Table I. Kinetic Parameters for Exchange of Bis(group 5)mercurials

| Compd | Solvent | E_{a} , kcal mol ⁻¹ | ΔH^{\ddagger} , kcal mol ⁻¹ | $\Delta S^{\ddagger},$ eu | k, l. mol ⁻¹ sec |
|--|-------------------------|--|--|------------------------------------|-----------------------------|
| $(Me_3Si)_2Hg^a$ | Xylene Triethylamine | 11.3 ± 0.3 11.1 + 0.7 | 10.7 ± 0.5 10.5 ± 0.7 | -21.8 ± 2.5 -22.8 ± 4.0 | 0.31 |
| $(Me_2ClSi)_2Hg^b$ $(Me_3Ge)_2Hg^a$ | Xylene Toluene | 11.1 ± 0.7 11.3 ± 0.7 12.1 ± 0.3 | 10.5 ± 0.7 11.2 ± 0.7 11.5 ± 0.5 | -23.4 ± 3.7 -18.4 ± 2.5 | 0.67 0.99 |

^a Reference 4. ^b Calculated from three separate determinations; error limits are the standard deviations from the least-squares fit for the activation parameters.

Bis(dimethylchlorosilyl)mercury is thermally stable enough to be sublimed at 80° under high vacuum and to permit the study of its self-exchange at elevated temperatures without undue decomposition. However, it is more sensitive to light than other similar compounds, discoloring under laboratory illumination in a day. This may account for the difficulty in the initial report since these authors¹ were using a photochemical preparation which would also induce decomposition. Like most other silvlmercury compounds, bis(dimethylchlorosilyl)mercury is sensitive to air, rapidly oxidizing and depositing metallic mercury.

We have previously studied the exchange of silvl groups on silylmercury compounds.⁴ Bis(trimethylsilyl)mercury scrambles trimethylsilyl groups by a second-order pathway. Exchange of dichloromethylsilyl groups in bis(dichloromethylsilyl)mercury is very much slower and was not detected on the NMR time scale in hydrocarbon solvents.

Bis(dimethylchlorosilyl)mercury in xylene also shows a second-order rate for exchange of silvl groups. The kinetic parameters are listed in Table I along with the values from previous studies for comparison. The rate of exchange is intermediate between that of bis(trimethylsilyl)mercury and bis(dichloromethylsilyl)mercury which only undergoes slow exchange.⁴ The order of the reaction and negative entropy of activation are consistent with a bridged transition state previously described.4

Experimental Section

All manipulations were performed with the exclusion of air and water. Dimethylchlorosilane was a commercial product obtained from both PCR and Pierce Chemical Co. It was degassed on the vacuum line and used without further purification. Di-tert-butylmercury was prepared by the method of Neumann⁵ and sublimed before use. All NMR spectra were obtained using a Varian A-60A operating at 60 mHz.

Bis(dimethylchlorosilyl)mercury. Into a Pyrex tube fitted with a breakseal and separated into two chambers with a coarse glass frit was distilled 16.16 g (51.33 mmol) of di-tert-butylmercury and 10.70 g (113.1 mmol) of dimethylchlorosilane. The tube was sealed off under vacuum and heated in an oil bath at 85°. After 2 days the solution was green and white crystals precipitated on cooling. The crystals were filtered on the glass frit by cooling one end of the tube. The crystals were washed by distilling back some of the reaction mixture. The tube was attached to the vacuum line, the breakseal was opened, and the volatile products were pumped out. The tube was broken open under argon to give 0.91 g of a gummy green solid, metallic mercury, and 7.03 g (18.1 mmol, 35.3% of the theoretical yield) of bis(dimethylchlorosilyl)mercury. Sublimation under high vacuum at 80° gave snow white crystals. A melting point determined by slow heating from room temperature was 128.5-130.5°; starting at 125° gave mp 130.5-131.8°. The ¹H NMR spectrum in xylene showed a single resonance characteristic of a methyl group on silicon at δ 0.32, flanked by mercury-199 and silicon-29 satellites: ${}^{3}J_{199}Hg^{-1}H = 36.6$ Hz, ${}^{3}J^{29}Si^{-1}H = 6.6$ Hz. The mass spectrum showed a parent ion at m/e 388 (1Hg, 2Cl isotope pattern): m/e 373, P – Me; m/e 353, P - Cl; m/e 295, P - Me2ClSi; m/e 202, Hg+; m/e 93, Me2ClSi+ (base peak). All fragments showed the appropriate isotopic patterns.

