

tially 40 g of potassium chloride (oven dried) was placed in the flask and carefully heated with a yellow gas flame under flowing nitrogen. Before attaching the "Tygon" tubing line to the trimethylaluminum cylinder, the line was carefully purged with nitrogen. The nitrogen inlet was then clamped off and 500 ml of trimethylaluminum solution was allowed to run into the reaction vessel. With the storage vessels used there was enough cylinder pressure to force the liquid out but as a precaution an auxiliary nitrogen line was connected to the gas phase of the cylinder to force solution out. It was found convenient to measure the solution volume with a calibrated addition funnel. After the alkylaluminum solution was added to the reaction vessel, the remaining liquid was drained from the tubing, the nitrogen inlet was unclamped, and the addition funnel was purged for about 30 min to remove the last traces of aluminum compound. The alkylaluminum line was then clamped in two places and cut with a pliers to remove the cylinder from the system. Trimethylchlorosilane, 108 g, was placed in the addition funnel with a syringe and was then added to the reaction mixture dropwise under a slow nitrogen flow. After the addition was complete, the system was set up for distillation by removal of the addition funnel between the nitrogen inlet and flask and replacement of the reflux condenser with a distillation head, condenser, and flask. In all reactions of this type it has been found necessary to heat the reaction mixture strongly while stirring to force the reaction to completion and to distill the product. The product in the reaction being tetramethylsilane made it necessary to cool the receiver in ice. In order to free the product from traces of the trimethylaluminum, the product was redistilled to yield 55 g of product boiling at 27°, 63% yield.

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A Chromatographic Study of the Diamine-Exchange Reaction between *trans*-Dichlorobis(diamine)cobalt(III) Compounds

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Suggested procedures for the preparation of the mixed diamine complexes *trans*-[Co(en)(pn)Cl₂]Cl¹ and *trans*-[Co(en)(tn)Cl₂]Cl² (where en = ethylenediamine, pn = propylenediamine, and tn = trimethylenediamine) call for treatment of the corresponding dinitro complexes with concentrated hydrochloric acid. Recent advances in the chromatography of diamine-cobalt(III) complexes³ have stimulated a more thorough

examination of the products obtained in a preparative reaction of the type mentioned above. We have found that treatment of Co(en)(NH₃)(NO₂)₂ with an aqueous solution of propylenediamine (1:1) followed by concentrated HCl results in the formation of *trans*-[Co(en)₂Cl₂]Cl, *trans*-[Co(en)(pn)Cl₂]Cl, and *trans*-[Co(pn)₂Cl₂]Cl.⁴ Furthermore, some *trans*-[Co(en)(pn)Cl₂]Cl is obtained on equilibration of a mixture of *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl in aqueous HCl or methanol. In both instances a statistical distribution of diamine ligands is attained at equilibrium.⁵ For the complexes under investigation, *trans* to *cis* isomerization and inner-sphere displacement of chloride by solvent are significant reactions in aqueous solution. Because these reactions are stoichiometrically insignificant in methanol, it was selected as the solvent for the exchange study.

We have found that the exchange of diamine between *trans*-dichlorobis(diamine)cobalt(III) compounds is relatively rapid in aqueous and methanolic solutions. This finding seriously alters the concept that the diamine ligands in such systems are nonlabile.

Experimental Section

Co(en)(NH₃)(NO₂)₂ and [Co(en)(pn)(NO₂)₂]NO₂ were prepared as described by Werner.^{6,7} *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl were obtained by the procedures of Bailar.⁸ ACS reagent grade methanol containing about 0.05% water was used without drying.⁹ Solutions of sodium methoxide in methanol were standardized by titration with aqueous HCl.

