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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CONTRIBUTION FROM THE CHEMICAL LABORATORIES
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Kinetics and Mechanisms of the Substitution Reactions of Cobalt Dithiolate Systems

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AND DWIGHT A. SWEIGART

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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

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

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-}.

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

Experimental Section

Most of the experimental details have been previously re-

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ported.[5] Ethylenediamine (en), bipyridine (bipy), and *o*-phenanthroline (phen) were purchased. Either a commercially available stopped-flow device or a Beckman DU-2 spectrophotometer equipped with a Gilford Model 220 optical density converter was used to follow the kinetics. The reactions were studied in methanol at an ionic strength of 0.1 *M* (sodium perchlorate). The Co(mnt)$_2$(L-L)$^{x-}$ complexes were prepared *in situ*. Spectra of reactants and products agree with those previously reported.[3] For the kinetic runs the cobalt complex was made 2 × 10^{-4} *M*. Runs were made under pseudo-first-order conditions with P(n-C$_4$H$_9$)$_3$ in at least 15-fold excess.

Results and Discussion

An interesting variance in kinetic behavior was found for the different leaving groups in reaction 2. The results for L-L = en are given in Figure 1. For L-L = bipy the reaction is much slower than for en and is independent of [P(n-C$_4$H$_9$)$_3$] over the range (3–75) × 10^{-3} *M* when no excess bipy is present. The rate constant for L-L = bipy is 9.8 × 10^{-4} sec^{-1} at 25°. With a 150-fold excess of bipy present (0.03 *M*) the k_{obsd} values are significantly lowered at low values of [P(n-C$_4$H$_9$)$_3$] and the intercept is zero while k_{obsd} approaches 9.8 × 10^{-4} sec^{-1} at high concentrations of nucleophile.

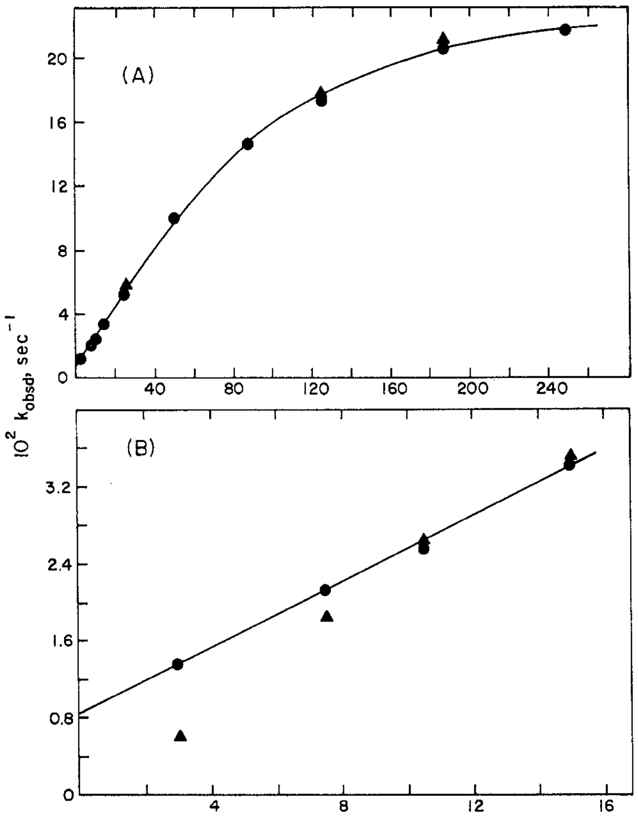

Figure 1.—The dependence of k_{obsd} on tributylphosphine concentration for L-L = ethylenediamine. Shown is the effect of excess en (A) over the entire concentration range and (B) at low concentration: ●, no excess en; ▲, 50-fold excess of leaving group ([en] = 0.01 *M*).

For L-L = phen the reaction times were of the order of days and good kinetic data could not be obtained owing to slow decomposition of the reactants. For Co(mnt)$_3^{3-}$, *i.e.*, L-L = mnt^{2-}, the reaction (eq 2) is first order in P(n-C$_4$H$_9$)$_3$ in the range (1–50) × 10^{-2} *M*.

$$k_{\text{obsd}}\ (\text{sec}^{-1}) = 3.0 \times 10^{-2}[\text{P}(n\text{-C}_4\text{H}_9)_3] \qquad (3)$$

Excess mnt^{2-} did not affect the reaction rates.

