days at 25°. At equilibrium the azobenzene bulb contained 4.419 ml of cyclopentane and the sample bulb 5.346 ml of cyclopentane which results in an experimental molecular weight of 224.

Acknowledgment.—We wish to thank the National Science Foundation for financial support of this work under Grant GP 9308, and Mr. J. Glore for carrying out the low-temperature nmr work.

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Synthesis of Optically Active 1,1-Dichloro-*trans*-3,5-bis(4-methylphenyl)-3,5-diphenylcyclotriphosphazatriene

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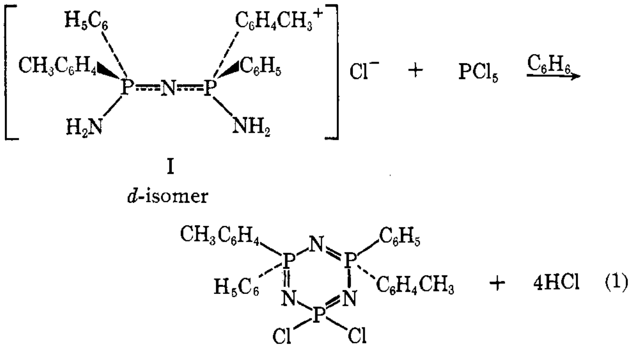
Received June 15, 1970

Numerous examples of cyclotriphosphazenes which possess the necessary asymmetry to exhibit optical isomerism have been reported, but no optical isomers have been isolated.[1] Because phosphazenes are neutral molecules, resolution of the racemic mixture presents a formidable experimental problem. By using an optically active phosphazenylphosphonium salt (I) in a cyclization reaction (eq 1), we have circumvented the difficult problem of resolving a neutral phosphazene and prepared the first optically active cyclotriphosphazatriene, *d*-1,1-dichloro-*trans*-3,5-bis(4-methylphenyl)-3,5-diphenylcyclotriphosphazatriene.



I

d-isomer

d-trans isomer
$[\alpha]^{32}{}_{5461}$ +4.2° (*c* 1.2
in methanol)

The general procedure for the synthesis of the optically active [amido(4-methylphenyl)phenylphosphazenyl]amido(4-methylphenyl)phenylphosphonium chloride (I) is outlined in eq 2–5. The final step in the synthesis of I is an adaptation of the method of Bezman and Smalley for the synthesis of $[(C_6H_5)_4P_2N_3H_4]Cl$.[4] In addition to the *dl* pair, the meso form is also possible. The racemic mixture of I was resolved in methanol by standard techniques with silver α-bromo-*d*-camphor-π-sulfonate monohydrate as the resolving agent. Colorless crystals of the diastereomer $[l\text{-}(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4][d\text{-}C_{10}H_{14}OBrSO_3]$ separated from the solution upon addition of 2-propanol and cooling. The diastereomer was twice recrystallized from methanol–2-propanol solution to give a sample, mp 201–202°, with a specific rotation $[\alpha]^{28}{}_{5461}$ +52.9° (*c* 1.90 in methanol). A slightly impure sample of the d^+,d^- diastereomer had a specific rotation $[\alpha]^{28}{}_{5461}$ +50.0° (*c* 1.64 in methanol).

$$CH_3C_6H_4NH_2 + HNO_2 \xrightarrow{H_2O} \xrightarrow{HBF_4} [CH_3C_6H_4N_2{}^+][BF_4{}^-] \quad (2)^2$$

$$[CH_3C_6H_4N_2{}^+][BF_4{}^-] + C_6H_5PCl_2 \xrightarrow[i\text{-}C_3H_7OAC]{Cu_2Br_2} \xrightarrow{Al} CH_3C_6H_4P(C_6H_5)Cl \quad (3)^3$$

$$(CH_3C_6H_4)P(C_6H_5)Cl + Cl_2 \xrightarrow[HCCl_3]{CCl_4\text{ or}} (CH_3C_6H_4)P(C_6H_5)Cl_3 \quad (4)$$

$$2(CH_3C_6H_4)P(C_6H_5)Cl_3 + 8NH_3 \xrightarrow{HCCl_3} \text{racemic mixture of I} + 5NH_4Cl \quad (5)$$

The diastereomers were converted to the respective chloride salts by passing them through a chloride-exchange column. The $l\text{-}[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$ sample, recrystallized from chloroform–ether, had a melting point of 215–218.5° and a specific rotation of $[\alpha]^{28}{}_{5461}$ −4.3° (*c* 1.43 in methanol). For the dextrorotatory phosphonium chloride, mp 215–218°, the $[\alpha]^{28}{}_{5461}$ is +4.7° (*c* 0.971 in methanol).

Experimental Section

Reagents.—Technical grade dichlorophenylphosphine (Victor) was used without further purification. Benzene was dried over sodium and fractionally distilled. The constant-boiling fraction was retained. All other organic solvents were used without further purification.