The similarities of the visible and ultraviolet spectra of the three dichlorodiamine complexes made a direct spectrophotometric determination of the extent of diamine exchange impossible. Therefore, a paper chromatographic method was developed for the separation and semiquantitative estimation of the three *trans*-dichlorodiamine complexes. A convenient total concentration of cobalt complexes in the samples to be analyzed chromatographically was 10⁻² M. The methanolic solutions in 1.5 × 10⁻² ml portions were spotted on Whatman No. 1 acid-washed paper. After evaporation of the methanol, the paper was coiled into a cylinder 25 cm long and stapled. The chromatogram was developed by standing it in a shallow container filled with 85% ethanol-15% water under a bell jar. When the solvent approached the top of the paper (6-7 hr), the chromatogram was removed from the bell jar and dried rapidly. The spots on the developed chromatogram were located by use of ultraviolet light in a darkroom. The R_f values¹⁰ determined for *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl were 0.32 ± 0.04 and 0.60 ± 0.02, respectively. Differences of 10% in sample concentrations could be distinguished by visual comparison of the spots on a developed chromatogram. *trans*-[Co(en)₂Cl₂]Cl could not be differentiated from *trans*-[Co(pn)₂Cl₂]Cl by spot intensity. There-

(4) Contrary to the findings of Mathieu,¹ who reported only *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl products.

(5) The statistical distribution of 1:2:1 was based on equal spot intensities for *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl in the same sample and for *trans*-[Co(en)(pn)Cl₂]Cl when this sample was diluted to half the original concentration. These spots were processed on the same chromatogram. In concentrated HCl at ~100° the half-time for the exchange is about 30 min.

(6) A. Werner, *Helv. Chim. Acta*, **1**, 10 (1918).

(7) L. A. P. Kane-Maguire and T. E. MacDermott, *Inorg. Chem.*, **7**, 769 (1968), have recently shown the material reported by Werner⁶ as [Co(en)(pn)(NO₂)₂]NO₂ to consist of bisethylenediamine and bispropylenediamine complexes as well as the mixed diamine complex.

(8) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

(9) Attempts to dry the methanol with magnesium resulted in an undesirable increase in basicity, which repeated distillations failed to reduce.

(10) R_f is defined as the ratio of the distance the spot moved up the paper to the maximum height reached by the solvent. The initial points for both solvent and complex were taken as the center of the original spot as placed on the paper.

(1) J. P. Mathieu, *Ann. Phys. (Paris)*, **19** (11) 340 (1944).

(2) J. C. Bailar, Jr., and J. B. Work, *J. Am. Chem. Soc.*, **68**, 234 (1946).

(3) See, for example, F. P. Dwyer, et al., *ibid.*, **86** 590 (1964), and earlier papers in that series.

fore, it was assumed that *trans*-[Co(en)(pn)Cl₂]Cl would show the same absorption intensity *via* the visual observation method.¹¹

When chromatographed, a solution containing *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl which had been equilibrated in methanol produced three spots. In addition to spots with the two expected *R_f* values, a third spot with an *R_f* value of 0.48 ± 0.02 appeared. This third spot with its intermediate *R_f* value was logically ascribed to the mixed diamine complex *trans*-[Co(en)(pn)Cl₂]Cl.¹² The diamine exchange in equilibrating methanol solutions was monitored by chromatographing samples at appropriate intervals. Time was recorded from the instant of mixing of the *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl solutions until application of the resulting solution to the acid-washed paper quenched the exchange reaction. When the spot intensities for *trans*-[Co(en)₂Cl₂]Cl, *trans*-[Co(pn)₂Cl₂]Cl, and *trans*-[Co(en)(pn)Cl₂]Cl on a developed chromatogram were all equal, the elapsed time was designated as *t*_{2/3}. The visual detection method was deemed most reliable under those conditions.

