

Redox Behavior of Rhenium Halides. IV.¹ Reactions of Rhenium(III) Chloride with Monodentate Tertiary Amines. Isolation and Characterization of a New Class of Rhenium(II) Derivatives^{2,3}

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The reactions of rhenium(III) chloride with pyridine, β - and γ -picolines, isoquinoline, quinaldine, and benzimidazole result in the formation of dark green-black rhenium(II) derivatives of stoichiometry $[\text{ReCl}_2 \cdot \text{L}]_n$. The appropriate amine hydrochloride is in all instances isolated as an organic by-product of these reductions. Related reactions are also observed using α -picoline, 2,6-lutidine, 2-vinylpyridine, and quinoline but the dark blue-purple reaction products precipitate before reduction to rhenium(II) is complete. Heterocyclic tertiary amines of low $\text{p}K_a$ (less than 3), such as pyrazine, 2,6-dimethylpyrazine, and 3-chloropyridine do not undergo redox reactions with rhenium(III) chloride but instead form the simple adducts $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$. By using very short reaction times, the reaction intermediates $\text{Re}_3\text{Cl}_9 \cdot 3\text{py}$ and $[\text{ReCl}_{2.5} \cdot \text{py}]_n$ have been isolated from the pyridine system. All the above products react with methanolic HCl to afford the rhenium(III) salts (amine) $\text{H}_2\text{Re}_3\text{Cl}_{11}$. On the basis of spectral, magnetic, and conductivity studies and the above reactions with methanolic HCl, it is proposed that the phases $[\text{ReCl}_2 \cdot \text{L}]_n$ and $[\text{ReCl}_{2.5} \cdot \text{py}]_n$ are best formulated as polymeric $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ and $[\text{Re}_3\text{Cl}_7 \cdot 5 \cdot 3\text{py}]_n$. The X-ray photoelectron spectra of $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ (L = pyrazine, dimethylformamide, and triphenylphosphine) and $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ (L = pyridine, γ -picoline, and benzimidazole) have been investigated and a comparison has been made of the rhenium $4f_{5/2,7/2}$ and chlorine $2p_{1/2,3/2}$ binding energies. These chlorine spectra have enabled chlorine atoms in different environments to be distinguished.

Introduction

The trimeric metal-metal bonded rhenium(III) chloride,⁵ bromide,⁶ and iodide⁷ are of interest as model species containing an M_3 cluster unit. Like other metal halides of the early transition series,⁸ they readily react with donor molecules to form simple adducts (e.g., $\text{Re}_3\text{Cl}_9 \cdot 3\text{PET}_2\text{Ph}$, $\text{Re}_3\text{Cl}_9 \cdot 3\text{AsPh}_3$, $\text{Re}_3\text{Cl}_9 \cdot 3\text{R}_2\text{SO}$, $\text{Re}_3\text{Cl}_{12}^{3-}$) and the rhenium-halogen bonds undergo solvolysis and replacement reactions with suitable ligand molecules. Thus acetylacetonate and sodium diethyldithiocarbamate react with Re_3Cl_9 and Re_3Br_9 to yield the complexes $\text{Re}_3\text{Cl}_6(\text{acac})_3$ and $\text{Re}_3\text{X}_6(\text{S}_2\text{CNET}_2)_3$ (X = Cl, Br).^{9,10} Furthermore, although the six terminal rhenium-chlorine bonds of the Re_3Cl_9 unit are readily replaced by bromide and thiocyanate ions,¹⁰⁻¹² the Re_3 cluster is generally not disrupted except under forcing reaction conditions.

On the other hand, in contrast to the behavior of other metal halides,⁸ the rhenium(III) halides have not previously been observed to undergo redox reactions in which an Re_3 cluster unit is preserved. The possibility of this latter behavior is of interest in view of the ability of the $\text{M}_6\text{X}_{12}^{n+}$ clusters (M = Nb, Ta) to undergo one-electron oxidations and reductions.¹³ We have now found that the reaction of rhenium(III) chloride with a variety of monodentate tertiary amines

leads to reduction of the Re_3Cl_9 cluster and formation of complexes of stoichiometry $[\text{ReCl}_2 \cdot \text{L}]_n$. The characterization of this new class of rhenium(II) derivatives is described in full, and studies of the X-ray photoelectron spectra of several such representative systems and of adducts of the type $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ are reported. Some of our studies on these new systems have previously been described in a preliminary report.¹⁴

Experimental Section

Rhenium(III) chloride was prepared by the thermal decomposition of rhenium(V) chloride in a nitrogen stream or obtained commercially from the S. W. Shattuck Co., Denver, Colo.

All heterocyclic tertiary amines were from commercial sources and were generally purified by distillation prior to use. Acetone was Analytical Reagent grade and was stored over anhydrous calcium sulfate prior to use.

Carbon, hydrogen, and nitrogen analyses were performed by the University of Reading, Reading, U. K., and Purdue University micro-analytical laboratories. Chlorine was determined gravimetrically and rhenium spectrophotometrically by the 2,2'-furaldioxime method. An oxidation-state analysis of the complex $[\text{ReCl}_2 \cdot \text{py}]_n$ was carried out using the procedure described previously.¹

Reaction Procedures. Most reactions were performed using dry deoxygenated acetone as the reaction solvent and allowing reaction of rhenium(III) chloride with the heterocyclic tertiary amine to proceed under a nitrogen atmosphere. However, rigorous exclusion of oxygen did not appear to be critical to the course of the reaction, since in the absence of the above precautions identical reaction products were isolated.

Reactions of Rhenium(III) Chloride. (i) **Pyridine.** (a) Rhenium(III) chloride (0.2 g) was dissolved in 10 ml of dry acetone; the solution was refluxed for a few minutes and then filtered. The filtrate was treated with a solution of pyridine (2 ml) in acetone (8 ml) and the reaction mixture was maintained at just below its boiling point for 15 min by which time the red Re_3Cl_9 color had changed to a very dark green and precipitation of a dark solid had commenced. The dark green, almost black, precipitate (0.15 g) was filtered off, washed well with acetone and ether, and dried *in vacuo*. Cautious addition of diethyl ether to the green filtrate produced a lighter green solid which was filtered off and worked up as above. Further addition of a large excess of ether to the remaining filtrate afforded a quantity of

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(2) This work was initiated at the University of Reading, Reading, England, and is abstracted in part from the Ph.D. thesis of D. G. Tisley, University of Reading, 1970.

