the volatiles were admitted to the vacuum system and distilled with U-traps held at −196, −160, −90, and −78 °C. The products were found to be Xe, PF_5, $(MeNPF_3)_2$, and unreacted $F_2PN(Me)PF_4$ on the basis of IR, mass, or NMR spectroscopy.

Reaction of F_2POPF_2 with XeF_2. Using the procedure described above, 3.2 mmol of XeF_2 was allowed to react with 1.4 mmol of F_2POPF_2 for 1 day at −78 °C. Fractionation of the volatiles with U-traps held at −90, −112, −160, and −196 °C afforded Xe, PF_5, and $F_3P(O)$ (characterized by IR spectroscopy[11]). Some unidentified solids remained in the reaction vessel. If the reaction was conducted at lower temperatures for shorter durations, unreacted F_2POPF_2 was detected among the products.

Reaction of F_2PSPF_2 with XeF_2. Using the procedure described above, 1.5 mmol of XeF_2 was treated with 1.5 mmol of F_2PSPF_2 at −130 °C for 2.5 h. Fractionation of the volatiles with U-traps held at −78, −140, −160, and −196 °C indicated that the products comprised Xe, PF_3, PF_5, and $F_3P(S)$ (characterized by IR spectroscopy[14]).

Synthesis of the Diphosphorus Zwitterion 1. In a typical reaction, $F_4PCH_2PF_4$ (1.59 mmol) and Me_3SiNMe_2 (5.95 mmol) were condensed into a ~8.0-mL Pyrex tube reactor at −196 °C. After being sealed, the reactor and its contents were allowed gradually to assume ambient temperature. After 1.5 h of standing at ambient temperature, the precipitation of white solids was complete and the reactor was opened to the vacuum line. Fractional vacuum condensation of the volatiles afforded unreacted Me_3SiNMe_2 (~3.0 mmol) in the −78 °C trap and Me_3SiF (3.4 mmol) in the −196 °C trap. Sublimation of the residual white solid (110 °C (10^{-5} torr)) produced 1.08 mmol of pure **1**, mp 115–117 °C (68.2% yield). Anal. Calcd for $C_5H_{14}N_2P_2F_6$: C, 21.59; H, 5.08; F, 40.99. Found: C, 21.78; H, 4.97; F, 40.66.

Spectroscopic Measurements. The ^1H and ^{19}F NMR spectra were recorded on Varian HA-100 or Varian A 56/60 spectrometers. The ^1H and ^{19}F chemical shifts were measured relative to external Me_4Si and CCl_3F, respectively. The ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WH-90 spectrometer and were referenced to external Me_4Si and 85% H_3PO_4, respectively. The mass spectra (70 eV) were determined on a CEC 21-491 spectrometer, and the infrared spectra were measured on a Perkin-Elmer 337 grating spectrophotometer.

Results and Discussion

Our attempts to prepare $F_4PN(Me)PF_4$ by eq 1–4 were

$$MeN(PF_2)_2 + SF_4 \rightarrow (MeNPF_3)_2 + MeN[P(S)F_2]_2 + PF_5 \quad (1)$$

$$F_2PN(Me)PF_4 + SF_4 \rightarrow (MeNPF_3)_2 + PF_5 + S_8 \quad (2)$$

$$MeN(PF_2)_2 + XeF_2 \rightarrow F_2PN(Me)PF_4 + PF_5 + Xe \quad (3)$$

$$F_2PN(Me)PF_4 + XeF_2 \rightarrow (MeNPF_3)_2 + PF_5 + Xe \quad (4)$$

unsuccessful.[15] It is apparent from reactions 1, 2, and 4 that facile decomposition of the desired product took place. In the case of reaction 3 only one of the phosphorus atoms underwent significant oxidative fluorination. Obvious driving forces for net fluorine migration process 5 are the volatility of PF_5 and

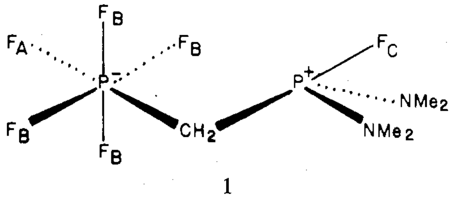
$$F_4PN(Me)PF_4 \rightarrow {}^1/_2(MeNPF_3)_2 + PF_5 \quad (5)$$

the enthalpy of dimerization of the iminophosphorane $MeN{=}PF_3$. Similarly, our attempts to produce oxygen- or sulfur-bridged F_4PXPF_4 or F_4PXPF_2 compounds via oxidative fluorination of the corresponding bis(difluorophosphine) precursors were thwarted by the elision of PF_5 and the formation of the rather stable molecules $F_3P(O)$ and $F_3P(S)$ (eq 6). In view of the foregoing results, it is clear that, in the

$$F_2PXPF_2 + XeF_2 \rightarrow F_3P(X) + PF_5 + Xe \quad (6)$$

domain of conventional synthesis, F_4PXPF_4 compounds will be isolable only when the potential product $F_3P{=}X$ is not particularly stable.

