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Preparaiton of Some Nitrile-Ruthenium(II) Complexes and Their Reactions with Carbon Monoxide

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A new series of complexes of the type dichlorotetra(nitrile)ruthenium(II) [$(RCN)_4RuCl_2$; R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, C_6H_5, $C_6H_5CH_2$] was prepared by the catalyzed reduction of "$RuCl_3$, $3H_2O$" by hydrogen gas over Adam's catalyst in solution in the appropriate nitrile. $(RCN)_4RuBr_2$ (R = CH_3, C_2H_5) were also prepared by both this direct method and by metathesis of the dichloride with lithium bromide in methanol. $(CH_3CN)_4RuBrCl$ was prepared by a similar short-term metathesis. Far i.r. spectroscopy indicated a trans *configuration for all the complexes. Reaction with carbon monoxide in boiling methanol produced $(RCN)_3(CO)RuCl_2$, while in boiling acetone $(RCN)_2(CO)_2RuCl_2$ resulted.*

Introduction

During the search for a simple general method for the preparation of ruthenium(II) complexes, the utility of the "blue solution", formed by the interaction of various reducing agents with commercial "$RuCl_3$, $3H_2O$" in solution, was investigated. The exact nature of the ruthenium species responsible for the blue color has been the subjiect of much investigation.[1-9] Recent conflicting reports have suggested that the cluster anion[8] $[Ru_5Cl_{12}]^{2-}$ or a mixture of dimeric ruthenium(II,III) species[9] is its correct formulation. Our initial experiments carried out in methanol using zinc amalgam as reductant, resulted in the preparation of mixtures of ruthenium and zinc complexes. To overcome this contamination problem, other reductants were tried. Reduction by molecular hydrogen over platinum[10] in methanol, at ambient temperature and pressure, gave a suitable method for the preparation of pure ruthenium complexes. A similar method, but with hydrogen under pressure, has been used recently to prepare ruthenium complexes from a wide variety of ligands.[11]

Our interest in the properties of coordinated nitriles prompted their use as ligands, but most gave only oils as products when added to the "blue solution". However, when the catalytic reduction was carried out with various nitriles as solvent, then solid products were obtained. This communication reports the preparation and some reactions of these dichlorotetra(nitrile)ruthenium(II) complexes.

Experimental Section

Materials. Ruthenium trichloride trihydrate ("$RuCl_3$, $3H_2O$") was obtained from Engelhard Industries; Adam's catalyst from K and K Laboratories, Inc.; acetonitrile, propionitrile, benzonitrile, and phenylacetonitrile from Aldrich Chemical Co., Inc.; n-butyronitrile, isobutyronitrile, and anhydrous lithium bromide from Matheson, Coleman and Bell; bis(1,2-diphenylphosphino)ethane from Strem Chemicals Inc.; carbon monoxide from Matheson Gas Products; all others were Mallinckroit AR grade.

All solvents were degassed and all reactions were carried out under anaerobic conditions.

Instrument and Analyses. Infrared spectra were obtained on a Beckman IR20A Spectrophotometer as KBr disks (4000-400 cm^{-1}) and Nujols mulls between polyethylene windows (600-250 cm^{-1}); conductance measurements with a Radiometer CDM2 bridge and CDC114 electrode; microanalyses with a Hewlett Packard 185 CHN Analyzer.

Halogen analyses and molecular weight data were

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Table I. Analytical Data.