(3) Presented in part at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, 1970; see Abstract No. 71.

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pyridinium hydrochloride, which was purified by sublimation at 100° *in vacuo*. *Anal.* Calcd for C_5H_5NCl : C, 52.0; H, 5.2; N, 12.2. Found: C, 51.4; H, 6.2; N, 12.0.

Analytical data for the insoluble (I) and soluble (II) green reaction products showed that both have the stoichiometry $[ReCl_2 \cdot py]_n$. *Anal.* Calcd for $[ReCl_2 \cdot C_5H_5N]_n$: C, 17.8; H, 1.5; N, 4.2; Cl, 21.1; Re, 55.4. Found (I): C, 17.7; H, 1.7; N, 3.95; Cl, 21.4; Re, 54.5. Found (II): C, 17.9; H, 2.2; N, 4.1; Cl, 22.6. The recovery of rhenium-containing species accounts for greater than 90% of the total rhenium content of the system.

If the initial Re_3Cl_9 -acetone-pyridine reaction mixture was left to stand at room temperature for 24 hr, the dark green-black solid slowly precipitated and addition of ether to the green filtrate once again produced the lighter green product and pyridinium chloride.

(b) In view of the apparent reduction of the rhenium(III) chloride to a derivative of rhenium(II) chloride, we decided to examine the reaction of rhenium(III) chloride with pyridine for *short* reaction periods, to establish whether any reaction intermediates involved in the reduction process could be isolated.

Rhenium(III) chloride (0.1 g) was dissolved in 5 ml of dry, pure pyridine. After 3 min, 100 ml of diethyl ether was added to the solution; an immediate precipitate separated and was filtered off, washed with acetone and diethyl ether, and dried. This afforded 0.08 g of gray-purple solid. *Anal.* Calcd for $[ReCl_2 \cdot C_5H_5N]_n$: C, 17.0; H, 1.4; N, 3.95; Cl, 25.0; Re, 52.8. Found: C, 17.4; H, 1.5; N, 4.0; Cl, 24.7; Re, 53.3. Like the green products of stoichiometry $[ReCl_2 \cdot py]_n$, the above purple phase was stable in air for periods in excess of 2 months.

The red filtrate was then treated with petroleum ether (bp 30–60°) until further precipitation almost began; the solution was agitated and then maintained in ice water to produce a crop of red needles (0.03 g) which were filtered off and washed with diethyl ether. *Anal.* Calcd for $[ReCl_2 \cdot C_5H_5N]_n$: C, 16.2; H, 1.3; N, 3.8; Cl, 28.7; Re, 50.0. Found: C, 16.3; H, 1.3; N, 3.7; Cl, 28.2; Re, 49.8. When maintained at room temperature the red crystals lost pyridine and darkened.

(c) Studies were also made of the reaction between rhenium(III) chloride and pyridine using long reaction times. Under these conditions the reactivity patterns appear to be rather complex and the products difficult to work up and characterize. However, the following reaction illustrates this behavior.

Rhenium(III) chloride (0.2 g) was dissolved in 20 ml of pyridine and refluxed for 7 days. At the end of this period 0.05 g of very dark brown, almost black, solid was found to have precipitated. This was filtered off and washed with acetone, ethanol, and ether. *Anal.* Calcd for $[ReCl_2 \cdot 2C_5H_5N]_n$: C, 28.9; H, 2.4; N, 6.7; Cl, 17.1; Re, 44.6. Found: C, 28.2; H, 2.5; N, 6.7; Cl, 16.1; Re, 45.4.

Addition of diethyl ether to the brown pyridine filtrate precipitated 0.14 g of a light brown material from which a little pyridinium chloride could be sublimed. The light brown solid was of variable composition and could be a mixture; the Re:Cl ratio was definitely less than 1:2.

(ii) β - and γ -Picolines, Benzimidazole, Isoquinoline, and Quinaldine. The reaction of these nitrogen donors with rhenium(III) chloride in acetone proceeded in a fashion similar to that described above for the related pyridine system.

The picolines (β and γ) yielded both insoluble and soluble materials with compositions $[ReCl_2 \cdot \beta\text{-pic}]_n$ and $[ReCl_2 \cdot \gamma\text{-pic}]_n$. *Anal.* Calcd for $[ReCl_2 \cdot C_6H_7N]_n$: C, 20.5; H, 2.0; N, 4.0; Cl, 20.3; Re, 53.2. Found (β -picoline insoluble product): C, 20.3; H, 1.9; N, 4.1; Cl, 19.8; Re, 54.0. Found (γ -picoline insoluble product): C, 19.1; H, 2.2; N, 3.8; Cl, 20.4; Re, 54.0. Found (β -picoline soluble product): C, 18.9; H, 1.8; N, 4.0; Cl, 21.3. Found (γ -picoline soluble product): C, 22.0; H, 2.6; N, 4.3; Cl, 22.6; Re, 49.0.

Benzimidazole, isoquinoline and quinaldine (2-methylquinoline) reacted with rhenium(III) chloride under conditions similar to those described above, except that the green-black complexes $[ReCl_2 \cdot \text{benz}]_n$, $[ReCl_2 \cdot \text{quin}]_n$ and $[ReCl_2 \cdot \text{quinal}]_n$ were allowed to precipitate without the addition of diethyl ether. *Anal.* (a) Calcd for $[ReCl_2 \cdot C_7H_7N_2]_n$: C, 22.4; H, 1.6; N, 7.5; Cl, 18.9; Re, 49.6. Found: C, 22.4; H, 1.9; N, 7.3; Cl, 18.8; Re, 49.9. (b) Calcd for $[ReCl_2 \cdot C_9H_9N]_n$: C, 28.0; H, 1.8; N, 3.6; Cl, 18.4; Re, 48.2. Found: C, 28.3; H, 2.0; N, 3.6; Cl, 18.3; Re, 48.7. (c) Calcd for $[ReCl_2 \cdot C_{10}H_9N]_n$: C, 30.0; H, 2.3; N, 3.5; Cl, 17.8. Found: C, 29.2; H, 2.3; N, 3.6; Cl, 18.2.

