(11) The pK_1 and pK_2 values for the trans-diaquo complex are, at 25 °C and $I = 0.5$ M ($NaClO_4$), 2.9 ± 0.1 and 7.2 ± 0.1, respectively, while for the cis congeners, the corresponding values are 4.9 ± 0.2 and 8.0 ± 0.2 (see ref 6). The spectrum for the *cis*-Co(cyclam)$(OH_2)(OH)^{2+}$ species was not recorded since it differs only slightly from the average of its diaquo and dihydroxy analogues.
(12) For the trans species, there is no need for the rapid mixing and scanning, nor for cooling below room temperature, since there is no isomerization and ring closure does not occur with these complexes.
(13) The same spectral result was obtained on long standing in excess of 0.5 M $NaHCO_3$-Na_2CO_3 buffer, but the subsequent ion-exchange experiment could not be carried out with this solution because of the excess of carbonate.
(14) To avoid any appreciable change in pH of the buffer solution, high buffer concentrations (0.2–0.3 M) were used.
(15) This is consistent with our earlier findings that $Co(NH_3)_5H_2O^{3+}$ (ref 16) and Co(tren)$(H_2O)_2^{3+}$ (ref 3) do not react with CO_2, and that the cis → trans isomerization of the acidified solution of Co(cyclam)$(H_2O)_2^{3+}$ complex is very slow (ref 6).
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(17) For the "tren" species (ref 3), small changes in K_2 with temperature were noted, but these are almost within experimental error. Possible similar variations in the present instance are therefore ignored and the published K_2 values at 25 °C (ref 6) are utilized over the 15–25 °C range.
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(20) See R. B. Martin, *J. Inorg. Nucl. Chem.*, **38,** 511 (1976). This correlation is based on consideration of the relative nucleophilicity of "bound" hydroxide ion as suggested by a modified form of the Swain-Scott relationship.
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Photochemistry of Coordination Compounds. 15. *trans*- and *cis*-$[Co(en)_2(NH_3)Cl](NO_3)_2$

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Abstract: The ligand field photolysis (488 nm) of *trans*- and *cis*-$[Co(en)_2(NH_3)Cl](NO_3)_2$ in acidic solution is reported. Quantum yields (all × 10^4) for ammonia aquation (14.8, 2.06, 50.7) and chloride aquation (2.96, 3.10, 17.1) for *trans*-$Co(en)_2(NH_3)Cl^{2+}$, *cis*-$Co(en)_2(NH_3)Cl^{2+}$, and $Co(NH_3)_5Cl^{2+}$, respectively, support a previous suggestion that photolysis rules similar to those for Cr(III) ammines are operative for Co(III) ammines as well. Isomer analysis shows that photoaquation of *trans*-$Co(en)_2(NH_3)Cl^{2+}$ occurs with essentially complete stereoretention. The principal photoaquation paths for *cis*-Co-$(en)_2(NH_3)Cl^{2+}$ are more complicated, yielding mainly *cis*-$Co(en)_2(NH_3)(H_2O)^{3+}$ as the chloride photoaquation product but mainly *trans*-$Co(en)_2(H_2O)Cl^{2+}$ as the ammonia photoaquation product. These results may be accounted for by the same photolysis rules, with the added mechanistic assumption that if one end of an ethylenediamine is labilized it may undergo an edge displacement to detach an adjacent monodentate ligand.

The photochemistry of Co(III) ammines has, until recently, been primarily that following irradiation in the wavelength region of the first charge transfer (CT) band; such irradiation leads to photochemistry dominated by redox decomposition.[2,3] Photochemistry in the wavelength region of the first (and, if uncomplicated by CT characteristics, the second) ligand field band was sparse until the advent of high power CW lasers because of the very low quantum yields. However, in a recent series of publications the ligand field photochemistry of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5(H_2O)^{3+}$, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5Cl^{2+}$, *trans*-$Co(en)_2Cl_2^+$, *trans*-Co(cyclam)Cl_2^+, *cis*-$Co(en)_2Cl_2^+$, and of various Co(III) trien and tren complexes was reported in some detail.[4-7] Results for several of these complexes have been confirmed and extended to irradiations in the wavelength region of the presumed triplet absorption long wavelength shoulder on the first ligand field band.[7]

The results of the above studies indicate that the ligand field photochemistry of Co(III) ammines is stereospecific and often antithermal—where two kinds of ligands are present the one predominantly photoaquated is often not the thermally labile one. The importance of stereochemistry is especially evident in the observation that *cis*-α-Co(trien)Cl_2^+ and *cis*-β-Co(trien)Cl_2^+ differ by a thousandfold in their photoreactivity. Further, it was suggested that the low quantum yields (10^{-3} to 10^{-5}) were more a consequence of enhanced radiationless deactivation rates than of reduced excited state reactivity, relative to the corresponding Cr(III) species. Reaction was regarded as taking place from a thermally equilibrated excited (thexi) state and to amount to heterolytic bond fission at a labilized position. This last was determined by the same photolysis rules as have been important for Cr(III) photochemistry.[8] Since they are central to the present paper, their restatement here is relevant. Rule (1): For a complex having octahedral geometry, the axis which is photoactivated is the one containing ligands of weakest average ligand field strength. Rule (2): If the labilized axis contains ligands having different ligand field strengths, the ligand with the greater ligand field strength is preferentially labilized. Thus, $Co(NH_3)_5Cl^{2+}$ preferentially photoaquates ammonia as expected by the rules, the yields for ammonia and for chloride photoaquation being 50.7×10^{-4} and 17.1×10^{-4}, respectively. The photochemistry is stereoretentive except in cases where, by the rules, an attachment of a chelate ligand would be expected to be labilized. Thus *cis*-$Co(en)_2Cl_2^+$ leads primarily to *trans*-$Co(en)_2(H_2O)Cl^{2+}$ and *cis*-β-$Co(trien)Cl_2^+$ gives primarily *trans*-$Co(trien)(H_2O)Cl^{2+}$. Such results were explained mechanistically by considering that the labilized end of a chelate ligand could undergo edge displacement of an adjacent other ligand (chloride in the cases cited). This displacement is probably concerted with coordination of water at the position vacated by the chelate, in view of the stereospecificity of the process. It was strongly corroborative of this mechanism that *cis*-α-$Co(trien)Cl_2^+$ was a thousand times less photoactive than the *cis*-β-$Co(trien)Cl_2^+$ complex; in the former case the labilized position is occupied by a secondary nitrogen, bound by the chelate chain and unable to undergo the edge displacement process.