Elemental Analyses.—All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Physical and Spectroscopic Measurements.—Infrared spectral measurements were made on a Beckman Model IR-8 or IR-10 spectrophotometer. A Bendix-Ericsson ETL-NPL automatic polarimeter, Type 143A, with filtered mercury light source, was used for the measurement of specific rotations. The concentration of solute in grams per 100 ml of solution is given in parentheses after the value of the specific rotation. Molecular weight determinations were made by Galbraith Laboratories, Knoxville, Tenn., on a vapor pressure osmometer.

Synthesis of [Amido(4-methylphenyl)phenylphosphazenyl]-amido(4-methylphenyl)phenylphosphonium chloride (I).—The compound 4-methylphenyldiazonium tetrafluoroborate, dec pt 108°, was prepared in 49% yield according to the method of Roe.[2] The diazonium salt was used to prepare (4-methylphenyl)phenylchlorophosphine, bp 130–135° (4–5 mm), 23% yield, by the method of Quin and Montgomery.[3]

To a solution of 23.3 g (0.0993 mol) of (4-methylphenyl)phenylchlorophosphine in 700 ml of pure chloroform was added an excess of chlorine gas (Matheson). After removing the unreacted chlorine with a nitrogen purge, an excess of anhydrous ammonia was then added to the solution containing the phosphorane, and the ammonium chloride which precipitated was removed by filtration. Treatment of the chloroform filtrate with diethyl ether resulted in the precipitation of 9.00 g (38% yield) of $[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$, mp 215–218°, which was removed by filtration. *Anal.* Calcd for $C_{26}H_{28}N_3ClP_2$:

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[2] A. Roe, "Organic Reactions," Vol. 5, Wiley, New York, N. Y., 1949, p 193.

[3] L. D. Quin and R. E.Montgomery, *J. Org. Chem.*, **27**, 4120 (1962).

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C, 65.07; H, 5.88; N, 8.76; Cl, 7.39; P, 12.91. Found: C, 65.06; H, 5.98; N, 8.71; Cl, 7.58; P, 12.91.

Evaporation of the chloroform–ether filtrate yielded a viscous brown oil which was dissolved in 100 ml of hot acetonitrile, filtered, and cooled to 0°. A 0.70-g sample of 1,3,5-tris(4-methylphenyl)-1,3,5-triphenylcyclotriphosphazatriene, mp 250–252° (recrystallized from acetonitrile), was precipitated from the cooled solution. *Anal.* Calcd for $C_{39}H_{36}P_3$: C, 73.23; H, 5.67; N, 6.57; P, 14.53; mol wt 640. Found: C, 72.04; H, 5.43; N, 6.43; P, 14.56; mol wt (vapor pressure osmometry in chloroform) 596.

The compound $[(4\text{-}ClC_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$, mp 288–291°, was prepared in 27% yield by the same procedure but no attempt was made to resolve it. *Anal.* Calcd for $C_{42}H_{22}N_3Cl_3P_2$: C, 55.35; H, 4.26; N, 8.07; Cl, 20.43; P, 11.90. Found: C, 55.66; H, 4.20; N, 7.88; Cl, 20.14; P, 12.10.

A small quantity of 1,3,5-(4-chlorophenyl)-1,3,5-triphenylcyclotriphosphazatriene, mp 235–236.5°, was isolated from the chilled acetonitrile. *Anal.* Calcd for $C_{36}H_{27}N_3Cl_3P_3$: C, 61.69; H, 3.88; N, 6.00; Cl, 15.18; P, 13.26; mol wt 700. Found: C, 61.54; H, 3.68; N, 5.94; Cl, 14.94; P, 13.13; mol wt (vapor pressure osmometry in benzene) 698.

Resolution of $[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$.—A 5.00-g (10.4-mmol) sample of racemic $[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$ was dissolved in 20 ml of methanol. A 4.22-g (9.68-mmol) sample of silver α-bromo-*d*-camphor-π-sulfonate monohydrate[5] was dissolved in 20 ml of methanol. The two solutions were mixed and 1.38 g (9.63 mmol) of silver chloride was removed by filtration. Ten milliliters of 2-propanol was then added to the filtrate, and the solution volume was adjusted to 25–30 ml. Colorless crystals of the l^+, d^- diasteriomer precipitated from the chilled solution. The crystals were removed by filtration, recrystallized twice from methanol–2-propanol, and dried under vacuum at 100° to give a product, mp 201–202°. *Anal.* Calcd for $[(CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4][C_{10}H_{14}OBrSO_3]$: C, 57.29; H, 5.57; N, 5.57; P, 8.22. Found: C, 57.15; H, 5.46; N, 5.47; P, 8.00.

An impure d^+,d^- diasteriomer was obtained as a second fraction.

