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Formation of Mononuclear and Dinuclear Halide Complexes of Rhenium from Reactions of the Polyhydrides $Re_2H_8(PR_3)_4$ and $ReH_7(PR_3)_2$ with Allyl Halides and Other Halogen-Containing Reagents

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Reactions occur between $ReH_7(PPh_3)_2$ and the allyl halides C_3H_5X (X = Cl, Br, and I) to afford the rhenium(IV) salts $(Ph_3PC_3H_5)_2ReX_6$; H_2 and propene (plus a trace of propane) are the principal gaseous products. Allyl thiocyanate reacts in an analogous fashion. The pentahydride complexes $ReH_5(PPh_3)_2L$ ($L = C_6H_{11}NH_2$ and $C_5H_{10}NH$) are also converted to $(Ph_3PC_3H_5)_2ReCl_6$, H_2, and propene by allyl chloride. The dinuclear core of $Re_2H_8(PPh_3)_4$ is preserved upon reaction with allyl chloride and bromide to give the quadruply bonded dirhenium species $(Ph_3PC_3H_5)_2Re_2X_8$ (X = Cl or Br) plus H_2 and propene. In contrast to this, the reaction with allyl iodide results in the cleavage of the Re–Re bond and the formation of $(Ph_3PC_3H_5)_2ReI_6$. The mononuclear polyhydride complex $ReH_7(PPh_3)_2$ also reacts with the chlorocarbons CCl_4, $CHCl_3$, CH_2Cl_2, Me_3CCl, and C_6H_5Cl to produce *trans*-$ReCl_4(PPh_3)_2$ with the concomitant evolution of H_2 and some hydrocarbons. The treatment of $Re_2H_8(PPh_3)_4$ with gaseous hydrogen chloride in methanol is unusual in that crystals of the mixed rhenium(III)–rhenium(IV) salt $(Ph_3PH)_2Re_2Cl_8{\cdot}5(Ph_3PH)ReCl_5(PPh_3)$ are formed. The course of these reactions is discussed, and the properties of the rhenium-containing complexes are described.

Introduction

Polyhydride complexes of rhenium[1] have recently become the focus of renewed interest from the point of view of both their photochemical properties[2-4] and their thermal reactions with various unsaturated organic molecules, especially arenes[5] and dienes.[6,7] Additionally, the discovery that they can activate the C–H bonds of cyclopentane[8] attests to the likelihood that they will continue to serve as vehicles for the development of new organometallic chemistry.

Our own interests in polyhydrides of the types $ReH_7(PR_3)_2$, $ReH_5(PR_3)_3$, and $Re_2H_8(PR_3)_4$ have, up to the present time, revolved around studies of their electrochemical redox properties[9] and their thermal reactions with isocyanide ligands,[9,10] the latter having led to high-yield syntheses of the rhenium(I) cations $[Re(CNR)_4(PR_3)_2]^+$, species which are not available by conventional substitution reactions of $[Re(CNR)_6]^+$ with tertiary phosphines. In a further development of the reaction chemistry of these polyhydride complexes, we now describe the results of our studies of their thermal reactions with halogen-containing organics (allyl halides, carbon tetrachloride, etc.) and, in the case of $Re_2H_8(PPh_3)_4$, reaction with concentrated hydrochloric acid. The reactions of $Re_2H_8(PPh_3)_4$ are of additional note since they are of relevance to the chemistry of multiply bonded dimetal species.[11]

Experimental Section

Starting Materials. Potassium perrhenate was purchased from Pressure Chemical Co. Triphenylphosphine was purchased from the Eastman Kodak Co. and used without recrystallization while the other tertiary phosphines were supplied by Strem Chemicals. Anhydrous sodium borohydride (98%) was obtained from the J. T. Baker Chemical Co. Allyl chloride, allyl bromide, allylamine, and allyl isothiocyanate were purchased from Aldrich Chemical Co. and used as received. Allyl iodide was obtained from Alfa and used without further purification. The following compounds were prepared by standard literature methods: $(n\text{-}Bu_4N)_2Re_2Cl_8$,[12] $Re_2Cl_6(PPh_3)_2$,[13] $ReH_5(PPh_3)_2L$ ($L = C_6H_{11}NH_2$ or $C_5H_{10}NH$),[14] $MoH_4(PMePh_2)_4$.[15] $ReH_7(PPh_3)_2$ was prepared by the procedure of Chatt and Coffey[14] using modifications previously reported.[10] $Re_2H_8(PPh_3)_2$ was prepared by one of two methods: either by heating under reflux for 2 h a suspension of $ReH_7(PPh_3)_2$ in ethanol[14] or by the reaction of $Re_2Cl_6(PPh_3)_2$ with $NaBH_4$.[16] The latter procedure was modified over that we used previously,[16] as a result of which the yields were improved considerably; these preparative details are described below.

Reaction Conditions. All reactions were run under an atmosphere of pure nitrogen, and all solvents were deoxygenated and purified prior to use.

