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Transition Metal-Hydrogen Compounds. IV.¹ Improved Synthesis of Enneahydridorhenates: the Sodium and Tetraethylammonium Salts of ReH_9 ²⁻

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The only enneahydridorhenate which has so far been characterized is the potassium salt, K_2ReH_9 .² The synthesis described for this compound³ gives only small yields of impure product. In this note we describe a simple procedure for preparing the sodium salt, Na_2ReH_9 , and from it the tetraethylammonium salt, $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{ReH}_9$, as well as K_2ReH_9 and the mixed-cation salt NaKReH_9 . Using the methods described, we have been able to prepare substantial amounts of these compounds and are carrying out an extensive investigation of their chemical reactions, for example, with tertiary phosphines⁴ and with carbon monoxide.⁵

Experimental Section

The hydride preparations were carried out under a nitrogen atmosphere, and the products were manipulated in an argon-filled drybox or under nitrogen. Infrared spectra were measured in the range 4000–250 cm^{-1} with Perkin-Elmer Model 337 and 457 grating spectrophotometers on samples in KBr disks and Nujol mulls. Decomposition points were determined in evacuated tubes, and the evolved gas was analyzed by mass spectrometry (Gollob Analytical Laboratory).

Anhydrous ether was distilled from LiAlH_4 in a nitrogen atmosphere. Acetonitrile was stirred with calcium hydride for 24 hr and then filtered, distilled, and degassed. Other solvents were reagent grade materials deaerated with a nitrogen stream. Reagent grade sodium spheres, $1/16$ to $1/4$ in. in diameter, were washed with pentane and cleaned by immersion in ethanol immediately before use. All aqueous alkali solutions used were carbonate free and passed the following test. On mixing 5 ml of the solution with 10 ml of methanol and 200 ml of ethanol, no turbidity was visible after 1 hr of standing on ice.

Hydride samples were oxidized to perrhenate with 5% H_2O_2 ³ for determination of Na, K, and Re. Sodium was determined by the magnesium uranyl acetate method,⁶ potassium by precipitation as the tetraphenylborate,⁷ and rhenium by precipitation as tetraphenylarsonium perrhenate.⁸ C, H, and N microanalyses were by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Compounds. Disodium Enneahydridorhenate.—Sodium spheres (2 g, 87 mg-atoms) were slowly added to a vigor-

ously stirred solution of NaReO_4 (3.0 g 11 mmol) in absolute ethanol (300 ml). When the solution turned dark brown, it was heated to reflux and additional sodium spheres (10 g, 435 mg-atoms) were gradually added. After the sodium had completely dissolved, the hot solution was centrifuged (2000 rpm, 5 min). The supernatant was reserved for recovery of perrhenate, and the precipitate was extracted with 3% ethanolic NaOC_2H_5 (two 25-ml portions, ~ 1 hr each time), after which it was washed consecutively with 2-propanol (three 25-ml portions) and ether (three 25-ml portions). After preliminary drying in a nitrogen stream the white product was pumped for 1 hr at 25° (10^{-3} mm) and then overnight at 82° (10^{-3} mm). The yield varied between 0.7 and 1.2 g (26–45% based on the starting perrhenate, 47–91% based on the amount of unrecovered perrhenate); the average yield of a large number of runs was 0.92 g (35% based on the starting perrhenate, 71% based on unrecovered perrhenate). A sample for analysis was purified as follows. The crude product (1.0 g) was dissolved in 5 ml of ice-cold 25% NaOH solution. Ice-cold methanol (10 ml) was added and the mixture was centrifuged (10,000 rpm, 0 – 20° , 5 min). The clear but colored supernatant was poured with stirring into 200 ml of ice-cold absolute ethanol. The resulting white precipitate was collected by centrifugation (2000 rpm, 5 min), then extracted once with ethanol (15 min) and twice with 2-propanol (15 min), and finally washed with anhydrous ether and dried as before to give 0.90 g (90% yield) of a white powder.