In the publication of Schmutzler et al.,[3] it was reported that $F_4PCH_2PF_4$ exhibited no perceptible spectral changes in the range +30 to −100 °C, thereby implying a small barrier to fluorine positional interchange. This is perhaps not surprising since the barrier to fluorine permutation of the analogous monophosphorane CH_3PF_4 is <4 kcal/mol.[16] Given that, in general, trifluorophosphoranes, X_2PF_3, possess larger ligand interchange barriers than the corresponding tetrafluorophosphoranes, XPF_4,[17] it seemed important to synthesize and examine spectroscopically a selection of bis(trifluorophosphoranes) of the genre $RPF_3CH_2PF_3R$. Since the interaction of active halides with silyl reagents represents an excellent means of effecting substitution by R groups, we decided to attempt the reaction of $F_4PCH_2PF_4$ with Me_2NSiMe_3 in the expectation of producing $Me_2NPF_3CH_2PF_3NMe_2$. Surprisingly, however, this reaction resulted in the formation of the novel zwitterion **1**. Formulation **1** is consistent with elemental analytical data and



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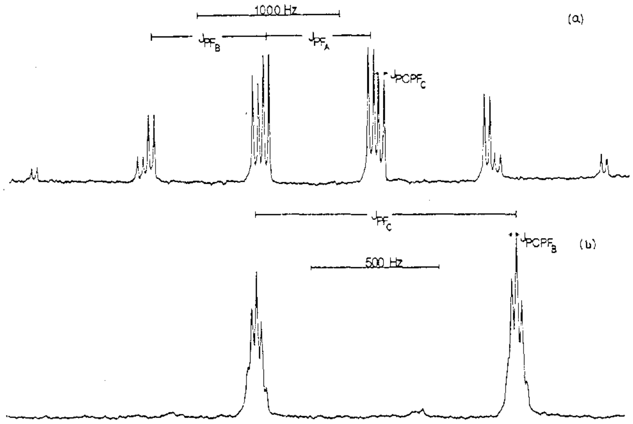

Figure 1. 36.4-MHz $^{31}P\{^1H\}$ Fourier transform NMR spectrum of the diphosphorus zwitterion **1**: (a) hexacoordinate phosphorus atom and (b) tetracoordinate phosphorus atom. The resonance due to trace quantities of PF_6^- has been omitted.

with the mass spectrum which exhibits a parent minus fluorine peak at *m*/*e* 259, together with the anticipated fragmentation pattern (Table I). $^{31}P\{^1H\}$ Fourier transform NMR spectroscopy has been very useful for establishing the structure of **1** in solution. The hexacoordinate portion of the zwitterion is established by a resonance at +141.0 ppm (Figure 1) which consists of a quintet of doublets of doublets with $J_{PF_B} = 806$, $J_{PF_A} = 731$, and $J_{F_CPCP} = 39.5$ Hz. The chemical shift of this resonance falls within the range anticipated for hexacoordinate phosphorus and, in particular, is in good agreement with the value of 126.4 ppm which has been reported for the $[MePF_5]^-$ anion.[18] The phosphonium portion of the zwitterion is also demonstrated by the presence of a doublet of quintets at −73.3 ppm with $J_{PF_C} = 1014$ and $J_{F_BPCP} = 17.1$ Hz (Figure 1). Our chemical shift and one-bond P–F coupling constant are in excellent accord with those reported[18] for the cation $[MePF(NMe_2)_2]^+$. Further confirmation of the zwitterionic structure of **1** is provided by ^{19}F NMR spectroscopy. For example, the F_A resonance, being a doublet of quintets with $J_{PF_A} = 734$ and $J_{F_BPF_A} = 44.3$ Hz, demonstrates clearly the presence of the $[RPF_5]^-$ moiety. The F_B and F_C resonances involve several more lines but we have been successful in effecting a spectral analysis on a first-order basis. Our proposed assignments are presented in Table II along with a summary of the experimental data. Some ^{13}C and ^1H NMR data for **1** are also detailed in Table II, even though these were not particularly informative for the purpose of structure assignment. Conspicuously absent are data pertaining to the ^{13}C resonance of the bridging methylene group—a consequence of the extensive coupling of this ^{13}C nucleus to the various ^{31}P and ^{19}F nuclei in the zwitterion. Note also that no value is cited for J_{PCP}. That the magnitude of this coupling should be very small is perhaps not surprising in view of the proclivity of two-bond couplings to changes of sign and of the sensitivity of, e.g., P–N–P couplings to conformational effects.[19]