Bulk separation of the mixed diamine complex from the two parent compounds was achieved in two ways. It was found that the room-temperature solubilities in ethanol of the three complexes were in an approximate 100:10:1 ratio for *trans*-[Co(pn)₂Cl₂]Cl, *trans*-[Co(en)(pn)Cl₂]Cl, and *trans*-[Co(en)₂Cl₂]Cl, respectively. Fractional solution with HCl-acidified ethanol thus enabled preparation of pure *trans*-[Co(en)(pn)Cl₂]Cl, using ethyl ether to precipitate the complex. The second preparative procedure employed a 5.0-cm diameter, 35 cm long column of Whatman acid-washed cellulose powder. The sample was dissolved in 85% ethanol and absorbed into some dry cellulose powder. This green powder was spread on the top of the column to a depth of about 0.16 cm and covered with 1.3 cm of wet powder. During elution with 85% ethanol, separation of the complexes into three green bands occurred. The pure separated products were identified by paper chromatography, as described above. The visible spectrum of *trans*-[Co(en)(pn)Cl₂]Cl has band profiles, positions, and intensities equivalent to an equimolar mixture of the two *trans*-bisdiamine compounds.

Results and Discussion

In methanolic solutions containing *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl, diamine exchange occurred under basic, neutral, or acidic conditions. The rate of this reaction was unaffected by the addition of small amounts of CoCl₂, LiCl, (CH₃)₄NCl, or H₂O but showed a strong, direct dependence on the concentration of base.

Several series of diamine-exchange rate studies were made at 25° with varying amounts of added sodium methoxide. The data given in Table I are representative of the results obtained. The initial solutions were 5.0 × 10⁻³ *M* in both *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(pn)₂Cl₂]Cl. The times required, *t*_{2/3},¹³ for the reactions to proceed until the concentrations of all three complexes were equal (*i.e.*, two-thirds of the way to equilibrium) are listed. These times have been converted into pseudo-first-order rate constants, based on complex concentrations (last column), which are seen to vary more or less linearly with the methoxide concentration. The experimental rate constant in pure methanol (3 × 10⁻⁶ sec⁻¹) is probably

(11) Elution of the material from the spots and comparison of the ultraviolet absorptions for these solutions may well lead to better quantitative estimates than the visual comparison method used.

(12) Obviously, the separation method does not distinguish the optical isomers resulting from the use of a *dl* mixture of propylenediamine in the preparations.

(13) *t*_{2/3} is inversely proportional to the rate of diamine exchange even if the rate constants for the forward and reverse exchange reactions are not identical.

TABLE I
RATE DATA FOR DIAMINE EXCHANGE BETWEEN
trans-[Co(en)₂Cl₂]Cl AND *trans*-[Co(pn)₂Cl₂]Cl
IN METHANOL AT 25°

Concn of added methoxide, <i>M</i> × 10 ⁴	<i>t</i> _{2/3} , hr	10 ⁶ <i>k</i> , sec ⁻¹
...	80 ± 10	3
0.65	28 ± 4	10
1.30	14 ± 2	20
2.60	7 ± 1	40

somewhat larger than the true value as a result of residual basicity of the solvent, since in 0.1 *M* methanolic HCl, the rate constant is found to be only about 8 × 10⁻⁸ sec⁻¹. The rate of the base-catalyzed reaction (obtained from the slope of the rate *vs.* methoxide concentration plot) is close to 1.5 × 10⁻¹ *M*⁻¹ sec⁻¹.

