where ϕ is the primary quantum yield for reaction 1 and I_a is the absorbed light intensity. If it is assumed that all the incident light is absorbed, which is a good approximation for the first 10–20% reaction where the product quantum yields were generally measured, it is seen that the rates and thus Φ (product quantum yield) are independent of initial concentration of $Mo(CN)_8^{3-}$ and that the expression leads to zero-order kinetics, in agreement with the experimental results. Furthermore, consideration of the expressions indicates Φ must also be independent of light intensity, also in agreement with the results. The rate expressions indicate the product quantum yield in acidic solution must lie between 1 and 2 and in basic solution between 4 and 5, depending on the values of k_4 and k_3, again in agreement with the results. Finally, if the mechanism is valid, the primary quantum yield, ϕ, using the observed values for Φ of 1.5 and 4.3 and assuming $k_4 \gg k_3$, must have a minimum value of 0.75 in acidic solution and 0.86 in basic solution. Using the observed product distribution (Table II) a ratio of k_3/k_4 can be calculated, which leads to a calculated value of ϕ of 1.1 ± 0.4, suggesting a primary quantum yield of unity.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA 29208

The Blue Ruthenium Chloride Complexes and Their Oxidation Products[1]

BY E. E. MERCER* AND P. E. DUMAS

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Three blue ruthenium chloride complexes have been identified as dimeric ruthenium(II,III) species of the type $Ru_2Cl_{3+n}^{(2-n)+}$, where $n = 0, 1, 2$. Chemical and controlled-potential oxidations produce corresponding dimeric ruthenium(III) complexes. The oxidation state of the metal was verified by redox titration and magnetic measurements. Ionic charges were measured by ion-exchange membrane equilibrations. The electrochemical behavior of these complexes is also reported.

The blue ruthenium chloride complexes were first observed by Claus,[2] who noted that when ruthenium trichloride was heated with strong reducing agents, intense blue solutions were obtained. Other investigators postulated on rather limited data that these blue solutions contained ruthenium(II) chloride complexes. The most recent reports on these complexes have been made by Adamson[3] and Wilkinson.[4] Although Adamson was able to elute a discrete band from an anion column with 4.0 *M* HCl, no attempt was made to characterize this species. The magnetic moment of this solution was determined in 10–11 *M* HCl and found to be on the order of 2.12–2.35 BM, which is inconsistent with both high-spin and low-spin ruthenium(II) complexes. He suggested an equilibrium between high- and low-spin complexes could account for the observed magnetic moment. Wilkinson[4] prepared blue ruthenium chloride solutions and was able to precipitate a dinegative ruthenium-containing ion, which he identified as $Ru_5Cl_{12}^{2-}$. He noted that these compounds were weakly paramagnetic and showed a single resonance in the esr spectrum.

Experimental Section

Analysis.—Ruthenium was determined spectrophotometrically as RuO_4[5] or RuO_4^{2-},[6] depending on whether the analysis was conducted in the presence or absence of free chloride.

Chloride coordinated to ruthenium was determined gravimetrically using a modification of the method reported by Connick and Fine.[7] Excess silver nitrate was added to an aliquot of the sample, and the ruthenium present was oxidized to ruthenium tetraoxide with ceric perchlorate. The RuO_4 was removed by heating. The solution was then filtered and the AgCl was thoroughly washed with 0.01 *M* HNO_3. This precipitate was dissolved in concentrated ammonia and reprecipitated by adjusting the pH to below 7 with nitric acid. This solution was filtered into preweighed crucibles and dried at 110°.

Lanthanum solutions were prepared by dissolving lanthanum oxide (American Potash and Chemical Corp.) in the appropriate acid. Lanthanum was determined gravimetrically by ignition of the oxalate.

Reagents.—Ruthenium chloride (≃38% Ru) was obtained from Engelhard Industries. This was converted into $K_2RuCl_5(H_2O)$ as previously reported.[8] This compound was used as the starting material in the preparation of all the blue complexes.

Ion-exchange resins used were Dowex 50-X8, 200–400 mesh (H^+ form), and Dowex 1-X8, 100–200 mesh (Cl^- form). The cation resin was always washed with 6 *M* HCl to remove iron impurities. The cation-exchange membranes were obtained from American Machine and Foundry Co. (Serial No. C 103 FE).

