Transactions of the Illinois State Academy of Science
(1995), Volume 88, 3 and 4, pp. 123-129

New Mixed-metal Polyhydride Compounds Containing the Ag_2Re and Ag_2Re_2 Cores

William Conroy, Tammy Stewart, and Gregory A. Moehring
Governors State University
University Park, Illinois 60466
USA

ABSTRACT

The reaction of $ReH_5(PPh_3)_3$ with AgX (X = PF_6^- or NO_3^-) produces the mixed silver rhenium polyhydride compounds, $[Ag_2ReH_5(PPh_3)_3]X_2$. The compound $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ has been found to react with alkenes such as cyclohexene, 1-pentene, or styrene to produce $[AgReH_4(PPh_3)_3]_2$ and finely divided silver metal.

INTRODUCTION

The synthesis of mixed-metal polyhydride clusters is an area of continuing interest. These mixed metal polyhydride clusters may afford one or more metal centers to coordinate organic substrates while the second metal center may provide hydride ligands to effect organic transformations. The goal of this work was to synthesize and investigate such a complex.

Previous work with the ReH_5L_3 (L = tertiary phosphine) class of polyhydride compounds has shown that these compounds readily form mixed metal polyhydride clusters *via* acid-base type reactions (Moehring and Walton, 1988; Carr, Fontaine, and Shaw, 1991). Other work has demonstrated that a silver containing polyhydride compound can contain a reactive, and possibly coordinativley unsaturated, silver center (Connelly, Howard, Spencer, and Woodley, 1984). We chose to pursue the reaction of silver salts with $ReH_5(PPh_3)_3$ in an attempt to obtain a reactive silver center bound to a rhenium polyhydride fragment. We found that $ReH_5(PPh_3)_3$ reacted with the silver salts AgX (X = PF_6^- or NO_3^-) to produce $[Ag_2ReH_5(PPh_3)_3]X_2$. A subsequent examination of the reactivity of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ found that alkenes would abstract one silver center per complex to produce $[AgReH_4(PPh_3)_3]_2$.

MATERIALS

Starting Materials

The complex $ReH_5(PPh_3)_3$ was prepared by the standard literature method (Cameron, Moehring, and Walton, 1990; Chatt and Coffey, 1969). All other reagents and solvents were obtained from commercial sources. Solvents were deoxygenated and/or distilled prior to use. All reactions were carried out under an atmosphere of nitrogen.

$[Ag_2ReH_5(PPh_3)_3](PF_6)_2$

Dichloromethane, 5 mL, was added to a flask which contained $AgPF_6$, 0.0515 g, (0.204 mmol) and $ReH_5(PPh_3)_3$, 0.1000 g (0.1022 mmol). The resultant yellow solution was stirred for 30 minutes and precipitation was then induced by the addition of 100 mL of diethyl ether. The resultant precipitate was filtered, washed with diethyl ether, and dried under vacuum; yield 0.0800 g (53%). Anal. Calcd for $C_{54}H_{50}Ag_2F_{12}P_5Re$: C, 43.71; H 3.40. Found: C, 44.25; H 3.79.

$[Ag_2ReH_5(PPh_3)_3](NO_3)_2$

A 50 mL round bottomed flask was loaded with 0.1010 g of $ReH_5(PPh_3)_3$ (0.1032 mmol) and 0.0960 g of $AgNO_3$ (0.565 mmol). Diethyl ether, 30 mL, was added and the mixture was stirred for 2.5 hours. A tan precipitate was isolated by filtration. The precipitate was extracted into 10 mL of dichloromethane. A white precipitate of $[Ag_2ReH_5(PPh_3)_3](NO_3)_2$ was induced from the extract by addition of 100 mL of pentane. The product was filtered and dried under vacuum; yield 0.0770 g (57 %). Anal. Calcd for $C_{54}H_{50}Ag_2N_2O_6P_3Re$: C, 49.21; H 3.82. Found: C, 48.43; H 4.31.

$[AgReH_4(PPh_3)_3]_2$

This compound can be prepared using a similar procedure and any of the following alkenes: cyclohexene, 1-pentene, or styrene. This procedure is given for styrene. In a 50 mL round bottomed flask, 0.0463 g of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ (0.031 mmol) was dissolved in 5 mL of dichloromethane. To this solution, 0.5 mL of styrene (3.8 mmol) was added. The solution was stirred for 16 hours and a precipitate of silver metal was removed by filtration. Diethyl ether, 100 mL, and pentane, 25 mL, were added to the filtrate to induce precipitation. The product was collected by filtration and dried under vacuum; yield 0.0293 g (87 %). Anal. Calcd for $C_{108}H_{98}Ag_2P_6Re_2$: C, 59.78; H 4.55. Found: C, 60.71; H 3.97.