Comupound	C Calc.	C Fd.	H Calc.	H Fd.	N Calc.	N Fd.	Cl Calc.	Cl Fd.	Mol. Wgt. Calc.	Mol. Wgt. Fd.	Conductance[a] Λ	Conductance[a] Conc.
$(CH_3CN)_4RuCl_2$ [b]	28.5	28.0	3.6	3.4	16.6	16.1	—	—	—	—	—	—
$(CH_3CN)_4RuBrCl$	25.2	25.1	3.2	3.4	14.7	14.5	21.0 9.3	20.3[c] 9.0	— —	— —	— —	— —
$(CH_3CN)_4RuBr_2$	22.6	22.4	2.9	2.5	13.2	12.8	37.6	36.3[c]	—	—	—	—
$(C_2H_5CN)_4RuCl_2$	36.7	36.4	5.1	5.1	14.3	13.8	18.1	18.5	392	400[d]	25.0 1.0	2.50[d] 2.14[e]
$(C_2H_5CN)_4RuBr_2$	29.9	29.7	4.2	4.3	11.6	11.6	33.2	33.3[c]	—	—	51.4	2.08[d]
$(n\text{-}C_3H_7CN)_4RuCl_2$	42.9	42.4	6.3	6.2	12.5	12.6	15.8	16.0	—	—	21.8	2.88[d]
$(i\text{-}C_3H_7CN)_4RuCl_2$	42.9	41.9	6.3	6.2	12.5	12.3	—	—	—	—	—	—
$(C_6H_5CN)_4RuCl_2$ [f]	57.5	57.4	3.5	3.5	9.6	9.4	12.1	12.6	584	619[g]	0.8	2.12[e]
$(C_6H_5CH_2CN)_4RuCl_2$	60.0	59.1	4.4	4.3	8.8	8.4	—	—	—	—	—	—
$(CH_3CN)_3(CO)RuCl_2$	26.0	25.7	2.8	3.3	13.0	13.8	—	—	—	—	40.5	3.17[d]
$(CH_3CN)_2(CO)_2RuCl_2$ [b]	23.2	22.8	1.9	2.6	9.0	8.9	—	—	—	—	—	—
$(C_2H_5CN)_3(CO)RuCl_2$	32.8	32.0	4.1	4.6	11.5	12.3	19.6	19.8	365	364[g]	34.2	2.77[d]
$(C_2H_5CN)_2(CO)_2RuCl_2$	28.4	28.2	3.0	3.4	8.3	8.5	—	—	—	—	35.3	2.01[d]
$(n\text{-}C_3H_7CN)_3(CO)RuCl_2$	38.3	38.5	5.2	6.1	10.3	11.0	—	—	—	—	—	—
$(i\text{-}C_3H_7CN)_3(CO)RuCl_2$	38.3	38.0	5.2	5.7	10.3	11.0	—	—	—	—	—	—
$(C_6H_5CN)_3(CO)RuCl_2$	51.8	52.4	3.0	3.6	8.2	8.6	—	—	—	—	—	—
$(C_2H_5CN)_2(diphos)RuCl_2$	56.4	55.3	5.0	5.1	4.1	4.3	10.6	10.6	680	820[g]	56.8 19.7	1.28[d] 0.97[e]
$(C_2H_5CN)(CO)(diphos)RuCl_2$	55.1	54.5	4.5	4.7	2.1	3.2	—	—	653	659[g]	51.2	1.42[d]

[a] In mho cm^2 mol^{-1}. concentrations are $\times 10^3 M$; typical values for 1:1 eliectrolytes are 50-80 in methanol and 50 in dichloromethane. [b] Ref. 10. [c] Bromine analysis. [d] Methanol solution. [e] Dichloromethane solution. [f] U.S. Patent No., 3,449,387. [g] Chloroform solution.

determined by Galbraith Laboratories, Inc., Knoxville, Tenn. or by Alfred Bernhardt, Mikroanalytische Laboratorium, Elbach über Engelskirchen, West Germany.

All analytical data are collected in Table I.

Preparation of dichlorotetra(nitrile)ruthenium(II) [$(RCN)_4RuCl_2$]. Typically, a solution of "$RuCl_3,3H_2O$" (1-2 g) in the appropriate nitrile (15-20 ml), with a trace of Adam's catalyst, was stirred in a slow stream of hydrogen. After *ca.* 15 hr. (sometimes longer depending on the nitrile used), the yellow *product*, which precipitated, was filtered off and washed with diethyl ether. Dissolution in a minimum of methanol, filtration and addition of diethyl ether gave good yields (65-95%) of crystalline *product*, which was dried at 25° (0.1 mm) for *ca.* 3 hr.

Reactions with Carbon Monoxide. (a) *In methanol.* A solution of $(RCN)_4RuCl_2$ (*ca.* 0.3 g in 25 ml) was heated under reflux in a stream of carbon monoxide for *ca.* 3 hr. After cooling and filtering, the solvent was removed and the yellow residue of $(RCN)_3(CO)RuCl_2$ washed with diethyl ether and dried at 75° (0.1 mm) for *ca.* 3 hr.