All other chemicals were reagent grade and were used without further purification.

Equipment.—All ultraviolet–visible spectra were recorded on a Cary Model 14 spectrophotometer using quartz cells. A Beckman Research pH meter was used for pH measurements and for

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all potentiometric titrations. Accurate pH measurements were made on small volumes ($\simeq$0.5 ml) employing a Corning combination electrode (Model 476051), which has an operating range from pH 0 to 14.

Electrochemical oxidations and reductions were carried out on a controlled-potential coulometer designed by Propst.[9] Electrochemical reductions were performed at mercury, platinum, or gold electrodes. Platinum or gold electrodes were used for oxidations. All potentials were referenced to an sce connected to the solution by a silicic acid bridge.

Polarograms were recorded on either a Sargent Model XV recording polarograph or a multipurpose instrument designed by Propst,[10] using a dme when possible. In the more positive region the rotating carbon-paste electrode[11] was employed.

Magnetic moments were measured at room temperature using the Gouy method. The equipment consisted of a Varian Model V-2301A 4-in. electromagnet and a Model H-16 Mettler balance. Standard solutions of nickel chloride and copper sulfate were used as references.

Electron spin resonance spectra were recorded using an Alpha Scientific Laboratories esr spectrometer.

Ion-exchange membrane equilibrations were performed in Teflon cells similar to those used by Wallace.[12]

Preparation and Isolation of the Dimeric Complexes.—A nearly saturated solution of $K_2RuCl_5(H_2O)$ in 0.01 *M* acid (approximately 10^{-2} *M* in Ru) was prepared. Potassium ions were replaced with hydrogen ions using a cation-exchange column in the hydrogen ion form. Twenty milliliters of the resulting solution was reduced at a controlled potential of -0.50 V *vs.* sce. Deoxygenated nitrogen was bubbled through the solutions throughout the electrolysis. The reduction was continued at room temperature until ruthenium metal was visible on the walls of the glass electrolysis cell. At this point, the solution was an intense blue. All the blue complexes which were characterized are present in this solution. Addition of hydrochloric acid prior to reduction was sometimes used to increase the fraction of the higher chloride complexes.

The stock solution which contained the blue complexes was loaded on a cation-exchange column (25 × 1 cm) in the hydrogen ion form. The column was thermostated at 0° and the solution was protected from the air with nitrogen. After loading, the column was washed with 0.01 *M* acid until the effluent was no longer blue. This deep blue solution contains anionic and neutral complexes of ruthenium. Three bands on the column are visible at this point: a red band at the top of the column, which is Ru^{2+},[8] a dark blue band immediately below, and a diffuse blue band on the remainder of the column. Elution with 0.1–0.2 *M* acid removes from the resin the broad blue band, which contains the $Ru_2Cl_4^+$ ion. The other blue complex, $Ru_2Cl_3^{2+}$, may be washed from the column with 0.5 *M* acid. These elutions have been performed using *p*-toluenesulfonic acid, sulfuric acid, tetrafluoroboric acid, and perchloric acid. When perchlorate solutions were needed, it was necessary to remove the resin loaded with Ru^{2+} prior to elution. The perchlorate ion oxidizes Ru^{2+} to a species which could not be completely separated from the blue complexes.

A third blue complex could be isolated using an anion-exchange column. The blue solution, removed from the cation column with 0.01 *M* acid, was loaded on an anion column (25 × 1 cm). After washing with distilled water, elution with 0.02 *M* acid removed a blue complex from the column, later identified as Ru_2Cl_5. The blue anionic complexes which remained on the column were so tightly retained that they could not be eluted without decomposition.

This procedure was modified when only one of the complexes was to be isolated. The more tightly retained cation, $Ru_2Cl_3^{2+}$, could be isolated using a cation column as short as 5 cm. The stock blue solution may be loaded directly on the anion-exchange column in the isolation of the Ru_2Cl_5 discussed above.

Each of the blue complexes, which were separated, could be oxidized to a yellow solution at a potential of $+0.70$ V *vs.* sce using a platinum electrode. Ion-exchange elutions, the electronic spectrum, and electrochemical behavior showed that a single yellow complex was present in each of these oxidized solutions. In each case the oxidation product was more tightly retained by a cation-exchange column than the corresponding blue complex from which it was prepared. After these oxidations, no free chloride could be detected in solution indicating that the Cl:Ru ratio in the pairs of yellow and blue complexes is the same.