A. Preparation of $Re_2H_8(PPh_3)_4$. A 100-mL, three-necked, round-bottom flask, equipped with a reflux condenser, was charged with 0.940 g (0.847 mmol) of $Re_2Cl_6(PPh_3)_2$, 0.475 g (1.81 mmol) of PPh_3, and 25 mL of absolute ethanol. The suspension was stirred at room temperature for 30 min, and 0.5 g of solid $NaBH_4$ was then added. The mixture was again stirred for 15 min and then heated to reflux (caution should be taken to minimize frothing). After 15 min of reflux, the mixture was filtered while still warm and the dark red precipitate collected and washed with ~100 mL of methanol (to dissolve any unreacted $NaBH_4$). Since the solid contained an appreciable quantity of sodium chloride, it was next washed with a 4:1 water–ethanol mixture, followed by ethanol and finally diethyl ether, and then vacuum dried; yield 1.06 g (87%). At this point the product may still contain some solvent of crystallization. We have found that this may be removed by refluxing a suspension of the complex in acetonitrile. Anal. Calcd for $C_{72}H_{68}P_4Re_2$: C, 60.49; H, 4.79. Found: C, 60.27; H, 5.05.

A crystalline carbon disulfide solvate $Re_2H_8(PPh_3)_4{\cdot}2CS_2$ was obtained by dissolving $Re_2H_8(PPh_3)_4$ in carbon disulfide and filtering this into 2-propanol. Anal. Calcd for $C_{74}H_{68}P_4Re_2S_4$: C, 56.19; H, 4.33. Found: C, 57.06; H, 4.40.

B. Reactions of $ReH_7(PPh_3)_2$ with Allyl Halides. (i) $(Ph_3PC_3H_5)_2ReCl_6$. A quantity of $ReH_7(PPh_3)_2$ (0.20 g, 0.28 mmol) was dissolved in 15 mL of tetrahydrofuran, and 1.0 mL (12.3 mmol)

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of allyl chloride was added. This mixture was refluxed for 1.5 h and then cooled to room temperature. The yellow-green precipitate was filtered off, washed with THF and diethyl ether, and dried under vacuum. Concentration of the mother liquor afforded a second batch of product. It was purified by recrystallization from dichloromethane–diethyl ether; yield 0.174 g (62%). Anal. Calcd for $C_{42}H_{40}Cl_6P_2Re$: C, 50.16; H, 4.01; Cl, 21.15. Found: C, 48.41; H, 3.61; Cl, 21.21. In spite of the slightly low carbon microanalysis for this complex, there is no hint from its spectroscopic properties for the presence of any impurities.

(ii) $(Ph_3PC_3H_5)_2ReBr_6$. A reaction procedure similar to that in section B(i), using 0.15 g of $ReH_7(PPh_3)_2$, 1.0 mL of allyl bromide, and 10 mL of diethyl ether as solvent, afforded a red solid that was recrystallized from dimethylformamide–diethyl ether; yield 0.113 g (43%). This compound was identified on the basis of its spectroscopic properties.

(iii) $(Ph_3PC_3H_5)_2ReI_6$. The reaction between $ReH_7(PPh_3)_2$ (0.20 g) and allyl iodide (0.5 mL) in 10 mL of THF was carried out by stirring the reactants at room temperature for 3 h. The resulting black precipitate was filtered off, washed with THF and diethyl ether, and recrystallized from dichloromethane–THF; yield 0.32 g (74%). Anal. Calcd for $C_{42}H_{40}I_6P_2Re$: C, 32.46; H, 2.59. Found: C, 32.14; H, 2.80.

C. Reactions of $Re_2H_8(PPh_3)_4$ with Allyl Halides. (i) $(Ph_3PC_3H_5)_2Re_2Cl_8$. A quantity of $Re_2H_8(PPh_3)_4$ (0.30 g, 0.21 mmol) was added to 25 mL of THF followed by 1.5 mL (18.4 mmol) of allyl chloride. The reaction mixture was refluxed for 2.5 h, after which the resulting blue-green solid was filtered off, washed with THF, and finally recrystallized from dichloromethane–diethyl ether; yield 0.197 g (74%). Anal. Calcd for $C_{42}H_{40}Cl_8P_2Re_2$: C, 39.95; H, 3.19; Cl, 22.46. Found: C, 40.37; H, 3.46; Cl, 22.46.

(ii) $(Ph_3PC_3H_5)_2Re_2Br_8$. A mixture containing 0.2 g of $Re_2H_8(PPh_3)_4$ and 1 mL of allyl bromide in 10 mL of THF was stirred at room temperature for 5 h. The resulting yellow-green suspension was filtered off, washed with THF and diethyl ether, and dried under vacuum; yield 0.173 g (76%). The product was recrystallized from dimethylformamide–diethyl ether and was identified on the basis of its spectroscopic properties, electrochemistry, and reaction chemistry.

(iii) $(Ph_3PC_3H_5)_2ReI_6$. This gray-black complex was prepared by stirring a mixture of 0.20 g of $Re_2H_8(PPh_3)_4$ and 0.5 mL of allyl iodide in 10 mL of THF for 3 h at room temperature. It was filtered off, washed with THF, and obtained as small black crystals upon recrystallization from dichloromethane–THF; yield 0.29 g (66%). Anal. Calcd for $C_{42}H_{40}I_6P_2Re$: C, 32.46; H, 2.59. Found: C, 31.86; H, 2.60.