Anal. Calcd for Na_2ReH_9 : Na, 19.05; Re, 77.18; H, 3.76. Found: Na, 19.11; Re, 76.66; H, 3.76; C, 0.36. Analysis of the crude product before purification gave the following results: Na, 18.22; Re, 75.82; H, 3.89; C, 0.44. The sample used for this analysis was from a mixture of the products of about 30 reactions. Analysis of the crude product from individual reactions showed some variation.

Unreacted perrhenate was recovered from the reaction mixture by stirring in 5 ml of 20% aqueous KOH and allowing the solution to stand overnight. A precipitate of KReO_4 settled out.

Bis(tetraethylammonium) Enneahydridorhenate.—Crude Na_2ReH_9 (1.10 g, 4.56 mmol, about 9% more than the amount required for stoichiometric metathesis) was dissolved in an ice-cold $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{SO}_4$ solution of known concentration (0.332 N, 25.0 ml) in 10% aqueous $(\text{C}_2\text{H}_5)_4\text{NOH}$. Ice-cold absolute ethanol (150 ml) was added and the mixture was allowed to stand on ice for ~ 5 min, after which it was rapidly filtered through a medium-porosity fritted disk; the filtrate was stripped to dryness on a rotary evaporator (25° (10^{-2} mm), liquid nitrogen trap). The residue from this evaporation was dissolved in 50 ml of 2-propanol, and after filtration through a fine-porosity fritted disk the solution was evaporated to dryness as above. The process of dissolving the residue in 2-propanol and evaporating to dryness was repeated until the OH stretching band (3400 cm^{-1}) in the infrared spectrum of the solid (KBr disk) had negligible intensity; a total of two or three evaporations was usually sufficient. The crude product (2.0 g, 100%) was white or slightly colored,⁹ and its infrared spectrum had an ReO stretching band at 910 cm^{-1} as well as several other impurity bands; it is, however, suitable for most synthetic purposes. Further purification was effected by dissolving the product in acetonitrile (40 ml) and immediately adding ether (50 ml) to give a white or light tan precipitate which was collected on a coarse fritted disk. After washing with ether (three 20-ml portions), the product was dried for 10 min in an argon stream and then for 8 hr at 56° (10^{-5} mm); yield, 1.6 g (81%). *Anal.* Calcd for $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{ReH}_9$: C, 42.15; H, 10.83; N, 6.14; Re, 40.87. Found: C, 41.82; H, 11.03; N, 5.86; Re, 40.72.

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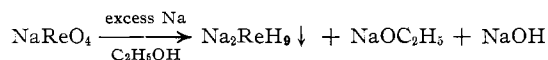
Sodium Potassium Enneahydridorhenate.—Unless otherwise noted, all solvents and solutions were kept ice cold. Purified Na_2ReH_9 (0.50 g, 2.1 mmol) was dissolved in 4 ml of 2 *N* KOH. The solution was centrifuged (10,000 rpm, 0–10°, 5 min) and the supernatant was decanted into 16 ml of methanol; a white precipitate formed and was collected by centrifugation. The product was washed successively at room temperature with 2-propanol (three 20-ml portions) and ether (three 20-ml portions) and then dried with a nitrogen stream, followed by overnight drying at 82° (10⁻³ mm); yield, 0.20 g (38%). *Anal.* Calcd for NaKReH_9 : Na, 8.93; K, 15.18; Re, 72.36. Found: Na, 8.76; K, 15.58; Re, 71.38.

In a second experiment, purified Na_2ReH_9 (0.60 g, 2.5 mmol) was converted to the sodium potassium salt by the above procedure but using 4 ml of 6 *N* KOH. The product was then dissolved in 4 ml of 6 *N* NaOH and after centrifuging (10,000 rpm, 0–10°, 5 min) the supernatant was poured into 16 ml of methanol to give a white precipitate which was washed and dried as before; yield, 0.33 g (52%). *Anal.* Found: Na, 9.14; K, 14.99; Re, 70.99.