Charge Determinations.—The charges on the complexes were determined using the membrane equilibration method reported by Wallace.[12] In this method solutions containing different anion concentrations are placed on either side of a cation-exchange membrane. Cations are transported through the membrane until an equilibrium distribution is reached. In our experimental application hydrogen ion and a single ruthenium-containing ion were the only cations present in solution. The exchange equilibrium may be represented by the equation

$$nH_L^+ + Ru_R^{n+} \rightleftarrows nH_R^+ + Ru_L^{n+} \tag{1}$$

where L and R represent the left and right chamber, respectively. The thermodynamic equilibrium constant for eq 1 is unity. Following the approximations for activity coefficients in perchloric acid solutions less than 0.20 *M*, which were made by Wallace,[12] the charge on the ruthenium ion is calculated by the expression

$$n = \frac{\log([Ru_R]/[Ru_L])}{\log([H_R]/[H_L])} + 0.055n(n - 1) \tag{2}$$

where n is the charge on the ruthenium-containing ion, $[Ru_R]$ and $[Ru_L]$ are molar concentrations of the ruthenium-containing species in the right and left chamber, respectively, and $[H_R]$ and $[H_L]$ are the hydrogen ion concentrations in each chamber. Since only the ratio of the concentrations of the ruthenium-containing complex is used in the calculation of the ionic charge, the concentration of ruthenium (gram-atoms per liter) may be used without altering the results of the charge determination. The charge calculated will be that of the complex actually present in solution, whether it is polymeric or monomeric.

The equilibration times in these experiments were greatly reduced by presaturation of the membrane with the ruthenium complex. At room temperature the blue complexes decomposed before equilibrium was reached so it was necessary to perform the experiments at 0°. Equilibrium was reached in 8–60 hr depending on the complex. In general, the higher the charge the more rapidly equilibrium was attained. After equilibrium was reached, the spectra of the solutions were recorded to check for decomposition and the solutions were analyzed for ruthenium and hydrogen ion.

The charge per atom on $Ru_2Cl_3^{3+}$ was determined by a charge balance on an ion-exchange column.[13] The ion was quantitatively displaced by acidic lanthanum solutions. The charge per atom is given by

$$\text{charge/Ru atom} = \frac{3[La^{3+}] + [H^+]_{in} - [H^+]_{out}}{[Ru]_{out}} \tag{3}$$

Results

The electronic spectra of the three blue complexes and their corresponding oxidation products are shown in Figures 1–3. The peaks observed in the 300–400-nm region for the blue complexes had extinction coefficients which did not change upon repeated purification by ion-exchange separation and therefore are probably not due to contamination by the oxidation product. As the number of coordinated chlorides increases, the maximum of the main band of the blue complexes shifts to longer wavelength and increases in intensity: $Ru_2Cl_3^{2+}$, ϵ_{max} 2370 (605 nm); $Ru_2Cl_4^+$, ϵ_{max} 2520 (620 nm); Ru_2Cl_5, ϵ_{max} 2740 (640 nm).

In Table I the results of the chloride analyses are pre-

TABLE I

Blue			Yellow		
Complex	No. of determins	Cl:Ru	Complex	No. of determins	Cl:Ru
$Ru_2Cl_3^{2+}$	3	1.49 ± 0.01	$Ru_2Cl_3^{3+}$	2	1.50 ± 0.01
$Ru_2Cl_4^+$	2	2.00 ± 0.01	$Ru_2Cl_4^{2+}$	1	2.04
Ru_2Cl_5	1	2.45	$Ru_2Cl_5^+$	3	2.50 ± 0.04

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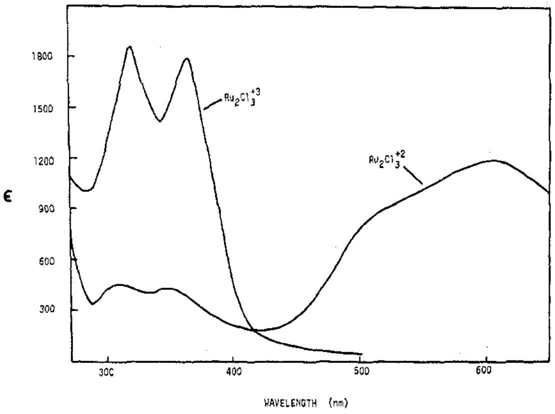

Figure 1.—The spectra of the ions identified as $Ru_2Cl_3^{3+}$ and $Ru_2Cl_3^{2+}$.