Exchange Studies. Rates of exchange were determined by NMR techniques. The lifetimes were calculated by the slow exchange approximation from the width at half-height of the mercury-199 satellites. A correction was made on the concentrations of Hg-(SiClMe2)2 to account for the thermal and photochemical decomposition which occurred during each kinetic run. This correction was made by integration of the methyl resonances of the Hg(SiClMe2)2 and of the decomposition product (Me₂ClSiSiClMe₂) and use of these data to calculate a new concentration of Hg(SiClMe₂)₂ from the ratio of its area to the total peak area and the original concentration. Absolute rates were determined by correcting for exchange between magnetically equivalent sites.4

Registry No. Bis(dimethylchlorosilyl)mercury, 55669-58-4; dimethylchlorosilane, 1066-35-9; di-tert-butylmercury, 23587-90-8.

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X-Ray Photoelectron Spectra of Inorganic Molecules. X.¹ Binding Energy Shifts within the Series of Metal-Metal Bonded Dimers $Re_2X_{6-n}(PR_3)_{2+n}$, Where X = Cl or Br and n = 0, 1, or 2

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In making comparisons of core electron binding energies between transition metal complexes in different oxidation states, account must be taken of changes in coordination number, ligands, and structure type. Since it is often impossible to keep most of these features unchanged as the metal oxidation state is varied, a meaningful interpretation of metal core binding energy shifts can become rather difficult. In our studies of the X-ray photoelectron spectra of complexes of the heavy transition elements²⁻⁴ such considerations were particularly important since charge variations occur at rather large metal centers and consequently binding energy shifts are proportionately smaller than those observed for the lighter elements. Our earlier comparative studies⁴⁻⁷ on low oxidation state halide complexes of rhenium, possessing widely different structures, showed only small variations in rhenium 4f5/2 and $4f_{7/2}$ binding energies and often no simple correlation between these energies and the formal metal oxidation state.

We have recently synthesized and structurally characterized^{8,9} a series of dinuclear tertiary phosphine complexes of rhenium of stoichiometries $Re_2X_5(PR_3)_3$ and $Re_2X_4(PR_3)_4$ (X = Cl or Br) which have structures closely related to those of the rhenium(III) dimers of the type Re₂X₆(PR₃)₂.^{10,11} An investigation of the X-ray photoelectron spectra of these complexes has revealed some striking differences in rhenium 4f binding energies. These results are now presented and their significance discussed.

| Table I. | X-Ray | Photoelectron | Spectra | of ! | Dinuclear | Rhenium | Complexes ^a |
|----------|-------|---------------|---------|------|-----------|---------|------------------------|
|----------|-------|---------------|---------|------|-----------|---------|------------------------|