The mechanism we propose to account for these results, given in Figure 2, is the microscopic reverse of the proposed mechanism[5] for reaction 1. Assuming a steady state for species B and C, Figure 2 predicts

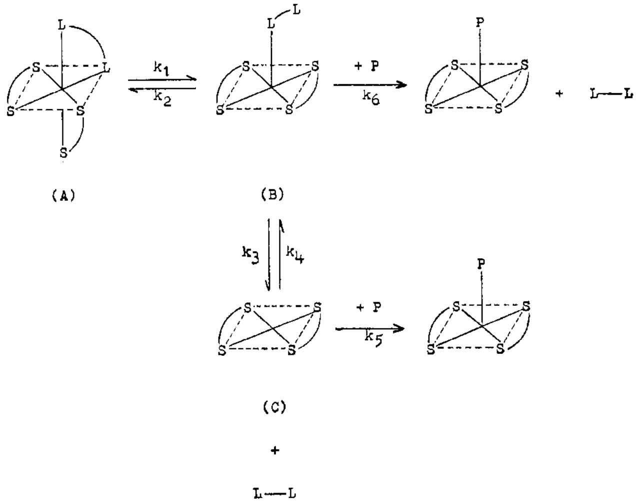

Figure 2.—Proposed mechanism for substitution reactions. P = tributylphosphine and L-L = leaving group. Charges are omitted.

$$k_{\text{obsd}} = \frac{k_1\{k_3k_5[\text{P}] + k_6[\text{P}](k_4[\text{L-L}] + k_5[\text{P}])\}}{k_3k_5[\text{P}] + (k_2 + k_6[\text{P}])(k_4[\text{L-L}] + k_5[\text{P}])} \qquad (4)$$

In the limit of large [P], k_{obsd} eventually reaches a limiting value equal to k_1. Furthermore, in the limit [P] = 0 eq 4 requires $k_{\text{obsd}} = 0$ when excess leaving group, L-L, is present. In the absence of excess leaving group k_{obsd} approaches $k_1k_3/(k_2 + k_3)$ as [P] goes to zero. Since L-L is released as the reaction proceeds, the value of the intercept observed for the runs with no initial excess of L-L may be between zero and $k_1k_3/(k_2 + k_3)$. The observed intercepts in this study are consistent with these predictions.

The en adduct shows a limiting rate at high concentrations of nucleophile (Figure 1). Also, as stated above, the bipy adduct reaction is independent of the nucleophile concentration. According to our mechanism this means that k_1 = 0.22 sec^{-1} for L-L = en and k_1 = 9.8 × 10^{-4} sec^{-1} for L-L = bipy. This difference may reflect a certain amount of inflexibility in bipy[5-7] not present with en.

As shown by eq 3, a limiting rate was not observed for L-L = mnt^{2-}. This is not necessarily inconsistent with eq 4 since an excess of nucleophile beyond experimental feasibility may be required to reach a limiting rate which depends, *e.g.*, on the relative magnitudes of k_2 and k_6[P].

It is clear that the mechanism in Figure 2 is not the only one that could be conjured up to explain the data.

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However, it is significant that it is possible to explain the kinetics of reaction 2 by a mechanism that is the microscopic reverse of that proposed to explain reaction 1. Hence the proposed mechanisms reinforce each other, although one should note that reactions 1 and 2 are not strictly the reverse of each other because the phosphines are different. Finally it is important to note that Figure 2 is essentially identical with the well-established mechanism for the acid hydrolysis of metal chelates.[6] This further strengthens the credibility of the proposed mechanism for (2) and, by the principle of microscopic reversibility, also for (1).

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Kinetics of the Chromium(II) Reduction of Isocyanatopentaamminecobalt(III)

BY R. J. BALAHURA AND R. B. JORDAN*

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In a recent study[1] on the preparation and reactivity of $(NH_3)_5CoNCO^{2+}$ Burmeister and DeStefano reported that the chromium(II) reduction of this complex fails to produce any $(H_2O)_5CrNCO^{2+}$ or its linkage isomer. This conclusion, combined with a discussion of why cyanate should not be as good a bridging group as CN^- or N_3^- and the long reaction times used, leaves the impression that the reaction is quite slow and that a bridging mechanism may not be operative. However in the concluding paragraph of the paper Burmeister and DeStefano note that they may never have actually observed the chromium(II) reduction reaction due to possible oxidation and/or hydrolysis.