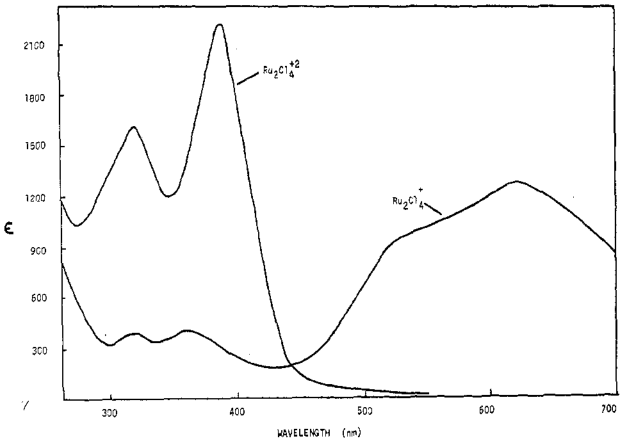

Figure 2.—The spectra of $Ru_2Cl_4^+$ and $Ru_2Cl_4^{2+}$.

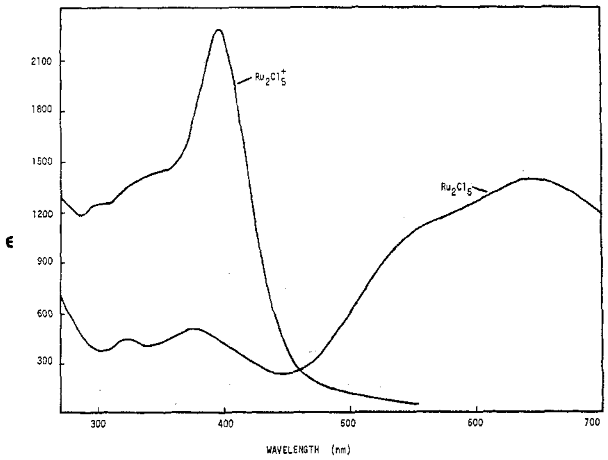

Figure 3.—The spectra of Ru_2Cl_5 and $Ru_2Cl_5^+$.

sented. The fractional atom ratios clearly show these complexes contain an even number of ruthenium atoms.

The charge per ruthenium atom determination was obtained on the yellow $Ru_2Cl_3^{3+}$ complex. In duplicate determinations the charge per ruthenium atom was 1.50 ± 0.05. Charge per atom determinations of the complexes of lower charge were not successful. These complexes were eluted by the lanthanum solution, so that the concentration of hydrogen ion in the column effluent was much greater than that of ruthenium, prohibiting an accurate charge determination (see eq 3). When conditions were such that this elution did not occur, the hydrogen ion concentration in solution was too low and the complexes decomposed.

The results of the ion-exchange membrane experiments are given in Table II. For all of these ions equilibrium was approached from both sides in the separate experiments. Since the charges of the ions are restricted to whole numbers, these determinations are sufficiently accurate to prove these complexes are all dimeric. In all cases where the charge found is 0.1 or greater from a whole number, the deviation is in the direction expected if some decomposition had occurred.