D. Reactions of $ReH_5(PPh_3)_2L$ ($L = C_6H_{11}NH_2$ or $C_5H_{10}NH$) with Allyl Chloride. In a typical reaction, 0.15 g of $ReH_5(PPh_3)_2L$ was dissolved in 20 mL of THF to which was added ~0.5 mL of allyl chloride. After the reaction mixture was refluxed for 2 h, the resulting yellow-green solid was filtered off, washed with THF, and dried under vacuum. The product was identified as $(Ph_3PC_3H_5)_2ReCl_6$ on the basis of its spectroscopic properties, but was contaminated with some of the corresponding amine salt, $[(C_6H_{11})(C_3H_5)NH_2]Cl$ or $[(C_5H_{10})(C_3H_5)NH_2]Cl$. The latter could be removed by washing the impure product with water; yield 40–60%.

E. Reactions of $ReH_7(PPh_3)_2$ with Allylamine and Allyl Thiocyanate. (i) $ReH_5(PPh_3)_2(H_2NC_3H_5)$. Allylamine (2.0 mL) was added to a solution of 0.15 g of $ReH_7(PPh_3)_2$ in 10 mL of THF. The solution was refluxed for 0.5 h and the solvent evaporated under reduced pressure. The resulting brown oil was dissolved in 2.0 mL of benzene, and ethanol was added until precipitation occurred. The solution was chilled at −10 °C for 10 h, and the resulting yellow powder was filtered off, washed with ethanol and diethyl ether, and dried under vacuum; yield 0.073 g (45%). The product was identified through the similarity of its spectroscopic and electrochemical properties to those of other complexes of the type $ReH_5(PPh_3)_2L$,[9] details of which are given in the Results and Discussion.

(ii) Reactions with Allyl Thiocyanate. A small quantity of $ReH_7(PPh_3)_2$ (0.10 g) was stirred with 0.5 mL of allyl thiocyanate in 4 mL of THF for 10 h at room temperature. The solvent was removed under reduced pressure to give a dark brown oil (IR $\delta(C{\equiv}N)$ 2065 cm^{-1}), which we were unable to crystallize. This product was not studied further.

F. Reaction of $Re_2H_8(PPh_3)_4$ with Allyl Thiocyanate. A reaction procedure similar to that described in section E(ii) but using 0.15 g of $Re_2H_8(PPh_3)_4$, 1.5 mL of allyl thiocyanate, and 15 mL of THF again produced a brown oil ($\delta(C{\equiv}N)$ 2060 cm^{-1}).

G. Reactions of $MoH_4(PMePh_2)_4$ with Allyl Chloride and Allyl Bromide. In a typical reaction, 0.15 g of $MoH_4(PMePh_2)_4$ was dissolved in 10 mL of THF to which was added 0.5 mL of allyl chloride. When the reaction mixture was stirred at room temperature for 24 h, a color change was observed, but when the reaction solvent was stripped off, only a red oil could be obtained. In the case of the reaction with allyl chloride, the resulting oil exhibited an IR-active $\nu(Mo{-}Cl)$ mode at 306 cm^{-1}, a value that is in accord with a Mo(IV) species such as $[MoCl_6]^{2-}$.[17]

H. Reactions of $ReH_7(PPh_3)_2$ with Other Organic Chlorides (CCl_4, $CHCl_3$, CH_2Cl_2, $(CH_3)_3CCl$, and C_6H_5Cl). All reactions of $ReH_7(PPh_3)_2$ with these organic chlorides proceeded in an analogous fashion. In a typical reaction, 0.1 g of $ReH_7(PPh_3)_2$ was dissolved in a small volume (~3 mL) of the appropriate chloride and the resulting solution allowed to stand for a day or so. The dark red crystals of *trans*-$ReCl_4(PPh_3)_2$ that separated were filtered off and dried; yield 60–80%. The identity of this complex was established by comparing its IR spectroscopic and electrochemical properties with those reported in the literature.[18,19]

I. Reaction of $Re_2H_8(PPh_3)_4$ with Carbon Tetrachloride. A suspension of $Re_2H_8(PPh_3)_4$ (0.224 g) in 25 mL of carbon tetrachloride was refluxed for 2 h to give 0.19 g of an insoluble blue-green product, which had spectroscopic properties consistent with a salt of the $[Re_2Cl_8]^{2-}$ anion (presumably $(Ph_3PCl)_2Re_2Cl_8$). This was confirmed by its conversion to the well-characterized salt $(Ph_4As)_2Re_2Cl_8$ by adding 0.2 g of Ph_4AsCl to a solution of this product in 25 mL of methanol containing 1 mL of 6 N HCl(aq). The insoluble $(Ph_4As)_2Re_2Cl_8$ was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Its identity was confirmed by the measurement of its IR and electronic absorption spectra.[20]

