CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS AT AUSTIN, AUSTIN, TEXAS 78712

Reactions of Deprotonated Ligands. V. Deprotonated Tris(ethylenediamine)rhodium(III) Ion[1]

BY GEORGE W. WATT AND PETER W. ALEXANDER

Received September 21, 1967

The deprotonated complex $[\mathrm{Rh(en\text{-}H)_2en}]\mathrm{I}$ has been shown to act as a nucleophile in reactions with CH_3I, CH_3Br, $SOCl_2$, and SO_2Cl_2 and as a strong Lewis base in the reaction with BF_3. A similar reaction of $[\mathrm{Rh(en\text{-}H)_3}]$ with CH_3I is described. The products of these reactions were isolated as crystalline solids and characterized by analytical, X-ray diffraction, and infrared spectral data as $[\mathrm{Rh(en\cdot CH_3)_2en}]\mathrm{I_3}$, $[\mathrm{Rh(en\cdot CH_3)_2en}]\mathrm{Br_2I}$, $[\mathrm{Rh(en\cdot CH_3)_3}]\mathrm{I_3}$, $[\mathrm{Rh(en\cdot BF_3)_2en}]\mathrm{I}$, $\{\mathrm{Rh(en)[(en\cdot H)_2SO_2]}\}\mathrm{Cl_2I}$, and $\{\mathrm{Rh(en)[(en\cdot H)_2SO]}\}\mathrm{Cl_2I}$. Possible structures of the products are discussed in terms of the infrared spectral data and reactivity toward hydrolysis.

Ewens and Gibson[2] report that a coordinated sulfur atom such as that in mercaptide complexes commonly behaves as a nucleophile. They found that β-mercaptoethylamine(diethyl)gold(III) reacts with methyl iodide to form the corresponding thioether. Such reactions have been extended to complexes of other metals, especially Ni and Pd with ligands of a similar nature, and represent an energy-transfer process. Methylation of the Ni–S–R group S atom which is quite strongly bound to the Ni atom produces the relatively weaker nickel–thioether bond, accompanied by a change from a square-planar diamagnetic complex to a paramagnetic octahedral one. With Pd(II) analogs, methylation decreases the M–S bond strength to such an extent that one ligand is lost to give the product $[\mathrm{Pd(NH_2CH_2SCH_3)I_2}]$.

Reactivity of coordinated mercaptides has shown[3] that terminal groups exhibit a greater tendency to act as nucleophiles than do bridging groups, but the nucleophilic power of a sulfide group is greatly impaired by replacing Ni(II) with Pd(II), an ion with little tendency for pentacoordination.

Reactions of this type have been successfully employed to prepare complexes containing macrocyclic rings. The product of the reaction between bis(β-mercaptoethylamine)nickel(II) and biacetyl, *i.e.*, 2,2′-dimethyl(ethanediylidenedinitrilo)(diethane)thiolnickel(II), reacts with 1 mol of *α,α′*-dibromo-*o*-xylene to give a product in which the Ni ion is completely enclosed by rings. Similar reactions with trimethylene diiodide and ethylene dibromide have not met with equal success perhaps because the ethylene dibromide is too short to span the distance between the S atoms. Much of the work involving mercapto complexes has been summarized in a recent review.[3]

The nucleophilic properties of atoms other than sulfur coordinated to metals are less well known even though proton dissociation from oxygen and nitrogen has long been known.[4,5] Coordinated aquo ions such as $[\mathrm{Cr(H_2O)_6}]^{3+}$ have been shown[4] to be reasonably acidic in aqueous solution as have certain ethylenediamine complexes of Au(III)[5] and Os(IV).[6] Acid dissociation constants of some en complexes have been measured in aqueous solution, *e.g.*

$$[\mathrm{Pt(en)_3}]^{4+} \rightleftharpoons [\mathrm{Pt(en\text{-}H)en_2}]^{3+} + \mathrm{H}^+$$

where pK_a is reported[7] to be 4.0, but in many cases the pK_a values are too large to be measured in aqueous solution. It has been shown[8] that, by working in solvents more basic than water, ammine complexes which are apparently not acidic at all in aqueous solution can be deprotonated in these solvents. The conjugate bases of such complexes should exhibit much stronger nucleophilic tendencies than complexes containing sulfur, oxygen, or nitrogen donor atoms with much lower pK_a values.

Watt and Upchurch[9] have methylated the deprotonated square-planar Pt(II) complexes $[\mathrm{Pt(bipy)(en\text{-}H)}]\mathrm{I}$ and $[\mathrm{Pt(bipy)(en\text{-}2H)}]$, where a π-bonding ligand is *trans* to the deprotonated N atoms of en. Solid products were characterized as $[\mathrm{Pt(bipy)(en\cdot CH_3)}]\mathrm{I_2}$ and $[\mathrm{Pt(bipy)(en\cdot 2CH_3)}]\mathrm{I_2}$. Such reactions have been extended[10] to the octahedral system, $[\mathrm{Co(en\text{-}H)_2en}]\mathrm{I}$, not involving a π-bonding ligand. The present paper describes nucleophilic substitution reactions of the Rh(III) octahedral complexes $[\mathrm{Rh(en\text{-}H)_2(en)}]\mathrm{I}$ and $[\mathrm{Rh(en\text{-}H)_3}]$.

Experimental Section

The equipment and procedures for reactions in liquid ammonia have been described previously.[11] Hygroscopic or air-unstable products were stored and handled in a drybox containing a helium atmosphere maintained oxygen and water free by continuous exposure to liquid Na–K alloy.