As indicated in the above summary, the principal evidence for the applicability of the photolysis rules is inferential rather than direct; the mechanism accounts for the photochemistry of various chelate complexes with the added assumption of the stereospecific edge displacement process. The applicability of the rules is less clear-cut in the case of complexes with only monodentate ligands. Thus for $Co(NH_3)_5Cl^{2+}$ the 3:1 ratio of ammonia to chloride aquation yields suggests that the rules are operative, but this ratio could result from a nearly indiscriminate aquation weighted by the 5:1 ratio of coordinated ammonia to chloride. It should be noted that Zink[9,10] has given a ligand field justification for the rules.

The purpose of the present study was to distinguish between these two alternative explanations. First, replacement of the four ammonias in the equatorial plane of the complex by two ethylenediamine ligands, by using *trans*-$Co(en)_2(NH_3)Cl^{2+}$, should not materially change the ligand field strengths of the octahedral axes. The spectrum of this complex is, in fact, very close to that of $Co(NH_3)_5Cl^{2+}$. Therefore, if the rules apply, the ammonia and chloride aquation yields should be about the same for the two complexes. Actually, since absolute yields could be affected by a change in radiationless deactivation rates, a minimum requirement would be that the ratio of the ammonia to chloride aquation yields be the same. If, on the other hand, nearly indiscriminate labilization occurs, this ratio should be much lower than 3:1 for *trans*-$Co(en)_2(NH_3)Cl^{2+}$; there should also be some indication of ethylenediamine labilization. Kirk and Kelly[11] have made use of this strategy in the case of the analogous Cr(III) systems.

Secondly, according to the rules, photolysis of *cis*-$Co(en)_2(NH_3)Cl^{2+}$ should lead to a much lower than a 3:1 ratio of ammonia to chloride aquation yields. Conversely, if the labilization were indiscriminate, the ratio should be about the same as for the trans isomer. It should be noted that a nonzero ammonia yield would be expected even if rule 2 were strongly obeyed. Our results with Co(III) trien and tren complexes[6] indicate that the labilized end of a multidentate ligand can recoordinate with edge displacement of a neighboring ligand. Rule 2 predicts labilization of that ethylenediamine nitrogen which is trans to the chloride, and the edge displacement process would lead to ammonia release and formation of *trans*-$Co(en)_2(H_2O)Cl^{2+}$. This was another prediction to be tested.

In summary, the photochemistry of *cis*- and *trans*-$Co(en)_2(NH_3)Cl^{2+}$ should be diagnostic on the matter of whether the photochemical rules apply to Co(III) ammines in designating not only the preferred type of ligand labilized but also the specific ligand position that is labilized. The above complexes are convenient from other points of view. They are very inert to thermal substitution, having aquation rate constants at 25 °C (for chloride aquation, the only thermal process observed) of 3.6×10^{-7} and 3.3×10^{-7} s^{-1},[12,13] respectively, thereby minimizing dark reaction corrections.

The similarity of the rate constants confirms that the complexes are chemically very similar. As already indicated, their spectra are very similar as well, and close to that of $Co(NH_3)_5Cl^{2+}$. The differences lie more in the intensity than in the position of the first and second ligand field band maxima. It seems safe to conclude that at any given wavelength in this region the same excited state is populated so that any differences in the photochemistry should be amenable to very direct interpretation.

It should be noted that there is recent evidence strongly indicating that an important relaxation process of the first singlet thexi state is to a lower lying triplet state.[7] This state may be relatively long lived[14,15] as well as having a substitutional chemistry more like that of the ground state.

Experimental Section

Materials. *trans*-$[Co(en)_2Cl_2]Cl$, prepared by the method of Bailar[16] or Krishnamurthy,[17] was recrystallized from saturated aqueous solution by the dropwise addition of concentrated hydrochloric acid and cooling in ice water. After washing with ethanol and ether, the complex was dried overnight at 110 °C in order to remove solvate water and HCl.

***trans*-$[Co(en)_2(NCS)Cl]NCS$.** This complex was prepared by a modified literature method.[18] *trans*-$[Co(en)_2Cl_2]Cl$ (20.0 g) was dissolved in 30 cm^3 of warm water and a solution of potassium thiocyanate (6.8 g in 15 cm^3 of water) was slowly added with constant stirring. Gentle heating was applied until the resulting paste dissolved, producing a purple solution which was immediately placed in an ice bath and allowed to cool for 2 h. A marked decrease in yield resulted from overheating during this state of the reaction. The precipitate of *cis*-$[Co(en)_2(NCS)Cl](NCS)$ was removed by filtration, and solid potassium thiocyanate (6.8 g) was added with stirring to the filtrate. *trans*-$[Co(en)_2(NCS)Cl](NCS)$, precipitated as a fine powder, was filtered off and washed with ethanol and water, and then vacuum dried overnight. The yield was 38%. The product was suitable for use in the next step without recrystallization.

***trans*-$[Co(en)_2(NH_3)Cl](NO_3)_2$.** A modified Werner synthesis was used in the preparation of the chloride salt of this complex.[18] *trans*-$[Co(en)_2(NCS)Cl]NCS$ (4.0 g) was mixed with 6 cm^3 of water and cooled in an ice bath. To the cold mixture was added 2 cm^3 of 1:3 (v:v) aqueous sulfuric acid, followed by the *cautious* addition of 10 cm^3 of 30% hydrogen peroxide. An exothermic reaction occurred, the color of the solution changing from red-violet to red. The reaction mixture was maintained at ice temperature for 2 h, after which 4 cm^3 of concentrated hydrochloric acid was added and the volume reduced on a steam bath until green crystals of *trans*-$[Co(en)_2Cl_2)]Cl$ precipitated, as noted by Nyholm and Tobe.[19] This impurity was removed and the solution further concentrated until red crystals of the desired product appeared. At this point, the solution was cooled and the crystals of a mixed chloride-sulfate salt of $Co(en)_2(NH_3)Cl^{2+}$ were collected, washed with alcohol and ether, and dried under vacuum.