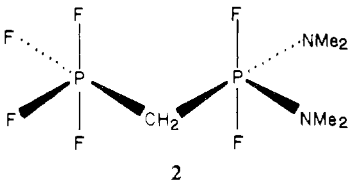

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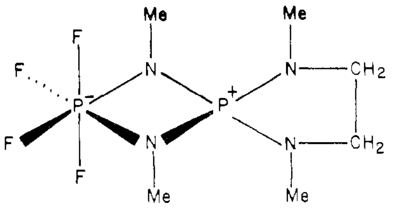
Table II. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR Data for Diphosphorus Zwitterion **1**[a]

	chemical shifts,[c] ppm					coupling constants, Hz
group[b]	^1H	^{13}C	^{19}F	^{31}P	multiplicity	
NMe_2	2.9				doublet of doublets	$J_{PNCH} = 10.7$, $J_{FPNCH} = 2.8$
CH_2	2.76				broad resonance	
NMe_2		36.5			doublet	$J_{PNC} = 6$
F_A			70.3		doublet of quintets	$J_{PF_A} = 734$, $J_{F_BPF_A} = 44.3$
F_B			45.0		doublet of doublets of 12 lines	$J_{PF_B} = 809$, $J_{F_APF_B} = 45$, $J_{PCPF_B} = 18.6$, $J_{HCPF_B} = 5.8$
F_C			80.4		doublet of doublets of 13 lines	$J_{PF_C} = 1016$, $J_{PCPF_C} = 39.6$, $J_{HCNPF_C} = 3.0$
P^-				141.0	quintet of doublets of doublets	$J_{PF_B} = 806$, $J_{PF_A} = 731$, $J_{PCPF_C} = 39.5$
P^+				−73.3	doublet of quintets	$J_{PF_C} = 1014$, $J_{PCPF_B} = 17.1$

[a] Near-saturated solution of **1** in $CHFCl_2$. [b] See text for proposed structure and labeling of groups. [c] ^1H and ^{13}C chemical shifts downfield from external Me_4Si; ^{19}F chemical shifts relative to external $CFCl_3$; ^{31}P chemical shifts relative to external 85% H_3PO_4.



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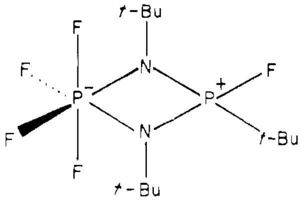

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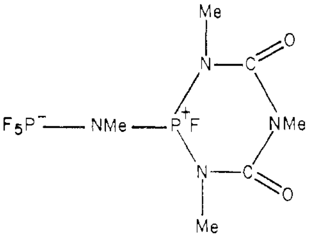

5

It is tempting to speculate that the zwitterion, **1**, is formed via intramolecular fluoride ion transfer of the initially formed bis(phosphorane), **2**. Indirect support for such a proposal stems from the fact that at 90 °C the F_A, F_B, and F_C resonances of **1** each change to very broad doublets, complete spectral collapse occurring at ca. 130 °C. We were unable to observe ^{19}F NMR specta above this temperature because of decomposition of the sample. Mindful that these obervations could be attributed to intramolecular fluoride transfer, to intermolecular fluoride transfer, or to a fluoride ion impurity catalyzed process, we deemed it important to investigate the concentration dependence of the spectra. Choosing the ^1H spectra on account of their simplicity, we found that the coalescence temperatures for the change from four- to two-line spectra were identical (77 °C) for 0.43, 0.56, and 0.82 M solutions of **1** in *sym*-tetrachloroethane. Unfortunately, the range of accessible concentrations was constrained on the one hand by the limited solubility of **1** in suitable solvents and on the other hand by the detectability of the various resonances at lower solute concentrations. Nevertheless, our data, while not proving the point rigorously, are indicative of an intramolecular transfer of F^- between **1** and **2**. Examination of molecular models suggests that this should be feasible stereochemically.