(b) *In acetone.* After heating under reflux a suspension of $(RCN)_4RuCl_2$ ($R = CH_3, C_2H_5$) in a stream of carbon monoxide for *ca.* 6 hr and removal of unreacted complex by filtration, the product $(RCN)_2(CO)_2RuCl_2$ was isolated as in (a).

Reactions of $(C_2H_5CN)_4RuCl_2$ *with bis(1,2-diphenylphosphino)ethane (diphos).* A suspension of $(C_2H_5CN)_4RuCl_2$ (0.21 g) and diphos (0.22 g, 1 mol) in methanol (20 ml) was heated under reflux for 1.2 hr to give a clear pale-green solution. After removal of solvent, heating at 75° (0.1 mm) for 9 hr gave yellow-green crystalline $(C_2H_5CN)_2(diphos)RuCl_2$ (0.4 g, 100%). When this *product* was heated under reflux in a stream of carbon monoxide in methanol (20 ml) for 4 hr, yellow $(C_2H_5CN)(CO)(diphos)RuCl_2$ was formed quantitatively.

Preparation of Bromides. (a) *Metathesis with Lithium Bromide.* (i) On shaking a solution of $(C_2H_5CN)_2RuCl_4$ (0.3 g) with lithium bromide (4.1 g, 62 mol) in methanol (25 ml) for 96 hr, pale orange $(C_2H_5CN)_4RuBr_2$ (0.1 g) precipitated.

(ii) Similarly, $(CH_3CN)_4RuCl_2$ (0.3 g) gave $(CH_3CN)_4RuBr_2$ (0.1 g).

(iii) In contrast, shaking for only 24 hr allowed $(CH_3CN)_4RuBrCl$ (30%) to be isolated.

(b) *Direct Method.* A ruthenium bromide compound was prepared by the metathesis of "$RuCl_3, 3H_2O$" and lithium bromide in boiling methanol, followed by removal of the solvent, extraction with acetonitrile and evaporation of this extract to dryness. This solid was then dissolved in the appropriate nitrile and reduced as before to give $(RCN)_4RuBr_2$ ($R = CH_3, C_2H_5$).

Results

The preparation of a new series of complexes of the type dichlorotetra(nitrile)ruthenium(II) [$(RCN)_4RuCl_2$; $R = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, C_6H_5, $C_6H_5CH_2$] has resulted from the catalytic reduction, using hydrogen gas over Adam's catalyst, of commercial ruthenium trichloride trihydrate in solution in the appropriate nitrile. The dibromides of the acetonitrile and propionitrile adducts were prepared by this method and also by the metathesis, over an extended period of time, of the appropriate dichloride with lithium bromide in methanol solution. Short time metathesis

Table II. Selected Infrared Spectral Data (cm^{-1}).

Compound	ν(CN)	ν(CO)	ν(RuCl)	Other bands
$(CH_3CN)_4RuCl_2$	2270	—	276	481,467,322(RuN)
$(CH_3CN)_4RuBrCl$	2275	—	278	482,461,323(RuN),301
$(CH_3CN)_4RuBr_2$	2278	—	—	479,458,321(RuN),299
$(CH_3CN)_3(CO)RuCl_2$	2280	1962	284,271	480,469,331sh.,320,303sh.
$(C_2H_5CN)_4RuCl_2$	2252	—	278	310(RuN),303sh.
$(C_2H_5CN)_4RuBr_2$	2265	—	—	312(RuN),299
$(C_2H_5CN)_3(CO)RuCl_2$	2252	1958	286,275	309,300sh.
$(C_2H_5CN)_2(CO)_2RuCl_2$	2270	2058,1965	270	314,300sh.
$(C_2H_5CN)_2(diphos)RuCl_2$	2255	—	—	530,513,485,453,424
$(C_2H_5CN)(CO)(diphos)RuCl_2$	2263	1963	—	529,511,488,453,420,309
$(n\text{-}C_3H_7CN)_4RuCl_2$	2262	—	267	565,547,462,440,405,312(RuN),300sh,283
$(n\text{-}C_3H_7CN)_3(CO)RuCl_2$	2267	1930	272,265	569,546,468,440,400,309(RuN),302sh.
$(i\text{-}C_3H_7CN)_4RuCl_2$	2250	—	281	558,418,370,312(RuN)
$(i\text{-}C_3H_7CN)_3(CO)RuCl_2$	2258	1950	280	558,419,369,302(RuN)
$(C_6H_5CN)_4RuCl_2$	2231	—	272	555,550sh.,507,400,346,286sh.
$(C_6H_5CN)_3(CO)RuCl_2$	2238	1960	284,274	551,540sh.,515sh.,506
$(C_6H_5CH_2CN)_4RuCl_2$	2255	—	265	481,464,321(RuN)

sh. = shoulder.

