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The Redox Behavior of Rhenium Halides. X.[1] The Reduction of Rhenium(III) Bromide by Tertiary Amines and Phosphines

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Rhenium(III) bromide reacts with pyridine, 3-chloropyridine, γ-picoline and benzimidazole to produce the rhenium(II) polymers $[Re_3Br_6L_3]_n$. *In contrast to this, pyrazine forms the unreduced adduct* $Re_3Br_9(pyz)_3$. *Prolonged reaction of rhenium(III) bromide with tri-n-propylphosphine and ethyldiphenylphosphine in refluxing methanol results in disruption of the trimer and reduction to metal–metal bonded dimers of the type* $Re_2Br_4L_4$. *Comparisons are made with the related reactions of rhenium(III) chloride.*

Introduction

We have demonstrated[2] that rhenium(III) chloride Re_3Cl_9 is readily reduced by the more basic heterocyclic tertiary amines such as pyridine, β- and γ-picoline, isoquinoline and benzimidazole to afford polymeric rhenium(II) species of stoichiometry $[Re_3Cl_6L_3]_n$. Although monodentate tertiary phosphines can also reduce this chloride, these reactions proceed with *disruption* of the trimeric structure and the formation of metal–metal bonded dimers.[3,4] The occurence and extent of reduction is dependent upon the basicity of the phosphine, so that reactions with PPh_3, PPh_2Et, $PPhEt_2$ and PEt_3 terminate at $Re_3Cl_9(PPh_3)_3$, $Re_2Cl_5(PPh_2Et)_3$, $Re_2Cl_4(PPhEt_2)_4$ and $Re_2Cl_4(PEt_3)_4$, respectively.[4]

A very convenient high yield synthesis of rhenium(III) bromide has recently been developed in this laboratory.[5] During the characterization of this phase we have taken the opportunity to investigate its reactivity with tertiary amines and phosphines with the object of assessing how its redox behavior compares to that of the related chloride systems.[2,4]

Experimental

Rhenium(III) bromide was prepared by the reaction of hydrogen bromide with the rhenium(III) acetate $Re_2(O_2CCH_3)_4Cl_2$.[5] All tertiary amines and phosphines were obtained from commercial sources. Solvents were normally deoxygenated by purging with N_2 gas for several hours and all reactions were carried out in a nitrogen atmosphere.

Reactions of Rhenium(III) Bromide

(i) Pyridine

Rhenium(III) bromide (0.12 g) was dissolved in 10 ml of dry acetone and the resultant dark red solution filtered to remove trace amounts of insoluble material. The filtrate was treated with pyridine (1.5 ml) and the reaction mixture heated until it changed to a dark green color. It was then cooled to room temperature, filtered and the filtrate treated with an excess of petroleum ether to produce a dark green precipitate of $[Re_3Br_6(py)_3]_n$. The complex was filtered off, washed freely with petroleum ether and then dried *in vacuo;* yield, 0.11 g (~90%). *Anal.* Calcd. for $[Re_3Br_6(C_5H_5N)_3]_n$: C, 14.1; H, 1.2; Br, 37.6; N, 3.3. Found: C, 13.8; H, 1.3; Br, 37.2; N, 3.3%.

(ii) 3-Chloropyridine

The dark green complex $[Re_3Br_6(3\text{-Clpy})_3]_n$ was prepared using a similar procedure to that described in (i). *Anal.* Calcd. for $[Re_3Br_6(C_5H_4ClN)_3]_n$: C, 13.1; H, 0.9; Br, 34.8; Cl, 7.7. Found: C, 13.0; H, 1.2; Br, 34.85; Cl, 7.7%.

(iii) Benzimidazole and γ-Picoline

The reactions of benzimidazole and γ-picoline with rhenium(III) bromide in acetone likewise afforded dark green insoluble products whose spectral properties were very similar to those of $[Re_3Br_6(py)_3]_n$ and $[Re_3Br_6(3\text{-Clpy})_3]_n$. While microanalytical data were not recorded for these complexes, there is little doubt that they can be formulated as rhenium(II) derivatives $[Re_3Br_6L_3]_n$ (see Results and Discussion Section).