Dipotassium Enneahydridorhenate.—Unless otherwise noted, all solvents and solutions were kept ice cold. Crude Na_2ReH_9 (0.57 g, 2.4 mmol) was dissolved in 20 ml of saturated $\text{Ba}(\text{OH})_2$ solution; after centrifugation (10,000 rpm, 0–10°, 5 min) the supernatant was mixed with 20 ml of methanol and centrifuged as before for 1 min. The clear, colorless supernatant was mixed with 200 ml of ethanol to give a white precipitate of $\text{BaReH}_9 + \text{Ba}(\text{OH})_2$ which was collected by centrifugation, washed successively, at room temperature, with 2-propanol and ether, and then dried with a nitrogen stream. The dry solid was stirred for several minutes with a mixture of 10 ml of 0.5 *M* $\text{K}_2\text{SO}_4 + 5$ ml of 2 *N* KOH, and the BaSO_4 precipitate which formed was centrifuged down. On adding the supernatant to 15 ml of methanol, excess K_2SO_4 precipitated and was centrifuged down. The clear supernatant was decanted into 200 ml of ethanol to give a white precipitate which was collected by centrifugation, washed successively, at room temperature, with ethanol and ether, and then dried first with a nitrogen stream and finally at 100° (10⁻³ mm); yield, 0.40 g (61%). An X-ray powder pattern (Cu $K\alpha$) and an infrared spectrum confirmed that the product was K_2ReH_9 . The infrared spectrum indicated the presence of a small amount of sulfate impurity ($\nu_3(\text{SO}_4^{2-})$, 1110 cm^{-1}). *Anal.* Calcd for K_2ReH_9 : Re, 68.10. Found: Re, 67.69.

Results and Discussion

Treatment of a solution of sodium perrhenate in ethanol with sodium metal gives a precipitate of Na_2ReH_9 . Infrared spectra of the dried precipitate show



weak impurity bands at ~ 3450 ($\nu(\text{OH})$), 2910 and 2840 ($\nu(\text{CH})$), 2700 (?), ~ 1640 ($\delta(\text{OH})$), 1450 ($\delta(\text{CH})$ and $\nu_3(\text{CO}_3^{2-})$), and 910–930 cm^{-1} ($\nu(\text{ReO})$). Re-precipitation from aqueous-methanolic sodium hydroxide solution gives a product with a satisfactory analysis. However, a small nonzero carbon analysis and the retention of some of the weak impurity bands in the infrared spectrum demonstrate that purification is not complete. The reaction is easily carried out in yields of about 35%; about 15% of the unconverted perrhenate is lost in side reactions, but the remainder may be recovered.

Na_2ReH_9 is soluble in water and methanol, slightly soluble in ethanol, and insoluble in 2-propanol, acetonitrile, ether, and tetrahydrofuran. By contrast, the dipotassium salt is soluble in water and only slightly soluble in methanol. The solutions are stabilized by

alkali. On heating Na_2ReH_9 under vacuum, visible decomposition begins at $\sim 245^\circ$ and becomes more rapid as the temperature is increased; hydrogen is evolved and at sufficiently high temperature sodium distills out.

Metathesis between Na_2ReH_9 and $((\text{C}_2\text{H}_5)_4\text{N})_2\text{SO}_4$ gives $((\text{C}_2\text{H}_5)_4\text{N})_2\text{ReH}_9$, which may be reprecipitated from acetonitrile to give a product with a good analysis and no significant impurity bands in its infrared spectrum. This compound is soluble in water, ethanol, 2-propanol, and acetonitrile; it is insoluble in ether and tetrahydrofuran. On heating under vacuum (2–4°/min), decomposition occurs in the range 115–120° with the evolution of hydrogen and ethane. The tetraethylammonium salt has proven to be a useful starting material in studying the reactions of ReH_9^{2-} .^{4,5}

Surprisingly, when a solution of Na_2ReH_9 in excess KOH was precipitated with methanol, a material with the composition NaKReH_9 was obtained, instead of the expected dipotassium salt. X-Ray powder patterns (Table I) demonstrate that NaKReH_9 is not a mixture of

