677. *Hydrido-complexes of Rhodium*(III) *Containing Nitrogen Ligands.*

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Hydrido-complexes of rhodium(III) containing nitrogen ligands such as ethylenediamine have been obtained by nucleophilic displacement of chloride ion, sodium borohydride being the source of hydride ion, in water; the species were characterised by spectroscopic techniques. Other systems believed to contain rhodium in oxidation states lower than III have been re-examined. Experiments on some analogous cobalt(III) complexes are described including a radiochemical study of a hydride-catalysed *cis–trans*-isomerisation.

The nucleophilic displacement of chloride by hydride in *cis*- or *trans*-dichlorobisethylenediaminerhodium(III) cations in aqueous solution with the borohydride ion as a source of hydride ion has been briefly described.[1] This paper gives fuller details of the work and its extensions to a variety of rhodium(III) and cobalt(III) octahedral complexes.

Rhodium Complexes.—Several chloro-complexes of rhodium(III), on treatment with sodium borohydride in aqueous solution, undergo a notable change in colour from yellow to pale brown, and examination of the solutions shows the presence in the nuclear magnetic resonance spectrum of the characteristic high-field proton-resonance line associated with a metal–hydrogen bond. The lines appear as sharp doublets due to spin–spin interaction with ^{103}Rh, as expected. In certain cases, the hydrido-complexes could be isolated as their insoluble tetraphenylborates whose infrared spectra contain, in addition to the bands expected for the nitrogen ligands and the anion, a band which can be assigned as an Rh–H stretching frequency. The spectroscopic results are given in Table 1. Hydrido-species could not be obtained when using sodium amalgam, hypophosphorous acid, or molecular hydrogen as reducing agent.

cis-*Dichlorotriethylenetetraminerhodium*(III) *cation.* The yellow complex ion [2] reacted with sodium borohydride in aqueous solution to give a brown solution which showed a strong proton resonance doublet line centred at 19·8 p.p.m. on the high-field side of the methyl line of an internal t-butyl alcohol reference (corresponding to $\tau \sim 28{\cdot}5$). This line we regard as due to the species *cis*-hydridochlorotriethylenetetraminerhodium(III). A second high-field line was just observable under optimum conditions centred at 18·4 p.p.m. on the high-field side of the reference (τ 27·1); this line was also split by about 30 c./sec. We attribute this line to the *cis*-dihydrido-species formed in low concentrations, *ca.* 5—10% of the hydridochloro-species. The visible and ultraviolet spectra (Table 2) were measured for an aqueous solution of known strength, and, from the absence of the band at 350 mμ characteristic of *cis*-dichlorotriethylenetetraminerhodium(III), it appears that for the reaction

$$cis\text{-}[\mathrm{Rh\ trienCl_2}]^+ + \mathrm{H}^- = cis\text{-}[\mathrm{Rh\ trienClH}]^+ + \mathrm{Cl}^-$$

the equilibrium in alkaline solution lies far to the right, also shown by the rapid reaction even in a solution 3M in chloride ion. The solution of the hydride is sufficiently stable to show the high-field line after being kept for a week under nitrogen, although metallic rhodium is slowly deposited. The other hydrido-species, discussed below, are very much less stable and decompose within an hour or so.

The highest-wavelength transitions may be assigned to $(t_{2g})^5(e_g)^1 \longleftarrow (t_{2g})^6$, and in these spin-paired complexes are an effective measure of the size of Δ, the ligand-field splitting. Hydride is a much stronger ligand than chloride, and fits into the halide spectrochemical series as $\mathrm{H^-} > \mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$. A previous attempt [3] to locate hydride

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[1] Wilkinson, *Proc. Chem. Soc.*, 1961, 72.
[2] Gillard and Wilkinson, *J.*, 1963, 3193.
[3] Chatt and Hayter, *J.*, 1961, 772.

TABLE 1.

Spectral data for hydrido-complexes of rhodium(III).