(iv) Pyrazine

A quantity of rhenium(III) bromide (0.11 g) was dissolved in 10 ml of acetone and treated with an acetone solution (10 ml) of pyrazine (0.15 g). The initial red color of the reaction mixture persisted over a period of several hours and when the solution was cooled overnight, dark purple crystals of the rhenium(III) complex $Re_3Br_9(pyz)_3$ separated. These were filtered off, washed with acetone and diethyl ether and dried; yield, 0.048 g (37%). *Anal.* Calcd. for $Re_3Br_9(C_4H_4N_2)_3$: C, 9.5; H, 0.8; Br, 47.4. Found: C, 9.4; H, 0.8; Br, 47.3%.

(v) Ethyldiphenylphosphine

Rhenium(III) bromide (0.18 g) was dissolved in 15 ml of dry methanol, the solution filtered and ethyldiphenylphosphine (1.0 ml) added to the filtrate. The reaction mixture was refluxed for 14 days, filtered and then concentrated to half-volume. It was set aside whereupon a small quantity of dark crystals slowly formed. After 4 weeks, the insoluble product was filtered off, washed with petroleum ether and dried *in vacuo;* yield, 0.04 g (12%). *Anal.* Calcd. for $Re_2Br_4[P(C_2H_5)(C_6H_5)_2]_4$: C, 43.4; H, 3.9; Br, 20.6. Found (for separate preparative samples): C, 43.6, 43.05; H, 4.3, 4.0; Br, 20.5, 20.3%.

(vi) Tri-n-propylphosphine

The reaction between rhenium(III) bromide (0.20 g) and tri-n-propylphosphine (1.0 ml) in refluxing methanol afforded a very small crop of glistening black crystals; yield, 0.03 g (~9%). *Anal.* Calcd. for $Re_2Br_4[P(C_3H_7)_3]_4$: C, 32.4; H, 6.3; Br, 24.0. Found: C, 34.6; H, 6.4; Br, 25.7%. While the microanalytical data are not very satisfactory for the suggested stoichiometry and indicate the presence of a significant amount of contaminant (~7%), the spectral properties of this product are in accord with its formulation (see Results and Discussion Section).

The Reaction of the Rhenium(III) Bromide–Tertiary Amine Products with Methanolic HBr

The complex $[Re_3Br_6(py)_3]_n$ was dissolved in a 4:1 mixture of methanol and 50% hydrobromic acid and the resultant solution left to evaporate to dryness to afford dark purple crystals of the rhenium(III) salt $[pyH]_2Re_3Br_{11}$. *Anal.* Calcd. for $(C_5H_6N)_2Re_3Br_{11}$: C, 7.5; H, 0.75; Br, 55.0. Found: C, 7.4; H, 1.0; Br, 54.4%.

The related salts of this type derived from the other amines (3-Clpy, benz, γ-pic and pyz), were prepared using this same procedure. Their identity was confirmed by spectral measurements (see Results and Discussion Section).

Physical Measurements

These were carried out using the procedures described previously.[4,6] Those electronic absorption spectra which were measured using the diffuse-reflectance technique were recorded on a Beckman DU-2 spectrophotometer.

Analytical Procedures

Elemental microanalyses were performed by Dr. C.S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Rhenium(III) bromide reacts with heterocyclic tertiary amines in an analogous fashion to that previously found[2] for the related chloride phase. In all cases except pyrazine, which reacts to form the adduct $Re_3Br_9(pyz)_3$, reduction occurs to afford rhenium(II) species of stoichiometry $[ReBr_2L]_n$. The only difference from the chloride systems[2], is that while 3-chloropyridine gives the unreduced complex $Re_3Cl_9(3\text{-}Clpy)_3$ with rhenium(III) chloride, the related bromide is, as expected,[7] more susceptible to reduction and yields $[ReBr_2(3\text{-}Clpy)]_n$. Pyrazine is not a sufficiently strong base to reduce either Re_3Cl_9 or Re_3Br_9.

A previously study which is of relevance to the present work, concerns the report[8] that rhenium(III) bromide reacts with pyridine in acetone to produce the green rhenium(III) complex $Re_3Br_9(py)_3$. This conclusion is in error since this complex is in fact the rhenium(II) complex.

