The assignment of a cis geometry to the initial reaction product is well supported by the following pieces of evidence: (1) the aqueous solution electronic absorption spectrum of the compound prepared in this study is in good agreement with that reported by Wirth and Linck,[5] who prepared solutions of the ion by photolysis of *trans*-$[Cr(en)_2FCl]ClO_4$; (2) the wavelengths of maximum absorption in the electronic spectrum are very close to those found for solutions of the ion produced by Ag^+-induced aquation of *cis*-$[Cr(en)_2FCl]Cl$;[4] (3) the infrared spectrum in the 400–600-cm^{-1} region is consistent with that previously reported for cis isomers of the type $[Cr(en)_2FX]^{n+}$.[9]

The anation of *cis*-$[Cr(en)_2F(OH_2)]^{2+}$ with thiocyanate ion proceeds with retention of geometric configuration to produce *cis*-$[Cr(en)_2FNCS]^+$. In this case the geometry of the F(NCS) product is unequivocally cis since the product was resolved into its optical antipodes. The optical rotatory dispersion studies indicate that $(+)_{5461}$-*cis*-$[Cr(en)_2FNCS]ClO_4$ and (+)-*cis*-$[Cr(en)_2F_2]I$ both have the same absolute configuration which is the same as $\Lambda(+)$-$[Co(en)_3]^{3+}$.

The *cis*-fluorothiocyanatobis(ethylenediamine)chromium(III) ion was prepared earlier by a longer, more tedious synthesis and the geometry was inferred from the electronic spectral data.[4] Resolution of the ion into its optical antipodes confirms the original assignment of the geometry.

The molar absorptivities of the *cis*-F(NCS) complex prepared in this study differ considerably from those reported earlier. This is due to the fact that the compound prepared earlier was impure.[4]

The purple product obtained in the latter stages of the aquation, $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$, appears to involve a cis arrangement of the iodo and aquo ligands. This geometry is consistent with the electronic absorption spectrum in aqueous solution, its infrared spectrum in the 400–600-cm^{-1} region, and the fact that aquation of the complex in dilute perchloric acid produces a solution whose electronic spectrum is identical with that of *cis*-$[Cr(en)_2(OH_2)_2]^{3+}$.[10]

The purple product on the basis of elemental analyses could be any one of three compounds. The complex $[Cr(en)_2(OH_2)_2]I_3$ can be eliminated at once since the electronic spectrum changes rapidly with time and $[Cr(en)_2(OH_2)_2]^{3+}$ is stable in aqueous solution. $[Cr(en)_2I_2]I \cdot 2H_2O$ was eliminated by rapid measurements of the resistance of aqueous solutions of the complex. The results always indicated three or more ions per complex ion. Thus the purple product was formulated as $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$.

Thermal dehydration of $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$ produced purple-green $[Cr(en)_2I_2]I$ as a final product.

Registry No. *cis*-$[Cr(en)_2F(OH_2)]I_2$, 59765-91-2; *cis*-$[Cr(en)_2FNCS]I$, 59765-92-3; *cis*-$[Cr(en)_2FNCS]ClO_4$, 59765-93-4; *cis*-$[Cr(en)_2FNCS]C_{10}H_{14}O_4BrS$, 59796-02-0; Λ-(+)-*cis*-$[Cr(en)_2FNCS]ClO_4$, 59796-03-1; $[Cr(en)_2IOH_2]I_2$, 59765-94-5; $[Cr(en)_2I_2]I$, 59765-95-6; *cis*-$[Cr(en)_2F_2]ClO_4$, 59765-96-7; *cis*-$[Cr(en)_2F_2][Cr(en)F_4]$, 13842-99-4; Λ-(+)-*cis*-$[Cr(en)_2F_2]I$, 14588-00-2.

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Correspondence

Phosphorus-31 Nuclear Magnetic Resonance Study of the Structure of Some "Triphosphites"

AIC60013V

Sir:

Condensation reactions between alkyl- or arylchlorophosphines and trialkyl phosphites have been shown to yield products which possess P–P bonds with the phosphorus atoms existing in different oxidation states, eq 1 and 2.[1,2] Conclusive

$$R_2PCl + P(OR')_3 \rightarrow R_2P\text{-}P(O)(OR')_2 + R'Cl \qquad (1)$$

$$RPCl_2 + 2P(OR')_3 \rightarrow RP[P(O)(OR')_2]_2 + 2R'Cl \qquad (2)$$

R = alkyl or aryl group; R′ = CH_3 or C_2H_5

evidence for the formation of these products in eq 1 and 2 was obtained from ^{31}P NMR spectroscopy. In the ^{31}P NMR spectra of these compounds the triply connected phosphorus atoms show positive chemical shifts from 85% H_3PO_4, whereas the quadruply connected phosphorus atoms exhibit negative chemical shifts from the same reference. Furthermore, these spectra exhibit the characteristic homonuclear P–P coupling constant values greater than 150 Hz.