The sulfate counterion was entirely replaced by chloride by dissolving the crude product in a minimum amount of water (1 g: 1 cm^3) and adding 1.0 M barium chloride dropwise until the precipitate of barium sulfate no longer formed. This last was removed by filtration and the *trans*-$[Co(en)_2(NH_3)Cl]Cl_2$ was recovered by addition of a tenfold volume of cold ethanol to the filtrate. After cooling to about 5 °C, the product was collected on a filter, washed, and dried as usual. The *trans*-$[Co(en)_2(NH_3)Cl]Cl_2$ was converted to the nitrate salt by dissolving the chloride salt in a minimun amount of water, adding an equivalent volume of concentrated nitric acid with stirring, and cooling the mixture in an ice bath for 15 min, producing pale red crystals. Additional product was obtained by adding cold ethanol to the filtrate. The two batches were combined, washed with cold ethanol until the washings were colorless and neutral to pH paper, and then washed with ether and vacuum dried. This recrystallization procedure was repeated until the residual free chloride was reduced to 0.6% and the visible absorption spectral parameters agreed with those previously reported,[19] or (λ_{max}, ϵ): (359.5, 51.5), (526, 45.9) as compared to the reported values of: (361, 52.4), and (526, 47.6) (nm, M^{-1} cm^{-1}). The spectrum is shown in Figure 1.

***cis*-[Co(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$.** A standard literature method was used to prepare the chloride salt of this complex.[20] *trans*-[Co(en)$_2$Cl$_2$]Cl was gound to a fine powder in a mortar and pestle and ammonium hydroxide (0.7 cm^3 per g of complex) was added with continued grinding. Ethanol (0.2 cm^3 per g of complex) was then added to the pink precipitate and the mixture filtered. The crude product was washed with ethanol, until the washings were colorless, then with ether and dried overnight under vacuum. The complex was converted to the nitrate salt as described above, the recrystallizations being repeated until the free chloride content was less than 0.2% and the absorption spectrum agreed with that in the literature, (λ_{max}, ϵ): (363, 78.2), (524, 73.3), as compared to the reported values of:[19] (365, 78), (524, 73) (nm, M^{-1} cm^{-1}). The spectrum is shown in Figure 1.

Photolysis Procedures. All procedures used in this work paralleled those used in the study of Co(NH$_3$)$_5$Cl^{2+} as closely as possible.[4] Photolyses were performed at 488.0 nm using the same argon laser (Coherent Radiation Model 52-G). The laser beam was expanded by means of a lens to the diameter of the window of either a jacketed 10-cm pathlength, 5-cm^3 volume Perkin-Elmer micropolarimeter cell, or a 10-cm pathlength, 27-cm^3 volume Cary spectrophotometer cell. Temperatures were maintained at 25 ± 0.5 °C by means of thermostated water flowing through the jacketed microcell, or with the use of a thermostated block holding the Cary cell.

Incident light intensities were taken directly from the internal power meter of the laser after calibration with Reineckate actinometry.[21] The Reineckate measurements averaged 0.706 of the power meter readings, but, after correction for reflection from the various surfaces (laser, lens, cell), the corrected measurements were within 10% of those of the power meter.

Photolyzed solutions were 10^{-3} to 10^{-2} M in complex, and 10^{-2} M in nitric acid. Light absorption at 488.0 nm by each solution was determined from absorption spectra obtained on a Cary Model 14 spectrophotometer immediately prior to photolysis. In order to minimize errors due to changes in light absorption, inner filter effects, and secondary photolysis, photolyses were restricted to 15% total reaction or less where chemical product analysis was to be used. Actually, secondary photolysis was found to be unimportant up to much greater degrees of reaction than the above, for both isomers. This point was established by photolyzing each complex, taking frequent absorption spectra, until spectral changes became negligible.

For reasons related to those above, absorption by the complex at 488.0 nm was kept to less than 80% for the 10-cm cell pathlength, except in the cases where quantum yields were needed for chloride release. In these cases, a quantitatively detectable amount of released chloride could be obtained only by irradiation of completely absorbing solution (to have enough total amount of material). The solution was agitated at frequent intervals, however, such that no part of it was photolyzed to more than 15% reaction. Completely absorbing solutions were also used in the photolysis of *cis*-Co(en)$_2$(NH$_3$)Cl^{2+} in order to generate enough Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ (in a 15% photolysis) to allow its isolation by ion exchange chromatography of the irradiated solution (see below).

Analytical Procedures. Ammonia release was determined, as in the previous study,[4] by the indophenol spectrophotometric method,[22] calibrated with standard ammonium chloride solutions. The latter were doubly standardized, first by the Volhard method, and then by using the chloride analysis technique that follows.

Released chloride was also determined as before,[4] by titration of free chloride with standard mercuric nitrate solution in the presence of diphenylcarbazone indicator.[23] The photolyzed solution was first passed through an SP-Sephadex C-25 cation exchange column in the acid form in order to eliminate the chloro complexes present; these are susceptible to mercury catalyzed aquation. Free chloride ion was not retained by the column and was easily eluted with 25-cm^3 aliquots of 10^{-2} M nitric acid (until a chloride test showed the concentration to be negligible).

In all analytical procedures, photolyzed solutions were compared to identically treated unphotolyzed ones. The difference in analysis was attributed to the photolysis.

Spectral changes on irradiation were recorded on a Cary Model 14 spectrophotometer, using the 5-cm^3 micropolarimeter cell. Spectra were taken against air, plus a 0.3 optical density Bausch and Lomb neutral density filter to provide a compensating absorption of the reference beam. The optical density baseline correction to spectra obtained in this manner could, of course, be made, since spectra taken in the normal manner were obtained for the initial solution. The *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} complex was followed for successive irradiation periods until no further spectral changes could be detected; photolysis of the cis complex was similarly followed.