J. Reaction of $Re_2H_8(PPh_3)_4$ with Gaseous Hydrogen Chloride. A quantity of $Re_2H_8(PPh_3)_4$ (0.32 g) was added to 25 mL of methanol that had previously been saturated with gaseous hydrogen chloride. The mixture was then heated to boiling *in air*. The wine red solution quickly became colorless, and a green precipitate formed. After the volume of solution had been reduced to ~5 mL, the reaction mixture was filtered and the green solid washed with diethyl ether. The microanalytical data were consistent with the green crystals being the *mixed salt* $(Ph_3PH)_2Re_2Cl_8{\cdot}5(Ph_3PH)ReCl_5(PPh_3)$;[21] yield 81%. Anal. Calcd for $C_{216}H_{187}Cl_{33}P_{12}Re_7$: C, 46.10; H, 3.35. Found: C, 45.83; H, 3.43. This formulation was confirmed by washing the crystals with dichloromethane, a procedure that led to their decomposition and left a blue-green solid (0.06 g) on the filter (i.e., $(Ph_3PH)_2Re_2Cl_8$) and produced a yellow-colored filtrate. The latter, when evaporated to dryness, gave 0.23 g of yellow $(Ph_3PH)ReCl_5(PPh_3)$. Anal. Calcd for $C_{36}H_{32}Cl_8P_2Re_2$ (i.e., $(Ph_3PH)_2Re_2Cl_8$): C, 36.56; H, 2.73. Found: C, 36.31; H, 2.93. Calcd for $C_{36}H_{31}Cl_5P_2Re$: C, 48.64; H, 3.51. Found: C, 48.08; H, 3.63.

When the complex $(Ph_3PH)_2Re_2Cl_8$ was dissolved in methanol, it decomposed with precipitation of the well-known complex $Re_2Cl_6(PPh_3)_2$.[13] The spectroscopic properties of $(Ph_3PH)_2Re_2Cl_8$ and $(Ph_3PH)ReCl_5(PPh_3)$ are fully in accord with this formulation. Each displays an IR-active $\nu(P{-}H)$ absorption (at 2410 (m) and 2380 (w, br) cm^{-1}, respectively). The electronic absorption spectrum of $(Ph_3PH)_2Re_2Cl_8$, recorded as a Nujol mull, displayed the intense, characteristic, $\delta \rightarrow \delta^*$ transition of the $[Re_2Cl_8]^{2-}$ anion[11] at 715 nm. A comparison of the electronic absorption spectra of $(Ph_3PH)_2Re_2Cl_8$ and $(Ph_3PH)ReCl_5(PPh_3)$ with that of the mixed salt showed clearly that the latter was a composite of these two species.

K. Reactions of $(Ph_3PC_3H_5)_2Re_2X_8$ (X = Cl or Br) with Triphenylphosphine and Acetic Acid. (i) $Re_2X_6(PPh_3)_2$. Triphenylphosphine (0.20 g) was dissolved in 10 mL of methanol (containing 0.5 mL of the appropriate concentrated acid HX) and then treated with 0.1 g of $(Ph_3PC_3H_5)_2Re_2X_8$. When the resulting solution was stirred for 30 min, the complex $Re_2X_6(PPh_3)_2$ precipitated and was

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filtered off, washed with methanol, and dried under vacuum; yield 75%. Both complexes were identified through a comparison of their spectroscopic properties with those of authentic samples.[13]

(ii) $Re_2(O_2CCH_3)_4X_2$. An acetic acid–acetic anhydride mixture (10 mL, 10:1 by volume) was added to 0.15 g of $(Ph_3PC_3H_5)_2Re_2Cl_8$ and the reaction solution refluxed for 45 min in a stream of N_2(g). During this time the color of the solution turned orange and an orange precipitate formed. The complex was filtered off, washed with ethanol and diethyl ether, and dried in vacuo; yield 40–50%. The rhenium(III) acetates were identified by IR and electronic absorption spectroscopy.[23]

L. Reaction of $(Ph_3PC_3H_5)_2ReI_6$ with Acetic Acid–Acetic Anhydride. A suspension of 0.1 g of $(Ph_3PC_3H_5)_2ReI_6$ in 8 mL of CH_3CO_2H–$(CH_3CO)_2O$ (10:1 by volume) was refluxed for 10 h and the orange complex $Re_2(O_2CCH_3)_4I_2$ filtered off, washed with ethanol, acetone, and diethyl ether, and dried in vacuo; yield 0.019 g (34%). The product was identified by its spectroscopic and electrochemical properties.[23]

Physical Measurements. Infrared measurements of Nujol mulls were recorded in the region 4000–200 cm^{-1}, with use of KBr and polyethylene plates and Beckman IR-12 and Acculab-6 spectrophotometers. Infrared spectra in the region 400–50 cm^{-1} were recorded with a Digilab FTS-20B spectrometer. ^1H NMR spectra were recorded at 90 MHz with a Perkin-Elmer R32 spectrometer. Resonances were referenced to the residual protons in the deuterated solvents. Magnetic moments were measured by the Evans method in either dichloromethane or dimethylformamide with the PE-R32 spectrometer. Cyclic voltammetry experiments were performed on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) were referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. Voltammetric measurements were taken with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder.

Analysis of volatile gases was carried out on a Carle Series-S analytical gas chromatograph (Model 111-H 156A) equipped with a Linear Model 1201 strip-chart recorder. The gas chromatograph was operated with an oven temperature of 56 °C and a hydrogen-transfer system operating at 600 °C. Reactions in which volatile gases were analyzed were carried out in a 25-mL, single-neck, round-bottom flask equipped with a rubber septum. The flask was charged with the starting material and flushed with N_2(g) for 30 min. The solvent and organic halide were then added via a syringe, and the reaction was allowed to proceed in the closed system. The gases for analysis were then extracted from the reaction headspace by use of a gas-tight syringe, and a 1-mL sample was injected into the gas chromatograph.

