$[RuBr_2(dpp)_2]$ in 1,2-dichloroethane is not repressed in the presence of excess Br^- ions and that addition of X^- ions to a 1,2-dichloroethane solution of $[RuX(dpp)_2]^+$ produces no detectable changes in the visible spectra even over long periods of time (1 week). Moreover, the dichloro derivative slowly reacts in 1,2-dichloroethane with Br^- ions, giving the cation $[RuBr(dpp)_2]^+$, probably through a $[RuClBr(dpp)_2]$ intermediate.

Monomeric five-coordinate structures are assigned to the diamagnetic $[RuX(dpp)_2]PF_6$ complexes, on the basis of their physical properties. Polymeric structures containing halogen bridges are ruled out from ir spectra (in Nujol mull) of $[RuCl(dpp)_2]PF_6$, which exhibit a single band assignable as Ru–Cl stretching at 280 cm^{-1}, in the range expected for terminal chlorine groups.[7] Both the chloro and the bromo derivatives behave as uni-univalent electrolytes in nitromethane solutions. The nature of a 1:1 electrolyte of $[RuCl(dpp)_2]PF_6$ has been confirmed by the method of Hayter.[9] The slope of the plot of equivalent conductance against the square root of the equivalent concentration is in good agreement with the values calculated for 1:1 electrolytes. Also ionic weight measurements of $[RuCl(dpp)_2]PF_6$ in 1,2-dichloroethane are consistent with a monomeric structure (see Table II).

Electronic absorption spectra of $[RuX(dpp)_2]^+$ complexes, which are very similar to each other and virtually identical both in the solid state and in solution, show two bands at 18,000 and 22,000 cm^{-1}, with a well-developed shoulder at higher frequencies. According to the simple crystal-field model for a five-coordinate d^6 ion in a strong field, the observed diamagnetism of the $[RuX(dpp)_2]PF_6$ complexes suggests a more or less distorted square pyramidal geometry. If we assume for the $[RuX(dpp)_2]^+$ chromophores a C_{4v} symmetry, the observed bands can be tentatively assigned, on the basis of the energy-levels diagram recently proposed by Sacconi,[10] to the transitions $^1A_1 \rightarrow {}^1B_2$, $^1A_1 \rightarrow {}^1E^a$, and $^1A_1 \rightarrow {}^1A_2$. A fourth transition ($^1A_1 \rightarrow {}^1E^b$), which is expected for such a symmetry, is probably masked by the charge-transfer bands.

It is interesting to note that attempts to obtain similar five-coordinate cations starting from the *trans*-$[RuX_2((C_6H_5)_2P(CH_2)_nP(C_6H_5)_2)]$ (n = 1, 2) have been unsuccessful. Presumably the increased chain length of the dpp ligand causes a larger crowding in the plane of the six-coordinate *trans*-$[RuX_2(dpp)_2]$ complexes, in such a manner that the elimination of one halide ion and the achievement of five coordination becomes favorable.

According to its coordinatively unsaturated nature, the compound $[RuCl(dpp)_2]PF_6$ readily adds in 1,2-dichloroethane 1 mol of CO per mol of complex, giving colorless solutions, from which the white diamagnetic solid $[RuCl(CO)(dpp)_2]PF_6$ may be recovered (ν_{CO} 1930 cm^{-1}). The carbonyl adduct can be assigned a trans configuration in view of the position of the Ru–Cl stretching frequency (300 cm^{-1}), which falls in the range expected for terminal chlorine trans to a CO group.[2,7] When the alkyl chain of the diphosphine is lengthened, ruthenium(II) complexes of unusual stoichiometry are obtained. Thus, the interaction of excess of 1,4-bis(diphenylphosphino)butane (dpb) with boiling aqueous ethanolic solutions of $K_2[RuCl_5(H_2O)]$ or with dichloromethane solutions of $[RuCl_2(P(C_6H_5)_3)_3]$ produces green compounds, which, depending on the excess of diphosphine used, appear to contain from 3 to 1.5 mol of diphosphine per ruthenium atom.

Repeated crystallizations of the crude products from chlorobenzene–diethyl ether give finally a green complex of composition $RuCl_2(dpb)_{1.5}$. The complex is diamagnetic and nonelectrolytic in nitromethane and, on the basis of spectroscopic data, is assigned a binuclear five-coordinate structure with a diphosphine molecule bridging two ruthenium atoms.