Work-up of the filtrates in the usual fashion afforded the appropriate amine hydrochlorides.

(iii) α -Picoline, 2-Vinylpyridine, Quinoline, and 2,6-Lutidine. These nitrogen bases showed very similar behavior in their reactivity toward rhenium(III) chloride although they differed from the sys-

tems discussed in sections (i) and (ii) above. In each instance, addition of the base to an acetone solution of rhenium(III) chloride resulted in the rapid and complete precipitation of a dark blue-purple, finely divided precipitate. These products were separated from the pale filtrates by centrifuging, washed with acetone and ether, and dried *in vacuo*. Their compositions were not very reproducible but approximated most closely to $[ReCl_2 \cdot 0.67L]_n$.

For all four systems the appropriate amine hydrochloride was identified (by infrared spectroscopy) as a reaction by-product.

(iv) 3-Chloropyridine. From the reaction of this base with rhenium(III) chloride in acetone, a clear red solution resulted which did not change color when maintained at room temperature for 12 hr and from which no product crystallized. Accordingly, an excess of the 2:1 mixed-solvent system petroleum ether (bp 30–60°)-diethyl ether was added, whereupon the red complex $[ReCl_2 \cdot 3\text{-Cl(py)}]_n$ precipitated. *Anal.* Calcd for $[ReCl_2 \cdot C_5H_4NCl]_n$: Cl, 26.3; Re, 45.8. Found: Cl, 26.1; Re, 46.1. The calculated figure for Cl refers only to the "inorganic" chlorine, since 3-chloropyridine did not decompose on heating with 1 M sodium hydroxide and hydrogen peroxide, the procedure which we used to disrupt the complex prior to rhenium and chlorine analyses.

(v) Pyrazine and 2,6-Dimethylpyrazine. These reactions were carried out by the usual procedure. The red crystalline products $[ReCl_2 \cdot \text{pyz}]_n$ and $[ReCl_2 \cdot 2,6\text{-Me}_2\text{pyz}]_n$ separated over a period of several hours. *Anal.* Calcd for $[ReCl_2 \cdot C_4H_6N_2]_n$: C, 12.9; H, 1.1; N, 7.4; Cl, 28.6. Found: C, 14.2; H, 1.3; N, 7.4; Cl, 29.0. Consistently high carbon analyses are attributed to trace amounts of lattice acetone, the presence of which was confirmed from the infrared spectrum of this product ($\nu_{C=O}$ 1710 cm^{-1}). *Anal.* Calcd for $[ReCl_2 \cdot C_6H_8N_2]_n$: C, 18.0; H, 2.0; N, 7.0; Cl, 26.6; Re, 46.4. Found: C, 18.3; H, 2.2; N, 6.9; Cl, 26.3; Re, 46.1.

(vi) Reaction of the Rhenium Chloride-Tertiary Amine Products with Methanolic HCl. In an effort to isolate a salt derived from $[ReCl_2 \cdot \text{py}]_n$, this complex together with $[ReCl_2 \cdot \text{py}]_n$ and $[ReCl_2 \cdot \text{py}]_n$ was dissolved in 4:1 mixtures of methanol and hydrochloric acid and the resultant solutions were left to evaporate in air. In all instances red crystals of the rhenium(III) salt $(\text{pyH})_2\text{Re}_3\text{Cl}_{11}$ were isolated. *Anal.* Calcd for $(C_5H_6N)_2\text{Re}_3\text{Cl}_{11}$: C, 10.8; H, 1.1; N, 2.5; Re, 35.2. Found: C, 10.3; H, 1.7; N, 2.4; Re, 35.0. The infrared spectrum (4000–400 cm^{-1}) of this complex agreed closely with that of pyridinium chloride and with pyridinium compounds generally.¹⁵

In a similar fashion, treatment of the other rhenium chloride-tertiary amine products, previously described in sections (ii)–(v), afforded salts of the type $(\text{amine})_2\text{Re}_3\text{Cl}_{11}$. Analytical data for these species, which in all instances are new compounds, are available on request to R. A. W.

(vii) Other Complexes of Rhenium(III) Chloride. The following complexes which were required for comparative purposes were prepared by literature methods: $Re_3Cl_9 \cdot 3\text{PPh}_3$,¹⁶ $Re_3Cl_9 \cdot 3\text{thiox}$ (thiox = 1,4-thioxane),¹⁷ $Re_3Cl_9 \cdot 1.5\text{diphos}$ (diphos = 1,2-bis(diphenylphosphino)ethane),¹⁷ and $(\text{Ph}_2\text{As})_2\text{Re}_3\text{Cl}_{11}$.¹⁸ The dimethylformamide adduct, of stoichiometry $[ReCl_2 \cdot \text{DMF}]_n$, was prepared by dissolving rhenium(III) chloride (0.2 g) in dimethylformamide (10 ml) and the red complex (0.22 g) was precipitated by the addition of a large excess of diethyl ether. *Anal.* Calcd for $[ReCl_2 \cdot C_3H_7NO]_n$: C, 9.8; H, 1.9; N, 3.8; Cl, 29.1. Found: C, 10.7; H, 2.1; N, 4.0; Cl, 28.8. The infrared spectrum of this complex (4000–400 cm^{-1}) confirmed that the ligand molecule was oxygen bonded, with $\nu_{C=O}$ at 1635 cm^{-1} in the complex, significantly lowered from that in free dimethylformamide (1670 cm^{-1}).