Physical Measurements

Infrared spectra were recorded as Nujol mulls between KBr plates on a Mattson Galaxy 2020 FT-IR spectrophotometer. Cyclic voltammetric experiments were performed with a Princeton Applied Research Model 173 potentiostat. A Pt disk working electrode was used. Dichloromethane was used as the solvent and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Potentials are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ V versus a Ag/AgCl reference electrode for a dichloromethane solution of ferrocene. ^{31}P NMR spectra were obtained on a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85 % H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4. ^1H NMR spectra were recorded at 60 MHz on a Hitachi Perkin Elmer R-24 B spectrometer or at 200 MHz on a Varian XL-200 spectrometer. Conductivity measurements were made with a Lab-Line Instruments Model MC-1 conductivity bridge. Microanalyses were performed by National Chemical Consulting Inc., Tenafly, New Jersey.

RESULTS AND DISCUSSION

The reaction of $ReH_5(PPh_3)_3$ with AgX (X = PF_6^- or NO_3^-) results in the mixed silver rhenium polyhydride complex $[Ag_2ReH_5(PPh_3)_3]X_2$; which is an interesting addition to the mixed-metal polyhydride compounds formed by combining ReH_5L_3 with gold or silver containing compounds. The mixed-metal cores Au_2Re, AuRe, and AgRe have previously been prepared in a similar fashion (Moehring and Walton, 1988; Carr, Fontaine, and Shaw, 1991). Unlike other such gold or silver containing cores, however, $[Ag_2ReH_5(PPh_3)_3]X_2$ does not contain a tertiary phosphine bound to silver. The compounds $[Ag_2ReH_5(PPh_3)_3]X_2$ most likely have silver atoms supported by significant interactions with the anions PF_6^- or NO_3^-. The reactivity of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ with alkenes, which leads to the loss of one silver center and the formation of $[AgReH_4(PPh_3)_3]_2$, is consistent with silver centers that are supported by easily displaced ligands.

The Nujol mull infrared spectrum of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ includes a very weak metal-hydride stretch at 1680 cm^{-1} and a weak absorption at 837 cm^{-1} due to the PF_6^- anion. We attribute the weakness of the PF_6^- absorption to interaction between the anion and the silver center. This interaction would effectively disturb the symmetry of the anion. The Nujol mull infrared spectrum of the nitrate salt exhibits a similar metal hydride stretch at 1680 cm^{-1}, but the absorption at 837 cm^{-1} is, of course, absent.

The ^1H NMR spectra of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ and $[Ag_2ReH_5(PPh_3)_3](NO_3)_2$, recorded in $CDCl_3$, are identical. The spectra consist of resonances at 7.2 ppm due to phenyl protons and resonances at -5.23 ppm due to the hydride ligands (Figure). The two resonances integrate as five hydride ligands for each three triphenylphosphine ligands. The hydride resonance is an apparent sextet which is best explained as an overlapping quartet of triplets. The quartet arises from hydride coupling to the three ^{31}P nuclei (J_{PH} = 17 Hz) and the triplet arises from hydride coupling with the two silver nuclei. Coupling to individual silver isotopes is not observed. The mean silver-hydride coupling constant is 20 Hz.

The ^{31}P NMR spectrum of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$, recorded in $CDCl_3$, consists of a singlet at 25.5 ppm due to the rhenium bound phosphorous atoms and a septet at -142.9 ppm due to the PF_6^- phosphorous atoms. As with all other silver containing rhenium polyhydride compounds, no coupling is observed between rhenium bound phosphorous nuclei and silver atoms (Carr, Fontaine, and Shaw, 1991; Connelly, Howard, Spencer, and Woodley, 1984).

Conductivity measurements of $[Ag_2ReH_5(PPh_3)_3]X_2$ solutions correspond to the formulation of $[Ag_2ReH_5(PPh_3)_3]X_2$ as a 2:1 electrolyte. In acetone, $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ produced a specific conductance, Λ, of 182 $ohm^{-1}cm^2mol^{-1}$ and $[Ag_2ReH_5(PPh_3)_3](NO_3)_2$ produced a specific conductance of 190 $ohm^{-1}cm^2mol^{-1}$ (Geary, 1971).

Other evidence in support of the formulation $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ includes the yields from reactions of $ReH_5(PPh_3)_3$ with varying amounts of $AgPF_6$. At stoichiometries of less than two equivalents of $AgPF_6$ per equivalent of $ReH_5(PPh_3)_3$, the yield of

$[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ decreased in proportion to the amount of $AgPF_6$ used. No effect upon the yield of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ was observed when stoichiometries of two or more equivalents of $AgPF_6$ were used. All attempts to isolate or observe other rhenium containing compounds from the above reactions were unsuccessful. We have no evidence of the fate of the unrecovered rhenium, be it unreacted starting material, unrecovered product, or some other rhenium containing product(s).