resulted in the formation of the bromochloride. These compounds were shown to be monomeric by osmometric mlecular weight determinations in chloroform solution. They are non-electrolytes in dichloromethane solution by molar conductance measurements, but significant ionization was observed in methanol. They are generally soluble in methanol, somewhat less soluble in cholorofrom and dichloromethane, only slightly soluble in acetone, and insoluble in diethyl ether.

These complexes underwent varying degrees of substitution with carbon monoxide, depending upon the solvent used. In methanol under reflux, only one nitrile group was replaced to give $(RCN)_3(CO)RuCl_2$ (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, C_6H_5), while in boiling acetone the disubstituted products $(RCN)_2(CO)_2$-$RuCl_2$ (R = CH_3[11],C_2H_5) were obtained. The six-coordinate, monomeric nature of these products was confirmed by molecular weight and conductance measurements. Boiling in 2-methoxyethanol in the presence of carbon monoxide resulted in a yellow solution from which a yellow solid was isolated. The infrared spectrum of this solid showed no absorption at ~2200 cm^{-1}, but did show several extremely strong bands at ~2000 cm^{-1}. These data indicate that all the nitrile groups had been displaced and that carbonyl ligands were present. The solution formed in this reaction may be of similar composition to that formed directly from "$RuCl_3$,$3H_2O$" and carbon monoxide in 2-methoxyethanol.[12]

The reaction in boiling methanol would not proceed significantly past monosubstitution, even after a 10 hr reflux period, while in boiling acetone, disubstituted product was present at 2 hr. Two nitrile ligands on $(C_2H_5CN)_4RuCl_2$ were also displaced by reaction with bis(1,2-diphenylphosphino)ethane (diphos) in methanol under reflux. Another nitrile in the resulting complex could also be substituted by reaction with carbon monoxide yielding (C_2H_5CN)-(diphos)(CO)$RuCl_2$.

The infrared spectra of the dichlorotetra(nitrile)-ruthenium(II) complexes (see Table II) ali showed a single strong band at ~2250 cm^{-1} [ν(CN)], confirming the presence of the nitrile group and indicating bonding through the nitrogen.[13] Also, bands at ~300 cm^{-1}, assignable to ruthenium-chloride [ν(Ru-Cl)] and ruthenium-nitrogen[ν(RuN)] stretching modes, were observed. For the acetonitrile and propionitrile complexes, only one absorption at ~275 cm^{-1} could be assigned to ν(Ru-Cl) on the basis of substitution of chloride by bromide. This observation suggests a *trans* chlorine configuration, and therefore, the point group D_{4h}, for these complexes. The spectra of the longer chain aliphatic nitrile complexes showed some asymmetry of the metal-halogen stretching vibration which may result from a general lowering of the symmetry of the molecule by the varying orientations of the organic groups, while still retaining a *trans* chlorine configuration. A similar effect was noted for the single band tentatively assigned to ν(RuN) at 320-310 cm^{-1}. The spectrum of the benzonitrile adduct showed only weak absorption between 400-300 cm^{-1}, but a strong, sharp bond at 270 cm^{-1}, probably due to ν(RuCl), with a much weaker absorption at 286 cm^{-1} again suggested a *trans* chlorine configuration.

