# The Synthesis of a Chloropraseodymium Hydride

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Complexes of transition metals containing M–H bonds are of importance in many catalytic reactions and in potential hydrogen storage applications [1]. Consequently, research into transition metal hydride chemistry has aroused great interest and is the focus of much activity. However, by comparison with transition metals, hydrides of rare earth metals have not been as extensively described even though nonstoichiometric binary hydrides and intermetallic hydrides of lanthanides are relatively well known [2].

Isolated examples of lanthanide hydrides have been reported. Silver reported [3] that the precipitates resulting from dissolution of rare earth metals in warm acetic acid or dilute mucochloric acid contain hydridic hydrogen, but their compositions are unknown and the products could be a mixed oxide-hydride phase. Kapur *et. al.* reportedly prepared hydrides of cerium(IV) complexed with cyclopentadienyl or indenyl ligands by the reaction of sodium hydride with tricyclopentadienylcerium(IV) chloride or bis(indenyl)cerium(IV) dichloride in THF [4]. Recently, Struss *et. al.* investigated the reactions of hydrogen with reduced lanthanide halides such as $LaI_2$ and $PrI_2$ and obtained some nonstoichiometric lanthanide hydrides containing halogens [5].

Here we report a new chloropraseodymium hydride, $Cl_2PrH\cdot 1.5$ THF (*1*) which we isolated from solutions of the components of lanthanide diene polymerization catalysts. This hydride was obtained by the reaction of $PrCl_3\cdot 2$ THF with $Et_3Al$ in THF as a green precipitate. Similar reactions with other lanthanum chlorides such as $LaCl_3$, $NdCl_3$, $SmCl_3$ and $LuCl_3$ were also investigated but stable hydrides could not be obtained from any of these reactions. The hydride *1* was prepared by reaction of 5:1 molar ratios of $Et_3Al$ and $PrCl_3\cdot 2$ THF in THF first at 0 °C and then at 25 °C. In this reaction, the $PrCl_3\cdot 2$ THF was initially present as a suspension which dissolved after dropwise addition of the $Et_3Al$ to give a transparent solution. The resulting solution was transferred to another Schlenk tube and concentrated to *ca.* one-half of its original volume. Subsequent stirring for 20 h at 25 °C led to formation of a greenish precipitate of the hydride *1*. This precipitate was washed with THF and dried in *vacuo* at 25 °C (77% yield). Characterization of *1* as $Cl_2PrH\cdot 1.5$ THF rests primarily on the analytical data for *1* (*Anal.* Calcd. for $C_6H_{13}Cl_2O_{1.5}Pr$: Pr, 43.90; Cl, 22.09; C, 22.45; H, 4.08%. Found: Pr, 43.75; Cl, 22.62; C, 23.47; H, 4.09%) and the chemistry of *1* described below. Elemental analysis showed no aluminum was present in *1*.

Compound *1* quickly decomposes in air but is stable in an inert atmosphere and can be stored in a drybox for long periods. Compound *1* reacts vigorously with $H_2O$ to release hydrogen and form insoluble $PrCl_2(OH)$ (or $Pr(OH)_3$). Compound *1* also undergoes alcoholysis reacting with alcohols to form hydrogen and an alcoholate of $PrCl_2(OR)$.

The presence of hydride in *1* was unambiguously demonstrated by reacting *1* with $D_2O$ and analyzing the resulting gas for HD and $D_2$. High resolution mass spectroscopy showed that no $H_2$ was formed and that no $D_2$ was formed. Only HD was present. Thus, hydridic ligands are present in *1* and the observed hydrogen evolution is not merely the result of reaction of a low oxidation state of praseodymium with $H_2O$. The elemental analysis excludes the possibility of aluminum hydrides since no aluminum was present in *1*. The volume of hydrogen evolved in a hydrolysis reaction was measured using a gas buret and was only 42% of what would be expected for an H:Pr ratio of 1:1. We have not ascertained whether this reflects incomplete reaction or a different H:Pr ratio (*e.g.* formulation as $Cl_2Pr\text{-}H\text{-}PrCl_2\cdot 3$ THF) since the volume of hydrogen evolved is not always a reliable indication of stoichiometry for metal hydrides [6]*.

Spectroscopic studies of *1* were generally inconclusive because of the nature of *1*. Specifically, NMR studies of *1* were unrevealing because praseodymium is paramagnetic and because *1* was too reactive (*1* decomposes in DMSO, HMPA, $CCl_4$, $CH_2Cl_2$ and $CHCl_3$) or too insoluble to obtain good spectra. Attempted solid state $^1H$ NMR did show three extremely broad peaks as expected for the hydride of *1* and the $\alpha$ and $\beta$ THF protons, but it was not possible to assign these peaks to *1* and coordinated THF with certainty. Solid state $^1H$ NMR did clearly show *1* was not $Pr(OH)_3$. Attempts to obtain mass spectra of *1* were also unsuccessful since the high (>500 m/e) m/e peaks seen when *1* was heated in the inlet of a mass spectrometer did not contain

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*The elemental analysis for *1* does not distinguish between a mono or dihydride.

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chlorine. However, IR spectra of *1* did have absorptions at 1210 (m) and 690 (m) $cm^{-1}$ which are not present in the IR spectrum of $PrCl_3 \cdot 2$ THF and which disappeared when *1* was decomposed with air or water. These absorptions are in regions characteristic of bridging hydrogen stretching frequencies and deformation frequencies of hydrides [7].

Attempts to obtain crystalline samples of *1* for structural studies proved to be impractical because of the microcrystalline nature of *1* and because of the difficulty of recrystallizing this insoluble compound.

We believe that the analytical results, the IR, and most importantly, the chemistry of *1* strongly support formulation of *1* as a praseodymium hydride, possibly with a hydrogen bridged structure. Although *1* is not a diene polymerization catalyst itself, it does form a diene polymerization catalyst on reaction with $Et_3Al$. Since *1* precipitates from solutions of the components of active lanthanide diene polymerization catalysts, *1* complexed with an organoaluminum reagent or a precursor of *1* (*e.g.* $CH_3CH_2PrCl_2$) possibly complexed with an organoaluminum reagent could be related to the heterogeneous lanthanide catalysts present in hydrocarbon solutions.

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