Insufficient data are available from this preliminary study to enable deduction of a mechanism for the process, but certain conclusions are warranted. It is known, for example, that chloride release by methoxide occurs at a rate several hundred times greater than the methoxide-catalyzed diamine-exchange reaction (500 × 10⁻¹ as compared to 1.5 × 10⁻¹ *M*⁻¹ sec⁻¹).¹⁴ The reactive species in the latter process therefore may well be methoxide-substituted complexes. However, spectrophotometric monitoring of the reactions gave no evidence of buildup of any new species. The products obtained after equilibration consisted entirely of the three dichlorochlorides specified, with complete retention of the *trans* configuration. This observation is particularly significant for reactions where *t*_{2/3} was less than 8 hr, since the half-times for *cis* to *trans* isomerization of [Co(en)₂Cl₂]Cl and [Co(pn)₂Cl₂]Cl in methanol were found to be about 8 hr at 25°. ^{15,16} Even after 3 months there was no spectrophotometric evidence for trisdiamine or tetrachloro complexes. The reaction between *cis*-dichlorobis(ethylenediamine)-cobalt(III) ion and propylenediamine in methanol has been shown to yield several different tris compounds within 2 days.¹⁷ Obviously, the transfer of diamine from one cobalt ion to the other must be some sort of concerted process, with no complete release of diamine at any stage and involving, perhaps, a binuclear diamine-bridged intermediate. Evidence for such bridged structures is scanty, but recent significant evidence concerning this type of combination has been reported in the case of a cobalt(III) complex involving *trans*-1,2-cyclopentanediamine.¹⁸ In addition to the diamine-exchange reaction discussed here, we have found an analogous base-catalyzed exchange reaction between *trans*-[Co(en)₂Cl₂]Cl and *trans*-[Co(*i*-bn)₂Cl₂]Cl in methanol (where *i*-bn = isobutylenediamine). The respective *R_f* values obtained for *trans*-[Co(*i*-bn)₂-

(14) D. W. Brown and C. K. Ingold, *J. Chem. Soc.*, 2674 (1953).

(15) R. C. Brasted and C. Hirayama, *J. Am. Chem. Soc.*, **80**, 788 (1958).

(16) *cis* to *trans* isomerization does occur in the solvent mixture used in development of the chromatograms (85% ethanol-15% water). In separate experiments when as little as 10% *cis* complex was present, spot trailing was observed. The respective values of *R_f*(*cis*) are much smaller than those of *R_f*(*trans*) for the two bis complexes. Accurate values of *R_f*(*cis*) could not, however, be determined because of the isomerization during development.

(17) R. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **81**, 5269 (1959).

(18) J. F. Phillips and D. J. Royer, *Inorg. Chem.*, **4**, 616 (1965).

$\text{Cl}_2\text{]Cl}$ and *trans*- $[\text{Co}(i\text{-bn})(\text{en})\text{Cl}_2]\text{Cl}$ in 85% ethanol-15% water are 0.79 ± 0.04 and 0.58 ± 0.02 . In view of our findings, we would like to join Kane-Maguire and MacDermott⁷ in emphasizing the importance of chromatographic monitoring in studying reactions of mixed diamine ligand systems.

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Amine-Substituted Iron Tetracarbonyl¹

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Because nitrogen ligands do not have available low-lying d orbitals, it has been questionable whether or not amines would form complexes with group VIII metals in low oxidation states, analogous to the phosphines, arsines, and stibines, *e.g.*, $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$. Knowledge of the stability and reactivity of the (amine) $\text{Fe}(\text{CO})_4$ compounds would shed light on the importance of d-orbital participation in the bonding of the P, As, and Sb analogs.

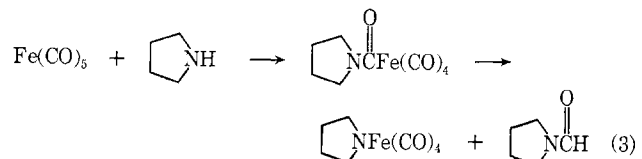
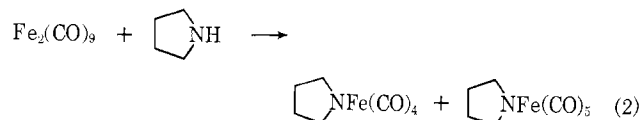
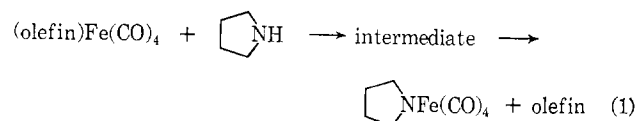
Edgell and coworkers² have reported that when $\text{Fe}(\text{CO})_5$ and amines react directly, using the amine itself as solvent, a first species, $>\text{NC}(=\text{O})\text{Fe}(\text{CO})_4$, is eventually converted into a species having infrared bands at 2045 (w), 1951 (m), and 1924 (s) cm^{-1} in the CO stretching region, proposed to be $>\text{NFe}(\text{CO})_4$ (see Figure 4 of ref 2 for spectra). Either the N-formylated amine or the CO gas or both are also formed in the reaction. The final metal carbonyl species was not isolated. We wish to report here the results of certain experiments which confirm that the species yielding the observed spectrum is the proposed amine-substituted iron tetracarbonyl.