The electronic spectrum of $[RuCl_2(dpb)_{1.5}]_2$ exhibits, both in the solid state and in solution of 1,2-dichloroethane, two bands at 14,700 and 21,700 cm^{-1}, with a shoulder at higher frequencies. This spectrum shows strong similarities to those reported recently by James[11] for the five-coordinate $[RuCl_2(P(C_6H_5)_3)_3]$ (two bands at 20,900 and 13,000 cm^{-1}) and is consistent with the presence of a five-coordinate ruthenium(II) with a P_3Cl_2 donor atom set. Trans arrangement of the chlorine atoms is indicated by the appearance of a single band at 320 cm^{-1} in the Ru–Cl stretching region.

In agreement with a five-coordinate structure, $[RuCl_2(dpb)_{1.5}]_2$ readily takes up in the solid state 1 mol of CO per ruthenium atom, to give a yellow monocarbonyl derivative $[RuCl_2(CO)(dpb)_{1.5}]_2$ (ν_{CO} 1990 cm^{-1}; ν_{RuCl} 320 cm^{-1}). When this complex is crystallized from dichloromethane–ethanol, isomerization occurs and a white compound of the same composition is obtained (ν_{CO} 1950 cm^{-1}; ν_{RuCl} 290 and 255 cm^{-1}), in which the carbonyl group is probably trans to a chlorine.[7]

Molecular weight determinations for $[RuCl_2(CO)(dpb)_{1.5}]_2$ (in $CHCl_3$: found, 1630; calcd, 1679) indirectly confirm the dimeric nature of $[RuCl_2(dpb)_{1.5}]_2$ which cannot directly be proved, owing to the low solubility of the compound in the usual solvents.

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Registry No. *trans*-$[RuCl_2(dpp)_2]$, 55669-28-8; *trans*-$[RuBr_2(dpp)_2]$, 55669-29-9; $[RuCl(dpp)_2]PF_6$, 55669-31-3; $[RuBr(dpp)_2]PF_6$, 55669-33-5; $[RuCl(CO)(dpp)_2]PF_6$, 55669-35-7; $[RuCl_2(dpb)_{1.5}]_2$, 55669-36-8; $[RuCl_2(CO)(dpb)_{1.5}]_2$, 55669-37-9; $K_2[RuCl_5(H_2O)]$, 14404-33-2; $[RuCl_2(P(C_6H_5)_3)_3]$, 15529-49-4.

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Preparation, Properties, and Self-Exchange of Bis(dimethylchlorosilyl)mercury

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Bettler, Sendra, and Urry reported that bis(dimethylchlorosilyl)mercury could be formed at low temperatures, but decomposed above −79°.[1] This is surprising since both bis(trimethylsilyl)mercury and bis(dichloromethylsilyl)mercury are thermally stable at room temperature.[1,2] This anomalous behavior prompted us to prepare and study bis(dimethylchlorosilyl)mercury.

Reaction of dimethylchlorosilane with di-*tert*-butylmercury at 85° gave a light green solution from which white crystals precipitated on cooling. NMR and mass spectra unequivocally established this material as bis(dimethylchlorosilyl)mercury.[3]

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

Compd	Solvent	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	k, l. mol^{-1} sec
$(Me_3Si)_2Hg$[a]	Xylene	11.3 ± 0.3	10.7 ± 0.5	−21.8 ± 2.5	0.31
	Triethylamine	11.1 ± 0.7	10.5 ± 0.7	−22.8 ± 4.0	0.17
$(Me_2ClSi)_2Hg$[b]	Xylene	11.3 ± 0.7	11.2 ± 0.7	−23.4 ± 3.7	0.67
$(Me_3Ge)_2Hg$[a]	Toluene	12.1 ± 0.3	11.5 ± 0.5	−18.4 ± 2.5	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 authors[1] were using a photochemical preparation which would also induce decomposition. Like most other silylmercury compounds, bis(dimethylchlorosilyl)mercury is sensitive to air, rapidly oxidizing and depositing metallic mercury.

We have previously studied the exchange of silyl 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 silyl 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 Neumann[5] 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: $^3J_{^{199}Hg-^1H} = 36.6$ Hz, $^3J_{^{29}Si-^1H} = 6.6$ 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 − Me_2ClSi; m/e 202, Hg^+; m/e 93, Me_2ClSi^+ (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 $Hg(SiClMe_2)_2$ 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 $Hg(SiClMe_2)_2$ and of the decomposition product ($Me_2ClSiSiClMe_2$) and use of these data to calculate a new concentration of $Hg(SiClMe_2)_2$ 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 elements[2–4] 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 studies[4–7] on low oxidation state halide complexes of rhenium, possessing widely different structures, showed only small variations in rhenium $4f_{5/2}$ 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 $Re_2X_6(PR_3)_2$.[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.