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Mechanism of Formation of $(\eta^5\text{-}C_5H_5)_2NbH_3$ from the Reaction of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ with Hydridoaluminate Reducing Agents

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Summary

The mechanism of the transformation of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ to $(\eta^5\text{-}C_5H_5)_2NbH_3$ by hydridoaluminate reducing agents has been investigated. Results suggest disproportionation of a niobium(IV) hydride, leading to the trihydride product and a niobium(III) hydridoaluminate, $(\eta^5\text{-}C_5H_5)_2NbH_2AlR_2$, which in turn is converted to the trihydride on hydrolysis. $(\eta^5\text{-}C_5H_5)_2NbH_2AlH_2$ has been isolated; deuterium labelling shows that hydrogens exchange between ring and metal-bridging positions in this molecule.

Introduction

One of the most general methods for preparation of transition metal hydride complexes is the reaction of a transition metal halide with a group III metal hydride, most commonly $NaBH_4$ or $LiAlH_4$ (1). An interesting feature of such reactions is that the formal oxidation state of the product is often higher than that of the starting halide, constituting an apparent oxidation by a reducing agent. In fact, in such cases it is not possible to write a reasonable balanced equation involving only the above two reagents, so that reaction with some other species--solvent, impurities, or water added to quench excess reducing agent (if this is done)--needs to be invoked. Several studies involving hydridoniobium complexes (2-4) required Cp_2NbH_3 ($Cp = \eta^5-C_5H_5$) which can be prepared in good yield from Cp_2NbCl_2 and a reducing agent such as Vitride (a commercially available benzene solution of $NaAlH_2(OCH_2CH_2OCH_3)_2$) (5); this reaction involves a formal oxidation of Nb(IV) to Nb(V). We here report studies aimed at elucidating the course of this transformation; a preliminary account of part of this work has previously appeared (6).

Results

Although Cp_2NbCl_2 is virtually insoluble in benzene, addition of excess Vitride to a suspension results in rapid dissolution and formation of a clear dark brown solution. The NMR of this solution shows two products; one is readily identified as Cp_2NbH_3 by the characteristic metal hydride pattern (7). The other shows two signals: a peak attributable to Cp hydrogens at 5.4 τ, and a very broad signal at about 20.2 τ; the relative intensity of these two peaks is approximately 5:1. These shifts and intensities are very similar to the previously reported $Cp_2NbH_2AlEt_2$ (8), suggesting identification of this second component as $Cp_2NbH_2Al(OCH_2CH_2OCH_3)_2$ (I); separation of the niobium-containing compounds from excess Vitride could not be achieved. The yields of these two compounds (based upon Cp_2NbCl_2) are quite variable, ranging from 40-80% for Cp_2NbH_3 and 0-40% for I, with the total of the two from 70-90%. After hydrolyzing with excess degassed water, however, the only benzene-soluble species detectable by NMR is Cp_2NbH_3 in 70-90% yield.

Use of $LiAlH_4$ as the reductant gives a much cleaner and more reproducible system. On adding solid $LiAlH_4$ to a suspension of Cp_2NbCl_2 in THF (no reaction occurs in benzene) an orange solution results, which by NMR consists of an equimolar (to within experimental uncertainty) mixture of Cp_2NbH_3 and a species with signals quite similar to those of I, which is therefore assigned as

$Cp_2NbH_2AlH_2$ (II). If the reaction mixture is allowed to stand for several hours, the peaks due to II gradually increase while those from Cp_2NbH_3 decrease. Evaporation of THF from this mixture, followed by extraction with benzene, gives a bright orange solution containing only II. In this case II can be isolated (in about 60% yield) as an orange solid and characterized (see Experimetanl section). Addition of water converts II quantitatively to Cp_2NbH_3.

Reduction by $NaAlH_2Et_2$ proceeds similarly: a yellow-brown solution is initially produced which contains two species in equimolar amounts; one is the previously-characterized $Cp_2NbH_2AlEt_2$ (III) (8). The other, however, is not Cp_2NbH_3; its hydride region shows two signals, intensity ratio 2:1, at 14.5 and 15.0 τ respectively. This pattern is very similar to that observed for the adduct formed from Cp_2NbH_3 and $AlEt_3$, in which the Lewis acid triethylaluminum is attached to the central hydrogen (8); hence this compound is formulated as $Cp_2NbH_3 \cdot AlHEt_2$ (IV). Again, on standing IV is gradually converted to III. Hydrolysis of III gives Cp_2NbH_3 quantitatively. Notably, the final product Cp_2NbH_3 obtained from hydrolysis of either II or III is colorless or very pale yellow, whereas that resulting from the procedure involving Vitride is always dark brown.