TABLE II

CHARGE PER ION DETERMINATION BY MEMBRANE EQUILIBRATION

	Equilibrium concns, *M*					
	Right		Left			
	$[H^+]$	$10^3[Ru]$	$[H^+]$	$10^3[Ru]$	n'[a]	Charge/ion
			Blue Complexes			
$Ru_2Cl_3^{2+}$	0.2000	4.17	0.1360	1.77	2.23	2.12
	0.2130	2.48	0.1050	0.50	2.26	2.15
	0.2130	2.02	0.1030	0.41	2.19	2.08
$Ru_2Cl_4^+$	0.0516	1.95	0.0836	3.06	0.93	0.93
	0.0334	0.52	0.1008	1.49	0.95	0.95
	0.0460	3.53	0.0926	7.53	1.08	1.08
			Yellow Complexes			
$Ru_2Cl_3^{3+}$	0.1875	7.79	0.1236	1.89	3.38	3.05
	0.2610	1.27	0.2010	0.54	3.26	2.93
	0.1590	1.97	0.1017	0.51	3.04	2.71
$Ru_2Cl_4^{2+}$	0.0965	0.22	0.1930	0.91	2.05	1.94
	0.1465	0.32	0.1840	0.51	2.04	1.93
	0.0931	0.21	0.1485	0.53	1.98	1.87
$Ru_2Cl_5^+$	0.1438	1.66	0.1030	1.21	0.94	0.94
	0.1739	2.18	0.1019	1.23	1.06	1.06
	0.0988	2.86	0.0508	1.40	1.07	1.07
	0.1600	1.96	0.0986	1.23	0.96	0.96

[a] n' is the apparent charge assuming concentrations are equal to activities (see Experimental Section and ref 11).

Unless other anions are present in these complexes, the results given above require that the blue complexes contain both ruthenium(II) and ruthenium(III). To verify this, potentiometric titrations using cerium(IV) perchlorate as the oxidant were performed. A typical titration curve is shown in Figure 4. The initial increase in potential was due to a small amount of reducing impurity, probably Ru^{2+}. This break, however, always accounted for less than 4% of the total ruthe-

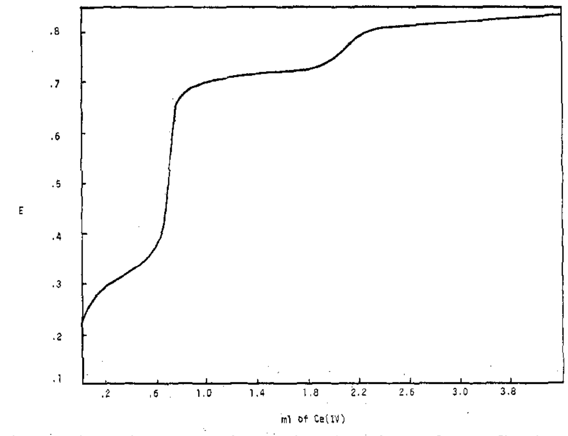

Figure 4.—The potentiometric titration of $Ru_2Cl_3^{3+}$ with cerium(IV) perchlorate. A 10.00-ml sample of a solution with $[Ru] = 5.06 \times 10^{-3}$ *M* was used. The Ce(IV) solution used was 3.64×10^{-2} *M*.

nium present. After oxidation of the impurity, the number of equivalents of cerium(IV) required to reach the next break in the curve corresponds to one electron per two ruthenium atoms. The spectrum of the solution at this break was identical with that of the yellow oxidation product for all of the complexes. Continued addition of the titrant produced further oxidation. In this region the potential was somewhat unstable, but a rather poorly defined break occurred with the addition of 1 additional equiv of cerium per gram-atom of ruthenium. The spectrum of the solution at the final break shown corresponds to that of uncomplexed ruthenium(IV).[14]

The reversibility of the blue to yellow conversion was demonstrated by titration of $Ru_2Cl_3^{3+}$ with tin(II). Ion-exchange elution and the absorption spectrum showed that the only ruthenium-containing product of this reduction was $Ru_2Cl_3^{2+}$. The results of the oxidation state determinations on all three complexes are summarized in Table III. These experiments confirm that the average oxidation state of ruthenium in the blue complexes is 2.5+ and is 3+ in the yellow complexes.

Table III

Complex	Titrant	No. of determns	Equiv of titrant: 1st end point	Equiv of titrant: 2nd end point
$Ru_2Cl_3^{2+}$	Ce(IV)	3	0.54[a]	1.55[b]
$Ru_2Cl_4^{+}$	Ce(IV)	2	0.51[a]	1.55[b]
Re_2Cl_5	Ce(IV)	3	0.50[a]	1.49[b]
$Ru_2Cl_3^{3+}$	Sn(II)		0.47[c]	

[a] Blue → yellow. [b] Blue → Ru(IV). [c] Yellow → blue.