The compounds $[Ag_2ReH_5(PPh_3)_3]X_2$ exhibit electrochemistry which is very different from that of the $ReH_5(PPh_3)_3$ starting material. $ReH_5(PPh_3)_3$ has a first oxidation potential, as measured by cyclic voltammetry, of +0.37 V versus SCE (Allison, Cameron, Wild, and Walton, 1981). The cyclic voltammogram of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ is characterized by an irreversible oxidation ($E_{p,a}$ = +1.70 V) and an irreversible reduction ($E_{p,c}$ = -1.05 V) with an associated product wave ($E_{p,a}$ = +0.29 V). The increase in first oxidation potential between the starting $ReH_5(PPh_3)_3$ and the $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ product of +1.33 V is very similar to the reported +1.35 V shift observed for the compound $Re_2H_8(PPh_3)_4$ and its bis coinage metal adduct, $[Re_2H_8(PPh_3)_4(AuPPh_3)_2](PF_6)_2$ (Moehring, Fanwick, and Walton, 1987).

As mentioned earlier, we were interested in preparing compounds such as $[Ag_2ReH_5(PPh_3)_3]X_2$ because we wanted to study their reactivity. An interaction between PF_6^- and silver, which was indicated in the infrared spectrum of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$, suggested the possibility of a reactive site at silver. We, therefore, chose to pursue the reactions of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ with alkenes. Alkenes have previously been shown to interact rather strongly with silver ions (Hartley, 1973; Crookes and Wolf, 1973). We found that the reactions of cyclohexene, 1-pentene, or styrene with $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ all produced the same rhenium containing product, namely $[AgReH_4(PPh_3)_3]_2$. These reactions also produce finely divided metallic silver as a gray precipitate. The silver precipitate has been identified by wet chemical tests. The silver most likely arises from reduction of a putative $[Ag(alkene)_n]^+$ complex formed during the reaction. Thus, $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ does indeed contain a reactive silver center. Interaction of an alkene at the center, however, leads to disruption of the silver rhenium bond and concomitant loss of silver from the complex.

This is not the first example of the removal of coinage metals from mixed coinage metal rhenium polyhydride compounds. The $(AuPR_3)^+$ (R = Ph or Et) fragments of $[Re_2H_8(PPh_3)_4(AuPR_3)]PF_6$ and $[Re_2H_8(PPh_3)_4(AuPR_3)_2](PF_6)_2$ were removed by soft bases such as halides or tertiary phosphines (Moehring, Fanwick, and Walton, 1987). This is the first report, however, of alkenes effecting the removal of a coinage metal from such a mixed metal compound.

The reaction of alkenes with $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ is also similar to the reaction of triethylamine with $[ReH_5(PPh_3)_3(AuPPh_3)]PF_6$ (Moehring and Walton, 1988). $[ReH_4(PPh_3)_3(AuPPh_3)_2]PF_6$, the product of the reaction of triethylamine with $[ReH_5(PPh_3)_3(AuPPh_3)]PF_6$, results from the loss of a hydride ligand as H^+ and the transfer of an $AuPPh_3^+$ fragment during the reaction. $[AgReH_4(PPh_3)_3]_2$, the product of the reaction of alkenes with $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$, results from the loss of a hydride ligand as H^+ and the loss of an Ag^+ during the reaction. Both reactions, then, consist of the loss of H^+ and the loss or transfer of a coinage metal fragment when the mixed metal polyhydride compound is exposed to a nucleophile.

We attempted to determine the fate of styrene in its reaction with $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ by performing the reaction in $CDCl_3$ and monitoring the reaction mixture periodically by ^1H NMR spectrosocpy. The ^1H NMR spectra revealed only free styrene. We were unable to observe any resonances that might be attributed to chemicals such as bound styrene, ethyl benzene, or styrene oligomers. Thus, any of these other possible styrene derivatives which might have formed are formed in concentrations below the detection limit for our ^1H NMR spectroscopy

The ^1H NMR spectrum of $[AgReH_4(PPh_3)_3]_2$, as measured in CD_2Cl_2, consists of only two resonances. The phenyl protons resonate at 7.2 ppm and the hydride ligands resonate at -4.70 ppm. No resonances corresponding to either bound or free alkene are observed in the spectrum. Integration of the resonances corresponds to four hydride ligands for each three triphenylphosphine ligands. The hydride resonance appears as a complex symmetrical multiplet due to coupling to with ^{31}P, ^{107}Ag, and ^{109}Ag nuclei. The ^{31}P NMR spectrum of $[AgReH_4(PPh_3)]$, recorded in $CDCl_3$, consists of a singlet at 21.6 ppm. Again, no coupling is observed between rhenium bound phosphorous and silver isotopes. No evidence of PF_6^- was observed in the ^{31}P spectrum of this compound.