Physical Measurements. Electronic spectra were recorded on a Unicam 700c spectrophotometer equipped with a diffuse-reflectance attachment and on a Cary 14 spectrophotometer. Infrared spectra in the region 4000–400 cm^{-1} were obtained with Perkin-Elmer 457 and Beckman IR 12 spectrophotometers and between 400 and 200 cm^{-1} on Grubb Parsons DM4 and Beckman IR 11 spectrophotometers. Studies on the X-ray photoelectron spectra of the rhenium complexes were carried out using a Hewlett-Packard Model 5950A ESCA spectrometer.¹⁹ Samples were diluted with graphite in an attempt to

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(19) This instrument was purchased through an equipment grant from the National Science Foundation which we gratefully acknowledge.

eliminate surface charging effects and the spectra were referenced to the C(1s) line on graphite at 284.0 eV. Full details of the experimental procedures we used to determine binding energies are described elsewhere.^{20,21}

The magnetic susceptibility of $[\text{ReCl}_2 \cdot \text{py}]_n$ was obtained on a conventional Gouy balance system. Dr. Robin Whyman of ICI, Runcorn, Cheshire, England, kindly measured the magnetic susceptibilities of $[\text{ReCl}_2 \cdot \text{py}]_n$ and $[\text{ReCl}_2 \cdot \text{benz}]_n$ using a Faraday balance.

Conductivities were measured using a Pye 11700 conductance bridge and a Mullard conductivity cell thermostated at 25°. X-Ray powder data were obtained using a Philips camera (Debye-Scherrer type) and Cu K α radiation (λ 1.5418 Å) with an exposure time of approximately 8 hr.

Results and Discussion

(a) **Synthesis and Preliminary Characterization.** In contrast to an early report¹⁶ that the reaction of acetone solutions of rhenium(III) chloride with pyridine affords a green complex of stoichiometry $[\text{ReCl}_3 \cdot \text{py}]_n$, we find that if the procedure of Colton, *et al.*,¹⁶ is followed, then this reaction product is in fact a rhenium(II) derivative $[\text{ReCl}_2 \cdot \text{py}]_n$. The stoichiometry of the material implied to us that a redox reaction had occurred involving reduction of the halide phase by pyridine, a reaction presumably analogous to the known pyridine reduction of other metal halides of the early transition series.⁸ In contrast to the insoluble product of composition $[\text{ReCl}_2 \cdot \text{py}]_n$, the green solid which precipitated on the addition of diethyl ether to the green Re_3Cl_9 -acetone-pyridine reaction solution was invariably found to have a slightly high chlorine analysis, implying that reduction had not proceeded to completion. Work-up of the reaction filtrates, after separation of the reduced rhenium chloride phases, afforded pyridinium chloride as the main reaction by-product. This result is in keeping with the observation that pyridinium halides are one of the main "oxidation" products from the pyridine reduction of the niobium(V), tantalum(V), and tungsten(V) halides.²²⁻²⁴

The unexpected course of this reaction led us to investigate this particular system in more detail and to establish whether similar behavior was observed with other monodentate tertiary amine systems. The results of these investigations are as follows.

(1) Analogous reduction reactions, to afford dark green complexes of the type $[\text{ReCl}_2 \cdot \text{L}]_n$, occur with β - and γ -picoline, isoquinoline, quinaldine (2-methylquinoline), and benzimidazole. On the other hand, with α -picoline, 2-vinylpyridine, 2,6-lutidine, and quinoline, very insoluble blue-purple reaction products were formed, in yields of greater than 90%, whose composition approximated to $[\text{ReCl}_2 \cdot 3.3 \cdot 0.67\text{L}]_n$, which implies that reduction to rhenium(II) was incomplete. In all instances, the appropriate amine hydrochloride was isolated by work-up of the reaction filtrates. The degree to which reduction occurs is not a function of any obvious steric effects, since, with quinaldine (2-methylquinoline), reduction to rhenium(II) is complete whereas with both quinoline and 2,6-lutidine only the partially reduced phases are isolated.

(2) Since these redox reactions result in the formation of the appropriate amine hydrochloride, it would seem reasonable to expect the course of the reactions to be dependent

in part on the $\text{p}K_a$ of the base. For all the systems discussed above, the $\text{p}K_a$ values are greater than 4.9. Accordingly, we next carried out reactions of rhenium(III) chloride in acetone with pyrazine, 2,6-dimethylpyrazine, and 3-chloropyridine, all of which have $\text{p}K_a$'s of less than 3. For these three systems, reduction did not occur and the resulting dark red complexes had the expected stoichiometry, $[\text{ReCl}_3 \cdot \text{L}]_n$.

(3) Since we had isolated the complexes $[\text{ReCl}_3 \cdot \text{L}]_n$, L = pyrazine, 2,6-dimethylpyrazine, and 3-chloropyridine, it seemed likely that adducts of this stoichiometry were intermediates in those systems in which reduction occurred. By using very short reaction times and rapidly isolating the reaction products, we successfully isolated $[\text{ReCl}_3 \cdot \text{py}]_n$ (red) and $[\text{ReCl}_2 \cdot 5 \cdot \text{py}]_n$ (gray-purple) from the pyridine system. The former complex, obtained as red needles, is unstable at room temperature, subsequent reduction slowly occurring even in the solid state.

(4) In an attempt to stabilize the rhenium(II) oxidation state as a complex chloro anion, the amine products were treated with methanolic HCl. In all instances they dissolved to afford dark red-purple solutions from which the rhenium(III) chloro anions $((\text{amine})\text{H})_2\text{Re}_3\text{Cl}_{11}$ crystallized. This oxidation was quite unexpected and led us to suspect that for all the phases $[\text{ReCl}_2 \cdot \text{L}]_n$, $[\text{ReCl}_2 \cdot 3.3 \cdot 0.67\text{L}]_n$, and $[\text{ReCl}_3 \cdot \text{L}]_n$, the trinuclear Re_3 cluster of the parent Re_3Cl_9 was retained, since to our knowledge there are no instances known where the Re_3 cluster is formed under such mild reaction conditions starting from mononuclear or dinuclear rhenium species. The formation of $((\text{amine})\text{H})_2\text{Re}_3\text{Cl}_{11}$ was expected for the phases of composition $[\text{ReCl}_3 \cdot \text{L}]_n$, where L = pyridine, pyrazine, and 2,6-dimethylpyrazine, since we had no reason to suspect that they were other than further examples of trinuclear derivatives of the type $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$, which are readily formed when rhenium(III) chloride is treated with a variety of donor molecules.^{18,25,26}