It is well known that amines displace olefins as ligands in metal carbonyl compounds. We have therefore synthesized (maleic anhydride) $\text{Fe}(\text{CO})_4$ from $\text{Fe}_2(\text{CO})_9$ and the olefin according to the method of Weiss and coworkers,³ as well as (cyclohexene) $\text{Fe}(\text{CO})_4$ (which has not been previously described to our knowledge, but can be made by a method identical with that used in ref 3). In each case, when pyrrolidine, $\text{C}_4\text{H}_8\text{NH}$, is added to a benzene solution of the (olefin) $\text{Fe}(\text{CO})_4$, an

immediate reaction takes place. This yields an intermediate which, over a period of several hours, is converted into the identical metal carbonyl species reported by Edgell, *et al.*,² *i.e.*, bands appear in the infrared spectrum at 2045 (w), 1951 (m), and 1924 (s) cm^{-1} in the CO stretching region. Although we have no evidence as yet, we speculate that the intermediate is either due to an equatorial to axial isomerization of the amine-substituted iron tetracarbonyl or represents a step of higher coordination before free olefin is liberated. In the case of maleic anhydride, if excess amine is present the expected reaction between the anhydride and the amine ensues. No CO is given off in these reactions, nor is there any evidence for any N-formylpyrrolidine being formed.

We have further found that when pyrrolidine is added to $\text{Fe}_2(\text{CO})_9$ directly at room temperature, the $\text{Fe}_2(\text{CO})_9$ dissolves yielding immediately a species, as shown by infrared spectra, identical with that obtained finally in the olefin-displacement reactions discussed above and in the direct $\text{Fe}(\text{CO})_5$ -amine reaction after some time. That this species is not due to a reaction of $\text{Fe}(\text{CO})_5$ formed in the decomposition of $\text{Fe}_2(\text{CO})_9$ is clear for three reasons: (1) the reaction of $\text{Fe}(\text{CO})_5$ with pyrrolidine takes 6.75 hr at 60°; (2) direct reaction with $\text{Fe}(\text{CO})_5$ yields large amounts of N-formylpyrrolidine, and none is found here; (3) if excess amine is present, we find that it reacts with $\text{Fe}(\text{CO})_5$ to give the expected first intermediate, $>\text{NC}(=\text{O})\text{Fe}(\text{CO})_4$. It is worthwhile to point out that this work again upholds the generalization that $\text{Fe}_2(\text{CO})_9$ often reacts as though it were $\text{Fe}(\text{CO})_4 + \text{Fe}(\text{CO})_5$.

It would appear that the series of reactions



all yielding identical products is excellent evidence for the proposal that this product is indeed amine-substituted iron tetracarbonyl. To date, however, all attempts to isolate the products of reactions 1 and 2 have led to decomposition, probably to polynuclear species. This is in sharp contrast to the phosphine, arsine, and stibine iron tetracarbonyls, which are generally quite stable and unreactive solids.

Experimental Section

$\text{Fe}_2(\text{CO})_9$ was prepared by Hg-lamp irradiation of a glacial acetic acid solution of $\text{Fe}(\text{CO})_5$ in a Vycor test tube, cooled by

(1) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 3080, (1965).

(3) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).