There is no doubt that these bromide complexes are close structural analogs of the related chloride derivatives. The oxidation of the rhenium(II) species $[ReBr_2L]_n$ to the rhenium(III) salts $[AmineH]_2Re_3Br_{11}$ when treated with methanol–HBr and the close similarity of the infrared (4000–600 cm^{-1}) and electronic absorption spectra (Table I) of the chlorides and bromides implies that the bromides are correctly formulated as the trimeric rhenium(II) polymers $[Re_3Br_6L_3]_n$. The electronic absorption spectra of the salts $[AmineH]_2Re_3Br_{11}$ (Table I) closely resemble the previously reported spectrum of the quinolinium derivative $[quinH]_2Re_3Br_{11}$,[8] with the exception that in our study we located an additional low energy band at ~9000 cm^{-1}. A band in this same spectral region has previously been noted[2,9] in the spectra of Re_3Cl_9 and its derivatives, so its association with the related bromides implies that the transition which is responsible must be a property of the $[Re^{III}]_3$ cluster. This spectral feature disappears when reduction to $[Re^{II}]_3$ occurs.

The X-ray photoelectron spectra of the new bromide complexes were recorded in the present investigation and the appropriate binding energies which were obtained are listed in Table II. The rhenium 4*f* binding energies are very similar to these reported previously[2,10] for the analogous chloride complexes. As before[2,10] we note that there is no significant difference in rhenium binding energies between the rhenium(III) and rhenium(II) complexes although the rhenium 4*f* peaks of $[Re_3X_6L_3]_n$ are somewhat broader than for $Re_3X_9L_3$. In the case of the γ-picoline product $[Re_3Br_6(\gamma\text{-pic})_3]_n$, the rhenium 4*f* binding energy spectrum showed that this complex was contaminated with perrhenate (rhenium $4f_{5/2,7/2}$ peaks at 47.4 and ~44.7 eV).[11] This contaminant was probably present as $[\gamma\text{-picH}]ReO_4$ since the nitrogen 1s binding energy spectrum of this product shows a peak at ~400.3eV (due to $[\gamma\text{-picH}]^+$?)

TABLE I. Electronic Absorption Spectra of Rhenium Bromide Complexes.

Complex	Medium[a]	Absorption Maxima, $\text{cm}^{-1} \times 10^{-3}$			
Rhenium(III) Derivatives					
$Re_3Br_9(pyz)_3$	DR	~8.3	12.7	~18.2sh	
	NM	8.3	12.7	17.7	21.5
$[pyH]_2Re_3Br_{11}$	MeOH/HBr	8.9	13.3	19.0sh	21.7
$[pyzH]_2Re_3Br_{11}$	MeOH/HBr	8.8	13.5	19.0sh	21.7
$[3\text{-ClpyH}]_2Re_3Br_{11}$	MeOH/HBr	8.85	13.3	19.0sh	21.8
$[\gamma\text{-picH}]_2Re_3Br_{11}$	MeOH/HBr	8.9	13.3	18.9sh	21.8
$[benzH]_2Re_3Br_{11}$	MeOH/HBr	~9.1	13.5	19.0sh	21.8
Rhenium(II) Derivatives					
$[Re_3Br_6(py)_3]_n$	DR	11.8	15.9		
$[Re_3Br_6(3\text{-Clpy})_3]_n$	DR	11.9	15.75		
$[Re_3Br_6(\gamma\text{-pic})_3]_n$	DR	11.6	15.75		
$[Re_3Br_6(benz)_3]_n$	DR	12.3	16.95		

[a] DR = diffuse reflectance; NM = nujol mull.

TABLE II. X-Ray Photoelectron Spectra of Rhenium Bromide Complexes of Heterocyclic Tertiary Amines[a].