Previously reported diphosphorus zwitterions include **3**, **4**, and **5**. Compound **1**, however, has two distinctive features: (i) it is acyclic and (ii) it involves a carbon rather than a nitrogen atom between the tetra- and hexacoordinate phosphorus centers.

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Registry No. **1**, 68036-86-2; $F_4PCH_2PF_4$, 57080-69-0; Me_3SiNMe_2, 2083-91-2.

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Transition-Metal Cyanocarbon Derivatives. 5. Reactions of (1-Chloro-2,2-dicyanovinyl)manganese Derivatives with Trialkyl Phosphites: A Novel Variant of the Michaelis–Arbusov Reaction Leading to [(2,2-Dicyanovinyl)phosphonato]metal Complexes[1,2]

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Ultraviolet irradiations of the (1-chloro-2,2-dicyanovinyl)manganese derivative $(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) (Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) with the trialkyl phosphites $(RO)_3P$ (R = CH_3, C_2H_5, $(CH_3)_2CH$) in tetrahydrofuran solutions result in Michaelis–Arbusov reactions to give the (2,2-dicyanovinyl)phosphonato derivatives $(NC)_2C{=}CP(O)(OR)_2Mn(CO)$(Pf-Pf)$[P(OR)_3]$ (R = CH_3, C_2H_5) and $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2$(Pf-Pf) (R = $(CH_3)_2CH$). The closely related compounds $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2$(Pf-Pf) (R = CH_3 and C_2H_5) can be prepared by ultraviolet irradiation of $(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with $LiP(O)(OR)_2$ (R = CH_3 and C_2H_5) in tetrahydrofuran solution. Ultraviolet irradiations of the dicarbonyls $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2$(Pf-Pf) with excess trialkyl phosphite $(R'O)_3P$ (R' = CH_3 and C_2H_5 but not $(CH_3)_2CH$) result in displacement of one of the two carbonyl groups to give the corresponding monocarbonyls $(NC)_2C{=}CP(O)(OR)_2Mn(CO)$(Pf-Pf)$[P(OR')_3]$ (R = CH_3, R' = CH_3; R = C_2H_5, R' = C_2H_5; R = $(CH_3)_2CH$, R' = CH_3). The spectroscopic properties of these complexes suggest that their (2,2-dicyanovinyl)phosphonato groups $(NC)_2C{=}CP(O)(OR)_2$ are bidentate ligands which are bonded to the metal through both a vinylic carbon atom and a phosphoryl oxygen atom leading to a four-membered Mn–C–P–O chelate ring.

Introduction

The thermal reactions of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with trivalent phosphorus ligands, including trialkyl phosphites, have been shown[4,5] to result in the replacement of three carbonyl groups with two trivalent phosphorus ligands to give terminal dicyanovinylidene complexes of the general type $C_5H_5M(PR_3)_2[C{=}C(CN)_2]Cl$ (M = Mo and W). In attempts to synthesize analogous dicyanovinylidene complexes of manganese, analogous thermal reactions of $(NC)_2C{=}C(Cl)Mn(CO)_5$ with trivalent phosphorus ligands were investigated.[1] However, such thermal reactions were found to result only in the replacement of two carbonyl groups by the trivalent phosphorus ligand to give complexes of the type *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(PR_3)_2$, containing an intact 1-chloro-2,2-dicyanovinyl group.

In view of the limited types of products obtained from thermal reactions of $(NC)_2C{=}C(Cl)Mn(CO)_5$ with trivalent phosphorus ligands, we began an investigation of photochemical reactions of $(NC)_2C{=}C(Cl)Mn(CO)_5$ and *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3L_2$ derivatives[1] with trivalent phosphorus ligands. Our idea was that such photochemical reactions would lead to more extensive CO substitution by the trivalent phosphorus ligand accompanied by rearrangement of the 1-chloro-2,2-dicyanovinyl group to the dicyanovinylidene ligand. However, up to the present time such reactions have not given any dicyanovinylidene complexes of manganese but instead have resulted in the isolation of other types of unusual and interesting cyanocarbon manganese carbonyl derivatives. This paper describes the preparation and properties of a series

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