Substitution of nitrile by carbon monoxide in these complexes lowers the symmetry of the molecule from the point group D_{4h} to C_{2v} for both mono- and disubstitution, assuming that the *trans* chlorine configuration is retained. This confers infrared activity on *both* ν(RuCl) modes and is manifested quite clearly in the spectra of $(RCN)_3(CO)RuCl_2$ (R = CH_3, C_6H_5) by the appearance of an additional weaker band at ~285 cm^{-1} (see Table II). A *cis* arrangement of the CO ligands in the disubstituted product was demonstrated by the observation of two ν(CO) modes at ~2000 cm^{-1} and although this imposes a *cis* arrangement on the two remaining nitriles only a single ν(CN) absorption was observed. This insensitivity to environment though is not an unusual phenomenon for ν(CN) in nitrile complexes.[13] The spectra of the other substituted adducts were more complex, but tentative assignments are indicated in Table II.

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Discussion

Of the dichlorotetra(nitrile)ruthenium(II) complexes prepared in this work, two have been reported previously. The acetonitrile adduct was prepared by a similar method[11] and the benzonitrile adduct, reported in a patent,[14] by the interaction of this nitrile with "$RuCl_3.3H_2O$" in 2-methoxyethanol. A related monomer[15,16] dichlorotetra(acrylonitrile)ruthenium(II) and the dimeric complex[11] $[(C_6H_5CN)_3RuCl_2]_2$ have also been prepared. This last product, prepared by the reaction of benzonitrile with the "blue methanolic solution of ruthenium",[11] contrasts with our observation for the direct reduction of "$RuCl_3.3H_2O$" in benzonitrile solution, where only the tetra(nitrile) monomer is formed.

Our investigation of the ease of substitution of nitrile ligands, particularly by gases, led to the observation of a solvent effect. All the tetra(nitrile) adducts underwent substituion of only one nitrile ligand on reaction with carbon monoxide in methanol solution under reflux, while, at the lower temperature of boiling acetone, two nitriles were replaced by carbon monoxide. In contrast, at the relatively high temperature of boiling 2-methoxyethanol all four nitrile ligands were displaced from the appropriate ruthenium (II) adduct. The monosubstitution observed for the benzonitrile adduct suggests the sequence of a reaction observed previously[11] for the chloro-bridged dimer $[(C_6H_5CN)_3RuCl_2]_2$ with carbon monoxide in methanol solution under reflux. If the chlorine bridge was first cleaved by carbon monoxide, then the product would be $(C_6H_5CN)_3(CO)RuCl_2$, which is now known to be stable to further substitution under these conditions. As the product isolated was in fact $(C_6H_5CN)_2(CO)_2RuCl_2$, the initial reaction must be one of nitrile substitution, followed by bridge cleavage. This latter reaction presumably occurs only when the more strongly electron-accepting carbon monoxide ligand becomes bound to ruthenium.

In the report[11] of the preparation of dichlorotetra(acetonitrile)ruthenium(II), an assignment for the infrared-active metal-halogen stretching frequency [ν(RuCl)] was made to a single, very strong band at 320 cm^{-1}, presumably based on a comparison with the spectra of the related dibromo- and dichlorotetra(pyridino)ruthenium(II) complexes. This was interpreted as indicating a *trans* chlorine configuration. However, the spectra of the analogous dibromo- and bromochlorotetra(acetonitrile)ruthenium(II) complexes obtained in the present work also showed a strong absorption at this frequency. Further, the strong band at 276 cm^{-1} observed in the dichloride spectrum was absent from the dibromide spectrum (see Table II). These observations suggest that the latter absorption may be better assigned to ν(RuCl) and the former at ~320 cm^{-1} tentatively assigned to ν(RuN). This conclusion is supported by the appearance of a weak absorption at 278 cm^{-1} in the bromochloride spectrum and also by the loss of a band at 278 cm^{-1} from the spectrum of dichlorotetra(propionitrile)ruthenium(II) on the replacement of chloride by bromide.

In the spectra of $(CH_3CN)_4RuBrCl$ and $(CH_3CN)_4RuBr_2$, a band at ~300 cm^{-1}, not present in the dichloride spectrum, appeared. In the former, it is relatively weak, while in the latter, it is of comparable intensity to the absorption at ~320 cm^{-1}. It might be considered as a second ν(RuN) thus indicating *cis* stereochemistry when bromide is present. This is unlikely, however, as increasing the size of the halogen atom should favor the *trans* configuration on steric grounds. Its assignment therefore remains uncertain. Generally, the spectra of all the tetra(nitrile) adducts were suggestive of a *trans* chlorine configuration.

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