Complex	Re		Br		N 1*s*[b]
	$4f_{5/2}$	$4f_{7/2}$[b]	$3p_{1/2}$	$3p_{3/2}$[b]	
$Re_3Br_9(pyz)_3$	44.7	42.3(1.2)	188.9	182.3(2.5)	399.7(1.6)
$[Re_3Br_6(py)_3]_n$	44.1	41.8(1.8)	188.7	182.0(2.9)	399.3(1.5)
$[Re_3Br_6(3\text{-Clpy})_3]_n$	44.3	41.9(1.7)	188.6	181.9(2.5)	399.3[d]
$[Re_3Br_6(\gamma\text{-pic})_3]_n$	44.7[c]	41.9[c]	188.5	181.7(2.6)	399.2(1.3)[e]
$[Re_3Br_6(benz)_3]_n$	44.6	42.1(1.8)	188.9	182.0(2.8)	399.6(2.2)[f]

[a] Binding energies (in eV) are quoted relative to a carbon 1*s* value of 284.0eV for graphite and are considered accurate to at least ±0.2eV. [b] FWHM values given in parentheses. [c] Additional Re 4*f* binding energies at ~44.7 and 47.4eV are due to perrhenate contaminant (see ref. 11). [d] Very weak peak. [e] Additional N 1*s* binding energy at ~400.3eV is due to $\gamma picH^+$ contaminant. [f] Large FWHM value reflects the presence of two different nitrogen environments in benzimidazole.

in addition to the nitrogen binding energy of the coordinated γ-picoline at 399.2 eV. These conclusions were supported by the infrared spectrum of this complex which revealed a broad band of medium intensity at ~900 cm^{-1} due to ReO_4^-.

Measurements of the chlorine 2*p* binding energy spectra of $Re_3Cl_9L_3$ and $[Re_3Cl_6L_3]_n$, have shown that the binding energy order is $Cl_b > Cl_t$, where Cl_b and Cl_t represent chlorine atoms in bridging and terminal Re–Cl bonds respectively, with a binding energy separation of ~1.4 eV.[2,10] In contrast to this situation, the bromine 3*p* binding energy spectra of $Re_3Br_9(pyz)_3$ and $[Re_3Br_6L_3]_n$ do not clearly show two sets of binding energies associated with Br_b and Br_t. While the bromine 3*p* peaks are significantly broader than those exhibited by complexes which contain only a *single* type of bromine environment, for example, K_2ReBr_6,[12] $[Bu_4N]_2Re_2Br_8$ and $Re_2(O_2CCH_3)_4Br_2$,[11] which have FWHM values* for the bromine $3p_{3/2}$ peaks of between 1.7 and 2.0 eV, the instrumental resolution is insufficient to separate the two sets of peaks in the spectra of $Re_3Br_9(pyz)_3$ and $[Re_3Br_6L_3]_n$. The smaller magnitude of $\Delta E_b(Br_b\text{–}Br_t)$ compared to $\Delta E_b(Cl_b\text{–}Cl_t)$[2,10] can be correlated with the different charge/size ratios for Cl and Br.

Although our studies on the reactions of rhenium(III) bromide with tertiary phosphines were not as extensive as those carried out with the tertiary amines, they are sufficient to show that reduction occurs to afford dinuclear metal–metal bonded species of the type $Re_2X_4L_4$.[4] In this respect, they closely resemble the related behavior of rhenium(III) chloride[4] in producing dinuclear species. These same complexes can usually be produced by the direct reaction of the

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* FWHM = full width at half-maximum.

octahalodirhenate(III) anions with the appropriate phosphines.[4] The one exception is the reaction of rhenium(III) bromide with ethyldiphenylphosphine. While rhenium(III) chloride and the salts, $[Bu_4N]_2Re_2Cl_8$ and $[Bu_4N]_2Re_2Br_8$ have been found to react with ethyldiphenylphosphine to yield the paramagnetic dimers $Re_2X_5(PEtPh_2)_3$,[4] rhenium(III) bromide is reduced further to produce the rhenium(II) complex $Re_2Br_4(PEtPh_2)_4$. Reasons for the different behavior of $[Bu_4N]_2Re_2Br_8$ and Re_3Br_9 with this phosphine are not obvious. Although methanol was used as the reaction solvent in both instances, in the former reaction[4] a small quantity of 48% HBr was added (to suppress hydrolysis). This latter reagent may have influenced the course of the reaction.

The spectral properties of $Re_2Br_4(PPr_3)_4$ and $Re_2Br_4(PEtPh_2)_4$ are consistent with the proposed structural formulation of these complexes, showing a close resemblance to the related spectra of $Re_2Br_4(PEt_3)_4$.[4]

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