By adding only 1 mol of silver α-bromo-*d*-camphor-π-sulfonate for every 2 mol of racemic phosphonium chloride, a relatively pure sample of *d*-phosphonium chloride remains in the methanol solution after the silver chloride and l^+,d^- diasteriomer have been removed. The specific rotation measurements of the *d*-[amido-(4-methylphenyl)phenylphosphazenyl]amido(4-methylphenyl)-phenylphosphonium chloride, mp 215–218°, were taken on samples resolved in this way and recrystallized from chloroform–ether.

The l^+,d^- diasteriomer, dissolved in methanol, was converted to the phosphonium chloride on a column of Amberlite CG-400 (50 mesh) chloride-exchange resin. Methanol was the eluent. The *l*-$[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$, recrystallized from chloroform–ether, had a melting point of 215–218° and a specific rotation of $[\alpha]^{28}{}_{5461}$ −4.3° (*c* 1.43 in methanol). *Anal.* Calcd for $C_{26}H_{28}N_3ClP_2$: C, 65.07; H, 5.88; N, 8.76; P, 12.91. Found: C, 64.88; H, 5.99; N, 8.67; P, 12.90.

Synthesis of *d*-1,1-Dichloro-3,5-(4-methylphenyl)-3,5-diphenylcyclotriphosphazatriene.—The method of preparation was like that described previously for 1,1-dichloro-3,3,5,5-tetraphenylcyclotriphosphazatriene.[6] A 0.356-g (0.743-mmol) sample of *d*-$[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$ in 50 ml of benzene was heated to reflux and 0.477 g (2.29 mmol) of resublimed phosphorus pentachloride (MCB) in 20 ml of benzene was added. After 21 hr the reaction was stopped; the benzene solution was treated with water to remove unreacted phosphorus pentachloride and was then dried over sodium sulfate. A 0.187-g sample of crude *d*-$(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2Cl_3P_3N_3$ (47% yield) was precipitated. A single recrystallization of the sample from acetonitrile gave 0.0215 g of a white solid, mp 96–103°, which has a specific rotation $[\alpha]^{32}{}_{5461}$ +4.2° (*c* 1.2 in methanol). The racemic mixture of $(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2Cl_2P_3N_3$, prepared in the same way with racemic $[(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4]Cl$, has a melting point of 116–118°.[7] The infrared spectra of the racemate and dextrorotatory salt are identical. *Anal.* Calcd for $C_{26}H_{24}N_3Cl_2P_3$: C, 57.58; H, 4.46; N, 7.75; Cl, 13.08; P, 17.13. Found (racemate): C, 57.35; H, 4.56; N, 7.92; Cl, 13.13; P, 17.02.

A summary of the strong infrared-active bands assigned to the P═N—P stretching vibration for compounds reported herein is given in Table I for identification purposes.

TABLE I

INFRARED-ACTIVE P═N—P VIBRATIONAL BANDS

Compound	ν, cm^{-1}
$(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2Cl_2P_3N_3$	1216, 1204, 1173
$(4\text{-}ClC_6H_4)_2(C_6H_5)_2Cl_2P_3N_3$	1229 sh, 1217, 1187, 1173
$[(4\text{-}CH_3C_6H_4)(C_6H_5)PN]_3$	1196 sh, 1159 br
$[(4\text{-}ClC_6H_4)(C_6H_5)PN]_3$	1190 sh, 1160 br
$(4\text{-}CH_3C_6H_4)_2(C_6H_5)_2P_2N_3H_4Cl$	1310, 1292, 1268
$(4\text{-}ClC_6H_4)_2(C_6H_5)_2P_2N_3H_4Cl$	1305, 1290, 1265

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Kinetics and Mechanisms of the Substitution Reactions of Cobalt Dithiolate Systems

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Received June 17, 1970

It has been shown[1–4] that $Co(mnt)_2^-$ (mnt = maleonitriledithiolate) displays many properties at variance with the usual behavior of cobalt(III) and the metal resembles a d^8 system more closely than a d^6 system. We previously reported[5] the kinetics for the transformation of the five-coordinate adducts to six-coordinate adducts according to reaction 1. Both a dissociative

$$Co(mnt)_2P(C_6H_5)_3^- + L\text{-}L \longrightarrow Co(mnt)_2(L\text{-}L)^{z-} + P(C_6H_5)_3 \qquad (1)$$

and an associative pathway were found to operate. Herein we report kinetic results for the transformation of six-coordinate adducts to five-coordinate adducts according to reaction 2 where L-L = en, bipy, phen, and mnt^{2-}.

$$Co(mnt)_2(L\text{-}L)^{z-} + P(n\text{-}C_4H_9)_3 \longrightarrow Co(mnt)_2P(n\text{-}C_4H_9)_3^- + L\text{-}L \qquad (2)$$

Experimental Section

Most of the experimental details have been previously re-

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