Compound *	ν(M–H) (cm.$^{-1}$) †	τ	Splitting (c./sec.)	Compound *	ν(M–H) (cm.$^{-1}$) †	τ	Splitting (c./sec.)
trans-[Rh en_2Cl_2]$^+$	2100	31	31	*cis*-[Rh trienCl_2]$^+$	2081	28·5	27
cis-[Rh en_2Cl_2]$^+$ ...	2093	31	31			27·1	30
[Rh(NH_3)$_5$Cl]$^+$ ...	2079	‡	—	*trans*-[Rh($DMG)_2Cl_2$]$^-$	—	26·4	—
				trans-[Rh py_4Cl_2]$^+$ ...	—	28·6	—

* These are the compounds which formed the hydrides. † In tetraphenylborates. ‡ The brown reduced solution (saturated) was too dilute to show the high-field line.

en = ethylenediamine, trien = triethylenetetramine, HDMG = dimethylglyoxime, py = pyridine.

TABLE 2.

Electronic spectra (λ in mμ) of rhodium(III) complexes.

Compound	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
cis-[Rh trienCl_2]$^+$	350	101	294	198	215	$\sim 3 \times 10^4$
cis-[Rh trienClH]$^+$ *	300	108	255 †	140	218	$\sim 3 \times 10^4$

* In aqueous solution at 0°. † Observed as shoulder.

ion in the spectrochemical series led to the same conclusion as this work but utilised complexes containing strong π-bonding ligands and was handicapped by the consequent overlapping of *d–d* transitions and charge-transfer bands.

The hydridochlorotriethylenetetraminerhodium(III) cation may be precipitated from aqueous solution by large anions. The pale brown tetraphenylborate showed a weak peak in the infrared spectrum at 2051 cm.$^{-1}$. Attempts at elemental microanalysis were discontinued after two severe explosions, although we were able to demonstrate the presence of chlorine in the tetraphenylborate. The pale brown solution of hydridochlorotriethylenetetraminerhodium(III) tetraphenylborate in acetone was not strong enough for the high-field line to be observed.

cis- *and* trans-*Dichlorobisethylenediaminerhodium*(III) *cations.* The observation [1] that hydride reacts with these species to form compounds containing rhodium–hydrogen bonds was confirmed; however, the product obtained by treating *trans*-dichlorobisethylenediaminerhodium(III) cation with borohydride and adding sodium tetraphenylborate did not contain chlorine, and we were able to show that all the chlorine was in the filtrate; this supports the reaction scheme

$$\textit{trans}\text{-}[\mathrm{Rh\ en_2Cl_2}]^+ + \mathrm{BH_4}^- \longrightarrow \textit{trans}\text{-}[\mathrm{Rh\ en_2ClH}]^+$$
$$\textit{trans}\text{-}[\mathrm{Rh\ en_2ClH}]^+ + \mathrm{BH_4}^- \longrightarrow [\mathrm{Rh\ en_2H_2}]^+$$

We assign *trans*-stereochemistry (Cl/H) to the monohydrido-cation because of the ready replacement of the second chloride, presumably due to the strong *trans*-effect of the hydride ion. It appears that the same species is obtained from *cis*- and *trans*-dichlorobisethylenediaminerhodium(III) cations on nucleophilic attack by hydride, since the high-field lines in their nuclear magnetic resonance spectra are in the same position (τ 31). The hydride from the *trans*-dichloro-isomer, when allowed to re-oxidise in presence of chloride ion, forms the *cis*-dichloro-isomer. This is considered below in connection with the similar isomerisation observed in the analogous complex of cobalt(III).

The electronic spectrum of the hydrido-species could not be obtained accurately, because of rapid decomposition to metallic rhodium, even at 0°, although the reduced solution from the *trans*-dichloro-isomer showed a new band at 387 mμ, probably due to the hydridic species.

Chloropentamminerhodium(III) *cation.* Although the brown solution obtained by treating the aqueous solution of this cation with borohydride was too dilute for observation of the high-field line, and decomposed (even at 0°) too rapidly for the electronic spectra to be measured accurately, the tetraphenylborate could be prepared; it exploded on heating but was shown to contain no chlorine. It showed a weak band at 2079 cm.$^{-1}$ (ν_{Rh-H}) in the infrared spectrum. The electronic spectrum of the brown solution did not show the band at 349 mμ characteristic of the chloropentamminerhodium(III) cation, but did show a new band at 295 mμ, which we attribute to the species $[Rh(NH_3)_5H]^{2+}$.