---

[1] Abbreviations: en = ethylenediamine; (en-H) = deprotonated en ligand; $(\mathrm{en\cdot CH_3})$ = (en-H) methylated at the deprotonated N atom; men = N-methylethylenediamine; dien = diethylenetriamine; bipy = 2,2′-bipyridyl.

[2] R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949).

[3] D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson, and M. L. Morris, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 125.

[4] J. C. Bailar, Jr., "Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956.

[5] B. P. Block and J. C. Bailar, *J. Am. Chem. Soc.*, **73**, 4722 (1951).

[6] F. P. Dwyer and J. W. Hogarth, *ibid.*, **75**, 1008 (1953).

[7] A. A. Grinberg, L. V. Vrublevskaya, Kh. I. Gel'dengershel, and A. I. Stetsenko, *Zh. Neorgan. Khim.*, **4**, 1018 (1959).

[8] G. W. Watt, *et al.*, *J. Am. Chem. Soc.*, **79**, 5163 (1957); **81**, 8 (1959); **82**, 4465 (1960); *Inorg. Chem.*, **1**, 6 (1962); **4**, 143 (1965).

[9] G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.*, **87**, 4212 (1965).

[10] G. W. Watt, P. W. Alexander, and B. S. Manhas, *ibid.*, **89**, 6483 (1967).

[11] G. W. Watt, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 311 (1959); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 46, 454 (1955).

Standard methods of analysis were used in all cases.

Infrared spectra were obtained with a Beckman IR-7 instrument with CsI interchange optics. Spectra were taken as potassium iodide disks in the range 270–4000 cm^{-1}. Ultraviolet–visible spectra were measured with a Cary Model 14 recording spectrophotometer using matched 1-cm quartz cells. The resulting data are listed in Table I.

Table I

Infrared Spectral Data[a]

I	II	III	IV	V	VI
3180 vs	3200 vs, br	3180 vs	3320 m	3200 vs	3190 vs, br
3090 vs	3100 vs, br	3090 vs	3180 vs	3105 vs	3100 vs, br
2980 sh	2980 sh	2980 sh	3090 vs	2980 sh	2980 sh
2900 sh	2895 sh	2895 sh	2980 sh	2900 sh	2900 sh
1565 s, br	1585 sh	1575 s, br	2895 sh	1572 s, br	1570 s, br
1485 sh	1567 s, br	1485 sh	1573 s, br	1459 s	1457 s
1459 s	1475 sh	1460 s	1462 s	1397 m	1397 w
1396 w	1461 s	1420 m	1430 s, br	1366 m	1366 m
1366 m	1399 w	1400 w	1398 ms	1324 m	1325 m
1327 m	1367 m	1366 m	1373 m	1268 s	1265 s
1300 m	1330 m	1329 m	1329 m	1253 s	1213 m
1279 w	1300 m	1300 m	1304 m	1210 m, br	1152 s
1230 w	1279 m	1280 w	1282 sh	1150 s	1108 m
1210 w	1230 w	1230 sh	1235 w	1118 s, br	1058 vs
1154 s	1213 w	1211 w	1210 w	1055 s	1032 sh
1120 m	1155 s	1154 s	1150 s	1030 sh	1005 w
1115 sh	1125 m	1124 m	1117 vs	1000 m	878 m
1056 s	1115 sh	1114 sh	1076 vs	880 m	806 s
1000 m	1057 s	1056 s	1055 vs	790 sh	745 vw
955 m	1000 m	1000 m	1038 sh	774 m	705 w
929 w	957 m	955 m	1000 vw, sh	740 w	623 m, sp
877 m	925 w	926 w	881 m	700 w	596 w
834 w	880 m	878 w	800 sh	623 s	573 m
880 m, br	858 vw	858 vw	775 m	598 m	557 m
783 sh	835 vw	832 w	760 w	575 m	501 m
758 sh	790 m, br	803 m, br	665 w	560 m	448 m
572 m	573 m	780 sh	571 m	500 m	403 w
559 m	557 w	730 vw	555 m	450 m	354 m
498 m	503 m	574 m	530 m	403 w	
448 m	498 sh	558 sh	523 sh	355 m	
350 ms	446 m	502 m	500 m		
250 ms	353 m	445 m	449 w		
		352 m	352 m		
		255 s	250 s, br		

[a] Symbols: vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; sp, sharp; br, broad; sh, shoulder.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter), 35-kV tube voltage, 15-mA filament current, and 13–15-hr exposure times. Relative intensities were estimated visually. The data are given in Table II.

Materials.—With the following exceptions all materials employed were reagent grade chemicals that were used without further purification.

Tris(ethylenediamine)rhodium(III) Iodide.—The method of preparation of $[Rh(en)_3]I_3$ has been described by Watt and Crum;[12] the yield was 48%. *Anal.* Calcd for $[Rh(en)_3]I_3$: Rh, 15.5; I, 57.3. Found: Rh, 15.3; I, 57.3.

Deprotonated Complexes.—Deprotonation was carried out by the method described elsewhere.[12] Titration of $[Rh(en)_3]I_3$ with 2 molar equiv of KNH_2 in liquid ammonia gave pale yellow, insoluble [Rh(en-H)$_2$en]I. *Anal.* Calcd for [Rh(en-H)$_2$en]I: Rh, 25.2; I, 31.1. Found: Rh, 25.6; I, 31.3.

