vide a basis for comparing the stabilities of other complexes of copper(II) with nitrogen and sulfur donors.

Experimental Section

The N-heterocyclic amines used in this investigation were commercial materials of highest available purity and were used as received.

Copper(I) thiocyanate was obtained from Alfa Inorganics. Complexes with those ligands which are liquids at 25° were prepared by dissolving the copper(I) thiocyanate in the pure liquid and precipitating the compound by dilution with ethanol. For the solid ligands, finely ground copper(I) thiocyanate was stirred at room temperature with an ethanol solution of the amine for periods of 18–36 hr. The unusual stoichiometries of the pyrazine, piperidine, and bipyridine complexes did not change when the preparations were carried out in refluxing ethanol.

The copper(II) thiocyanate complexes were obtained from the corresponding copper(II) chloride compounds by treatment with the stoichiometric quantity of potassium thiocyanate in ethanol. All of the compounds were washed with absolute ethanol and were dried under vacuum at 25°.

Infrared spectra were recorded from KBr pellets and Nujol mulls using a Beckman IR-10 spectrophotometer calibrated with polystyrene. For those compounds containing organic ligands with absorption bands near the thiocyanate bands, location of the latter was accomplished by comparison with the spectra of the corresponding copper(II) chloride–base complex. The spectrum of a copper(II) chloride complex was essentially identical with that of the free ligand.[13]

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New Synthesis of a π-Crotylrhodium Complex

BY HAROLD E. SWIFT AND ROBERT J. CAPWELL, JR.

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The reaction of ethanolic rhodium trichloride with olefins and dienes has been investigated quite extensively in recent years and the results have been varied. For example, a reaction between ethanol and butadiene to form ethers where rhodium trichloride acts as a catalyst has been reported.[1]

Butadiene has been polymerized to both crystalline and oily polymers in ethanol[2–4] using rhodium trichloride as a catalyst. Ethylene[5,6] and propylene[7] have been dimerized in ethanol using rhodium trichloride as a catalyst. Olefins have been isomerized with ethanolic[8] rhodium trichloride. In other cases complex formation between rhodium and olefins and/or dienes has been reported.[1,9,10]

We now wish to report the synthesis of what is believed to be a new reaction in which a π-crotylrhodium complex is formed.

Experimental Section

The complex was formed by adding 5 g of butadiene to a flask immersed in a Dry Ice–acetone bath which contained 1.2 g of rhodium trichloride trihydrate ($RhCl_3 \cdot 3H_2O$) dissolved in 150 ml of absolute ethanol and 35 g of 10–20 mesh granular zinc metal. After the addition of butadiene, the flask was removed from the Dry Ice–acetone bath and set aside to warm slowly at room temperature. Approximately 30 min after the flask was removed from the bath, a light brown precipitate started to form around the zinc granules. After the reaction ceased, the precipitate was filtered and washed several times with absolute ethanol. Separation of the precipitate from the zinc granules presented no problem since the precipitate could be easily suspended in ethanol, whereas the zinc granules remained at the bottom of the flask. After thoroughly washing the precipitate with absolute ethanol, it was dried under vacuum at 70°. The solid obtained weighed 0.45 g. No precautions were taken to carry out the reaction and separation in an inert atmosphere.

Zinc concentrations in solutions were determined by X-ray emission spectroscopy (X-ray fluorescence). Zinc metal was dissolved in dilute HCl for the primary standards. Aliquots were diluted with ethanol for use as working standards. Copper was added to the standards and the samples as an internal standard to correct for absorption effects by rhodium. The Zn Kα/Cu Kα intensity ratios were then determined for standards and samples.

Infrared spectra were recorded in the 4000–550-cm^{-1} region with a Perkin-Elmer Model 421 spectrophotometer. The vibrational frequencies were measured both with a KBr wafer and in Nujol mull. In the 550–200-cm^{-1} region, a Perkin-Elmer Model 621 was used and the spectra were obtained in Nujol between polyethylene windows.

Results and Discussion

The reaction described above was an attempt to form a rhodium(I) butadiene complex using a similar type of reaction where copper has been used to prepare a rhodium(I) carbonyl complex[11]

$$\mathrm{RhX_3 + 2CO + 2Cu \longrightarrow Rh(CO)_2X + Cu_2X_2} \qquad (1)$$

The complex reported in this paper contained 19.1% carbon, 3.6% hydrogen, 24.1% chlorine and 40.1% rhodium. The only analysis which was questionable was the rhodium where there was a ±2% spread among three samples from the same batch.