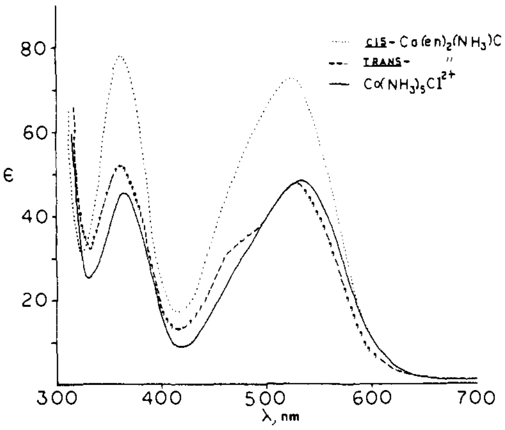

Figure 1. Absorption spectra of aqueous Co(NH$_3$)$_5$Cl^{2+}, *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}, and *trans*-Co(en)$_2$(NH$_3$)Cl^{2+}.

Table I. Analytical Quantum Yields (× 10^4)[a]

Complex	ϕ_{NH_3}	ϕ_{Cl^-}	ϕ_{NH_3}/ϕ_{Cl^-}	Ref
trans-Co(en)$_2$-(NH$_3$)Cl^{2+}	14.8 ± 0.5 (4)	2.96 ± 0.18 (4)	5.0	This work
cis-Co(en)$_2$-(NH$_3$)Cl^{2+}	2.06 ± 0.12 (5)	3.10 ± 0.06 (5)	0.66	This work
Co(NH$_3$)$_5$-Cl^{2+}	50.7 ± 1.3 (3)	17.1 ± 1.2 (3)	3.0	4
Co(NH$_3$)$_5$-H$_2$O^{3+}	1.8 ± 0.1 (3)			4

[a] Number of runs given in parentheses.

In the case of *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}, the stereochemistry of the product resulting from photoaquation of chloride was appraised as follows. A solution of optical density about 1 at 488.0 nm was purified of trace impurities by ion exchange chromatography using the SP Sephadex C-25 cation exchanger in the acid form. The complex was eluted with 0.15 M HNO$_3$, approximately 6–7 cm^3 being collected. A tenfold dilution was then made to give a solution having an absorbance of about 1 in a 10-cm cell with a concentration of acid similar to that in the other solutions photolyzed.

After photolysis to 15% total reaction, the solution was placed on a short (approximately 2 mm) column of Dowex 50W-X2 in the acid form containing in a 2-cm^3 coarse glass fritted funnel. The +2 charged species were separated from the +3 charged material by elution with 1 M sodium perchlorate in 10^{-2} M perchloric acid. After about 25 cm^3 had been eluted, 3 cm^3 of 3 M HCl was added to elute the +3 charged species. The spectrum of this eluate was then taken in a 10-cm micropolarimeter cell (of 0.8 cm^3 total volume) and compared to that of a blank prepared in an identical manner. The correction for absorption by the blank was negligible in the wavelength region of the L$_1$ band maximum of the +3 charged isomers (*cis*- and *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$), but amounted to about 30% at the wavelength of the L$_2$ band maximum. This last was due to some UV absorbing impurities that leached from the exchanger.

The cis-trans isomer ratio of aquoammines was estimated from the ratio of absorbance at the L$_1$ to that at the L$_2$ band maxima. This ratio is 1.08 for pure cis isomer and 0.86 for pure trans isomer.

Results

Analytical Quantum Yields. Our results are summarized in Table I. The reported yields are averages of the several runs and the precision should be reliable to the indicated limits. The absolute yields may be somewhat less accurate, but, as seen in the Discussion, the principal significance of the results lies

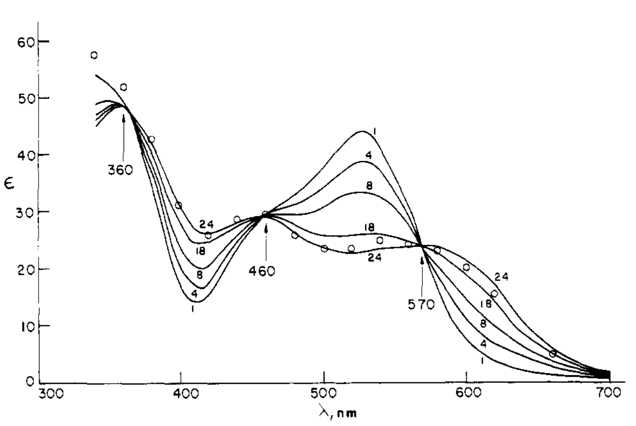

Figure 2. Photolysis at 488 nm of acidified aqueous *trans*-Co(en)$_2$(NH$_3$)Cl^{2+}. Curves 1, 4, 8, 18, and 24 are for successive photolyses, curve 1 being the initial spectrum and curve 24 the terminal spectrum. Circles: calculated spectrum for 75% photolysis to give the product composition 81% *trans*-Co(en)$_2$(H$_2$O)Cl^{2+}, 19% *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$.