(5) The infrared spectra of all the complexes were recorded in the region 4000–400 cm^{-1} . The spectra of the α -picoline, 2,6-lutidine, quinoline, and 2-vinylpyridine products revealed contamination by $[(\text{amine})\text{H}]^+$ impurities, which are presumably trapped in the lattice as these very insoluble reaction products precipitated from solution. For $[\text{ReCl}_2 \cdot \text{py}]_n$ and $[\text{ReCl}_2 \cdot \gamma\text{-pic}]_n$, broad bands at $\sim 890 \text{ cm}^{-1}$ of medium intensity indicated that these products are contaminated by trace amounts of perhenate. This species is possibly present as the $[(\text{amine})\text{H}]\text{ReO}_4$ salt since a weak band at $\sim 1540 \text{ cm}^{-1}$ in the spectrum of $[\text{ReCl}_2 \cdot \text{py}]_n$ could be due to pyH^+ . We were not able to prepare these two products free from this contaminant, but since it is present in very low levels, as judged by the analytical data and infrared spectroscopy, its presence in these two compounds did not hinder their subsequent characterization. This conclusion was further confirmed by X-ray photoelectron spectroscopy. Measurements in the oxygen 1s binding energy region showed only small amounts of oxygen-containing species with binding energies of ca. 531 eV, which could be attributable to the perhenate anion.²⁷

(b) **Electronic and Low-Frequency Vibration Spectra of the Rhenium(III) and Rhenium(II) Derivatives.** Since we do not have a detailed knowledge of the electronic structure of Re_3Cl_9 or its derivatives, any lengthy discussion of their

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Table I. Electronic Absorption Spectra of Complexes of Rhenium(III) and Rhenium(II)

Compound	Medium ^b	Absorption maxima, $\text{cm}^{-1} \times 10^{-3}$ ^a		
		λ_1	λ_2	λ_3
1. Rhenium(III) Derivatives				
Re_3Cl_9	DR	~ 8.3	12.7	19.0
$\text{Re}_3\text{Cl}_9 \cdot 3\text{PPh}_3$	DR	7.6	12.2	18.4
$\text{Re}_3\text{Cl}_9 \cdot 1.5\text{diphos}$	DR	7.6	12.2	18.2
$\text{Re}_3\text{Cl}_9 \cdot 3\text{thioxane}$	DR	8.5	12.8	19.0
$\text{Re}_3\text{Cl}_9 \cdot 3\text{DMF}$	DR	8.0	12.6	19.2
$\text{Re}_3\text{Cl}_9 \cdot 3\text{py}$	DR	8.3	13.0	19.0
$\text{Re}_3\text{Cl}_9 \cdot 3(3\text{-Cl(py)})$	DR	8.2 br	12.9	18.9
$\text{Re}_3\text{Cl}_9 \cdot 3\text{pyz}$	DR	8.2	13.0	19.0
$\text{Re}_3\text{Cl}_9 \cdot 3(2,6\text{-Me}_2\text{pyz})$	DR	8.2	13.0	19.0
$[\text{Ph}_3\text{As}]_2\text{Re}_3\text{Cl}_{11}$	CH_3CN	8.4 (40)	12.6 (270)	18.8 (1450)
$[\text{pyH}]_2\text{Re}_3\text{Cl}_{11}$	DR	8.2	12.4	18.4
	CH_3CN	8.2 (40)	12.4 (480)	18.6 (1500)
$[\text{pyzH}]_2\text{Re}_3\text{Cl}_{11}$	DR	8.2	13.1	19.3
$[2,6\text{-Me}_2\text{pyzH}]_2\text{Re}_3\text{Cl}_{11}$	DR	8.3	13.2	19.4
$[\text{quinalH}]_2\text{Re}_3\text{Cl}_{11}$	DR	8.2	12.6	18.6
	CH_3CN	8.2 (35)	12.6 (450)	18.8 (1500)
$[\text{quinH}]_2\text{Re}_3\text{Cl}_{11}$	DR	8.3	12.6	18.7
	CH_3CN	8.3 (33)	12.7 (480)	18.8 (1640)
2. Rhenium(II) Derivatives ^{c,d}				
$[\text{ReCl}_2 \cdot \text{py}]_n$	DR		10.8	15.4
$[\text{ReCl}_2 \cdot \beta\text{-pic}]_n$	DR		11.1	15.8
$[\text{ReCl}_2 \cdot \gamma\text{-pic}]_n$	DR		11.2	15.8
$[\text{ReCl}_2 \cdot \text{benz}]_n$	DR		12.2	16.8
$[\text{ReCl}_2 \cdot i\text{-quin}]_n$	DR		11.8	15.8
$[\text{ReCl}_2 \cdot \text{quinal}]_n$	DR		10.8	15.8

^a Molar extinction coefficients are given in parentheses. ^b DR = diffuse reflectance. ^c The related, partially reduced but impure α -picoline, 2,6-lutidine, 2-vinylpyridine, and quinoline phases have very similar diffuse-reflectance spectra. ^d Solutions in polar solvents such as acetonitrile and dimethylformamide were unstable, so that solution spectral data are not reported.

electronic spectra is at present unprofitable. However, we can make the following important general observations. In the past, the observation of two sharp bands in the 11,000–20,000- cm^{-1} region of the visible absorption spectra of the rhenium(III) halides and their adducts, in which the lower frequency band is the least intense, has been assumed to be characteristic of the rhenium(III) cluster.^{17,18,25,26} However, as we show in Table I, two absorption bands are also observed in the spectra of the rhenium(II) derivatives in this same spectral region, although they are shifted slightly to lower energies relative to $\text{Re}_3\text{X}_9 \cdot 3\text{L}$. Therefore this previous spectral criterion is incorrect. However, if these measurements are extended into the near-infrared region, we have now found that an absorption band is always located at $\sim 8000 \text{ cm}^{-1}$ for the rhenium(III) cluster whereas no comparable band is present in the spectra of $[\text{ReCl}_2 \cdot \text{L}]_n$ or the partially reduced species. For this study we chose as our model rhenium(III) species several previously synthesized derivatives of rhenium(III) chloride, together with the salts of the type $(\text{amine})_2\text{Re}_3\text{Cl}_{11}$ and the adduct $\text{Re}_3\text{Cl}_9 \cdot 3\text{DMF}$, reported here for the first time. Also, it can be seen that the new derivatives $[\text{ReCl}_2 \cdot \text{L}]_n$ (L = pyridine, 3-chloropyridine, pyrazine, and 2,6-dimethylpyrazine) are clearly the adducts $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$, since their spectra show the characteristic three-band pattern with the intensity order $\lambda_3 > \lambda_2 > \lambda_1$.²⁸ As a result of the above investigations, measurements in the 5000–25,000- cm^{-1} region are necessary to detect this change in

(28) We note that, in an earlier study by Cotton and Mague,⁵ published spectral traces of Re_3Cl_9 in acetone and $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$ in 12 M HCl do show weak features at $\sim 8500 \text{ cm}^{-1}$, which we believe are the related λ_1 bands for the ones we have located for the complexes listed in Table I.