Microanalyses were performed by Dr. C. S. Yeh and Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

Reactions of Halocarbons with the Mononuclear Polyhydrides $ReH_7(PPh_3)_2$ and $ReH_5(PPh_3)_2L$. Our interest in the reactions of the heptahydride $ReH_7(PPh_3)_2$ with chlorocarbons arose when we found that its dissolution in carbon tetrachloride led to the generation of a dark red solution and the precipitation of carmine red crystals of *trans*-$ReCl_4(PPh_3)_2$. Subsequently, related reactions were found to occur with other organic chlorides, namely, $CHCl_3$, CH_2Cl_2, Me_3CCl, and C_6H_5Cl. Since the metal-containing product is one that can be more conveniently prepared by other methods,[24] we chose not to pursue these reactions further. However, a few additional comments are perhaps appropriate. This reaction course is that which is to be expected on the basis of the reactions of other transition-metal hydrides with chlorocarbons such as CCl_4.[25] We note that, while these reactions of $ReH_7(PPh_3)_2$ proceed in the dark, they are inhibited by hydroquinone, thereby suggesting a radical mechanism. Finally, in subjecting the evolved gases from the reactions of $ReH_7(PPh_3)_2$ with $CHCl_3$ and CH_2Cl_2 to a GC analysis, we found that H_2 was, as expected, the major product and was evolved quite rapidly. In addition, there was a somewhat slower buildup of much smaller amounts of CH_4, C_2H_6 (a trace), C_4H_8 (in the case of the CH_2Cl_2 reaction only), and C_5H_{12} as the reactions proceeded.

We next investigated the question of how this reaction course might be affected by the introduction of an unsaturated functionality into the organic chloride. Since 3,3-dimethylbut-1-ene has been found[5,8] to serve as a hydrogen acceptor upon its reaction with $ReH_7(PPh_3)_2$ (following loss of 1 equiv of H_2 and the coordination of the double bond), we thought that the use of allyl chloride might dictate a reaction course different from that encountered with the other organic chlorides (vide supra). The treatment of $ReH_7(PPh_3)_2$ with allyl chloride in refluxing tetrahydrofuran for 1.5 h afforded yellow-green $(Ph_3PC_3H_5)_2ReCl_6$ in good yield. Extending this study to include the analogous allyl bromide and allyl iodide showed that this was a convenient method of preparing the series of salts $(Ph_3PC_3H_5)_2ReX_6$ (X = Cl, Br, I). The phosphine ligands that are released during the reductive elimination of H_2 (GC analysis) and the concomitant chlorination of the metal center react with the excess allyl halide present to produce the $(Ph_3PC_3H_5)^+$ cations[26,27] that subsequently stabilize the $[ReX_6]^{2-}$ species. In all three reactions, GC analysis of the gases that are evolved showed that propene plus a trace of propane are evolved in addition to the aforementioned H_2. Clearly, the course of these reactions resembles those of $ReH_7(PPh_3)_2$ with the organic chlorides discussed previously, in that the final metal-containing product is a stable Re(IV) entity. The large organic cation $(Ph_3PC_3H_5)^+$ renders the rhenium compounds soluble in most common organic solvents (acetone, CH_2Cl_2, CH_3CN, DMF, etc.), thereby making possible the enhancement of many of their chemical reactions.

The spectroscopic properties of these salts are fully in accord with their formulation. The low-frequency IR spectra (Nujol mulls) show ν(Re–X) modes at 326 (s) (X = Cl), 229 (s) (X = Br), and 160 (s) (X = I) cm^{-1},[28] while the ν(C=C) vibration that is associated with the allyl moiety of the $(Ph_3PC_3H_5)^+$ cation is located at ~1590 (m) cm^{-1}. The ^1H NMR spectra of all three complexes gave broad, poorly defined resonances because of their paramagnetic nature. In the case of $(Ph_3PC_3H_5)_2ReCl_6$, a magnetic-moment determination by the Evans method gave $\mu_{eff} = 3.2\ (\pm 0.1)\ \mu_B$.

While the reaction of allyl thiocyanate with $ReH_7(PPh_3)_2$ failed to give a well-characterized metal-containing product (only oils were obtained), analysis of the evolved gases (vide supra) indicated a reaction course similar to that occurring with the allyl halides.

The C_3H_5X (X = Cl, Br, I, and NCS) reactions described so far can be contrasted with that found to occur with allylamine. Chatt and Coffey[14] had previously described this reaction as affording a yellow product, but they did not provide any microanalytical or spectroscopic data to shed any light on its true nature. We find that this material is the complex $ReH_5(PPh_3)_2(NH_2C_3H_5)$, a member of a series of complexes of the type $ReH_5(PPh_3)_2L$,[14] where L represents an amine or phosphine σ-donor. The cyclic voltammogram of this complex shows an oxidation at $E_{p,a} = +0.22$ V vs. SCE in tetra-*n*-butylammonium hexafluorophosphate–dichloromethane. This behavior is expected on the basis of CV measurements on other complexes of this type.[9] The IR and ^1H NMR spectroscopic

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properties[29] are likewise strong support for the formulation we propose. Presumably, this different reaction course reflects the preference of rhenium for bonding to the strong σ-donor amine nitrogen plus the minimizing of steric crowding.