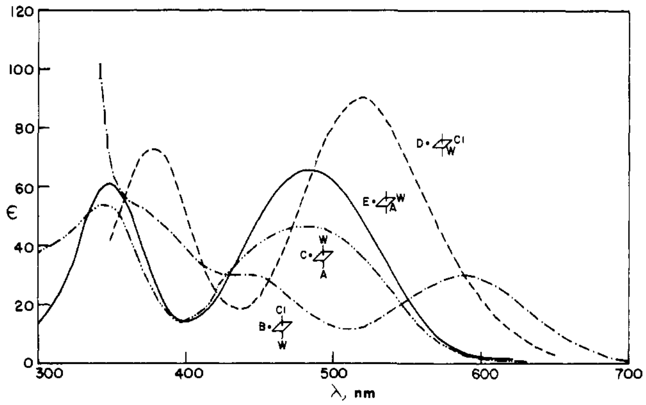

Figure 3. Absorption spectra of possible photolysis products: B, *trans*-Co(en)$_2$(H$_2$O)Cl^{2+}; C, *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$; D, *cis*-Co(en)$_2$(H$_2$O)Cl^{2+}; E, *cis*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$.

in ratio comparisons and isomer identifications. The table includes some related quantum yields for purposes of comparison. We could find no indication of other than chloride or ammonia aquation. There was negligible redox decomposition, and any appreciable ethylenediamine aquation would have led to noticeable spectral anomalies. Nor does it appear that protonated, monodentate ethylenediamine complexes are important for Co(III).[5]

The summary findings are that all yields are in the range of 10^{-4} to 10^{-3}, as now seems standard for Co(III) ammines, and that the ratio ϕ_{NH_3}/ϕ_{Cl} is 5.0 for *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} and 0.66 for *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}, as compared to 3.0 for Co(NH$_3$)$_5$Cl^{2+}.

Stereophotochemistry of *trans*-Co(en)$_2$(NH$_3$)Cl^{2+}. It was important to this investigation to know the isomeric assignments of the photolysis products. The case of *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} proved to be relatively straightforward. Figure 2 shows a near-terminal spectrum for a solution photolyzed to 75% reaction. The isosbestic points at 570, 460, and 360 nm were maintained throughout this extensive photolysis, indicating that secondary photolysis (or thermal reaction) was not important. Thermal reaction of the parent complex was also not important as the spectrum of a dark solution was stable over the photolyses times.

The final spectrum is dominated by features characteristic of *trans*-Co(en)$_2$(H$_2$O)Cl^{2+},[24] see Figure 3. Of the possible photolysis products, *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} had the most clearly distinguishable spectrum. The absorption peak at 600 nm does not occur with the other species, whose lowest lying ligand field bands are in the 525-nm region. Also, since *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} had the lowest energy charge transfer band of the four possible products, extending well into the visible region, its second ligand field band, at about 300 nm, appears merely as a shoulder in a region of rapidly ascending absorption. By contrast, *cis*-Co(en)$_2$(H$_2$O)Cl^{2+} and *cis*- and *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ all have a distinct second ligand field absorption band, occurring between 340 and 390 nm, followed by a minimum below 340 nm, the region in which *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} and the photolyzed solution absorb strongly. Qualitatively, then, the spectra of Figure 2 indicated this last species to be the principal photoproduct.

The observed isosbestic points are predicted for a product mixture of 80-82% *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} and 20-18% *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$, although because of the similarity of the spectra of *trans*- and *cis*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$, up to perhaps 10% of the latter complex could be present, that is, a just allowable product composition would be 80, 10, and 10% trans aquochloro and trans and cis aquoammine, respectively. However, as shown in Figure 2, an 81-19% trans aquochloro-trans aquoammine composition well reproduces the entire terminal photolysis spectrum (75% photolysis). This is essentially the product composition which corresponds to the ratio ϕ_{NH_3}/ϕ_{Cl}. The only significant discrepancy is around 540 nm, in a direction that might be due to some *trans*-Co(en)$_2$(H$_2$O)$_2$$^{3+}$ finally being formed by secondary photolysis. Product compositions including some cis aquoammine do not give as good an overall fit because of the relatively high extinction coefficient of this complex in the 480-500-nm region. We conclude that no appreciable *cis*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ forms.

The above approach requires knowledge of the degree of reaction, but allowed inclusion of both isomers of the aquoammine in test calculations. Alternatively, the ratio of trans aquochloro to trans aquoammine in the product can be determined without knowing the degree of reaction, if no other products are assumed. The triangular graphical procedure involved is that previously described.[5] Briefly stated, if a species A photolyzes (or, in general, reacts) to give products B and C, it follows that for any mixture the apparent extinction coefficient (optical density/path length times total concentration) is

$$\epsilon_{\text{obsd}} = F_A\epsilon_A + F_B\epsilon_B + F_C\epsilon_C \tag{1}$$

where ϵ_A, ϵ_B, and ϵ_C are the extinction coefficients at that wavelength for the respective pure species, and the *F*'s denote the fraction of the total concentration that is present in the indicated form. Manipulation gives

$$F_A = \frac{\epsilon_{\text{obsd}} - \epsilon_C}{\epsilon_A - \epsilon_C} - F_B\frac{\epsilon_B - \epsilon_C}{\epsilon_A - \epsilon_C} \tag{2}$$

Equation 2 plots as a straight line in a triangular composition diagram. The slope of the line will vary with the wavelength chosen, since the various extinction coefficients will vary. However, since the mixture can only have one composition, all lines must pass through a common point. As shown in Figure 4, the lines for each of a series of wavelengths do indeed cross. Four solutions are shown, representing successive stages of irradiation. Extrapolation of the line from the left origin (the starting complex) through these four crossing points to the B-C baseline gives the composition at 100% reaction, that is, the product ratio. This extrapolation gives 85% *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} and 15% *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$. There is an uncertainty of several percent in this result, but it should be borne in mind that the treatment makes use of essentially all of the spectral data. Were more than two products present, the lines for a given solution would not have a common

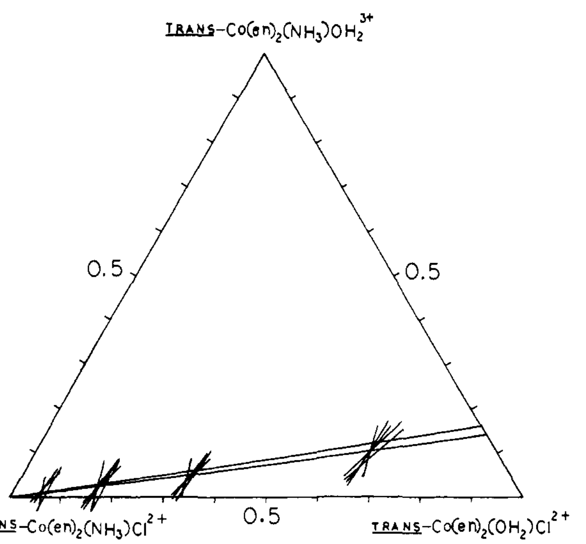

Figure 4. Triangular composition diagram showing plots of eq 2 for various wavelengths and for successive irradiations of *trans*-Co(en)$_2$(NH$_3$)Cl^{2+}, assuming that B and C (see Figure 2) are the only products.