Titration of $[Rh(en)_3]I_3$ with 3 molar equiv of KNH_2 in liquid ammonia gave yellow, insoluble [Rh(en-H)$_3$]. *Anal.* Calcd for [Rh(en-H)$_3$]: Rh, 36.7; I, 0.0. Found: Rh, 36.6; I, 0.0.

Both of these complexes are unstable in air and were stored and sampled in a dry helium atmosphere.

Reaction of [Rh(en-H)$_2$en]I with Methyl Iodide.—Approximately 20 ml of CH_3I was added by distillation *in vacuo* to 0.2 g of [Rh(en-H)$_2$en]I in a reaction vessel containing a magnetic stirring bar. The vessel was sealed and the reaction mixture stirred for 3 weeks at 25°. The excess CH_3I was removed by distillation and the residual solid dried *in vacuo* for 24 hr. The product was yellow-tan and appeared stable in air. *Anal.* Calcd for $[Rh(en\cdot CH_3)_2en]I_3$ (I): Rh, 14.9; C, 13.9; H, 4.05. Found: Rh, 15.0; C, 13.8; H, 4.26. This product was soluble and stable in water, The ultraviolet–visible spectrum showed two maxima at 270 and 345 mμ (ϵ ~900 and 300, respectively); the spectrum did not change with time.

Table II

X-Ray Diffraction Data[a]

I		II		III		IV		V		VI	
d, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$
9.93	0.6	10.27	1.0	7.16	0.7	7.79	0.8	10.52	0.3	6.17	0.8[b]
4.28	1.0	6.63	0.8	5.82	0.2	6.78	1.0	6.02	1.0[b]	5.11	1.0[b]
3.81	0.7	6.25	0.7	4.58	0.3	6.60	0.8	5.50	0.7	4.54	0.2
3.61	0.4	4.20	0.7	4.31	1.0	5.14	0.7	4.41	0.5	4.07	0.4
3.41	1.0	3.98	0.7	4.15	0.1	4.29	0.9[b]	3.93	1.0	3.87	0.4
3.23	0.7	3.67	0.9	3.78	0.3	4.07	0.6	3.70	0.4	3.55	0.3
2.27	0.4	3.45	0.8	3.44	0.5	3.92	0.8	3.48	0.5[b]	3.34	0.3
1.95	0.5	3.30	0.8			3.83	0.8	2.94	0.3	2.49	0.2
						2.95	0.6				

[a] Less intense lines not included. [b] Broad line.

Reaction of [Rh(en-H)$_2$en]I with Methyl Bromide.—Gaseous CH_3Br was condensed at reduced pressure and −72° in a reaction vessel which had previously been evacuated and contained 0.3 g of [Rh(en-H)$_2$en]I. The reaction vessel was sealed and the mixture stirred at 25° for 2 months, and, as in the previous reaction, the solid changed from pale yellow to yellow-tan. Excess CH_3Br was removed by distillation and the residue was dried *in vacuo* for 24 hr. The product was stable in air but slightly hygroscopic. *Anal.* Calcd for $[Rh(en\cdot CH_3)_2en]Br_2I$ (II): Rh, 17.2; C, 16.1; H, 4.70. Found: Rh, 17.1; C, 16.3; H, 5.07.

Reaction of [Rh(en-H)$_3$] with Methyl Iodide.—A sample of 0.5 g of [Rh(en-H)$_3$] was treated with a large excess of CH_3I as described above for the methyl iodide reaction. The mixture was stirred continuously for 1 month at 25° and the excess CH_3I removed by distillation. After drying *in vacuo* for 24 hr, the remaining solid was washed with two 50-ml portions of anhydrous ether by distillation of the ether *in vacuo* into the reaction vessel. The ether was filtered off, and the solid dried once more for 24 hr *in vacuo*. The product was yellow-tan and appeared stable in air but slightly hygroscopic. *Anal.* Calcd for $[Rh(en\cdot CH_3)_3]I_3$ (III): Rh, 14.6; C, 15.3; H, 4.25; I, 54.0. Found: Rh, 14.4; C, 15.0; H, 4.12; I, 53.9. This product dissolved in water to form a solution, the ultraviolet–visible spectrum of which did not change with time. Maxima were observed at 276 and 352 mμ (ϵ ~1800 and 700, respectively).

Reaction of [Rh(en-H)$_2$en]I with Boron Trifluoride.—Approximately 10 ml of chloroform, followed by 20 ml of anhydrous ether, was distilled *in vacuo* into a reaction vessel containing 0.8 g of [Rh(en-H)$_2$en]I. Gaseous BF_3 was bubbled through the solvent until manometer pressure readings indicated that the solvent mixture was almost saturated. The solution turned orange in color and was allowed to stir for 5 days. After filtration, a yellow-orange solid was obtained, washed *in vacuo* with three 50-ml portions of anhydrous ether, and dried *in vacuo* for 24 hr. The product appeared stable in air but was slightly hygroscopic. *Anal.* Calcd for $[Rh(en\cdot BF_3)_2en]I$ (IV): C, 13.3; H, 4.05; I, 23.3. Found: C, 13.4; H, 4.50; I, 23.4. The infrared spectrum is shown in Figure 1. An aqueous solution of this product was initially pale yellow but became colorless almost immediately. This solution gave an ultraviolet spectrum with only one band at 300 mμ.