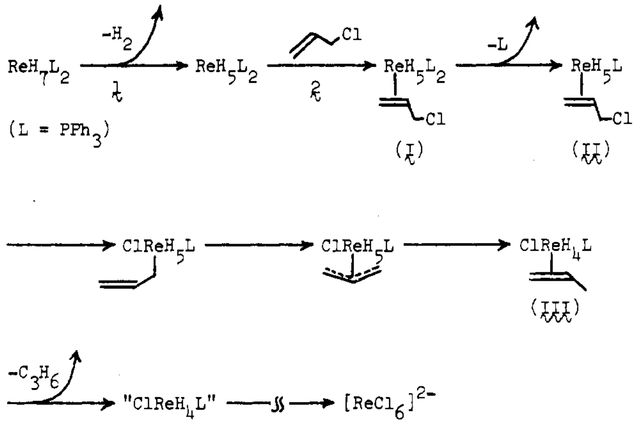
While the thermal reactions of $ReH_5(PPh_3)_2L$ complexes with σ-donors and π-acceptors are exceedingly sluggish,[10,14,30,31] this is not the case upon treatment with allyl chloride. When tetrahydrofuran solutions containing $ReH_5(PPh_3)_2L$ ($L = C_6H_{11}NH_2$ or $C_5H_{10}NH$) and C_3H_5Cl are refluxed for 2 h, $(Ph_3PC_3H_5)_2ReCl_6$ is isolated in about 50% yield, together with the appropriate amine salt $(LC_3H_5)Cl$, and H_2 and propene (plus a trace of propane) are the gaseous products. The reaction course resembles that observed starting with $ReH_7(PPh_3)_2$.

Reactions of Allyl Halides with the Dinuclear Polyhydride $Re_2H_8(PPh_3)_4$. Previously, very little in the way of substitution reaction chemistry of complexes of the type $Re_2H_8(PR_3)_4$ has been reported. These molecules possess the structure $(PR_3)_2H_2Re(\mu\text{-}H)_4ReH_2(PR_3)_2$ as established by a neutron-diffraction analysis,[32] and exhibit a well-defined electrochemical redox chemistry.[9,33] The one example of a well-defined substitution reaction is that in which $Re_2H_8(PMe_2Ph)_4$ reacts with the unusual phosphite ligand $P(OCH_2)_3CEt$ (abbreviated L′), but here the reaction is nontrivial, resulting in the loss of hydrogen and the formation of the interesting molecule $L'(PMe_2Ph)_2HRe(\mu\text{-}H)_3Re(PMe_2Ph)_2L'$.[34] In the present study we find that reactions of $Re_2H_8(PPh_3)_4$ with C_3H_5X (X = Cl or Br) proceed cleanly and relatively fast in tetrahydrofuran to form products, viz. $(Ph_3PC_3H_5)_2Re_2X_8$, via the reductive elimination of H_2 (accompanied by the evolution of propene) and with the retention of the dirhenium core (as present in the quadruply bonded $[Re_2X_8]^{2-}$ anions). The IR spectra of these two complexes show ν(Re–X) modes at 335 (X = Cl) and 233 (X = Br) cm^{-1}, in excellent agreement with the spectroscopic results for other salts containing these anions.[35] Also, the ^1H NMR spectrum of the cation in these complexes agrees well with previously reported data,[27] with δ 7.70 (multiplet, C_6H_5), 5.40 (multiplet, $-CH_2C\mathit{H}{=}C\mathit{H}_2$), and 4.42 (doublet of doublets, $-C\mathit{H}_2CH{=}CH_2$).

The reaction between $Re_2H_8(PPh_3)_4$ and C_3H_5I provides an interesting contrast to the reactions with C_3H_5X (X = Cl, Br) since the Re(IV) complex $(Ph_3PC_3H_5)_2ReI_6$ is isolated. It is suspected that the reaction course is similar to the reactions with C_3H_5Cl and C_3H_5Br, since the same volatile gases are detected by GC. However, the presence of small amounts of free iodine in the reaction mixture probably results in the oxidative cleavage of $[Re_2I_8]^{2-}$ to give $[ReI_6]^{2-}$. Unfortunately, we have been unable to confirm this as we did not isolate $(Ph_3PC_3H_5)_2Re_2I_8$ during the course of the reaction, even though salts containing the $[Re_2I_8]^{2-}$ anion have been prepared by other methods.[36]

Mechanistic Considerations. In all reactions of the rhenium polyhydrides (mononuclear and dinuclear) with C_3H_5X (X = Cl, Br, I, NCS), both H_2 and propene were evolved initially. In timed studies, a small amount of propane slowly grew into the chromatogram. We postulate that this represents a portion of the propene being reduced to propane by H_2, although there could be a competing side reaction in which propene is reduced directly by the rhenium hydride. The consistency of these reactions for all of the rhenium polyhydrides studied tends to suggest a common mechanism.