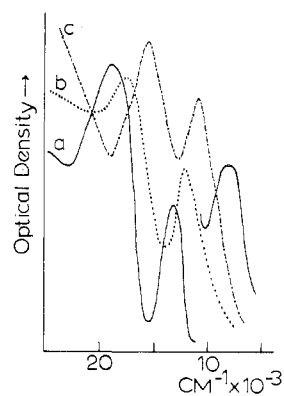


Figure 1. Diffuse-reflectance electronic absorption spectra: (a) $\text{Re}_3\text{Cl}_9 \cdot 3\text{py}$; (b) $[\text{ReCl}_{2.5} \cdot \text{py}]_n$; (c) $[\text{ReCl}_2 \cdot \text{py}]_n$.

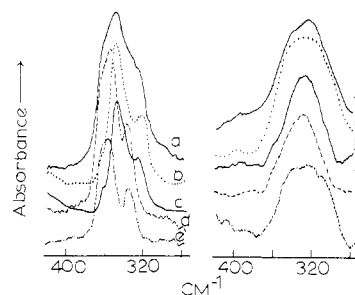


Figure 2. Far-infrared spectra (Nujol mulls) of complexes of the types $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ and $[\text{ReCl}_2 \cdot \text{L}]_n$: L = py (a), $1/2$ diphos (b), PPh_3 (c), pyz (d), 2,6-Me₂pyz (e), β -pic (f), γ -pic (g), *i*-quin (h), quinal (i), and benz (j).

oxidation state if this spectral region is to be used for diagnostic purposes.

The diffuse-reflectance spectrum of the compound of stoichiometry $[\text{ReCl}_{2.5} \cdot \text{py}]_n$ was also recorded and shown to resemble the two-band pattern of $[\text{ReCl}_2 \cdot \text{py}]_n$, although the band positions were intermediate between those of $[\text{ReCl}_2 \cdot \text{py}]_n$ and the λ_2, λ_3 pair of $[\text{Re}_3\text{Cl}_9 \cdot 3\text{py}]$. The observed shift to lower energies of the bands in the 20,000–10,000- cm^{-1} region in the order $\text{Re}_3\text{Cl}_9 \cdot 3\text{py} > [\text{ReCl}_{2.5} \cdot \text{py}]_n > [\text{ReCl}_2 \cdot \text{py}]_n$ (see Figure 1) implies that they do not originate from halogen (π) \rightarrow Re transitions, since if this were the case then they should decrease in energy with increase in oxidation state, *i.e.*, with increase in optical electronegativity χ_{opt}^{29} . This observation in turn suggests that for Re_3Cl_9 , λ_2 and λ_3 involve transitions within the Re_3 cluster.

A comparison was also made of the low-frequency infrared spectra of $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ and $[\text{ReCl}_2 \cdot \text{L}]_n$ in the region 400–200 cm^{-1} . As shown in Figure 2 these spectra are very similar within each series and are dominated by an intense band in the region 360–310 cm^{-1} , which we assigned as essentially involving stretching of the Re-Cl bonds. For $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$, the band maximum centered at $\sim 350 \text{ cm}^{-1}$ is probably associated in large part with vibrations of the terminal Re-Cl bonds. The shift of the band maximum to lower energies and the increase in its half-bandwidth for $[\text{ReCl}_2 \cdot \text{L}]_n$ are consistent with the oxidation state change from rhenium(III) to rhenium(II) and/or the transformation of terminal Re-Cl bonds to bridging Re-Cl units.

(c) **Structural Considerations.** While the above electronic and vibrational absorption spectra do not provide any definitive structural data on the phases $[\text{ReCl}_2 \cdot \text{L}]_n$, they certainly suggest that independent of the nature of L, the same struc-

tural $[\text{ReCl}_2]_n$ unit persists. Also, the relative simplicity of the far-infrared spectra of $[\text{ReCl}_2 \cdot \text{L}]_n$ further indicates that this structural unit does not involve a complex Re-Cl framework. Furthermore, from the known chemistry of rhenium,³⁰ the ease with which $[\text{ReCl}_2 \cdot \text{L}]_n$ is converted into ((amine)H)₂Re₃Cl₁₁ is evidence in favor of the retention of the Re₃ unit in these derivatives, so that they are probably best represented as $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$. This would not, of course, rule out the possibility that they are in fact the octahedral clusters $[\text{Re}_6\text{Cl}_{12} \cdot 6\text{L}]$, structurally related to the known niobium and tantalum derivatives of the type $[\text{M}_6\text{X}_{12} \cdot 6\text{L}]^{n+}$. However, a consideration of the likely electronic structure of such an Re₆ cluster does, we believe, make this unlikely. Using the approximate molecular orbital energy level diagram devised by Cotton and Haas³¹ for the $\text{Re}_3\text{Cl}_{12}^{3-}$ anion, we can allot 15 electrons to the orbitals associated with the Re₃ core of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ in the following fashion: $(A_1')^2(A_2'')^2(E')^4(E_a'')^4(E_b'')^3$. Thus with the exception of three electrons in the antibonding E_b'' set, the remaining 12 electrons are in bonding orbitals. Consequently, there is still a net bonding effect for a rhenium(II) species containing the triangular Re₃ cluster. On the other hand, for $[\text{Re}_6\text{Cl}_{12} \cdot 6\text{L}]$, if we now use the related diagram for the M₆ cluster orbitals of $\text{M}_6\text{X}_{12}^{n+}$,³¹ we find that for this species so many electrons have to be allotted to essentially antibonding orbitals that there is little net M-M bonding in this cluster. This does not immediately rule out the existence of the $[\text{Re}_6\text{Cl}_{12}]$ cluster, since Pt₆Cl₁₂, for which the net Pt-Pt bond order approaches zero, is known, but it does indicate that *such a species would be unstable with respect to $[\text{Re}_3\text{Cl}_6]$* . Evidence in favor of this conclusion is presented below.