TABLE I
THE d SPACINGS AND RELATIVE INTENSITIES (Cu $K\alpha$)
FOR Na_2ReH_9 , NaKReH_9 , AND K_2ReH_9 ^a

| $d_{\text{obsd}}, \text{\AA}$ | | |
|-------------------------------|-------------------|---------------------------------------|
| Na_2ReH_9 | NaKReH_9 | K_2ReH_9 ^b |
| 4.40 (10) | 4.60 (10) | 4.770 (10) |
| 3.65 (3) | 4.45 (10) | 4.581 (7) |
| 3.34 (2) | 4.25 (7) | 3.605 (3) |
| 3.20 (1) | 3.78 (7) | 3.311 (8) |
| 3.10 (1) | 3.45 (4) | 3.137 (1) |
| 2.78 (6) | 3.30 (4) | 2.758 (9) |
| 2.60 (7) | 2.88 (10) | 2.718 (7) |
| 2.52 (7) | 2.68 (4) | 3.393 (6) |
| 2.23 (8) | 2.60 (5) | 2.122 (2) |
| 1.81 (7) | 2.31 (10) | 2.080 (1) |
| 1.64–1.68 (5) | 2.23 (1) | 1.954 (6) |
| 1.53 (1) | 2.12 (2) | 1.805 (6) |
| 1.47 (1) | 2.06 (2) | 1.720 (1) |
| 1.38–1.40 (3) | 1.89 (4) | 1.684 (1) |
| 1.295 (1) | 1.86 (4) | 1.589 (3) |
| 1.275 (1) | 1.75 (3) | 1.513 (3) |
| 1.245 (2) | 1.72 (3) | 1.438 (2) |
| 1.154 (2) | 1.69 (4) | 1.381 (2) |
| | 1.67 (1) | 1.325 (2) |
| | 1.63 (1) | 1.235 (2) |
| | 1.53 (1) | 1.197 (2) |
| | 1.59 (2) | 1.1590 (1) |
| | 1.47 (2) | 1.0996 (2) |
| | 1.450 (1) | |
| | 1.435 (1) | |
| | 1.330 (2) | |
| | 1.300 (1) | |
| | 1.285 (1) | |
| | 1.265 (1) | |

^a Intensities are indicated by the numbers in parentheses on the scale: 10, most intense; 1, least intense. ^b From ref 1; several lines with $d < 1.0996$ are omitted.

Na_2ReH_9 and K_2ReH_9 . When NaKReH_9 is dissolved in excess NaOH and the solution is precipitated with methanol, the product has the same composition. Evidently, NaKReH_9 is a well-defined compound formed because it is less soluble in alkaline methanol-

water than either the disodium or the dipotassium salts. In order to obtain K_2ReH_9 from Na_2ReH_9 , it is necessary first to convert the latter to $BaReH_9$ from which the dipotassium salt may be prepared by metathesis with K_2SO_4 . The *d*-spacing data also show that Na_2ReH_9 and $NaKReH_9$ are not isomorphous with K_2ReH_9 or with each other.

An isolated ReH_9^{2-} ion (point group symmetry² D_{3h}) should give rise to three infrared-active ReH stretching frequencies, $\nu(ReH)$ ($2 E' + A_2''$), and five infrared-active ReH bending frequencies, $\delta(ReH)$ ($3 E' + 2 A_2''$). Alkaline aqueous solutions of M_2ReH_9 ($M_2 = Na_2, NaK, K_2, ((C_2H_5)_4N)_2$) have only a single rather broad $\nu(ReH)$ band at 1845 cm^{-1} . For $((C_2H_5)_4N)_2ReH_9$ in acetonitrile solution, the $\nu(ReH)$ frequency is shifted to 1808 cm^{-1} and the band is still unresolved. The $\nu(ReH)$ and $\delta(ReH)$ frequencies in the solid state are listed in Table II; the most notable feature is the