An infrared spectrum of the solid showed strong water bands at 3300 and 1607 cm^{-1}. This water was tenaciously held since it could not be removed under vacuum at 100°. Also, between 4000 and 500 cm^{-1}, absorptions were found at 1456 (m), 1434 (s), 1370 (ms), 1245 (w), 1181 (w), 1023 (s), 964 (ms), 868 (m), and 535 (m, br) cm^{-1}. Fritz[12] and Fischer and Werner[13] have reported these bands as characteristic of the π-crotyl system. However, the 1434-cm^{-1} band has remained unassigned, and, therefore, we suggest it is a methyl deformation. Between 500 and 200 cm^{-1}, a very strong band at 330 cm^{-1} and a medium intense one at 280 cm^{-1} were observed. Following the assignments made by Powell and Shaw[9] for

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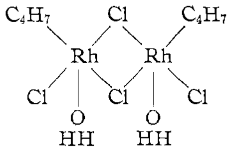
the 320- and 240-cm^{-1} absorptions found in their crotyl complex of rhodium, we assign the 330-cm^{-1} band to the terminal Rh–Cl stretch and the 280-cm^{-1} band to the bridged Rh–Cl–Rh stretching vibration. Recently Brookes and Shaw[14] investigated the low-frequency infrared spectra of a large number of rhodium chloride complexes and found Rh–Cl stretching vibrations in two ranges: 345–293 and 278–264 cm^{-1}.

The complex was insoluble in benzene, methanol, dimethylformamide, dimethyl sulfoxide, carbon tetrachloride, and water suggesting a binuclear or polymeric material. Because of the insolubility, molecular weight measurements and nmr studies could not be carried out.

Reaction of the complex with 10% KOH in ethylene glycol at 70° liberated a hydrocarbon gas mixture consisting of 51% *trans*-2-butene, 18% isobutane, 19% *cis*-2-butene, 5% 1-butene, and 7% lighter hydrocarbons. Reaction with concentrated HCl at 70° liberated a gaseous mixture consisting of 33% 1-butene, 31% *trans*-2-butene, 12.5% *cis*-2-butene, 2.5% butadiene, and 21% chlorinated hydrocarbons. The complex started to decompose at 240° upon heating in air at the rate of 1.8°/min. The weight loss amounted to approximately 32% of the sample weight. The hydrocarbon products obtained on decomposition were butenes, ethylbenzene, and ethylnaphthalene according to mass spectrographic analysis. Rhodium metal and an unidentified material were left in the tga cell as determined by X-ray diffraction.

Based on the elemental analyses and infrared data, it is believed that a π-crotylrhodium(III) complex and not a rhodium(I) complex has been formed. I and II are proposed as likely structures for the complex where the theoretical values of carbon, hydrogen, chlorine, and rhodium are 19.4, 3.6, 28.7, and 41.7% respectively. These values agree very well with the experimentally determined values. These structures are based mainly on a similar structure reported by Powell and Shaw[9] where butadiene is coordinated to the rhodium instead of the two water molecules. No evidence of coordinated butadiene was found in the complex reported in this paper, but very strong evidence for coordinated water has been obtained.



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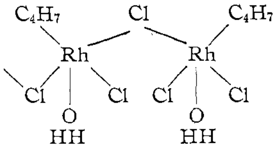

II

It is essential that metallic zinc be used in the preparation of this complex since it did not form when butadiene was added to ethanolic rhodium trichloride in the absence of zinc or when butadiene was added to an ethanolic rhodium trichloride–zinc chloride solution.

It is believed that a necessary step in preparing the complex is the reduction of Rh(III) with zinc to form a rhodium(I)–butadiene complex

$$\mathrm{RhCl_3 + C_4H_6 + Zn \longrightarrow [RhClC_4H_6] + ZnCl_2} \qquad (2)$$

Evidence of the reduction of rhodium with zinc was obtained by determining the zinc concentration under various conditions as shown in Table I. In the absence of butadiene there was a slow deposition of rhodium metal on the zinc granules with a corresponding oxidation of the zinc. In the presence of butadiene, the complex was formed and some rhodium metal deposited on the zinc. The calculated value of zinc ions in solution based on the amount of complex found and metal deposited agreed very well with the experimental value reported in Table I.

TABLE I

ZINC CONCENTRATION IN ETHANOLIC RHODIUM TRICHLORIDE

Reaction time, hr	Zinc concn, mg/ml	Conditions
1	0.20	Zinc metal added to ethanolic rhodium trichloride at 26° in the absence of butadiene; concentrations same as described in the Experimental Section
2	0.98	
3	2.30	
4	2.82	
3	1.36	Butadiene added; reaction conditions and concentrations same as discussed in the Experimental Section

To explain the formation of the π-crotylrhodium(III) complex, the rhodium(I) complex which is proposed in (2) would have to be oxidized with HCl[15] to form a dichlororhodium(III) hydrido complex. This complex would then react with the coordinated butadiene to form the crotyl complex.[16]

HCl was detected in solution and could be formed by a reaction between ethanol and rhodium trichloride as reported by Paiaro and coworkers.[17] The source of HCl and the mechanism for the formation of the crotyl complex will have to be established and work in this area is continuing.

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The Stability Constant of the Monochloro Complex of Iron(II)[1]

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Recently Wells and Salam[2] reported that the rate of the iron(II)–hydrogen peroxide reaction was increased

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

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