trans-*Dichlorotetrapyridinerhodium*(III) *cation*. When a slightly alkaline ice-cold solution of the chloride of this cation is treated with a cold aqueous solution of borohydride, a brown solution is obtained, which almost immediately deposits a brown solid, too unstable to be isolated. The diamagnetic suspension showed no high-field line. However, when methanolic solutions of the reactants were used, the brown material remained in solution, giving a high-field line at 1047 c./sec. on the high-field side of the methyl line of an internal reference (tetramethylsilane), corresponding to τ 28·6. The methanolic solution of the hydrido-complex, when shaken with carbon tetrachloride, under nitrogen, formed chloroform and *trans*-dichlorotetrapyridinerhodium(III) chloride.

Martin and Waind[4] studied the reduction of bipyridyl complexes of cobalt(III) and rhodium(III), and postulated that the products were complexes of the univalent metals. They found[4b] no high-field line in the nuclear magnetic resonance spectra of the complexes of cobalt, and we have been unable to find a high-field line in the corresponding compounds of rhodium. However, both they and we have observed that reduction of the yellow dichlorobisbipyridylrhodium(III) cation gives first a brown solution, which we find to be diamagnetic, then the blue product, "$[Rh(bipy)_2]ClO_4,3H_2O$," which they report as showing a weak peak at 1980 cm.$^{-1}$. The tetraphenylborate which we obtained from the brown solution had a weak peak at 2016 cm.$^{-1}$. These absorptions may be due to ν_{Rh-H} stretching. Since the analogous dichlorotetrapyridinerhodium(III) cation gives a hydride on treatment with borohydride, a common first-stage may occur, of the type

$$[Rh^{III}B_4Cl_2]^+ \xrightarrow{H^-} [Rh^{III}B_4ClH]^+ \longrightarrow [Rh^{I}B_4]^+ + HCl$$

The second stage then appears to occur only with the complex containing bipyridyl; this is presumably a reflection of the greater π-bonding capacity of bipyridyl and its well-known ability to stabilise lower oxidation states.

Other reduced species. When a solution of sodium *trans*-dichlorobisdimethylglyoximatorhodate(III) is treated with an aqueous solution of borohydride, the diamagnetic green solution obtained shows a rather weak high-field line at 17·7 p.p.m. relative to t-butyl alcohol (*i.e.*, τ 26·4), presumably due to a hydridic species. The green solution rapidly deposited metallic rhodium and left a brown solution. No splitting of the proton resonance was found, nor have we been able to isolate a solid salt. Although compounds formulated as containing rhodium(II) were obtained[5a] by the action of hypophosphorous acid on dichlorobisdimethylglyoximatorhodium(III), these red-brown reduced solutions do not show high-field signals. They are, however, diamagnetic which suggests that they contain either rhodium(III) or rhodium(I). Other complexes supposedly of rhodium(II) obtained by treating sodium hexachlororhodate(III) with hypophosphorous acid[5b] again do not show high-field lines although the solutions are diamagnetic, indicating that rhodium(II) species are not present. Similarly the reduction of rhodium trichloride by boiling hypophosphorous acid gives first a dark-red solution, said to contain rhodium(II), then a yellow solution said to contain rhodium(I).[5b] Neither the red nor the yellow solution showed a high-field proton resonance line but in the yellow solution there was a broad peak near the high-field component of the P–H doublet of hypophosphorous acid. This peak showed no splitting and disappeared after four days. These reduced species have not been further investigated.

Hydrogen-transfer reactions. Trisbipyridylcobalt(III) ion acts as a catalyst in the

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[4] (*a*) Martin and Waind, *J.*, 1958, 4284; (*b*) Martin, McWhinnie, and Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

[5] Dwyer and Nyholm, *Proc. Roy. Soc. New South Wales*, (*a*) 1946, **78**, 266; (*b*) 1942, **75**, 122.

reduction of several aromatic nitro-compounds by borohydride.[6] This is equally true for the complexes of rhodium(III) which form hydrides; in each case, nitrobenzene is reduced to aniline, when an aqueous-methanolic solution of the complex of rhodium is used to achieve homogeneity. A possible alternative to the electron-transfer mechanism for such catalyses is therefore a hydride transfer. This is certainly the case with the hydridochlorotriethylenetetraminerhodium(III) cation. When an aqueous-methanolic suspension of the tetraphenylborate in excess was shaken with an aqueous solution of quinone, quinol could be extracted from the mixture, indicating that the cation acts as a hydride-transferring agent. The rhodium-containing product of this reaction unfortunately formed a red gum.