TABLE II
SOLID-STATE INFRARED SPECTRA OF
ENNEAHYDRIDORHENATE SALTS^a

| Compound | $\nu(ReH), \text{cm}^{-1}$ | $\delta(ReH), \text{cm}^{-1}$ |
|------------------------|--|-------------------------------------|
| Na_2ReH_9 | 1835 s, br | 745 s, ~ 720 sh, ~ 630 sh |
| $NaKReH_9$ | ~ 1950 sh, 1845 s, ~ 1700 sh | 738 s |
| $K_2ReH_9^b$ | 1931 w, sh, 1846 s, 1814 sh | 735 s |
| $((C_2H_5)_4N)_2ReH_9$ | 1780 s, br | ~ 720 sh, 675 s, ~ 610 sh |

^a Nujol oil mull spectra: s, strong; sh, shoulder; br, broad; w, weak. ^b From ref 1.

appreciable shift to lower frequencies of both the stretching and bending vibrations in the bis-tetraethylammonium salt.

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Evidence of Ligand Motion in Tris(ethylenediamine)- and Tris(propylenediamine)cobalt(III) Complexes¹

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The most difficult problem encountered in applying pmr spectroscopy to the study of cobalt(III) complexes is finding a suitable solvent. Clifton and Pratt³ have shown that the pmr spectra of cobalt(III)-amine complexes could be obtained in acidified deuterium oxide solutions. Using this solvent, Spees, *et al.*,⁴ observed

the pmr spectra of several hexaminecobalt(III) complexes including those of ethylenediamine and propylenediamine. However, these spectra were not sufficiently well resolved to make unambiguous assignments of the different conformations of the individual chelate rings. Yoneda and Morimoto⁵ have found that several acids could be used as solvents for pmr studies of these compounds. They were also able to relate the stereochemistry of $Co(en)_3^{3+}$ and $Co(tn)_3^{3+}$ complexes to the spectra obtained using trifluoroacetic acid (TFA) as a solvent.

The present investigation was undertaken to obtain a more complete understanding of the behavior of these complexes in solution. The dependence of the spectra on the nature of the solvent and temperature is reported herein.

Results and Discussion

The pmr spectrum of the $Co(en)_3^{3+}$ complex shows a marked dependence on the solvent. In TFA and 70% $HClO_4$, a broad doublet at lower fields and a broad singlet at higher field are observed. The chemical shift of the doublet changes greatly in different solvents while the singlet remains relatively fixed. When DMSO was employed as a solvent, only one peak, a broad singlet, was observed at lower fields. Since the sharpest lines were obtained, TFA appears to be the best solvent for this work.

The spectrum of this complex is easily understood by considering its stereochemistry. The X-ray structure of this compound, obtained by Nakatsu, *et al.*,⁶ is shown in Figure 1A. The complex ion has a threefold axis about which the three ethylenediamine ligands have a nonplanar twisted structure. If the nitrogen atoms are assumed to have tetrahedral bonds, we can distinguish two kinds of $-NH_2$ protons, such that, of the six upper N-H hydrogens, three are directed upward from the N(I)-N(II)-N(III) plane and three outward, nearly perpendicular to the threefold axis.

If this rigid structure is present in solution, we would expect to observe two distinct chemically shifted NH_2 protons. If the complex is not rigid in solution, with a flipping of the NH_2 groups taking place, the magnetic environment of these protons would be time averaged to a single chemical shift. The nitrogen quadrupole moment and the electric field asymmetry around the nitrogen would cause neighboring proton resonances to be broadened. Various unresolved spin-spin splittings would also cause the spectrum to appear broad.

The room-temperature spectra of $Co(en)_3^{3+}$ dissolved in TFA or 70% $HClO_4$ are consistent with the predictions for a rigid structure. The low-field doublet can be assigned to the NH_2 protons and the broad singlet to the $-CH_2-$ protons. The spectrum obtained in DMSO indicates that the complex is no longer rigid.

In some solvents a variation of the spectrum at different temperatures is observed. The spectrum of $Co(en)_3^{3+}$ in TFA is independent of the temperature

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