Reaction of [Rh(en-H)$_2$en]I with Sulfuryl Chloride.—Fractional distillation of SO_2Cl_2 was used to remove a low-boiling yellow impurity. The reagent (*ca.* 20 ml) was then added by distillation *in vacuo* to a 0.7-g sample of [Rh(en-H)$_2$en]I. The pale yellow complex changed to bright yellow almost immediately, and, after stirring for 1 day at 25°, excess SO_2Cl_2 was removed by filtration. The remaining solid was dried *in vacuo* for 24 hr, washed *in vacuo* with two 50-ml portions of anhydrous ether, and dried *in vacuo* for 24 hr. The product was a bright yellow, finely

---

[12] G. W. Watt and J. K. Crum, *J. Am. Chem. Soc.*, **87**, 5366 (1965).

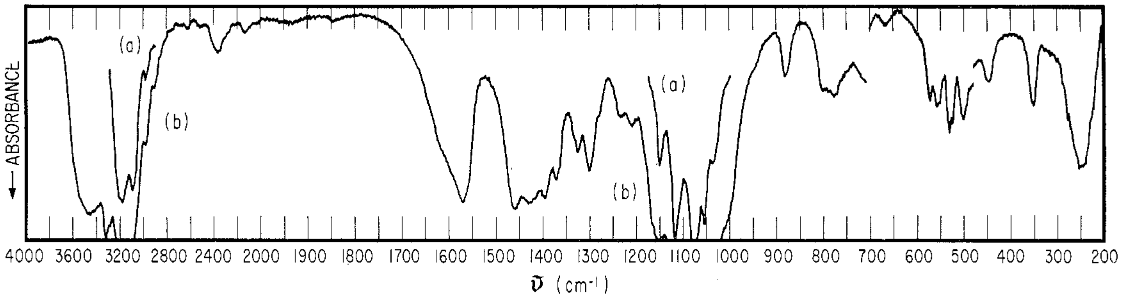


Figure 1.—The infrared spectrum of $[\mathrm{Rh(en\cdot BF_3)_2en}]\mathrm{I}$: (a) 0.3% in KI; (b) 1.0% in KI.

divided powder, stable in air, but slightly hygroscopic. *Anal.* Calcd for $\{\mathrm{Rh(en)[(en\text{-}H)_2SO_2]}\}\mathrm{Cl_2I}$ (V): Rh, 18.9; C, 13.3; H, 4.05; N, 15.4. Found: Rh, 18.5; C, 13.1; H, 4.27; N, 15.4. The infrared spectrum is shown in Figure 2. A pale yellow aqueous solution of this product gave an ultraviolet–visible spectrum with bands at 297 and 455 mμ (ϵ ~500 and 280, respectively). Over 1 week the solution became colorless and this solution exhibited one band at 300 mμ. The spectrum of a solution prepared and stored under nitrogen showed very little change after 1 week.

Reaction of $[\mathrm{Rh(en\text{-}H)_2en}]\mathrm{I}$ with Thionyl Chloride.—Approximately 0.5 g of $[\mathrm{Rh(en\text{-}H)_2en}]\mathrm{I}$ was treated with excess $\mathrm{SOCl_2}$ (20 ml) as described for the foregoing reaction. The pale yellow solid immediately began to turn to a darker yellow, and, after stirring for 24 hr at 25°, the solid was filtered and dried *in vacuo* for 24 hr. The product was a finely divided orange powder; in air, it slowly decomposed and after exposure for 1 week turned black. *Anal.* Calcd for $\{\mathrm{Rh(en)[(en\text{-}H)_2SO]}\}\mathrm{Cl_2I}$ (VI): Rh, 19.52; C, 13.66; H, 4.21; N, 15.94. Found: Rh, 19.87; C, 13.37; H, 4.16; N, 15.67. The ultraviolet–visible spectrum of an initially pale yellow aqueous solution of this product showed bands at 288 and 348 mμ and a broad band at *ca.* 450 mμ (ϵ ~900, 500, and 150, respectively); this spectrum remained unchanged when the solution was stored under nitrogen for 3 days. In the presence of air, however, the solutions became colorless on standing overnight and the spectrum consisted of only one band at 300 mμ.

Discussion

Analytical data for the solid products described above reveal the following stoichiometry. The mole ratio of $[\mathrm{Rh(en\text{-}H)_2en}]\mathrm{I}$ to reagent is 1:2 with $\mathrm{CH_3I}$, 1:2 with $\mathrm{CH_3Br}$, 1:1 with $\mathrm{SO_2Cl_2}$, 1:1 with $\mathrm{SOCl_2}$, and 1:2 with $\mathrm{BF_3}$. The mole ratio of $[\mathrm{Rh(en\text{-}H)_3}]$ to reagent has been shown to be 1:3 with $\mathrm{CH_3I}$. The X-ray diffraction data in Table II were obtained to supplement the characterization of the reaction products and, by comparison with analogous data for the deprotonated species,[12] to provide the initial evidence for the occurrence of reaction with the various reagents.

In Table I are listed the band positions and relative intensities in the infrared spectra of the reaction products. These spectra provide evidence for the presence of the attacking groups in the solid products and partial assignments have been made. As might be expected, modification of only a small part of the tris(ethylenediamine) structure in these reactions does not alter the over-all spectral features to any great extent, and the main skeletal vibrations of $[\mathrm{Rh(en)_3}]\mathrm{I_3}$ are still obvious in the spectra of the reaction products. However, the appearance of new bands can be attributed to the presence of the added groups.