Metallic rhodium produced by borohydride reduction of simple compounds of rhodium(III) is very effective in reducing olefins.[7] We have treated dec-1-ene, in aqueous alcohol, with borohydride in the presence of the compounds of rhodium(III) which we know to form hydrides. Except in one case (*cis*-[Rh en_2Cl_2]) where metallic rhodium was accidentally formed, no reduction of the olefin occurred.

Cobalt(III) *Complexes.*—Where we have demonstrated the formation of rhodium–hydrogen bonds in complexes containing non-π-bonding ligands, the analogous complex of cobalt(III) has been studied. We have not obtained any direct evidence for cobalt–hydrogen bonds; in nearly all cases, reduction occurs readily through cobalt(II), sometimes not detected, to metallic cobalt [*e.g.*, *cis*-dichlorotriethylenetetraminecobalt(III) cation, and chlorobisdimethylglyoximatoamminocobalt(III)].

The green *trans*-dichlorobisethylenediaminecobalt(III) chloride, in excess, when treated carefully with borohydride in ice-cold aqueous solution formed the purple *cis*-dichloro-isomer very rapidly; even at 0°, no evidence for a hydridic species was obtained. Addition of sodium tetraphenylborate to the purple solution caused the unchanged *trans*-isomer to be precipitated as its pale green tetraphenylborate. The *cis*-dichloro-isomer could be recovered from the purple mother-liquor. This difference in solubilities of the tetraphenylborates is presumably due to a difference in lattice energies. It is not a general phenomenon; there is no marked difference in the solubilities of the tetraphenylborates of *cis*- and *trans*-dichlorobisethylenediaminerhodium(III) or *cis*- and *trans*-dinitrobisethylenediaminecobalt(III). *cis*-Dichlorotriethylenetetraminecobalt(III) tetraphenylborate is slightly soluble in water; the *trans*-isomer [2] is instantly isomerised by water. The tetraphenylborates of the monopositive cations *trans*-dichlorotetraminecobalt(III), bisdimethylglyoximatobisamminecobalt(III), and bisdimethylglyoximatobisamminerhodium(III) are all very insoluble in water.

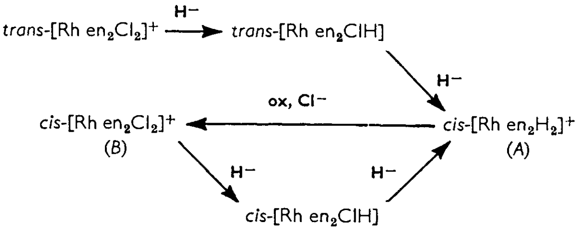
The mechanism of the catalysis by hydride ion of this *trans–cis* isomerisation is not clear. Hypophosphorous acid at 65° also effects the change, although solutions of chromous compounds have no apparent effect on the green solution of *trans*-dichlorobisethylenediaminecobalt(III) chloride. We have found, by radiochemical exchange experiments with ^{36}Cl, that only one of the co-ordinated chloride ions in the *trans*-dichloro-compound is involved in the reaction. After the isomerisation and removal of the complex ion, the supernatant liquid contained 60% of the initial activity, compared with 59·3% calculated for displacement of one chloride. If no chloride had been displaced, only 33% of the initial activity should be in the supernatant liquid; and if both were displaced, 81%. We therefore postulate the scheme *trans*-$[Co\ en_2Cl_2]^+ + BH_4^- \longrightarrow$ *cis*-$[Co\ en_2ClH]^+ + ox + Cl^- \longrightarrow$ *cis*-$[Co\ en_2Cl_2]^+$, where ox represents a general oxidant; the reaction occurs with equal facility under nitrogen. We assign *cis*-stereochemistry (Cl/H) to the intermediate hydrido-species, because a chloride ion *trans* to hydride could be displaced very readily and, in that case, both chlorides would be expected to participate in the radiochemical exchange. The alternative *trans*-stereochemistry is, however, found in the analogous reaction of rhodium(III).