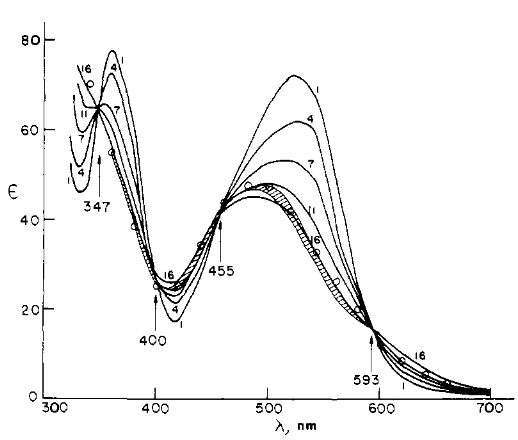

Figure 5. Photolysis at 488 nm of acidified aqueous *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}. Curves 1, 4, 7, 11, and 16 are for successive photolyses, curve 1 being the initial spectrum and curve 16 the terminal spectrum. Circles: Calculated spectrum for 95% photolysis and product composition 32% B, 12% C, 8% D, and 48% E (see Figure 3). The hashed spectrum is the terminal spectrum calculated from extrapolation of photolyses in the 15-25% range of photolysis, the span of the hashing being an indication of the uncertainty in the extrapolation.

crossing point. We concluded from this analysis that the main photolysis products are indeed *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} and *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$, produced in 80-85% and 20-15% yield, respectively. Since this treatment makes use of data representing relatively small degrees of photolysis, the possible complication of some *trans*-Co(en)$_2$(H$_2$O)$_2{}^{3+}$ in the observed terminal irradiation spectrum of Figure 2 is not likely.

Stereophotochemistry of *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}. Prolonged photolysis of *cis*-Co(en)$_2$(NH$_3$)Cl^{2+} produced successive spectral changes which maintained isosbestic points at 593, 457, 398, and 347 nm. A spectrum corresponding to about 90-95% photolysis is shown in Figure 5. As with the trans isomer, it appeared that secondary photolysis was not a major importance. The fact that the products absorbed more strongly than the starting material for wavelengths greater than 593 nm clearly indicates that *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} is a major product. Moreover, in view of the analytical result of $\phi_{NH_3}/\phi_{Cl} = 0.66$ (so that only 40% of the photosubstitution consisted of ammonia aquation), the additional qualitative conclusion is that relatively little *cis*-Co(en)$_2$(H$_2$O)Cl^{2+} forms. This conclusion is reinforced by the rising product absorption below 360 nm; of the possible products, only *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} can supply this behavior.

Detailed analysis made it clear, however, that there was some contribution to the product spectrum from all four possible products. Two approaches were followed in extracting the complete product composition from the data. The spectral changes on extensive irradiation, such as shown in Figure 5, were large enough that the difference quantities involved in the algebraic solution of the simultaneous equations were relatively precise, but the solutions were sensitive to small inaccuracies such as might be present if some minor degree of secondary photolysis had occurred. The second approach was to use spectra for 15-25% photolysis; for these, secondary photolysis was not important, but the precision of the spectral changes was reduced. The consequent error in the calculated spectrum for the product mixture was not trivial; this is indicated by the hashed spectrum in Figure 5. The small deviations from the observed terminal spectrum and the hashed one may reflect the presence of some secondary photolysis after prolonged irradiations.

The compositions giving spectra falling within the hashed region (and conforming to the analytical ϕ_{NH_3}/ϕ_{Cl}) cover a range of values. For chloride aquation, the products are 60 ± 20% *cis*- and 40 ± 20% *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ and for ammonia aquation they are 70 ± 15% *trans*- and 30 ± 15% *cis*-Co(en)$_2$(H$_2$O)Cl^{2+}.

The above rather wide limits were, unfortunately, not narrowed by the spectral analyses of the chromatographically isolated fraction containing the aquoammine product. A number of such analyses (each on separate runs) were made and these give L_1/L_2 absorbance ratios ranging from 0.92 to 1.01, the corresponding percent of cis isomer being 30-70%. The problem, never satisfactorily resolved, was that the blank correction in the region of the L_2 absorption was large and variable from one blank to another so that accurate correction was never possible.

Allowing for error in both the spectral and the chromatographic analyses, we conclude that the photoproducts consisted of an approximate 80/20 ratio of *cis*- to *trans*-Co(en)$_2$(NH$_3$)(H$_2$O$_2$)$^{3+}$ and (to fit the spectral changes on photolysis) likewise, an 80/20 ratio of *trans*- to *cis*-Co(en)$_2$(H$_2$O)Cl^{2+}. The calculated points of Figure 5 are for this isomer composition.

Discussion

The results do provide considerable support for the applicability of the photolysis rules to Co(III) ammine complexes. We consider first the case of *trans*-Co(en)$_2$(NH$_3$)Cl^{2+}. The only photochemistry observed is that of the ligands on the weak field axis, and, as predicted by rule 2, ammonia aquation predominates over chloride aquation. Unlike the case of Co(NH$_3$)$_5$Cl^{2+}, the result is unambiguous in that the only source of ammonia is from the axial position. Furthermore, the ratio ϕ_{NH_3}/ϕ_{Cl} of 5.0 is similar to the 3.0 ratio observed for the chloropentaammine complex, which indicates that the relative bond weakening effects of the axial labilization are about the same for the two compounds, as would be expected.