The spectrum of $[\mathrm{Rh(en\cdot CH_3)_2en}]\mathrm{I_3}$ exhibits several bands not present for $[\mathrm{Rh(en)_3}]\mathrm{I_3}$ or $[\mathrm{Rh(en\text{-}H)_2en}]\mathrm{I}$. These appear at 1485 sh, 1396, 1230, 955, 929, and 834 cm^{-1}, and are assigned by comparison with the roughly similar ions $\mathrm{(CH_3)_2NH_2^+}$ and $\mathrm{(CH_3)_3NH^+}$ studied by Ebsworth and Sheppard.[13] They assigned bands near 1470 and 1400 cm^{-1} as asymmetric and symmetric bending deformations of $\mathrm{CH_3}$ and on this basis similar assignments are made for the bands at 1485 and 1396 cm^{-1} of the methylated product. The bands at 1230 and 955 cm^{-1} are then assigned by the same correlations as $\mathrm{CH_3}$ rocking motions and those at 929 and 834 cm^{-1} as C–N stretches. Previous work[14] on diethylenetriamine complexes of Pd(II) is also in agreement with the assignment of ν(C–N). The NH bending deformations for $[\mathrm{Rh(en)_3}]\mathrm{I_3}$ have been assigned at 1580 and 1550 cm^{-1}. For the methylated complex only one strong, broad band appears in this region at 1565 cm^{-1}. In all other respects, the spectrum closely resembles that of $[\mathrm{Rh(en)_3}]\mathrm{I_3}$ and of particular interest are the Rh–N stretching modes at 572 and 559 cm^{-1}, not significantly different from ν(Rh–N) for the en complex[12] at 570 and 558 cm^{-1}.

The methyl bromide reaction product, as expected, exhibits a spectrum virtually the same as that of $[\mathrm{Rh(en\cdot CH_3)_2en}]\mathrm{I_3}$ as shown in Table I. The one noticeable difference concerns the intensities of the Rh–N stretching vibrations where there is an increase in the relative intensity of the band near 570 cm^{-1} with respect to that of the band at 557 cm^{-1}. For $[\mathrm{Rh(en)_3}]\mathrm{I_3}$, the band at the lower wavenumber is the more intense whereas for both methylated derivatives the opposite is true.

Somewhat surprisingly, the spectrum of $[\mathrm{Rh(en\cdot CH_3)_3}]\mathrm{I_3}$ (III) is similar in nearly every respect to those of the two complexes discussed above. A medium band appears at 1420 cm^{-1} which seems likely[13–15] to be due to the NH bending deformation of the secondary amino grouping, $\mathrm{CH_3}$–NH. N substitution of the third methyl group is apparently required to produce the increase in intensity necessary to observe this band. In the absence of deuteration experiments, little certainty can be attached to this assignment, however. The Rh–N stretches are also significantly

---

[13] E. A. V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, **13**, 261 (1959).

[14] G. W. Watt and D. S. Klett, *ibid.*, **20**, 1053 (1964).

[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 257.

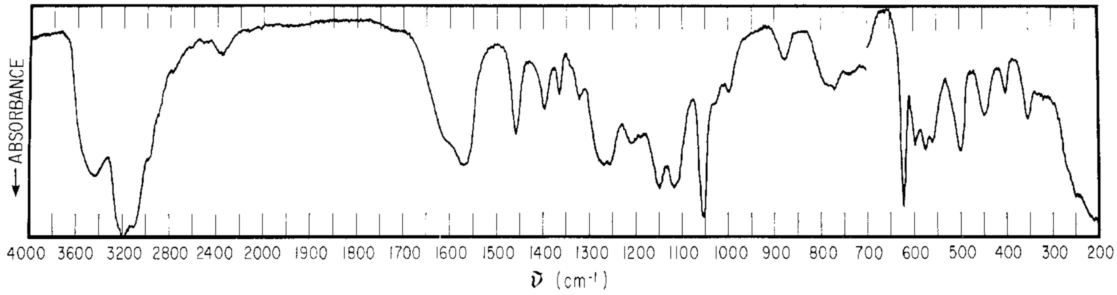


Figure 2.—The infrared spectrum of $\{Rh(en)[(en\text{-}H)_2SO_2]\}Cl_2I$.

affected since a large increase in intensity of the 573-cm^{-1} band was observed while the band at 558 cm^{-1} appears only as a weak shoulder. These are the only obvious spectral changes brought about by the reaction of 3 mol of CH_3I with $[Rh(en\text{-}H)_3]$. The reasons for this close similarity between spectra of the di- and trimethylated products is not clear when it is considered that the infrared spectrum[16] of $[Rh(men)_3]I_3$, prepared by direct synthesis, is distinctly different from any of the spectra discussed here. This point is discussed further below.