Attempts to obtain mass spectra of the derivatives $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ were thwarted by their thermal decomposition in the spectrometer; only the amine base and its fragmentation pattern was detected in the vapor phase in each case. Measurement of the X-ray powder photographs of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$, the partially reduced α -picoline product, and the intermediate pyridine product $[\text{ReCl}_{2.5} \cdot \text{py}]_n$ showed that all three systems were amorphous, suggesting that they possessed disordered polymeric structures. Further support for this conclusion is provided from magnetic susceptibility measurements. The magnetic moment of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ at room temperature was 0.86 BM, as determined by the Gouy method. This low value suggests that we do not have isolated Re₃ clusters but rather a condensed system in which interactions between clusters could exist. Independent measurements of the magnetic properties of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ and the related benzimidazole complex were kindly carried out for us by Dr. Robin Whyman using a Faraday balance system. Both systems were found to be essentially "diamagnetic" within experimental error.

A freshly prepared solution of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ in pyridine ($3.6 \times 10^{-3} M$) had a molar conductivity of $11 \text{ ohm}^{-1} \text{ cm}^2$, which increased to $30 \text{ ohm}^{-1} \text{ cm}^2$ as the solution was diluted to $0.2 \times 10^{-3} M$. These conductance values were much lower than those expected for a 1:1 electrolyte in this solvent and are indicative of weak electrolyte behavior. However, that these observed modest conductances are in part due to reaction with the solvent is shown by the time dependence of the Λ_m values. The above pyridine solution ($3.6 \times 10^{-3} M$) when set aside for 24 hr showed an increase in its conductance from the initial value of $11 \text{ ohm}^{-1} \text{ cm}^2$ to a final one of $24 \text{ ohm}^{-1} \text{ cm}^2$. Similar behavior was observed for

Scheme I. Possible Reactions for the Conversion of Rhenium(III) Chloride to the Rhenium(II) Derivative $[\text{ReCl}_2 \cdot \text{py}]_n$

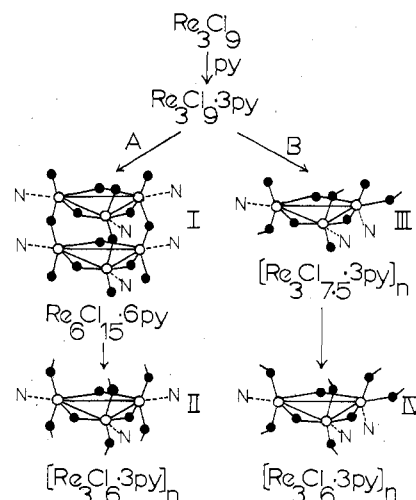


Table II. Rhenium 4f and Chlorine 2p Binding Energies (eV) of Rhenium Halide Clusters $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ and $[\text{ReCl}_2 \cdot \text{L}]_n^a$

	Re 4f _{5/2, 7/2}		Cl 2p _{1/2, 3/2}		
$\text{Re}_3\text{Cl}_9 \cdot 3\text{pyz}$	44.8	42.5	200.6	199.3	197.9
$\text{Re}_3\text{Cl}_9 \cdot 3\text{DMF}$	44.8	42.2	200.3	199.1	197.7
$\text{Re}_3\text{Cl}_9 \cdot 3\text{PPH}_3$	44.7	42.5	200.6	199.3	198.0
$[\text{ReCl}_2 \cdot \text{py}]_n$	44.5	42.1	200.5	198.7	197.6
$[\text{ReCl}_2 \cdot \text{benz}]_n$	43.6	41.8	<i>b</i>	<i>b</i>	<i>b</i>
$[\text{ReCl}_2 \cdot \gamma\text{-pic}]_n$	44.5	42.3	200.7	198.8	197.7

^a All spectra are referenced to the C 1s binding energy of graphite at 284.0 eV. ^b This spectrum was poorly resolved and the Cl 2p binding energies are therefore not reported.

solutions in dimethylformamide. The low Λ_m values for the *freshly prepared* solutions indicate that $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ possesses a nonionic structure in the solid state. If our conclusions are correct, then the formation of a polymeric $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ structure, in which the triangular Re₃ units are preserved, can be envisaged as occurring in one of two ways, as shown in Scheme I, A and B. These differ in that A involves a symmetric polymerization to afford the linear "polymer of trimers," structure II, *via* the intermediate I, whereas B presents the alternative process which leads to disordered structures II and IV in which no *preferential* polymerization *via* Re-Cl-Re bridges is envisaged. For both A and B, we would expect the intermediate formation of I or III, and our isolation of the phase of stoichiometry $[\text{ReCl}_{2.5} \cdot \text{py}]_n$ from the pyridine system certainly supports the essential features of either of the proposed schemes. However, the amorphous nature of these two reaction products perhaps favors III and IV, which have the least ordered structures.

Since these compounds are amorphous to X-rays, an unambiguous structure determination is not feasible. We have, however, explored the X-ray photoelectron spectra of several of the compounds. Both the rhenium 4f_{5/2, 7/2} and chlorine 2p_{1/2, 3/2} binding energies of several complexes of the types $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ and $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ were recorded and these data are presented in Table II. The spectra of $\text{Re}_3\text{Cl}_9 \cdot 3\text{pyz}$ and $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ which are shown in Figure 3 are representative of these systems. Further, comparisons between $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ and $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ are, we feel, justified since these species probably have closely related structures.

Our first conclusion is that the rhenium 4f binding energies for these low oxidation state Re(III) and Re(II) species differ

(30) J. E. Fergusson, *Coord. Chem. Rev.*, **1**, 459 (1966).