| | R | le | Cl | | | | Br | | |
|---|------------|-------------------|-------|-------|-------------------|-------------|-------------|-------------------|-------------------|
| Complex | 4f 5/2 | 4f _{7/2} | 2p, | /2 | 2p _{3/2} | P 2p | C 1s | 3p _{1/2} | 3p _{3/2} |
| Re ₂ Cl ₄ (PEt ₂) ₄ | 43.3 (1.4) | 40.9 (1.4) | 200.1 | | 198.5 (1.3) | 130.9 (1.7) | 284.9 (1.4) | | |
| $\operatorname{Re}_{2}\operatorname{Cl}_{4}(\operatorname{P}(n-\operatorname{Pr})_{2})_{4}$ | 43.5 (1.2) | 41.2 (1.2) | 200.1 | | 198.4 (1.2) | 130.9 (1.6) | 284.9 (1.4) | | |
| Re, Cl, (PEt, Ph) | 43.5 (1.4) | 41.1 (1.3) | 200.0 | | 198.4 (1.3) | 131.0 (1.7) | 284.7 (1.3) | | |
| Re, Br, (PEt) | 43.5 (1.4) | 41.1 (1.2) | | | | 130.9 (1.6) | 284.8 (1.3) | 188.8 | 182.3 (2.1) |
| Re, Cl, (PEtPh,) | 44.1 (1.7) | 41.7 (1.7) | 200.1 | | 198.5 (1.3) | 131.2 (1.6) | 284.6 (1.3) | | |
| Re, Cl, (PMePh,), | 44.2 (2.0) | 41.8 (1.8) | 199.9 | | 198.4 (1.4) | 131.2 (1.8) | 284.5 (1.3) | | |
| Re ₂ Br ₂ (PEtPh ₂) ₃ | 43.9 (2.1) | 41.6 (1.9) | | | | 131.0 (1.9) | 284.3 (1.3) | 188.6 | 182.0 (2.3) |
| Re, Br, (PMePh,), | 43.9 (1.9) | 41.5 (1.7) | | | | 131.1 (1.9) | 284.2 (1.3) | 188.7 | 182.0 (2.0) |
| $\operatorname{Re}_{2}\operatorname{Cl}_{5}(\operatorname{PEt}_{3})_{2}$ | 44.9 (1.4) | 42.5 (1.4) | 200.2 | | 198.5 (1.4) | 131.3 (1.8) | 284.7 (1.5) | | |
| $\operatorname{Re}_{2}\operatorname{Cl}_{6}(\operatorname{P}(n-\operatorname{Pr})_{3})_{2}$ | 45.0 (1.4) | 42.5 (1.4) | 200.3 | | 198.7 (1.3) | 131.5 (1.7) | 284.7 (1.3) | | |
| Re ₂ Cl ₆ (PEt, Ph), | 45.1 (1.4) | 42.6 (1.3) | 200.1 | | 198.5 (1.3) | 131.4 (1.7) | 284.6 (1.3) | | |
| Re, Cl, (PEtPh,), | 44.9 (1.4) | 42.5 (1.3) | 200.1 | | 198.6 (1.4) | 131.4 (1.7) | 284.5 (1.4) | | |
| Re ₂ Cl ₆ (PMePh ₂) ₂ | 45.1 (1.4) | 42.7 (1.3) | 199.9 | | 198.4 (1.3) | 131.3 (1.5) | 284.5 (1.2) | | |
| $\operatorname{Re}_{2}\operatorname{Br}_{6}(\operatorname{PEt}_{3})_{2}$ | 44.7 (1.1) | 42.3 (1.0) | | | | 131.1 (1.6) | 284.2 (1.0) | 188.7 | 182.0 (1.8) |
| Re ₂ Br ₆ (PEt, Ph), | 44.8 (1.1) | 42.3 (1.1) | | | | 131.3 (1.7) | 284.2 (1.0) | 188.7 | 182.0 (1.9) |
| $\operatorname{Re}_{2}\operatorname{Br}_{6}(\operatorname{PEtPh}_{2})_{2}$ | 44.9 (1.3) | 42.5 (1.2) | | | | 131.4 (1.7) | 284.3 (1.3) | 188.8 | 182.1 (2.0) |
| $\operatorname{Re}_{2}\operatorname{Br}_{6}(\operatorname{PMePh}_{2})_{2}$ | 44.7 (1.3) | 42.2 (1.2) | | | | 131.0 (1.7) | 284.0 (1.2) | 188.6 | 181.9 (2.0) |
| $\operatorname{Re}_{2}\operatorname{Br}_{6}(\operatorname{PPh}_{3}),$ | 44.7 (1.3) | 42.3 (1.3) | | | | 131.3 (1.9) | 284.2 (1.2) | 188.6 | 182.0 (1.9) |
| $\operatorname{Re}_{2}\operatorname{Cl}_{4}\operatorname{Br}_{2}(\operatorname{PEt}_{3})_{2}$ | 44.9 (1.6) | 42.4 (1.5) | 199.7 | | 198.1 (1.4) | 132.2 (1.9) | 284.4 (1.5) | 188.5 | 181.7 (2.3) |
| $\operatorname{Re}_{2}\operatorname{Cl}_{4}\operatorname{Br}_{2}(\operatorname{PPh}_{3})_{2}$ | 44.8 (1.5) | 42.2 (1.5) | 199.8 | | 198.1 (1.2) | 131.6 (1.9) | 284.2 (1.3) | 188.6 | 182.1 (2.0) |
| $(Et_3PCl)_2Re_2Cl_8$ | 45.3 (1.5) | 42.9 (1.5) | 202.3 | 200.0 | 198.3 (1.4) | 132.6 (1.6) | 284.8 (1.5) | | |
| $(Bu_4N)_2Re_2Cl_8$ | 45.2 (1.4) | 42.8 (1.3) | 199.9 | | 198.4 (1.3) | | | | |
| $(Et_3PCl)_2Re_2Br_4Cl_4$ | 44.8 (2.0) | 42.4 (1.8) | 202.2 | 200.3 | 198.2 (1.4) | 132.5 (1.7) | 284.7 (1.3) | 188.7 | 182.0 (2.2) |