The spectrum of $[Rh(en\cdot BF_3)_2en]I$ (IV) is reproduced in Figure 1 and band positions are listed in Table I. The presence of BF_3 is clearly indicated by the extremely strong absorption in the range 1030–1150 cm^{-1} characteristic of boron–fluorine vibrations.[17] The BF_3 molecule is planar and belongs to the D_{3h} point group. On coordination to a deprotonated nitrogen atom of the Rh(III) complex, formation of the tetrahedral $[NBF_3]^-$ group is expected, with consequent lowering of symmetry to C_{3v} as a first approximation to the local symmetry of the BF_3 group although the real symmetry in the molecular framework is probably C_1. The number of infrared-active normal vibrations is then increased from four for BF_3 to six[18] for molecules of type ZXY_3. Three of these are easily assigned by comparison with the spectrum[19] of $NH_3\cdot BF_3$ so that the bands at 1117 and 1076 cm^{-1} are the $\nu_4(E)$ fundamentals of the ^{10}B and ^{11}B isotopes and those at 1055 and 1038 cm^{-1} are the $\nu_1(A_1)$ frequencies. The doublet at 523 and 530 cm^{-1} is the $\nu_5(E)$ fundamental of the BF_3 bending deformation; the splitting has been attributed[17] in $[BF_4]^-$ to the isotopic effect of ^{10}B and ^{11}B. The $\nu_3(A_1)$ fundamental was not observed[19] in the infrared spectrum of $NH_3\cdot BF_3$ but was found[19] at 450 cm^{-1} in the Raman spectrum, while $\nu_6(E)$, the rocking mode, was assigned at 330 cm^{-1}. Neither of these modes is obvious in the spectrum of complex IV and apparently they are both obscured by en skeletal vibrations in these regions. This leaves the $\nu_2(A_1)$ frequency for the B–N stretching vibration unassigned, and there is a very wide spread in the frequency values assigned for similar compounds such as 735 cm^{-1} for $NH_3\cdot BF_3$,[19] 1113 cm^{-1} for the py–BCl_3 adduct,[20] 1249 cm^{-1} for $(CH_3)_3N\cdot BF_3$,[21] and 1255 cm^{-1} for $(CH_3)_3N\cdot BH_3$.[22] This latter assignment, however, has been found doubtful by Taylor and Cuff,[23] who, from Raman spectroscopy, propose that ν(B–N) occurs at 667 cm^{-1}. For the Rh(III) complex, two other bands appear which are not present in the starting materials, *viz.*, a strong, broad band at 1430 cm^{-1} and a weak band at 630 cm^{-1}. It seems likely from the $NH_3\cdot BF_3$ assignments[19] that the band at 1430 cm^{-1} is the NH bending deformation of the $BF_3\cdot NH$ group, and we therefore assign 665 cm^{-1} as ν(B–N). In other respects, the spectrum of $[Rh(en\cdot BF_3)en]I$ resembles that of $[Rh(en)_3]I_3$ and again the Rh–N stretching modes at 571 and 555 cm^{-1} are virtually unchanged.

The infrared spectrum of $\{Rh(en)[(en\text{-}H)_2SO_2]\}Cl_2I$ is given in Figure 2 and the band positions are listed in Table I. Assignments have been made by comparison with the spectra of sulfuryl chloride and sulfamide as reported by Robinson[24] and by Martz and Langeman.[25] A straight-line correlation was found[24] between the symmetric and antisymmetric stretching frequencies of the SO_2 group contained in a wide variety of compounds. In addition, $\nu(SO_2)$ was found to increase with the electronegativities of the attached groups, X and Y, in $XYSO_2$, thus indicating an increase in the strength of the S=O bonds. For example, $\nu_a(SO_2)$ and $\nu_s(SO_2)$ are found, respectively, at 1501 and 1269 cm^{-1} for SO_2F_2, 1414 and 1182 cm^{-1} for SO_2Cl_2, and 1350 and 1163 cm^{-1} for $SO_2(NH_2)_2$.[24] For the Rh(III) complex reaction product with SO_2Cl_2, strong bands are observed at 1268 and 1118 cm^{-1} which lie close to the straight-line plot of Robinson. The relative intensities of these bands are considerably more intense than those observed in this range for $[Rh(en)_3]I_3$ and they are therefore assigned as $\nu_a(SO_2)$ and $\nu_s(SO_2)$, respectively. It is interesting to note that the bands occur at frequencies significantly lower than those for sulfamide. The low frequencies of these vibrations provide evidence for the bonding of S to two N atoms.

The remaining characteristic changes in the spectrum occur in the far-infrared region with the ap-

---

[16] G. W. Watt and P. W. Alexander, *J. Am. Chem. Soc.*, **89**, 1814 (1967).

[17] N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

[18] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 110.

[19] J. Goubeau and H. Mitschelen, *Z. Physik. Chem.*, **14**, 61 (1958).

[20] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).

[21] A. R. Katritzky, *ibid.*, 2049 (1959).

[22] B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

[23] R. C. Taylor and C. L. Cuff, *Nature*, **182**, 390 (1958).

[24] E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

[25] D. E. Martz and R. T. Langeman, *J. Chem. Phys.*, **22**, 1193 (1954).

pearance of a strong, sharp band at 623 cm^{-1}, and less intense bands at 598 and 403 cm^{-1}. Assignments in this region are complicated by possible overlap with the metal–ligand vibrations and the large number of bands predicted for the X_2SO_2 system (where X = Cl, NH_2, etc.). For tetrahedral molecules of this type, the symmetry is C_{2v} and nine infrared-active normal vibrations are expected.[18] All of these bands have been found for SO_2Cl_2, and seven occur in the region 250–600 cm^{-1}.

In the spectrum of the complex, the band at 623 cm^{-1} is most characteristic but is absent in the spectrum of SO_2Cl_2. By comparison with literature values for other molecules, this band is assigned as an S–N stretching frequency. There is some uncertainty in the literature[26] as to the frequency range expected for ν(S–N), but it has been assigned at 550 cm^{-1} for sulfamide[27] and at 688 cm^{-1} for $NH_3 \cdot SO_3$,[28] and the several S–N vibrational modes of the cyclic S_4N_4 have been assigned[29] in the region 460–790 cm^{-1}. The origin of the remaining bands at 598 and 403 cm^{-1} is uncertain. As for the previous products, there is again very little change in ν(Rh–N), observed at 575 and 560 cm^{-1}, for the SO_2Cl_2 reaction product.