Scheme I



In contrast, the reactions of $ReH_7(PPh_3)_2$ with CCl_4, $CHCl_3$, etc. show the fast evolution of H_2 with the subsequent buildup of small amounts of hydrocarbons. The molybdenum tetrahydride $MoH_4(PMePh_2)_4$ also reacts with C_3H_5Cl to evolve H_2 and propene, again with a slight buildup of propane. Attempts at the isolation and identification of the metal-containing product(s) of this reaction were unsuccessful.

The mild conditions under which $ReH_7(PPh_3)_2$ reacts with the allyl halides are similar to those used by Baudry and co-workers[7] in the reaction between the heptahydride and olefins. This suggests to us that allyl chloride initially coordinates as an olefin following the previous loss of dihydrogen (steps 1 and 2 in Scheme I). The pentahydride (I) may then lose one phosphine ligand (L) to give a solvent-stabilized intermediate (II). Note that the release of free phosphine is the most logical route to the triphenylallylphosphonium cation,[26,27,37] which is subsequently formed and which stabilizes the resulting rhenium haloanions. The coordinated allyl halide could then proceed through an allylic substitution reaction via an oxidative addition and $\eta^1 \leftrightarrow \eta^3$ rearrangement[38] to form the tetrahydridochloro intermediate (III). The bound propylene is then presumably eliminated to give a coordinatively unsaturated rhenium species that is open to further attack. Although further speculation is not justified, we note that the reaction between $ReH_7(PPh_3)_2$ and allyl chloride proceeds in the dark and in the presence of a radical inhibitor (hydroquinone), thereby favoring such a nonradical mechanism. Furthermore, we find no evidence for intermediate rhenium hydrido species when monitoring the reaction by ^1H NMR spectroscopy. The hydride resonance at δ −4.2 (triplet, J_{P-H} = 17 Hz) diminishes in intensity as the reaction between $ReH_7(PPh_3)_2$ and allyl chloride proceeds, but no new resonances appear that can be attributed to ReH_5 or ReH_4 intermediates. It appears that reaction is very rapid once loss of H_2 and initial coordination of allyl chloride have occurred.

Reaction of $Re_2H_8(PPh_3)_4$ with Gaseous Hydrogen Chloride. The reactions of the mononuclear polyhydride complexes of the types ReH_7L_2 and ReH_5L_3 (where L is a tertiary phosphine) with hydrogen chloride lead[14] to the evolution of H_2 and the formation of the nonhydridic complexes $ReCl_4L_2$ and $ReCl_3L_3$, respectively; there is no evidence for mixed chloro-

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(29) IR (Nujol mull): δ(N–H) at 3320 (m–w) cm^{-1}; ν(Re–H) at 2010 (m), 1910 (m), and 1833 (m) cm^{-1}; ν(C=C) of $-CH_2CH{=}CH_2$ at 1585 (m–w) cm^{-1}. ^1H NMR (C_6D_6): δ 6.70 (multiplet, C_6H_5), 4.30 (multiplet, $-CH_2C\mathit{H}{=}CH_2$), 4.10 (multiplet, $-CH_2CH{=}C\mathit{H}_2$), 3.75 (doublet, $-C\mathit{H}_2CH{=}CH_2$), −5.3 (triplet, Re–H). See ref 14 for comparable data on other complexes of this type.

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hydride intermediates in these reactions. In a slightly earlier report, Ginsberg[39] had mentioned that the polyhydride anion $[ReH_8(PPh_3)]^-$ was converted to $(Ph_3PH)_2Re_2Cl_8$ upon treatment with HCl. The "deficiency" of phosphine ligand in this anion (compared to $ReH_7(PR_3)_2$) clearly has a dramatic effect on this reaction, but it is not obvious why the alternative reaction $[ReH_8(PPh_3)]^- + 5HCl \rightarrow [ReCl_5(PPh_3)]^- + 6.5H_2$ does not occur. Nonetheless, this reaction constituted an interesting early example of a single step conversion of a mononuclear complex to a multiply bonded dinuclear species.[11] In the present study, we have taken the opportunity to carry out the analogous reaction between $Re_2H_8(PPh_3)_4$ and gaseous HCl. To our surprise, this turned out to afford an unusual species, the major product being the mixed salt $(Ph_3PH)_2Re_2Cl_8 \cdot 5(Ph_3PH)ReCl_5(PPh_3)$ containing both mononuclear Re(IV) and dinuclear Re(III) components. Separation and purification of the two components can be accomplished by treating the crystals with dichloromethane. The explanation for this reaction is not obvious, although it is in accord with other work that has shown that nonhydridic products are the rule.[14,39-41]