The stereochemistry, furthermore, is consistent with that found for other Co(III) ammines.[5,6] The photoaquations are almost entirely, if not entirely, stereoretentive; both aquoproducts are trans. As noted previously, the mechanistic appearance is one of direct water substitution at the labilized position, the octahedral framework remaining intact. That is, it does not appear likely that complete loss of ligand (ammonia or chloride) occurs to give a pentacoordinated intermediate (which then coordinates solvent). Were this the case, some isomerization would be expected. Note that Nyholm and Tobe[19] found base hydrolysis to give primarily the *cis*-chlo-

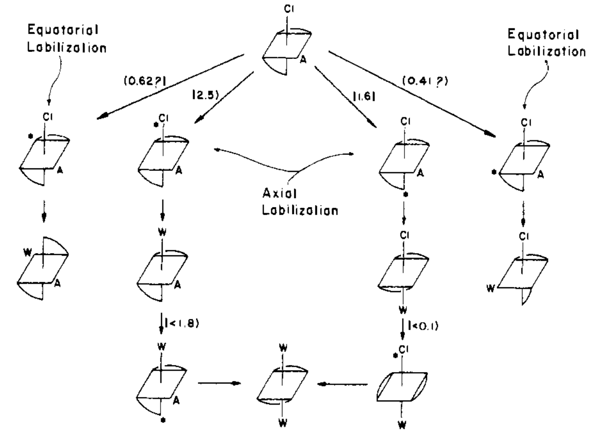

Figure 6. Expected photolysis products for *cis*-Co(en)$_2$(NH$_3$)Cl^{2+} assuming either axial or equatorial ligand labilizations.

rohydroxy isomer; the counter-base mechanism for this reaction involves a five-coordinated species. These workers were unable to determine the steric course of the aquation or acid hydrolysis reaction (exclusively chloride replacement), but comment that both aquochloro isomers are present at equilibrium. Thus the stereospecificity of the photoreaction seems properly attributed to kinetic rather than to thermodynamic control.

One point of difference between the photochemistries of *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} and Co(NH$_3$)$_5$Cl^{2+} is in the absolute quantum yields. These are lower by about fourfold for the former complex. There seems no basis for attributing this difference to any change in the type of ligand field excited state populated. The spectra of the two complexes are nearly identical both as to positions and to intensities of the band maxima, except for a more pronounced long wavelength shoulder on the first ligand band of the trans chloroammine complex. We assume that for both complexes, irradiation leads to population of the lowest excited singlet state which, in the C_{4v} microsymmetry, is presumably ^1E_g.[9] We suggested earlier[4] that the generally low photoaquation yields for Co(III) as compared to Cr(III) ammines are due more to higher radiationless deactivation rates than to reduced excited state chemical reactivities. The same type of explanation may apply here; that is, the radiationless deactivation may be faster for *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} than for Co(NH$_3$)$_5$Cl^{2+}.

The recent observation of presumably triplet state photochemistry of Co(III) ammines[7] adds a potential complication. Some of the first singlet thexi state may disappear by intersystem crossing and the lower quantum yields for our system could be due to an enhanced rate of such crossing. The substitutional quantum yields found on excitation to the likely triplet state (646 nm) were smaller, in the case of Co(NH$_3$)$_5$Cl^{2+}, than those we found earlier for the 500-nm wavelength region, 50 vs. 1 for NH$_3$ aquation, and 17 vs. 10 for Cl$^-$ aquation (all $\times 10^{-4}$). Since we find about the same ratio of ammonia to chloride aquation for *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} as for Co(NH$_3$)$_5$Cl^{2+} it seems likely that most of our photoreaction was from the first singlet thexi state; were photochemistry from a lower lying triplet important, something like the 10:1 ratio of Cl$^-$ to NH$_3$ aquation found for the triplet of Co(NH$_3$)$_5$Cl^{2+} would be expected. Thus while the excited state assignment of our present results contains an uncertainty, it probably is not a massive one. Certainly, the stereochemical conclusions stand, regardless of excited state designations.

The ability to photolyze to near completion without secondary photolysis is to be expected according to the photolysis rules. One product, *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} is known to be photoinert.[5] The other, *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$, probably has a very low quantum yield for ammonia aquation, the preferred process. Thus the yield for ammonia aquation of Co(NH$_3$)$_5$(H$_2$O)$^{3+}$ is only 1.8×10^{-4},[4] and would be even less for the trans aquoammine if the general pattern of lower yields for Co(en)$_2$(NH$_3$)Cl^{2+} vs. Co(NH$_3$)$_5$Cl^{2+} species is followed. We now attribute, incidentially, the relative low yield for Co(NH$_3$)$_5$(H$_2$O)$^{3+}$ to an especially rapid radiationless deactivation rate for the excited state involved. Emission studies with room temperature aqueous Cr(III) ammines indicate that lifetimes are especially small for complexes that have coordinated water.[25] We suppose that such water is in good vibrational communication with the solvent through hydrogen bonding, and that this favors the coupling of the excited state with the ground-state-solvent system.

Turning next to the *cis*-Co(en)$_2$(NH$_3$)Cl^{2+} case, the first observation is that the quantum yield results are roughly consistent with the rule based expectations. That is, the yield for chloride aquation is about the same as for the trans complex, while that for ammonia aquation is sharply reduced. This last is to be expected since ammonia is now not on the axis predicted to be labilized.

The overall situation is more involved, of course, than for the trans isomer, in that a mixture of all four product isomers is produced. As noted, the principal products are readily accounted for. Referring to Figure 6, labilization of the Cl-end of the weak field axis should lead to *cis*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$, the experimentally favored aquoammine isomer. Labilization of the N-end of the axis activates one end of an ethylenediamine ligand, and, following a previously proposed mechanism[5,6] we suppose that (a) recoordination and hence no net reaction occurs, or (b), edge displacement of ammonia takes place, leading to the observed main isomer, *trans*-Co(en)$_2$(H$_2$O)Cl^{2+}. The scheme is shown in Figure 6. A third possibility, that of edge displacement of chloride, is considered to be unlikely in view of its remote position.