Reduction of Cp_2NbCl_2 in the presence of potential ligands L (CO, $PMePh_2$, ethylene) gave some Cp_2NbHL in addition to the products previously described. These are not formed by subsequent reaction of the latter, since they are completely stable to added ligand under the reaction conditions. The yields of ligand-containing product appear significant; for example, on reducing Cp_2NbCl_2 with Vitride with variable amounts of added $PMePh_2$, the yield of $Cp_2NbH(PMePh_2)$ by NMR varied as follows: 0.3 eq. L/Nb, 14%; 1.0 eq./Nb, 48%; 3.0 eq./Nb, 50%. Similar behavior was obtained using $LiAlH_4$; in no case was any yield of Cp_2NbHL greater than 50%. (For the gaseous ligands, CO and C_2H_4, yields were considerably less, presumably because of the low concentration of ligand in solution.)

Hydrolysis of benzene solutions of II or III gives Cp_2NbH_3 quantitatively, as mentioned before. The mode of this reaction was investigated by deuterium labelling: when II is treated with excess D_2O the ratio of the hydride peaks to the Cp peak in the NMR of the resulting product is very close to 2:10 instead of the 3:10 value expected for Cp_2NbH_3; thus exactly one deuterium has been incorporated into the product. The hydride region shows a broad, unresolved signal at 12.6 and a partially resolved signal centered at 13.5 τ, which consists of the doublet observed for undeuterated Cp_2NbH_3 plus a broader peak in the middle; the intensities of these two signals are in the ratio 1:2. This is consistent with a statistical mixture of the two possible mono-deuterated isomers of Cp_2NbH_2D (deuterium inside or outside).

An attempt to carry out the converse labelling procedure led to a surprising result: treatment of Cp_2NbCl_2 with $LiAlD_4$ gave a reaction mixture which initially showed no peak in the metal hydride region, as expected. However, after evaporating THF and extracting into benzene, the hydride peak of III at 19.8 τ was present, albeit weak; on standing this peak grew until, after several hours, its intensity was 1/5 that of the Cp signal; the latter showed a corresponding decrease relative to an added reference signal (toluene). From the growth of the high-field signal during the first 15 minutes after extraction, the rate constant for the process giving rise to the growth was estimated as 6×10^{-4} sec^{-1}. Growth of the high-field signal was also observed in the initial THF solution, but its rate was much slower.

Discussion

It is most noteworthy that the initial products of the reduction of the Nb(IV) complex, Cp_2NbCl_2, are (with $LiAlH_4$ or

$NaAlH_2Et_2$) equimolar quantities of a Nb(V) species, Cp_2NbH_3, and a Nb(III) species, $Cp_2NbH_2AlR_2$. This strongly suggests that the primary product of the reaction is the Nb(IV) hydride, Cp_2NbH_2 (or possibly an Al-complexed form, such as $Cp_2NbH(HAlHR_2)$), which undergoes rapid disproportionation to Cp_2NbH_3 and Cp_2NbH. The key intermediate, Cp_2NbH_2, has previously been observed in low-temperature ESR studies; it is known to decompose rapidly even below 0° C, although the stable products of this decomposition were not examined (an ESR signal attributed to Cp_2Nb was detected) (9). The Nb(III) intermediate, Cp_2NbH, is coordinatively unsaturated and would be expected to be highly reactive; it has been suggested as the intermediate leading to C-H bond cleavage in the H-D exchange in benzene catalyzed by Cp_2NbH_3, as well as to the formation of the dimeric form of niobocene, $[CpNbH(\mu\text{-}C_5H_4)]_2$ (7). The fate of this intermediate should depend upon specific reaction conditions; all of the above results may be thus interpreted.