Reactions of the Salts $(Ph_3PC_3H_5)_2Re_2X_8$ and $(Ph_3PC_3H_5)_2ReI_6$ with Triphenylphosphine and Acetic Acid–Acetic Anhydride. The complexes $(Ph_3PC_3H_5)_2Re_2X_8$ (X = Cl or Br) react in the predicted fashion[11] with PPh_3 and with $CH_3CO_2H-(CH_3CO)_2O$ to give the quadruply bonded dirhenium(III) species $Re_2X_6(PPh_3)_2$ and $Re_2(O_2CCH_3)_4X_2$, respectively. In other words, retention of the quadruple bond is observed. At the time when we first reacted $Re_2H_8(PPh_3)_4$ with allyl iodide, we had anticipated that the product would be $(Ph_3PC_3H_5)_2Re_2I_8$. Accordingly, when we first began to characterize this material and reacted it with refluxing acetic acid–acetic anhydride, our isolation of $Re_2(O_2CCH_3)_4I_2$ did not surprise us. Later, when we realized that the correct formulation was $(Ph_3PC_3H_5)_2ReI_6$ rather than $(Ph_3PC_3H_5)_2Re_2I_8$, it became apparent that the formation of $Re_2(O_2CCH_3)_4I_2$ constituted a relatively rare example of the reductive coupling of two higher oxidation state rhenium centers to give a dinuclear multiply bonded species. The conversion of *trans*-$ReOX_3(PPh_3)_2$ (X = Cl or Br) to $Re_2(O_2CCH_3)_4X_2$ is another such example.[18]

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Registry No. $Re_2H_8(PPh_3)_4$, 66984-37-0; $ReH_7(PPh_3)_2$, 12103-40-1; $ReH_5(PPh_3)_2C_6H_{11}NH_2$, 25702-61-8; $ReH_5(PPh_3)_2C_5H_{10}NH$, 25702-62-9; $MoH_4(PMePh_2)_4$, 32109-07-2; $Re_2Cl_6(PPh_3)_2$, 11087-98-2; $(Ph_3PC_3H_5)_2ReCl_6$, 85319-88-6; $(Ph_3PC_3H_5)_2ReBr_6$, 85335-12-2; $(Ph_3PC_3H_5)_2ReI_6$, 85335-13-3; $(Ph_3PC_3H_5)_2Re_2Cl_8$, 85335-14-4; $(Ph_3PC_3H_5)_2Re_2Br_8$, 85335-15-5; $ReH_5(PPh_3)_2(H_2NC_3H_5)$, 85319-89-7; *trans*-$ReCl_4(PPh_3)_2$, 34248-10-7; $(Ph_4As)_2Re_2Cl_8$, 14649-98-0; $(Ph_3PH)_2Re_2Cl_8 \cdot 5(Ph_3PH)ReCl_5(PPh_3)$, 85335-17-7; $(Ph_3PH)ReCl_5(PPh_3)$, 36550-27-3; $(Ph_3PH)_2Re_2Cl_8$, 83511-36-8; $NH_2C_3H_5$, 107-11-9; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; $(CH_3)_3CCl$, 507-20-0; C_6H_5Cl, 108-90-7; HCl, 7647-01-0; PPh_3, 603-35-0; C_3H_5Cl, 107-05-1; C_3H_5Br, 106-95-6; C_3H_5I, 556-56-9; C_3H_5NCS, 764-49-8; CH_3CO_2H, 64-19-7; Re, 7440-15-5.

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Crystal Structure of Tris(2,5-dimethyl-2,5-diisocyanohexane)disilver(I) Diperchlorate: A Unidimensional, Ladderlike, Polymeric Metal Complex

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Reaction of $AgClO_4$ with 2,5-dimethyl-2,5-diisocyanohexane (TMB) in methanol/acetonitrile gives rise to colorless crystals of $[Ag_2(TMB)_3](ClO_4)_2$, which were investigated by X-ray diffraction. The complex belongs to the triclinic space group $P\bar{1}$, a = 8.951 (5) Å, b = 9.018 (9) Å, c = 15.500 (10) Å, α = 93.54 (7)°, β = 90.73 (5)°, γ = 115.86 (6)°, and Z = 1. The structure consists of pairs of $\cdots Ag—C\overline{N\ N}C—Ag—C\overline{N\ N}C—Ag\cdots$ infinite chains containing the TMB ligand in an extended form. Pairs of chains are cross-linked at every step by another TMB ligand joining a silver atom in one chain to the corresponding silver on the opposite chain. Each silver atom is thus bonded to three CN groups defining a distorted-trigonal plane. The Ag–CN distances (average 2.14 Å) are significantly longer than in the rhodium complex (average 1.94 Å). A weak interaction with one oxygen of the perchlorate anion is also apparent (Ag–O = 2.73 (1) Å). The complex is slightly soluble in acetonitrile, and its ^{13}C NMR spectrum has been obtained.

Introduction

Diisocyanide ligands are of special interest due to their versatility in bonding with metal complexes and to their ability to give rise to complexes with unusual properties.[2-4] The differences in bonding may be related to the design of the diisocyanide ligand (geometrical requirements imposed by the relative location of the two isocyanide groups, nature of the bridge), as well as to the nature of the metal atom and of the remaining ligands.

Until now, few well-characterized diisocyanide metal complexes have been reported. Gray et al.[5,6] have shown by x-ray crystallography that 2,5-dimethyl-2,5-diisocyanohexane (TMB = "tetramethyl bridge") gives rise to a ligand-bridged dinuclear cationic complex $[Rh_2(TMB)_4](PF_6)_2 \cdot 2CH_3CN$ when reacting with a Rh(I) complex and to a cubane-like structure $[Ni_4(OCH_3)_4(TMB)_4(OAc)_2](BPh_4)_2$ when reacting with Ni(O-

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