The Nujol mull infrared spectrum of $[AgReH_4(PPh_3)_3]_2$ exhibits only monosubstituted phenyl ring overtones in the metal-hydride stretching region. No absorption due to PF_6^- is observed. Because the compound is insoluble in any appropriate solvent, conductivity measurements were not attempted. The compound is, however, quite soluble in benzene, corresponding to the formulation of $[AgReH_4(PPh_3)_3]_2$ as a nonelectrolyte.

The determination that $[AgReH_4(PPh_3)_3]_2$ is dimeric in nature was made from molecular weight measurements. The molecular weight of $[AgReH_4(PPh_3)]_2$ was determined by the freezing point depression of a benzene/$[AgReH_4(PPh_3)_3]_2$ solution. The molecular weight was determined to be approximately 2000 g/mol. This corresponds to the formulation of the compound as $[AgReH_4(PPh_3)_3]_2$ rather than $AgReH_4(PPh_3)_3$. The most likely structure for this compound would be one in which the silver centers bridge two $ReH_4(PPh_3)_3$ fragments. Another compound which contains a silver atom bridge between two rhenium centers has previously been reported (Connelly, Howard, Spencer, and Woodley, 1984).

The cyclic voltammogram of $[AgReH_4(PPh_3)_3]_2$ consists of a single irreversible oxidation at +0.65 V versus Ag/AgCl. The shift in oxidation potential from the +1.70 V found for $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$ to the +0.65 V for $[AgReH_4(PPh_3)_3]_2$ is entirely consistent with the loss of positive charge that occurs at the rhenium centers during the reaction.

ACKNOWLEDGMENTS

We thank Robert Thomas and Professor Richard A. Walton of Purdue University for their assistance with the Varian XL-200 NMR spectra. We also thank the Governors State University Grant Fund for financial support of this work.

LITERATURE CITED

Allison, J. D., C. J. Cameron, R. E. Wild, and R. A. Walton. 1981. Redox Reactions of Polyhydride Complexes of Rhenium: Electrochemistry and Reactions with Alkyl Isocyanides. J. Organomet. Chem. 218:C62-C66.

Cameron, C. J., G. A. Moehring, and R. A. Walton. 1990. Heptahydridobis(triphenylphos-phosphine)rhenium(VII) and Octahydridotetrakis(triphenylphosphine)dirhenium(IV). Inorg. Synth. 27:14-18.

Carr, S. W., S. L. R. Fontaine, and B. L. J. Shaw. 1991. Bimetallic Complexes of Rhenium Multihydrides with Silver, Copper or Mercury containing Diphosphine Ligands. J. Chem. Soc., Dalton Trans. 1991:1025-1027.

Chatt J., and R. S. Coffey. 1969. Hydrido-complexes of Rhenium-containing Tertiary Phosphines. J. Chem. Soc., A 1969:1963-1972.

Connelly, N. G., J. A. K. Howard, J. L. Spencer, and P. K. Woodley. 1984. Complexes of Rhenium and Osmium Polyhydrides with Metallic Lewis Acids: X-Ray Crystal Structure of $[Ag\{ReH_7(PPhPri_2)_2\}_2][PF_6]$. J. Chem. Soc., Dalton Trans. 1984:2003-2009.

Crookes, J. V. and A. A. Wolf. 1973. Competitive Interactions in the complexing of Ethylene with Silver(I) Salt Solutions. J. Chem. Soc., Dalton Trans. 1973:1241-1247.

Geary, W. J. 1971. The use of Conductivity Measurements in Organic Solvents for the Characterization of Coordination Compounds. Coord. Chem. Rev. 7:81-122.

Hartley, F. R. 1973. Thermodynamic Data for Olefin and Acetylene Complexes of Transition Metals. Chem. Rev. 1973:163-190.

Moehring, G. A., P. E. Fanwick, and R. A. Walton. Mixed Polyhydride-Phosphine Clusters That Contain the Re_2Au and Re_2Au_2 Cores: Reversible Protonation and Auration of the Dirhenium Polyhydride Complex Re2(m-H)4H4(PPh3)4. Inorg. Chem. 26:1861-1866.

Moehring, G. A., and R. A. Walton. 1988. Mixed Rhenium-Gold Polyhydrides that contain ReAu and $ReAu_2$ Cores. J. Chem. Soc., Dalton Trans. 1988:1701-1703.

Figure 1. The ^{1}H NMR hydride resonance of $[Ag_2ReH_5(PPh_3)_3](PF_6)_2$.

Sorry, data not available for this volume's on-line version. Contact library or author for reproduction of Figure 1.