^a All spectra are referenced to the C 1s binding energy of graphite taken as 284.0 eV; fwhm values are given in parentheses.

Experimental Section

Spectral Measurements. The X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum K $\alpha_{1,2}$ line (1486.6 eV) was used as the X-ray excitation source. Sample preparation and full details of the experimental procedure are described fully elsewhere.^{1,12}

Preparation of Metal Complexes. Samples of the crystalline complexes $Re_2X_6(PR_3)_2$, $Re_2X_5(PR_3)_3$, and $Re_2X_4(PR_3)_4$, where X = Cl or Br, were available from an earlier study.^{8,9} The complexes $(Et_3PCl)_2Re_2Br_4Cl_4$, $(Et_3PCl)_2Re_2Cl_8$, and $Re_2Cl_4Br_2(PEt_3)_2$ were products of the carbon tetrachloride oxidation of $Re_2X_4(PEt_3)_4$, where X = Cl or Br.⁹ The mixed-halide complex $Re_2Cl_4Br_2(PEt_3)_2$ was prepared by the addition of triphenylphosphine to an acetone solution of $(Et_3PCl)_2Re_2Br_4Cl_4$.⁹ The salt $(Bu_4N)_2Re_2Cl_8$ was prepared by the usual literature procedure.¹⁰

Microanalytical data and infrared and electronic absorption spectral measurements confirmed the purity and identity of these complexes.

Results and Discussion

Rhenium 4f, chlorine 2p, bromine 3p, phosphorus 2p, and carbon 1s binding energies of the tertiary phosphine complexes are presented in Table I. The appropriate fwhm values are also given in this table. Binding energy measurements were usually conducted in triplicate on different preparative samples of the compounds. The binding energies were located with a precision of ± 0.1 eV and are considered accurate to at least ± 0.2 eV, relative to a carbon 1s binding energy of graphite at 284.0 eV.² To check the instrumental performance, we recorded the related binding energy spectrum of the salt (Bu4N)₂Re₂Cl₈ and compared these data with those reported in an earlier study.7 The agreement between the corresponding energies and fwhm values was excellent. Typical rhenium 4f7/2 and chlorine 2p3/2 fwhm values in Table I are similar to those observed for other rhenium chloride complexes,^{4,7} and the data are therefore considered to be of acceptable quality.

For the group of 20 complexes in Table I which comprise the series $\text{Re}_2X_{6-n}(\text{PR}_3)_{2+n}$, the rhenium $4f_{7/2}$ binding energies occur in the range 40.9-42.7 eV and reveal a clear dependence upon the *formal* metal oxidation state: 40.9-41.2 eV for Re(+2); 41.5-41.8 eV for Re(+2.5); 42.2-42.7 eV for $\text{Re}(+3).^{13}$ The magnitudes of these energy shifts are significantly greater than those observed in our earlier studies on rhenium complexes.^{4,7} This we attribute to the very close structural similarity within the present series of complexes, wherein the replacement of halide by tertiary phosphine ligands occurs in a systematic and regular fashion $(I \rightarrow II \rightarrow III)$.^{8,9}