It remains to account for the relatively minor anti-rules products, that is, *trans*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ and *cis*-Co(en)$_2$(H$_2$O)Cl^{2+}. First, these are not expected from secondary photolysis. Neither of the favored isomers should be appreciably photosensitive. As noted above, *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} is known to be photoinert. Also following the previous discussion, *cis*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ should not be very photosensitive if its behavior is similar to that of Co(NH$_3$)$_5$(H$_2$O)$^{3+}$. Furthermore, as shown in Figure 6, the only expected secondary photolysis product is *trans*-Co(en)$_2$(H$_2$O)$_2$$^{2+}$, not only a species whose presence would have been noted, but also one which corresponds to neither of the observed minor products. The minor products could come from a component of equatorial as opposed to axial labilization, as shown in Figure 6. We are not certain of this as a possibility, in view of the cleanness of axial labilization in the case of the trans starting material. A similar lack of exact rules-predicted stereochemistry was found for *cis*-Co(en)$_2$Cl$_2$$^+$, which produced only 70% of the expected trans aquochloro isomer; there the alternative explanation of displacement of the remote chloride by labilized ethylenediamine was available—such an alternative is of no help here as such displacement would not account for the minor products. Another perhaps equally acceptable explanation is that part of the time a give-coordinated intermediate is formed, with some consequent loss of stereochemical memory. Finally, of course, we cannot rule out that an enhanced intersystem crossing efficiency to a lower lying triplet is leading to the anti-rules components of our photoproducts.

Returning to the main products, the rules-based mechanism gives the quantum yield for reactive Cl-end labilization as $3.10 \times 10^{-4} \times 0.80$ or 2.5×10^{-4} and for reactive N-end labilization as $2.06 \times 10^{-4} \times 0.80$ or 1.6×10^{-4}. If the same ratio of

N-end to Cl-end labilization applies as for the *trans*-$Co(en)_2(NH_3)Cl^{2+}$ complex, the predicted N-end labilization should be $2.5 \times 10^{-4} \times 5.0$ or 12.5×10^{-4}. The discrepancy, 12.5×10^{-4} to 1.6×10^{-4} then indicates that 87% of the time labilization of the N-end terminates in recoordination of the ethlenediamine and hence no net reaction. We have used our preferred 80/20 isomer ratios in the above calculations, but use of the middle figures of the uncertainty ranges would not change the qualitative conclusions.

From the spectroscopic point of view, we would still suppose the lowest excited singlet state to be essentially the same as for $Co(NH_3)_5Cl^{2+}$, although the microsymmetry is not exactly C_{4v} for the cis chloroammine complex. The position of the absorption band maxima is the same as for the chloropentaammine, however, although the intensities are considerably higher.

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Oxidative Additions of Aryl, Vinyl, and Acyl Halides to Triethylphosphinenickel(0) Complexes

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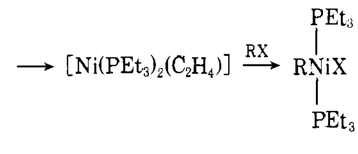
Abstract: Aryl, vinyl, and acyl halides, but not alkyl halides, react with $Ni(PEt_3)_2(C_2H_4)$, $Ni(PEt_3)_2(1,5\text{-}C_8H_{12})$, and $Ni(PEt_3)_4$ complexes to yield square-planar *trans*-$NiX(R)(PEt_3)_2$ compounds. Structure assignments are based on infrared and NMR spectra. Carbonylation of aryl nickel compounds provides aroyl derivatives. Template, radical, and aromatic-nucleophilic-substitution processes are involved in the nickel–organic halide interactions.

Reactions of aryl halides with zero-valent nickel complexes have attracted considerable interest in organic[1] and organometallic[2] synthesis. Several years ago, one of us communicated a method for the preparation of aryl nickel complexes by the reaction of aryl halides with $Ni(PEt_3)_2(C_2H_4)$, prepared and reacted in situ (eq 1).[3] Since that time, a large



$$\mathrm{Ni(acac)_2 + 2PEt_3 + 1.5Et_2AlOEt} \longrightarrow [\mathrm{Ni(PEt_3)_2(C_2H_4)}] \xrightarrow{\mathrm{RX}} \mathrm{R}\overset{\mathrm{PEt_3}}{\underset{\mathrm{PEt_3}}{\mathrm{Ni}}}\mathrm{X} \qquad (1)$$

number of related examples have surfaced.[4] This article presents details of our communicated method, and, more importantly, defines the scope of organonickel synthesis from nickel(0) complexes bearing triethylphosphine ligands, especially from $Ni(PEt_3)_2(1,5\text{-}C_8H_{12})$ and $Ni(PEt_3)_4$. Our studies were largely confined to complexes with triethylphosphine ligands, since this ligand imparts a high reactivity to nickel(0) reagents[4j] and good stability to the organonickel(II) products.[4i]

Results and Discussion

Reactivities of Nickel(0) Reagents. (A) $Ni(PEt_3)_2(1,5\text{-}C_8H_{12})$. The addition of 2 molar equiv of triethylphosphine to a yellow solution of bis(1,5-cyclooctadiene)nickel(0) in hexane causes the solution to turn red-brown. The color change is attributed to the formation of $Ni(PEt_3)_2(1,5\text{-}C_8H_{12})$ as a 1,5-cyclooctadiene ligand is liberated.[5,6] When this solution was added to an acyl halide, vinyl halide, or perfluoroaryl halide, rapid (sometimes exothermic) oxidative-addition reactions occurred. Products of formula $NiX(R)(PEt_3)_2$ were isolated in 61–83% yields by low temperature crystallization and filtration. When the final isolation steps were performed in air rather than under an inert atmosphere, the isolated yields dropped below 40% even for moderately air-stable compounds. The best results were always obtained when the nickel(0) reagent was added to the organic halide, thus keeping the organic halide present in excess at all times during the mixing process. The reaction of $Ni(PEt_3)_2(1,5\text{-}C_8H_{12})$ with chlorobenzene, bromobenzene, and the dichlorobenzenes required elevated temperatures (50–60 °C) or extended reaction times (24–48 h). Elemental nickel precipitated during these reactions and yellow-green impure products were isolated in 6–64% yields. Recrystallization of these products yielded the yellow-brown aryl nickel