In contrast to this observation, the products resulting from the treatment of alkylchlorophosphines with the sodium salt of dialkyl phosphites and those obtained from alkylchlorophosphines and dialkyl phosphites in the presence of triethylamine have been assigned[3] structures with P–O–P linkages, eq 3 and 4, based on triply connected phosphorus atoms. Apparently, there has been no ^{31}P spectral study reported for the products of eq 3 and 4 and, therefore, these structural assignments are far from conclusive. Furthermore, in some reactions related to eq 3, Michalski and co-workers[4] obtained phosphorus products which contain P–P bonds, eq 5. While spectroscopic evidence[5] on the dialkyl phosphites is overwhelmingly in favor of the structure $(RO)_2P(O)H$, based on quadruply connected phosphorus, spectral data on their sodium salt strongly indicate[5] the structure $(RO)_2PONa$ based on triply connected phosphorus. Since both of the reactions 3 and 4 gave identical products, it was not unreasonable nearly 20 years ago[3] to assign to these compounds a structure based on triply connected phosphorus atoms.

$$RPCl_2 + 2NaOP(OC_2H_5)_2 \rightarrow RP[OP(OC_2H_5)_2]_2 + 2NaCl \qquad (3)$$

$$RPCl_2 + 2HOP(OC_2H_5)_2 \xrightarrow{2N(C_2H_5)_3} RP[OP(OC_2H_5)_2]_2 + 2N(C_2H_5)_3HCl \qquad (4)$$

R = alkyl group

$$(RO)_2PONa + ClP(O)(OR)_2 \rightarrow (RO)_2(O)P\text{-}P(O)(OR)_2 + NaCl \qquad (5)$$

R = alkyl group

Because of our recent interest[2,6,7] in the catenation compounds of group 5 elements, we thought it desirable to reexamine the products of reactions 3 and 4 and establish their structures from ^{31}P NMR spectra.

Experimental Work. The ^{31}P NMR measurements were carried out on a Varian XL-100-15 spectrometer equipped with

Table I. ^{31}P NMR Parameters for the $RP[P(O)(OR')_2]_2$ Compounds[a]

	Chem shifts, ppm			
Compd	RP<	$(RO)_2P$-(O)-	$J_{1,2}$, Hz	$J_{2,3}$, Hz
$C_6H_5P[P(O)(OCH_3)_2]_2$	+63.4	−29.7	160.9	163.6
$C_6H_5P[P(O)(OC_2H_5)_2]_2$	+61.4	−27.1	157.2	160.5
$CH_3P[P(O)(OCH_3)_2]_2$	+87.3	−34.1	175.0	178.0
$CH_3P[P(O)(OC_2H_5)_2]_2$	+84.8	−31.4	170.5	173.1

[a] The chemical shifts and coupling constants are taken from the calculated spectra which best fit the observed ones. $J_{1,2}$ and $J_{2,3}$ refer to the calculated P-P coupling constants in $P_2(O)$-P_2-$P_3(O)$. Presumably $J_{1,2}$ equals $J_{2,3}$.

Fourier-transform accessories. The spectra were recorded both in the Fourier-transform and continuous-wave modes. Broad-band proton noise decoupling was employed and the chemical shifts were referenced to 85% H_3PO_4. Analysis of the spectra was carried out on the Nicolet 1080 minicomputer using the programs ITRCL1 and ITRCL2. In this study, it was possible to fit the experimental spectra using the iterative approach developed by Castellano and Bothner-By.[8]

Dichloromethylphosphine was obtained from Edgewood Arsenal and dichlorophenylphosphine was purchased from Orgmet, Inc., Hampstead, N.H. Trimethyl phosphite, triethyl phosphite, dimethyl phosphite, and diethyl phosphite were procured from Aldrich, Inc., Milwaukee, Wis. All of these reagents were distilled prior to use. Triethylamine obtained from J. T. Baker Chemical Co. was distilled over NaOH. Anhydrous ether from Mallinckrodt Chemical Works was dried over metallic sodium prior to use. All operations were performed in the absence of air and moisture.