The fwhm values for the rhenium 4f binding energies of the paramagnetic complexes $Re_2X_5(PR_3)_3$ are greater than comparable data for diamagnetic $Re_2X_6(PR_3)_2$ and Re_2X_4 - $(PR_3)_4$. The explanation for this broadening effect is either that it reflects the occurrence of "multiplet splittings",16,17 due to coupling of the hole in the metal 4f core with the unfilled rhenium valence shell, or that it arises from the presence of two dissimilar rhenium environments (see structure II) within these dinuclear species. We favor the latter explanation since no such broadening effects arising from "multiplet splittings" are observed with the paramagnetic complexes ReCl4(PPh3)27 and $K_2 Re X_{6.4}$ Also, a significant peak broadening has been previously noted for the unsymmetrical dinuclear 2,5dithiahexane complex Re₂Cl₅(DTH)₂ (fwhm of 2.2 eV for the Re $4f_{7/2}$ peak).⁴ The greater magnitude of this effect for the latter complex (i.e., 2.2 eV vs. ~ 1.8 eV for Re₂X₅(PR₃)₃) is in agreement with the greater disparity in the environments of the two rhenium centers in $Re_2Cl_5(DTH)_2^{18}$ compared to $Re_2Cl_5(PR_3)_3$ (see structure II).

In explaining the rhenium 4f binding energy chemical shifts within the series $\text{Re}_2X_{6-n}(\text{PR}_3)_{2+n}$, it is tempting to conclude that the variation in binding energies is only a reflection of differences in the initial state charge distributions, with the order of decreasing metal charge being $Re_2X_6(PR_3)_2 >$ $Re_2X_5(PR_3)_3 > Re_2X_4(PR_3)_4$, i.e., Re(+3) > Re(+2.5) >Re(+2). While this may be true, it is also quite possible that final state relaxation effects^{19,20} enhance this trend. Although the treatment of relaxation effects is much more complicated for the condensed than the gaseous phase, it is perhaps reasonable (to a first approximation) if we ignore secondary intermolecular interactions for the series of insulators $\operatorname{Re}_{2}X_{6-n}(\operatorname{PR}_{3})_{n+2}$. Certainly, crystallographic data for Re₂Cl₆(PEt₃)²¹¹ and Re₂Cl₄(PEt₃)⁴⁸ support such a premise. In the studies by Martin and Shirley²¹ on the binding energy shifts in simple aliphatic alcohols, it was found that the relaxation energy (E_R) increased with the molecular size of a substituent group, thereby resulting in a decrease in observed



Figure 1. Chlorine 2p binding energy spectra of (a) (Et₃PCl)₂Re₂Br₄Cl₄ and (b) (Et₃PCl)₂Re₂Cl₈ showing deconvolutions into two sets of $Cl 2p_{1/2}$, $2p_{3/2}$ doublets.

binding energy at the oxygen atom. Applying such an argument to $\operatorname{Re}_2 X_{6-n}(\operatorname{PR}_3)_{n+2}$ would imply that as the halide ligands are progressively replaced by the larger tertiary phosphines, the relaxation energy should increase, since the latter ligands are more able to distribute excess positive charge effectively. In other words, both differences in initial state charge distributions and final state relaxation effects probably contribute (in the same sense) to the observed rhenium 4f binding energy shifts. It is clearly impossible to unravel the relative magnitudes of these different contributions to the overall binding energy shifts for these particular complexes.

The other core binding energies recorded on these phosphine complexes (Table I) are, with the exception of the phosphorus 2p energies, quite normal and are not further discussed. The phosphorus 2p binding energies span the range 130.9-132.2 eV, which approaches the spread of values (131.1-132.0 eV) observed for a series of phosphine complexes of platinum(II).15 If we internally reference these data to a carbon 1s binding energy of 285.0 eV for the tertiary phosphine ligands,¹⁵ the phosphorus 2p binding energy order becomes Re₂X₆(PR₃)₂ $\gtrsim \text{Re}_2 X_5(\text{PR}_3)_3 > \text{Re}_2 X_4(\text{PR}_3)_4$. Such a trend may reflect an increasing degree of rhenium to phosphorus π -back bonding as the rhenium oxidation state decreases.