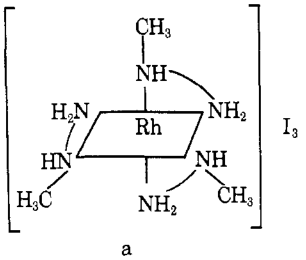
The spectrum of the thionyl chloride reaction product (VI), $\{Rh(en)[(en\text{-}H)_2SO]\}Cl_2I$, is very similar to that of the sulfuryl chloride product; the band positions and intensities are listed in Table I. Assignments for thionyl chloride have been reported,[30] the S–O stretching frequency occurring at 1229 cm^{-1} and the asymmetric and symmetric stretching frequencies S–Cl at 490 and 443 cm^{-1}. Several bands appear in the spectrum of the complex, not observed in either $[Rh(en\text{-}H)_2en]I$ or $[Rh(en)_3]I_3$, at 1265, 623, 596, and 403 cm^{-1}. By comparison with $SOCl_2$, the strong band at 1265 cm^{-1} is assigned as ν(S–O) at a somewhat higher frequency than for thionyl chloride, thus indicating an increase in the S–O bond strength on coordination of the S atom with the N atom nucleophile of the deprotonated complex. The far-infrared region is remarkably similar to that observed for the sulfuryl chloride reaction product, and the band at 623 cm^{-1} is again assigned as an S–N stretching vibration. The origin of the bands at 596 and 403 cm^{-1} remains uncertain.

With regard to the comparative stabilities of the products of concern here, the methylated species are stable both in air and in aqueous solution. The products of reactions with BF_3 and SO_2Cl_2 are stable in air but the $SOCl_2$ reaction product decomposes slowly. All three of these products are somewhat hygroscopic and undergo hydrolysis in aqueous solution to form colorless solutions the ultraviolet–visible spectra of which show only a band at 300 mμ that is characteristic of $[Rh(en)_3]^{3+}$.[31] Hydrolysis is almost instantaneous for the BF_3 product and less rapid for the SO_2Cl_2 and $SOCl_2$ products; in both of the latter two cases, hydrolysis can be inhibited by exclusion of oxygen. The relatively greater stability of the SO_2Cl_2 product suggests that the hydrolysis of the $SOCl_2$ product in the presence of air is accompanied by an oxidation step which evidently increases the rate of hydrolysis. Such a step cannot occur when air is excluded from the solution or in the case of the SO_2Cl_2 reaction product, a solution of which hydrolyzes only very slowly even in the presence of air.

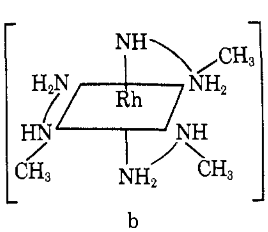
Conclusive evidence concerning the structures of these complexes is not yet available. The analytical, X-ray diffraction, and infrared spectral data demonstrate that reaction between the deprotonated Rh(III) complexes and the added reagents occurred with established stoichiometry and provide data concerning the mode of bonding in the reaction products. To obtain direct evidence of structural configuration would require synthesis by other routes which has not been found possible. The present syntheses are therefore useful for preparing such complexes which cannot be prepared by other methods.

The reaction products with CH_3I, SO_2Cl_2, and $SOCl_2$ are analogous to those reported[10] for $[Co(en\text{-}H)_2en]I$, and their properties are similar.

In connection with the methylated Co complex, it was suggested that two methyl groups reacted with two different en molecules at the deprotonated N atom nucleophiles in *cis* positions. The *cis* configuration could be present initially or be formed by anionic site migration. The synthesis of $[Rh(en \cdot CH_3)_3]I_3$ now indirectly indicates that this suggestion is plausible since this product is not identical with $[Rh(men)_3]I_3$ prepared directly[16] by reaction of $RhCl_3$ with N-methylethylenediamine. The latter product could have structure a wherein the three methyl groups are in *cis* positions. Another geometric isomer, structure b,



a



b

could then be assigned to the $[Rh(en \cdot CH_3)_3]I_3$ prepared in the present work, thus accounting for the observed differences in X-ray, infrared, and ultraviolet–visible data, although geometric isomerism is not normally associated with such significant changes in the infrared region.

The nucleophilic reaction with the sulfur compounds could occur with bridging of two deprotonated nitrogen atoms of the complex by the sulfur atom, as suggested[10] for the analogous Co complexes. The

---

(26) J. N. Baxter, J. Cymerman-Craig, and J. B. Willis, *J. Chem. Soc.*, 669 (1955).

(27) H. J. Hoffmann and K. R. Andress, *Naturwissenschaften*, **4**, 94 (1954).

(28) T. J. Lane, I. Nakagawa, S. I. Mizushima, A. J. Saraceno, and J. V. Quagliano, *Spectrochim. Acta*, **12**, 239 (1958).

(29) E. R. Lippincott and M. C. Tobin, *J. Chem. Phys.*, **21**, 1559 (1953).

(30) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2171 (1961).

(31) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

two chlorine atoms of either SO_2Cl_2 or $SOCl_2$ are then replaced by two deprotonated N atoms of the en complex. For bridging to occur in this manner, the two N atom nucleophiles would be required to occupy a *cis* configuration at some stage during the reaction. The infrared data support these conclusions since S–N stretching frequencies are observed and the SO_2 stretching frequencies are shifted to much lower values in comparison with those of SO_2Cl_2.