All the compounds examined in this study were prepared by using methods reported previously.[1,3] Thus, $C_6H_5P[P(O)(OCH_3)_2]_2$ was made either from $C_6H_5PCl_2$ and $P(OCH_3)_3$ or from $C_6H_5PCl_2$ and $(CH_3O)_2POH$ in the presence of triethylamine. $CH_3P[P(O)(OCH_3)_2]_2$ was prepared from CH_3PCl_2 and $P(OCH_3)_3$ or from CH_3PCl_2 and $(CH_3O)_2POH$ in the presence of triethylamine. Since $(CH_3O)_2PONa$ is an insoluble solid in ether, its reaction with CH_3PCl_2 or $C_6H_5PCl_2$ in this solvent gave an intractable yellow precipitate and essentially no soluble products. To circumvent this, $C_6H_5P[P(O)(OC_2H_5)_2]_2$ and $CH_3P[P(O)(OC_2H_5)_2]_2$ were made by treating $C_6H_5PCl_2$ or CH_3PCl_2, respectively, with $(C_2H_5O)_2PONa$ in Et_2O. $C_6H_5P[P(O)(OC_2H_5)_2]_2$ and $CH_3P[P(O)(OC_2H_5)_2]_2$ were also obtained by the methods used for $CH_3P[P(O)(OCH_3)_2]_2$. All operations were performed at room temperature or below. Typically, after the removal of either NaCl or $(C_2H_5)_3NHCl$ by filtration from the reaction mixture, the solvent was volatilized under vacuum and the resulting product was examined by ^{31}P NMR.

Results and Discussion. Since the structures of the phosphorus compounds resulting from the reactions of $C_6H_5PCl_2$ with either $P(OCH_3)_3$ or $P(OC_2H_5)_3$ are known[1] to be molecules of the type $C_6H_5P[P(O)(OR')_2]_2$ with P–P bonds, we first examined the derivatives of $C_6H_5PCl_2$ obtained via reactions 3 and 4 using the corresponding dialkyl phosphites. Our results show that all the three preparative methods, i.e. eq 2–4, result in the same type of products, namely, $RP[P(O)(OR')_2]_2$. Also, we have obtained the same compound, $CH_3P[P(O)(OCH_3)_2]_2$, either from CH_3PCl_2 and $P(OCH_3)_3$ or from CH_3PCl_2 and $(CH_3O)_2POH$ in the presence of triethylamine. Furthermore, the compound obtained from CH_3PCl_2 and $NaOP(OC_2H_5)_2$ exhibited a ^{31}P NMR pattern very similar to that of $CH_3P[P(O)(OCH_3)_2]_2$ showing that it too has the structure $CH_3P[P(O)(OC_2H_5)_2]_2$. It should be pointed out that the crude products resulting from CH_3PCl_2 and $NaOP(OC_2H_5)_2$ as well as from CH_3PCl_2 and $(CH_3O)_2POH$ in the presence of triethylamine showed several unidentified minor peaks in their NMR spectra. However, these peaks, presumably attributable to impurities appeared in the "phosphate region" of the spectrum, i.e., above −50 ppm, and hence are not assignable to any compounds with the structure $RP[OP(OR')_2]_2$.

It has been suggested[2] previously that a reasonable mechanism for the formation of P–P bonded compounds from a chlorophosphine and a trialkyl phosphite might involve an onium intermediate proceeding via an Arbusov-type rearrangement. A similar mechanism may well be operating in reactions 3 and 4 to give P–P bonded compounds.

The ^{31}P NMR spectra of these triphosphine derivatives exhibit some interesting features. The ^{31}P{^{1}H} spectra of $C_6H_5P[P(O)(OCH_3)_2]_2$ and $C_6H_5P[P(O)(OC_2H_5)_2]_2$ were reported[1] by Fluck and Binder as exhibiting a triplet in the positive region of the spectrum ($C_6H_5P<$ moiety) and a doublet in the negative region ($(R'O)_2P(O)$– moiety). Although this is roughly true, under optimum conditions of resolution it can be seen that all the $RP[P(O)(OR')_2]_2$ compounds reported in this study show an AXX′ NMR pattern so that the center peak of the triplet really consists of a close-lying doublet. The pertinent NMR data on these compounds are given in Table I.

It is interesting to note that these spectra to some extent resemble the spectrum of the tripolyphosphate anion.[9] In the latter case, under optimum experimental conditions, the center resonance of the tripoly middle-group triplet is also seen to be composed of two closely spaced transitions.

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Registry No. $C_6H_5P[P(O)(OCH_3)_2]_2$, 17052-31-2; $C_6H_5P[P(O)(OC_2H_5)_2]_2$, 17052-29-8; $CH_3P[P(O)(OCH_3)_2]_2$, 59389-80-9; $CH_3P[P(O)(OC_2H_5)_2]_2$, 59389-81-0; ^{31}P, 7723-14-0.

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Direct Injection Chemical Ionization Mass Spectrometry. Mechanism of Aquation of (Dimethylformamide)pentaamminecobalt(III) and (Dimethyl sulfoxide)pentaamminecobalt(III) in Oxygen-18-Labeled Water

AIC60014N

Sir:

The use of isotopically labeled compounds is an extremely useful, powerful, and general method of studying mechanisms of chemical reactions since the method often furnishes information which can be obtained in no other way and since