Finally, we wish to comment upon the X-ray photoelectron spectra of the salts (Et₃PCl)₂Re₂Cl₈ and (Et₃PCl)₂Re₂Br₄Cl₄, which are formed⁹ by the carbon tetrachloride oxidation of Re₂Cl₄(PEt₃)₄ and Re₂Br₄(PEt₃)₄, respectively. The values of the rhenium 4f binding energies are in accord with their formulation as rhenium(III) dimers. However, of considerably more interest is the observation that the fwhm values for the Re₂Br₄Cl_{4²⁻} anion are greater than for the chloro anion Re₂Cl_{8²⁻} (Table I), consistent with the presence of dissimilar rhenium environments in the former species. We have previously noted⁹ that the salt (Et₃PCl)₂Re₂Br₄Cl₄ exhibits an infrared-active $\nu(Re-Re)$ mode, implying that this anion is noncentrosymmetric. Such a situation would arise if the isomer we have isolated is one in which unequal numbers of chloride and bromide ligands are bonded to the two rhenium centers, i.e., [Br₃ClRe–ReBrCl₃]^{2-.} In this same connection we note that the phosphine complexes Re₂Cl₄Br₂(PR₃)₂ possess fwhm values for their rhenium 4f binding energies which are the largest for those of any of the complexes of the type $Re_2X_6(PR_3)_2$. This again parallels our observation of an infrared-active $\nu(Re-Re)$ mode for the triethylphosphine derivative⁹ and supports a structure in which the two rhenium environments are different, as in the isomer [(PR3)- $Br_2ClRe-ReCl_3(PR_3)$].

The chlorine 2p spectra of the complexes (Et₃PCl)₂Re₂Cl₈ and (Et₃PCl)₂Re₂Br₄Cl₄ both exhibit a three-peak pattern (Figure 1) arising from a near coincidence in the energy of a chlorine $2p_{1/2}$ component of one type of chlorine with the energy of a $2p_{3/2}$ component of another type. Deconvolution of the chlorine 2p binding energy spectra was carried out using the procedure previously described.¹ The deconvoluted spectrum for (Et₃PCl)₂Re₂Br₄Cl₄ exhibited four components in the intensity ratio 1.0:1.9:1.9:3.9, in excellent agreement with the ratio of 1:2:2:4 expected for a complex which possesses two types of chlorine environments in the stoichiometric ratio 1:2. The corresponding deconvoluted spectrum of (Et₃PCl)₂Re₂Cl₈ had peak intensity ratios of 1.0:2.0:3.9:7.5, again in satisfactory agreement with the ratio 1:2:4:8 which is expected for a 1:4 stoichiometric ratio of chlorines. The binding energies for the deconvoluted peaks were 202.1, 200.7, 199.9, and 198.3 eV for (Et₃PCl)₂Re₂Br₄Cl₄ and 201.8, 200.4, 199.8, and 198.3 eV for (Et₃PCl)₂Re₂Cl₈. The high binding energy doublet in each spectrum is clearly assigned to the chlorine in the phosphonium cation based upon the observed intensity ratios. This binding energy order presumably reflects a strong electron-withdrawing effect by the phosphorus atom, which lowers the electron density of the chlorine atom within the (Et₃PCl)⁺ cation and, consequently, increases its core electron binding energies relative to chlorine bound to rhenium.

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Registry No. Re₂Cl₄(PEt₃)₄, 52359-06-5; Re₂Cl₄(P(n-Pr)₃)₄, 52359-07-6; Re2Cl4(PEt2Ph)4, 52359-08-7; Re2Br4(PEt3)4, 52359-09-8; Re2Cl5(PEtPh2)3, 55450-45-8; Re2Cl5(PMePh2)3, 55450-43-6; Re2Br5(PEtPh2)3, 55450-46-9; Re2Br5(PMePh2)3, 55450-44-7; $\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2$, 19584-31-7; $\text{Re}_2\text{Cl}_6(\text{P}(n-\text{Pr})_3)_2$, 41021-44-7; Re₂Cl₆(PEt₂Ph)₂, 55333-38-5; Re₂Cl₆(PEtPh₂)₂, 55661-10-4; Re2Cl6(PMePh2)2, 55661-11-5; Re2Br6(PEt3)2, 55661-12-6; Re2Br6(PEt2Ph)2, 55661-13-7; Re2Br6(PEtPh2)2, 55661-14-8; Re2Br6(PMePh2)2, 55661-15-9; Re2Br6(PPh3)2, 51826-46-1; Re2Cl4Br2(PEt3)2, 55661-16-0; Re2Cl4Br2(PPh3)2, 55661-17-1; $(Et_3PCl)_2Re_2Cl_8$, 52325-11-8; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0; (Et3PCl)2Re2Br4Cl4, 52325-13-0.

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