The S–N stretch in $\{Rh(en)[(en\text{-}H)_2SO]\}Cl_2I$ occurs at approximately the same frequency as for the sulfuryl chloride reaction product. However $\nu(SO)$ at 1265 cm^{-1} is higher than the corresponding vibration for $SOCl_2$ indicating an increase in the double-bond character of the (S═O) group. The influence of resonance hybrid structures responsible for this effect apparently contributes to the instability in air.

The nucleophilic properties of the deprotonated N atoms in $[Rh(en\text{-}H)_2en]I$ are further demonstrated by its ability to act as a Lewis base toward boron trifluoride. Although Watt and Crum have shown[12] that delocalization does occur to some extent, the deprotonated site must retain a substantial electron density in order for this reaction to proceed.

Acknowledgments.—This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

Contribution from the Department of Chemistry, Imperial College, London, England, and the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Fluorocarbon Complexes of Rhodium Containing Triphenylstibine and Triphenylarsine

By J. T. MAGUE and G. WILKINSON

Received October 5, 1967

Tris(triphenylstibine)chlororhodium(I) reacts readily with tetrafluoroethylene to produce the complex $RhCl(C_2F_4)(Sb(C_6H_5)_3)_2$. With hexafluorobut-2-yne, the complexes $RhCl(C_4F_6)(Sb(C_6H_5)_3)_3$ and $RhCl(C_8F_{12})(Sb(C_6H_5)_3)_2$ are formed. The latter five-coordinate complex contains a rhodiacyclopentadiene ring and being coordinatively unsaturated for rhodium(III) readily forms adducts with donor molecules such as carbon monoxide, phosphorus trifluoride, and pyridine. An analogous rhodiacyclopentadiene derivative is formed from tris(triphenylarsine)chlororhodium(I) and hexafluorobut-2-yne.

Introduction

The large variety of substitution and oxidative addition reactions undergone by the versatile hydrogenation catalyst tris(triphenylphosphine)chlororhodium(I)[1] suggested that similar results could be obtained with the analogous triphenylarsine and triphenylstibine complexes.[2] In view of the enhanced stability of a number of the derivatives of the complexes $RhCl(M(C_6H_5)_3)_3$ (M = As, Sb) over that noted for the analogous triphenylphosphine-containing complexes[2] it was hoped a wider range of derivatives could be prepared from these.

Experimental Section

Microanalyses were by the Microanalytical Laboratory, Imperial College, London, A. Bernhardt, Mühlheim, Germany, and Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were determined on a Mechrolab osmometer at 37°. Infrared spectra were recorded using Beckman IR-5A and Grubb-Parsons Spectromaster instruments on Nujol mulls unless otherwise stated. All of the compounds reported contain absorptions due to triphenylarsine or -stibine; thus only additional bands are reported. Nmr spectra were taken on a Varian HR-60 spectrometer in chloroform solutions. The ^{19}F resonances are referred to benzotrifluoride as an internal standard. Melting points were determined on a conventional hot-stage microscope and are uncorrected. The benzene used was distilled from calcium hydride and stored over sodium. Dichloromethane was distilled from calcium chloride and stored over the same.

$RhCl(C_2F_4)(Sb(C_6H_5)_3)_2$.—A dichloromethane solution (5 ml) of $RhCl(Sb(C_6H_5)_3)_3$ (0.3 g) was placed in a thick glass tube which was then frozen and evacuated. Tetrafluoroethylene was condensed in and the tube sealed. The tube was shaken for *ca.* 0.5 hr at room temperature, at the end of which time yellow-orange crystals of the *complex* had formed (mp 154–156°). These were collected, washed with diethyl ether, and air dried (yield 0.2 g, 85%). Recrystallization was effected from hot 1,1-dichloroethane.

Anal. Calcd for $C_{38}H_{30}Sb_2F_4ClRh$: C, 48.3; H, 3.2; mol wt, 945. Found: C, 48.7; H, 3.7; mol wt, 927 ($CHCl_3$). ν_{max}: 1401 w, 1333 w, 1304 m, 1263 m, 1100 vs, 1020 vs, 855 w, 803 vs, 763 vs cm^{-1}.

Reaction of this complex with carbon monoxide produced $Rh(CO)Cl(Sb(C_6H_5)_3)_4$.

Anal. Calcd for $C_{73}H_{60}Sb_4OClRh$: C, 55.53; H, 3.83; Cl, 2.24. Found: C, 55.56; H, 4.21; Cl, 2.89.

$RhCl(C_8F_{12})(Sb(C_6H_5)_3)_2$.—Hexafluorobut-2-yne was condensed into an evacuated, thick glass tube containing $RhCl(Sb(C_6H_5)_3)_3$ (0.3 g) which had been completely dissolved in dry benzene (5 ml). The tube was sealed and held at 75–80° for 3 hr. The tube was then cooled, left to stand 24 hr, and opened, and the excess fluorocarbon was recovered. The crude crystalline product was filtered off and recrystallized from 1,1-dichloroethane–petroleum ether (bp 30–60°) affording yellow-orange crystals, mp 208–210° dec (0.23 g, 80%).

Anal. Calcd for $C_{44}H_{30}Sb_2F_{12}ClRh$: C, 45.2; H, 2.6; F, 19.5; mol wt, 1170. Found: C, 44.9; H, 2.7; F, 20.4; mol wt,

---

[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1711 (1966).

[2] J. T. Mague and G. Wilkinson, *ibid.*, 1736 (1966).