Our preliminary studies indicated that the reduction of $(NH_3)_5CoNCO^+$ by chromium(II) was much faster than indicated by the previous work. In fact the reaction is complete in ~10 sec at the concentrations used by Burmeister and DeStefano. In order to obtain a quantitative measure of the reduction rate, a more detailed kinetic study was undertaken as reported here.

Experimental Section

The $((NH_3)_5CoNCO)(ClO_4)_2$ used in this study was prepared from aquopentaamminecobalt(III) perchlorate and either urea in trimethyl phosphate or molten urea or urea in *N,N*-dimethylacetamide as described previously.[2] The compound from the molten urea preparation has been further purified by cation-exchange chromatography on Rexyn 102(H) in the sodium ion form. The visible spectrum of the chromatographed sample had maxima at 353 (ϵ 82.6) and 501 nm (ϵ 128) and an infrared spectrum with a characteristic maximum at 2265 cm^{-1}. The chromatographed material has extinction coefficients almost identical with those reported previously[2] but somewhat different from those reported by Burmeister and DeStefano.[1]

The rate of the chromium(II) reduction was followed spectrophotometrically at 500 nm using standard syringe techniques and temperature control apparatus as described previously.[3] The lithium perchlorate, perchloric acid, and chromous perchlorate solutions were prepared and standardized also as previously described.[3] The reduction was initiated by adding a degassed solution of cobalt complex to a solution of chromous perchlorate, $HClO_4$, and $LiClO_4$, at the appropriate concentrations and temperature, in a spectrophotometric cell.

Results and Discussion

The kinetics of the reduction were studied as a function of hydrogen ion and chromium(II) concentrations. The results are summarized in Table I. The concentration dependence of the rate is given by

TABLE I

KINETIC DATA FOR THE REDUCTION OF $(NH_3)_5CoNCO^{2+}$ BY CHROMIUM(II) (1 *M* $LiClO_4$–$HClO_4$)

Temp, °C	10^3[oxidant][a]	10^2[reductant][a]	$10^2[HClO_4]$[a]	10^2k, sec^{-1} Obsd	10^2k, sec^{-1} Calcd[b]
25	1.7	1.05	5.62	1.47	1.44
25	1.7	1.05	5.62	1.47	1.44
25	2.1	1.61	5.67	1.76	1.72
25	2.0	1.61	5.67	1.76	1.72
25	1.4	2.42	5.65	2.11	2.13
25	1.4	2.91	5.58	2.31	2.36
25	1.2	3.23	5.67	2.43	2.53
25	2.0	3.88	5.56	2.94	2.84
25	1.7	4.20	5.64	3.15	3.01
25	1.2	3.23	0.87	1.58	1.76
25	1.5	3.23	3.27	2.24	2.14
25	1.5	3.23	3.27	2.27	2.14
25	1.2	3.23	8.01	2.89	2.95
25	1.3	3.23	12.8	3.59	3.69
25	1.4	3.23	19.9	4.78	4.84
25	1.4	3.23	19.9	4.47	4.84
10	1.4	1.61	5.20	0.578	0.572
10	1.7	1.50	5.59	0.533	0.565
10	1.7	1.50	5.59	0.530	0.565
10	1.8	3.00	5.57	0.856	0.894
10	1.6	3.00	5.57	0.856	0.894
10	1.7	4.50	5.56	1.22	1.22
10	1.8	6.00	5.54	1.56	1.55

[a] Initial concentrations in molar units. [b] Calculated from eq 1 with $k_1 = 0.500\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 0.162\ M^{-1}\ \text{sec}^{-1}$ at 25° and with $k_1 = 0.22\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 0.042\ M^{-1}\ \text{sec}^{-1}$ at 10°. The activation parameters for k_1 are $\Delta H^* = 8.8$ kcal mol^{-1} and $\Delta S^* = -30.4$ eu, calculated from k_1 at 25 and 10°.

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} = k_1[Cr^{2+}] + k_2[H^+] \qquad (1)$$

The results in Table I give $k_1 = 0.51\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 0.162\ M^{-1}\ \text{sec}^{-1}$ at 25° in 1 *M* $LiClO_4$–$HClO_4$, while at 10° $k_1 = 0.22\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 0.042\ M^{-1}\ \text{sec}^{-1}$.

It would seem most probable that the k_2 path, which

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