[6] Vlček and Rusina, *Proc. Chem. Soc.*, 1961, 161.

[7] Brown and Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 1495.

When *trans*-dichlorobisethylenediaminerhodium(III) cation is treated with borohydride, and the solution of the hydrido-complex produced allowed to oxidise in air, *cis*-dichlorobisethylenediaminerhodium(III) cation is formed. This fact, and the formation of the same hydride from both isomers of dichlorobisethylenediaminerhodium(III) chloride may be explained by the tentative reaction scheme below, in which ox represents a general oxidant, such as water.

The replacements of chloride by hydride are probably S_N2 in character, since qualitative observations show that increasing the concentration of borohydride increases the rate of formation of the hydride. The infrared spectrum of the tetraphenylborate of (*A*) in the characteristic region[8] for the bisethylenediamine series suggests that it has the *cis*-configuration. However, the tetraphenylborate anion has absorptions in the same region so that the spectra are not completely unequivocal. It is noteworthy that two hydridic species are produced from the *cis*-dichlorotriethylenetetraminerhodium(III) cation, which is unlikely to rearrange. The product of replacing the first chloride in *cis*-dichlorobisethylenediaminerhodium(III) by hydride may be either the *cis*- or the *trans*-hydridochloro-compound since the second chloride is here so readily replaced. The oxidation of (*A*) to (*B*) occurs through unknown stages since chloride ion itself does not replace the hydride in (*A*) even at very high concentrations.



EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained in tubes of 15 mm. outside diameter, in a Varian Associates V-4311 spectrometer, operating at 56·43 Mc./sec. Infrared spectra were measured on a Perkin-Elmer model 21 spectrophotometer, with calcium fluoride or sodium chloride optics, and electronic spectra were obtained by using a Perkin-Elmer model 4000 spectrophotometer.

Solvents used were degassed, then saturated with nitrogen, and all operations were conducted under nitrogen. The procedure used is illustrated by the following example.

Dihydridobisethylenediaminerhodium(III) *Tetraphenylborate.*—*trans*- or *cis*-Dichlorobisethylenediaminerhodium(III) chloride (0·31 g., 1 mmole) in water (5 ml.) at 0° was treated dropwise with an ice-cold solution (5 ml.) of sodium borohydride (0·18 g., 5 mmoles). An ice-cold solution (5 ml.) of sodium tetraphenylborate (0·75 g., 2 mmoles) was added slowly, and the pale brown precipitate of the desired salt was collected, washed with ice-cold water, and dried in a rotary drier at 15°. The *salt* contained no chlorine (Found: C, 65·0; H, 7·0; N, 9·5. $C_{28}H_{38}BN_4Rh$ requires C, 62·0; H, 7·0; N, 10·4%).

This procedure was repeated with 0·0132 g. of the dichloro-complex. After the addition of sodium tetraphenylborate and removal of the precipitate, an excess of silver nitrate solution was added to the filtrate, giving a mixed precipitate of silver chloride and silver tetraphenylborate, contaminated with a little metallic silver formed by residual borohydride ions. This precipitate was collected, washed several times with acetone (which dissolves the silver tetraphenylborate), and redissolved in ammonia. The solution was acidified with nitric acid, and the precipitated silver chloride collected, washed with water, dried, and weighed (0·0158 g.; calc. for complete chlorine displacement from complex, 0·0166 g.).

When the brown solution of dihydridobisethylenediaminerhodium(III) chloride was set aside under nitrogen, metallic rhodium was slowly deposited, and, after 3 days, the solution had

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[8] Baldwin, *J.*, 1960, 4369.

become yellow. The rhodium was removed by filtration, and the absorption spectrum of the filtrate was measured (see Table 3). The tetraphenylborate was isolated from the " oxidised " solution and had an infrared spectrum identical with that of authentic *cis*-dichlorobisethylenediaminerhodium(III) tetraphenylborate.

TABLE 3.

trans–cis-Isomerisation in dichlorobisethylenediaminerhodium(III) cations *via* the hydridic compound (λ in mμ).