The magnetic moment of $Ru_2Cl_3^{2+}$ and $Ru_2Cl_3^{3+}$ offers confirmatory evidence that the formulation of these complexes is correct. The susceptibility per gram-atom of ruthenium was $(900 \pm 90) \times 10^{-6}$ esu for the blue $Ru_2Cl_3^{2+}$. This value is consistent with one unpaired electron per two ruthenium atoms. The diamagnetism of the yellow complex, $Ru_2Cl_3^{3+}$, requires an even number of electrons and is consistent with our formulation of this complex as a dimeric ruthenium(III) complex. Solutions of the blue complexes exhibited a broad esr absorption at room temperature identical with those reported by Rose and Wilkinson.[4]

The electrochemical behavior of the three blue complexes was studied polarographically and by coulometry. These complexes all showed a reversible oxidation wave and a reduction wave. The half-wave potentials for these waves are given in Table IV. The complete reversibility of the oxidation waves was demonstrated by recording polarograms of partially oxidized samples of the blue complexes. The oxidation and reduction portions of the polarograms appeared as a single wave with no change in the half-wave potential.

Table IV
Polarographic Waves of the Blue Complexes in 0.10 *M* Acid

Complex	$E_{1/2}$,[a] V: Oxidation	$E_{1/2}$,[a] V: Reduction
$Ru_2Cl_3^{2+}$	+0.55	−0.44
$Ru_2Cl_4^{+}$	+0.45	−0.48
Ru_2Cl_5	+0.42	−0.52

[a] Half-wave potentials are referred to the sce and the usual polarographic sign convention is used.

The nature of the reduction wave which appears in the polarograms of the blue complexes is not entirely clear. They are only partially resolved from the hydrogen discharge wave at the dme. Prolonged electrolysis of mixtures of the blue complexes at −0.50 V caused no diminishing in the height of this wave or any change in the absorption spectrum of the solution. The product of the electrochemical reduction probably is reoxidized chemically to its initial form. No accumulation of the Ru(II,II) dimer could be detected.

Coulometric determinations were made on several electrolytic oxidations and reductions. Particularly pertinent are the following. When the solutions of $K_2RuCl_5(H_2O)$ are reduced, approximately one electron per ruthenium atom is needed to reach the limiting current. There is always evidence of ruthenium metal in the resulting blue solutions. Visual observations of dilute solutions of this compound at low temperature suggest that during the electrolysis all the metal is first reduced to ruthenium(II), and then the blue complexes form from this. The presence of metal would suggest that this occurs by a disproportionation. When the blue solutions are oxidized and then rereduced, both steps involve the transfer of one electron for each two ruthenium atoms.

Discussion

The results show that the blue ruthenium complexes which have previously been assumed to contain only ruthenium(II) are, in fact, another example of mixed oxidation state complexes. Several other examples of this have been observed in ruthenium compounds. Moderately stable Ru(III,IV) complexes have been observed in the reduction of $K_4Ru_2Cl_{10}O$[15] and ruthenium(IV) perchlorate solutions.[16] Complexes containing ruthenium(II,III) are also known. Wilkinson[17] prepared compounds with the formula $Ru_2(RCO_2)_4Cl$ with several carboxylates. Cotton[18] determined the structure of the *n*-butyrato complex of this series. He found that the four carboxylate groups were each coordinated to both ruthenium atoms. Since the two metal atoms were crystallographically equivalent, he described the oxidation state of the ruthenium as 2.5+.

Another ruthenium(2.5+) complex has been prepared by Nicholson.[19] The structure of this complex $Ru_2Cl_5(PR_3)_4$, where R = *n*-butyl, has been determined.[20] Three of the chloride atoms serve as bridges between the two crystallographically equivalent ruthenium atoms. The coordination of the metal atoms was that of a distorted octahedron. The magnetic susceptibility of this complex is similar to the blue chloride complexes.