(31) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

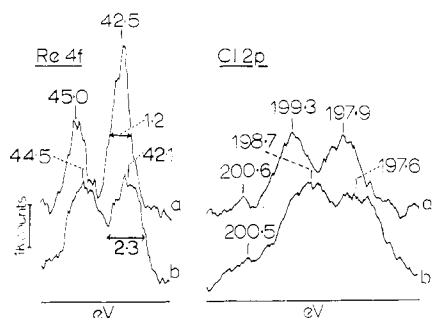


Figure 3. X-Ray photoelectron spectra: (a) $\text{Re}_3\text{Cl}_9 \cdot 3\text{pyz}$; (b) $[\text{ReCl}_2 \cdot \text{py}]_n$.

very little. This is not unexpected since, with the large metal ions of the second and third transition series, changes in oxidation state by one unit are unlikely to be reflected by large changes in effective nuclear charge at the central metal center.

Of rather more interest are the chlorine 2p spectra which are quite different from those expected for species with only *one* type of Re-Cl bond. For the ReCl_6^{2-} anion, or in fact for any chlorine-containing compound possessing one type of chlorine atom, the spectra show two binding energies, separated by ~ 1.5 eV, which are in the intensity ratio 1:2; the $2p_{1/2}$ component, which is at higher energy, has the lower intensity of the two. For the molecules $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$, which possess two types of chlorine atoms, these are six equivalent out-of-plane terminal Re-Cl bonds and three in-plane chlorines in Re-Cl-Re bridging units. The crystal structure of $\text{Re}_3\text{Cl}_9 \cdot 3\text{PEt}_2\text{Ph}$ provides a model for a detailed analysis of these spectra.²⁵ In this molecule the terminal Re-Cl bond lengths of 2.32 ± 0.03 Å are slightly shorter than those of the comparable bridging bonds (2.38 ± 0.03 Å) but the latter are fairly tightly bound to *two* metal centers. Accordingly, the electron drift from the latter chlorine centers may reasonably be expected to exceed that of a terminal chlorine, so that the positive charge will be greater and the 2p binding energies consequently greater. Therefore, if the above structural features are preserved in the adducts $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$ considered in the present report, we would expect overlap of the two different chlorine 2p spectra such that the binding energies for the bridging chlorines are located at the higher energies. The spectra of $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$, for L = pyrazine, dimethylformamide, and triphenylphosphine, show that this is the case, and since the separations between the three components is ~ 1.3 eV, then the overlap is such that the chlorine $2p_{3/2}$ peak of the Re-Cl_b nearly coincides with the chlorine $2p_{1/2}$ of Re-Cl_t . Further, the relative intensities are close to the anticipated ratio of 1:4:4 for such a system.

A similar chlorine 2p binding energy pattern exists for the

reduced phases $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ and $[\text{Re}_3\text{Cl}_6 \cdot 3\gamma\text{-pic}]_n$ (Table II and Figure 3), which immediately rules out the possibility that $[\text{ReCl}_2 \cdot \text{L}]_n$ compounds are in reality $[\text{Re}_6\text{Cl}_{12} \cdot 6\text{L}]$, since in this structure there would be only one type of chlorine atom. On the other hand, this spectrum is consistent with our proposed structures II or IV if we make the reasonable assumption that the chlorine atoms in the intracuster Re-Cl-Re bridges have higher binding energies than those involved in the weaker intercluster bridges.

The rhenium 4f and chlorine 2p binding energies of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ were significantly broader than for $\text{Re}_3\text{Cl}_9 \cdot 3\text{L}$. For instance, the full width at half-maximum for the rhenium $4f_{7/2}$ component of $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ was almost twice that for $\text{Re}_3\text{Cl}_9 \cdot 3\text{pyz}$ (Figure 3). These differences can probably be attributed to the amorphous nature of the rhenium(II) phases in which we have slight variations in the rhenium and chlorine environments giving rise to peak broadening. This complicates any discussion of relative peak intensities and for this reason our arguments have not dealt with a detailed consideration of this point.

One further point which should be considered is the possibility that the phases $[\text{Re}_3\text{Cl}_6 \cdot 3\text{L}]_n$ are really the hydrido derivatives $[\text{ReHCl}_2 \cdot \text{L}]_n$. We consider this unlikely for the following reasons. (i) The conditions used to generate these compounds are similar to the tertiary amine reductions of other metal halides of the early transition series for which metal hydride formation has not been observed.⁸ (ii) No modes assignable to $\nu(\text{Re-H})$ have been located in the infrared spectra. (iii) An oxidation-state titration on $[\text{Re}_3\text{Cl}_6 \cdot 3\text{py}]_n$ gave an oxidation state of 1.9 ± 0.1 . (iv) Treatment with methanol-HCl with resulting oxidation to $(\text{amine})_2\text{Re}_3\text{Cl}_{11}$ was not accompanied by the evolution of hydrogen gas.

Registry No. Rhenium(III) chloride, 14973-59-2; $[\text{ReCl}_2 \cdot \text{py}]_n$, 27614-34-2; $[\text{ReCl}_2 \cdot 5\text{-py}]_n$, 27614-34-2; $[\text{ReCl}_3 \cdot \text{py}]_n$, 37191-65-4; $[\text{ReCl}_2 \cdot 2\text{py}]_n$, 37191-67-6; $[\text{ReCl}_2 \cdot \beta\text{-pic}]_n$, 27614-35-3; $[\text{ReCl}_2 \cdot \gamma\text{-pic}]_n$, 27614-36-4; $[\text{ReCl}_2 \cdot \text{benz}]_n$, 27661-14-9; $[\text{ReCl}_2 \cdot i\text{-quin}]_n$, 37540-80-0; $[\text{ReCl}_2 \cdot \text{quinal}]_n$, 27614-37-5; $[\text{ReCl}_3 \cdot 3(\text{Cl})\text{-py}]_n$, 37191-64-3; $[\text{ReCl}_3 \cdot \text{pyz}]_n$, 37191-63-2; $[\text{ReCl}_3 \cdot 2,6\text{-Me}_2\text{-pyz}]_n$, 37191-66-5; $(\text{pyH})_2 \cdot \text{Re}_3\text{Cl}_{11}$, 37191-62-1; $[\text{ReCl}_3 \cdot \text{DMF}]_n$, 37191-61-0.

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