In the presence of a potential ligand, Cp_2NbH will be trapped to form the 18-electron Cp_2NbHL. The yield of the latter will depend upon the concentration of L and its ability to compete with other species for the unsaturated intermediate, but according to the suggested mechanism, it cannot exceed 50%, as is observed. It should be emphasized that Cp_2NbHL is apparently formed only by capturing an unstable intermediate: $Cp_2NbH_2AlH_2$ is completely stable to ligands such as $PMePh_2$ under the reaction conditions, in contrast to the related borohydride complex, $Cp_2NbH_2BH_2$, which reacts rapidly with phosphines to give Cp_2NbHL (10).

Without any added ligand, Cp_2NbH reacts with hydridoaluminum species present in the reaction mixture to give the hydrogen-bridged aluminate complex, $Cp_2NbH_2AlR_2$. In the case of R = H this species could be isolated and characterized; the most useful spectral feature is the NMR signal at around 20 τ, assigned to the bridging hydrides. (No signal is observed for hydrogens terminal on aluminum; this is not uncommon because of interactions with the Al nucleus.) Related complexes which have been reported are $Cp_2NbH_2BH_2$ (10) and $Cp_2TiH_2AlH_2$ (11); the latter was characterized only by ESR. The corresponding products for R = Et or $-OCH_2CH_2OCH_3$ could not be isolated, as the excess reducing agents present have virtually identical solubility properties. However, the hydride region of the NMR allows fairly conclusive identification. The overall transformation leading to the equimolar mixtures thus follows Scheme I.

For the cases R = H or Et, subsequent transformations of the reaction mixture are observed. In the first, Cp_2NbH_3 gradually is converted to <u>II</u>. This must involve reaction of the former with an aluminum hydride species (represented in Scheme I as AlH_3, but others are possible). A model for this reaction is found in the addition of $AlEt_3$ to Cp_2NbH_3, giving (at low temperature) the adduct $Cp_2NbH_3 \cdot AlEt_3$ which on warming loses ethane and forms <u>III</u> (8). In the present case the corresponding adduct would be $Cp_2NbH_3 \cdot AlH_3$ which would give <u>II</u> by elimination of H_2. When R = Et, the Nb(V) species present in solution <u>is</u> the adduct (according to the hydride region of the NMR), presumably $Cp_2NbH_3 \cdot AlHEt_2$, which slowly loses hydrogen to give <u>III</u>.* These reactions are apparently inhibited by THF, since after evaporation of THF and extraction into benzene only the $Cp_2NbH_2AlR_2$

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*An alternate possibility is that the product assigned as <u>III</u> is actually Cp_2NbH_2AlHEt, obtained by loss of ethane from <u>IV</u>. This cannot be readily distinguished by NMR, since the groups terminal on aluminum are not detectable and the shift of the bridging hydrides may be relatively insensitive to substitution in this case. In principle, characterization of the gas phase over the reaction could answer this question, but since the product cannot be separated from excess reductant it would be difficult to do this cleanly. In any case, the choice of the correct structure for <u>III</u> does not affect the overall mechanistic conclusions.

Scheme I:

$$2\ Cp_2NbCl_2 + 4\ MAlH_2R_2 \longrightarrow 2\ Cp_2NbH_2 + 4\ AlHR_2 + 4\ MCl$$

$$2\ Cp_2NbH_2 \longrightarrow Cp_2NbH_3 + Cp_2NbH$$

$$Cp_2NbH + AlHR_2 \longrightarrow Cp_2NbH_2AlR_2$$

products are found; probably the THF coordinates to the aluminum hydride species and prevents it from binding to the hydrogen on niobium. It appears reasonable to propose that the formation of $Cp_2NbH_2BH_2$ from Cp_2NbCl_2 and $NaBH_4$ (10) proceeds by a similar route. Still another model for the chemistry observed here may be found in the titanium analog $(Cp_2TiH)_2$, which reacts with phosphine ligands to give Cp_2TiHL and with diborane to give $Cp_2TiH_2BH_2$ (12).