Considering our experimental data and the other known ruthenium (2.5+) complexes, the most reasonable structure for the blue ruthenium complexes would be a tri-μ-chloro bridge with water molecules completing octahedral coordination about each metal. No direct experimental proof of this could be obtained. How-

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ever, the absence of complexes containing less than three chlorides may mean that this number is necessary to form the bridges in the dimeric structure. Whether these complexes should be viewed as containing ruthenium(II) and -(III) or two equivalent metal atoms is moot. However, the other similar ruthenium complexes on which structural data are available would favor the latter interpretation. Supporting this is the very broad, intense absorption in the visible spectrum and the diamagnetism of the corresponding ruthenium(III) dimers. In the absence of hyperfine splitting by the nuclei, the single resonance observed in the esr spectrum is consistent with both interpretations of the oxidation state. However, it should be pointed out that this resonance was assumed to arise from ruthenium(III) chloride complexes by Garif'yanov.[21] We have shown that neither the monomeric nor dimeric ruthenium(III) chloride complexes have an absorption at room temperature in aqueous solution.

The relation between our blue complexes and the ion identified by Wilkinson,[4] *et al.*, as $Ru_5Cl_{12}^{2-}$ is not clear. He assigned the oxidation state as 2+ on the basis of chemical and electrochemical reduction of ruthenium(III) chlorides. Our coulometric experiments show that this criterion may be insufficient to assign the oxidation state in the final blue complexes. Furthermore, as Wilkinson pointed out, the weak paramagnetism and esr signal which he observed is not consistent with a complex containing only ruthenium(II).

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CONTRIBUTION FROM THE CENTRO NAZIONALE DI CHIMICA DEI COMPOSTI DI COORDINAZIONE ED ELEMENTO ORGANICI DEL CNR, LABORATORIO DI PISA, PISA, ITALY, THE ISTITUTO DI CHIMICA ORGANICA INDUSTRIALE, UNIVERSITÀ DI PISA, PISA, ITALY, AND THE CATTEDRA DI CHIMICA ORGANICA INDUSTRIALE, UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY

Preparation and Reactivity of Some Ruthenium Carbonyl Hydrides

BY FRANCO PIACENTI,* MARIO BIANCHI, PIERO FREDIANI, AND ENZO BENEDETTI

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Triruthenium dodecacarbonyl reacts with CO and H_2 under convenient pressure to give $Ru(CO)_5$ and $H_4Ru_4(CO)_{12}$. Appropriate conditions are indicated for a quantitative synthesis of $H_4Ru_4(CO)_{12}$. By reaction of $H_4Ru_4(CO)_{12}$ with $P(C_4H_9)_3$ and $P(C_6H_5)_3$ the corresponding mono-, di-, tri-, and tetraphosphine-substituted ruthenium carbonyl hydrides were synthesized. The properties of $H_4Ru_4(CO)_{12}$ are compared with those reported in the literature and discussed.

Several ruthenium carbonyl hydrides have been described up to now: besides the mononuclear *cis*-$H_2Ru(CO)_4$,[1] the tri- and tetranuclear hydrides $H_4Ru_3(CO)_{10}$,[2] α-$H_2Ru_4(CO)_{13}$,[3] β-$H_2Ru_4(CO)_{13}$,[4] $H_nRu_4(CO)_{12}$,[5] α-$H_4Ru_4(CO)_{12}$,[3,4] β-$H_4Ru_4(CO)_{12}$,[4] and $H_2Ru_6(CO)_{18}$[6] have been reported. Very little however is known on their reactivity and stability.

As a result of some investigations on the catalytic activity of $Ru_3(CO)_{12}$ (I) we became interested in the stability and reactivity of ruthenium carbonyl hydrides. We had in fact found that I was an effective catalyst in the carbonylation of olefins[7-9] and acetylene[10,11] and in the hydrogenation of olefins and aldehydes.[9] By analogy with what was already suggested to rationalize the course of the hydroformylation of olefins in the presence of $Co_2(CO)_8$[12] and $RhCl[P(C_6H_5)_3]_3$[13] we have tentatively attributed this catalytic activity to the presence of one or more catalytically active ruthenium carbonyl hydrides.

In order to give experimental support to this hypothesis we started investigating the behavior of I in the presence of carbon monoxide and hydrogen at various temperatures and pressures.

Our aim was to detect, recover, and identify the ruthenium carbonyl hydrides eventually formed under hydroformylation conditions.[14]

Infrared spectroscopy was the technique chosen to detect the presence of the carbonyl derivatives in the reaction medium. By the use of a cell capable of withstanding high pressures and temperatures the deter-

* Address correspondence to this author at the University of Pisa.

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