Compound	$\lambda_{max.}$	ε_1	$\lambda_{max.}$	ε_2	λ	ε	λ	ε	$\varepsilon_2/\varepsilon_1$
cis-[Rh en_2Cl_2]$^+$	350	130	292	170	—	—	210	10^4	1·30
trans-[Rh en_2Cl_2]$^+$	407	75	289	130	240	1500	210	10^4	1·73
" Oxidised "-[Rh en_2H_2]$^+$ ...	350	—	292	—	—	—	210	—	1·35

Hydrido-complexes were obtained from *cis*- and *trans*-dichlorobisethylenediaminerhodium(III) chlorides, chloropentamminerhodium(III) chloride, *cis*-dichlorotriethylenetetraminerhodium(III) perchlorate, dichlorotetrapyridinerhodium(III) chloride, and sodium dichlorobisdimethylglyoximatorhodate(III). The following compounds were also studied, with negative results: trisbipyridylrhodium(III) chloride, dichlorobisbipyridylrhodium(III) chloride, sodium dichloro-*NN'*-bisacetylacetonatoethylenedi-iminorhodate(III), sodium hexachlororhodate(III), trisacetylacetonatorhodium(III), bisdimethylglyoximatodiamminorhodium(III) chloride, and monoaquoethylenediaminetetra-acetatorhodate(III).

Reduction of Quinone by Hydride Transfer.—Quinone (0·05 g., 5×10^{-4} mole) in water (2 ml.) was added to a suspension of hydridochlorotriethylenetetraminerhodium(III) tetraphenylborate (0·6 g., 10^{-3} mole) in a mixture of water (3 ml.) and methanol (1·5 ml.). The mixture was shaken under nitrogen for ½ hr. at 30°, cooled, and extracted with ether. On evaporation of the ether, white crystals of quinol (~0·03 g.) were obtained, which, after recrystallisation from ether, had m. p. and mixed m. p. 170° (lit., 170·3°). The aqueous layer had deposited a red gum, which contained all the rhodium.

Radiochemical Experiments on Cobalt(III).—A solution of the unlabelled complex (0·3 g.) in ^{36}Cl-labelled hydrochloric acid (A.E.R.E., Harwell, 4 ml., 2M, with an activity of 10 μc) was set to reflux for 2 hr., whereafter the solution was cherry-red, then allowed to evaporate to dryness. The green crystals of active *trans*-dichlorobisethylenediaminecobalt(III) chloride hydrochloride were collected, and heated at 110°; the desired labelled compound was obtained.

After unsuccessful attempts involving (i) precipitation of free chloride with silver nitrate (this removed all the chloride from the complex as well) or (ii) precipitation with tetraphenylborate (this was incomplete), a 0·01M-solution of the labelled complex in potassium chloride solution (0·1M) was counted. An ice-cold 5-ml. aliquot part was treated with freshly prepared sodium borohydride solution in excess; this was necessary because aged solutions were sufficiently alkaline to promote the base-catalysed hydrolysis of the complex ions, which effectively increased the exchange. The solution was immediately acidified with concentrated nitric acid and shaken with Dowex 50 cation-exchange resin (0·5 g.) which removed all the complex ion from solution. The resin was removed by centrifugation and washed with ice-water, and the combined supernatant solutions were made up to 10 ml. An aliquot part (5 ml.) was counted. The activity of the free chloride in the supernatant liquid was found to be 60% of the original (mean of 3 runs: 58, 66, 56%), indicating that only one chloride of the original had exchanged.

Other Experiments on Cobalt(III).—No evidence for formation of hydrides was obtained when the following complexes were treated with reducing agents: *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chloride, *cis*-dichlorotriethylenetetraminecobalt(III) chloride, chlorobisdimethylglyoximatoamminocobalt(III), chlorobisdimethylglyoximatopyridinocobalt(III), bisdimethylglyoximatobisamminocobalt(III) chloride, trisacetylacetonatocobalt(III), and potassium ethylenediaminetetra-acetatocobaltate(III).

We thank Dr. A. J. Poë for his kind assistance with the design and prosecution of the radiochemical experiments, Johnson, Matthey and Co. Ltd. for a loan of rhodium, and the United States Rubber Company for financial assistance.

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[*Received, February 9th*, 1963.]