The reduction with Vitride appears more complicated, in that yields are variable and, particularly, the initial yield of Cp_2NbH_3 is frequently greater than 50%. This requires an alternate source of hydrogen, and an attractive possibility is the ether-like groups on the reductant. It has been noted that hydridoniobium species can be obtained by reducing Cp_2NbCl_2 with sodium amalgam in THF (13), where the solvent is the only possible hydrogen source; hydrogen atoms on carbon adjacent to oxygen, as in Vitride, should be particularly susceptible to abstraction by a metal center. If such a step can compete with other possible reactions, at either the Cp_2NbH_2 or Cp_2NbH stage, this would result in an increased yield of Cp_2NbH_3. In this regard, the different color of the products obtained using Vitride compared to that from $LiAlH_4$ or $NaAlH_2Et_2$ is suggestive: although the products are indistinguishable by NMR, the former is dark brown, indicating that an NMR-silent impurity is present, most likely a complex of Nb(IV). (Cp_2NbCl_2 is a similar dark-brown color.) Also, as reported earlier, methanol can be obtained following thermal decomposition of $Cp_2NbH(CO)$ derived from Vitride but not from $LiAlH_4$ (6). These results are compatible with a pathway involving homolytic hydrogen abstraction from the Vitride alkoxide groups, leading to side-products which incorporate part of the Vitride molecule, as well as to the occasionally observed yields of Cp_2NbH_3 greater than 50%.

The conversion of bridged hydridoaluminates such as II and III to Cp_2NbH_3 on hydrolysis appears to be completely quantitative. Incorporation of a single deuterium on treatment with D_2O suggests that the bridges are cleaved asymmetrically--that is, that both bridging hydrides remain on niobium, and the H-Al bonds are broken. The absence of regioselectivity in the location of the deuterium could result either from a random position of attack, or else the two types of hydrogen in Cp_2NbH_3 may be exchanging. (Such a process is not rapid on the NMR time scale, since two distinct signals are observed, but might well be fast on the preparative time scale.) An alternate possibility is that symmetric cleavage to Cp_2NbH occurs, with the latter rapidly adding HD liberated in the hydrolysis of Al-H bonds; this would give the same isotopic distribution. However, hydrolysis in the presence of $PMePh_2$ gives only Cp_2NbH_3 and no Cp_2NbHL; the latter would be anticipated if the intermediate Cp_2NbH were involved here. It may also be significant that fragmentation of II to Cp_2NbH_2 and AlH_2 is observed in the mass spectrum.

Observation of the growth of NMR peaks assigned to Nb-H-Al bridging hydrides in the reaction of Cp_2NbCl_2 with $LiAlD_4$ indicates that hydrogen exchange between hydride and Cp sites is occurring. A similar process has been observed in related borohydride complexes $Cp_2M(BH_4)_2$ (M = Zr, Hf) (14); in the latter case, exchange is fast enough to measure by NMR line broadening. No line broadening can be observed in II up to about 100^o, by which temperature decomposition is significant, but the exchange rate can be roughly estimated from the rate of growth of the hydride peak at early stages, and is (in benzene) approximately 6×10^{-4} sec^{-1}. In THF exchange is much slower; perhaps THF blocks a vacant site on Nb or Al needed for the exchange process. In the $Cp_2M(BH_4)_2$ complexes cited above all four hydrogens on each boron are involved in the exchange process. Since the hydrogens terminal on Al in II are not observed, it cannot be determined directly whether all four, or only the two bridging hydrogens participate in the exchange. The relative rate of the decrease of the Cp signal compared to the increase of the hydride signals agrees more closely with the value expected for exchange of only the bridging hydrogens, but the magnitude of experimental uncertainty in this determination is too large to reach a definite conclusion.

Experimental

All manipulations were performed using standard inert-atmosphere techniques (15). $NbCl_5$ and all reducing agents were commercially available products, used without additional purification. Cp_2NbCl_2 was prepared by a literature procedure (16). NMR spectra were recorded on Varian A-60 and XL-100 spectrometers; mass spectra on an AEI-MS9 instrument.

General procedure. An accurately weighed sample of Cp_2NbCl_2 was suspended in benzene (for reduction with Vitride or $NaAlH_2Et_2$) or THF (for $LiAlH_4$); typical quantities are 100 mg Cp_2NbCl_2 in 1-2 ml solvent. A weighed amount of toluene was added as a reference standard for quantitation by NMR. In the cases where trapping by added ligand was being studied, a weighed quantity of $PMePh_2$ was added; or, alternatively, the solution was placed under an atmosphere of CO or C_2H_4. An excess of reducing agent (usually 5-10 fold based on Nb) was added, and the mixture stirred for five minutes, after which an aliquot was removed by syringe, transferred to an argon-flushed, serum-capped NMR tube, centrifuged if necessary to remove small amounts of solid, and the ^1H NMR spectrum recorded. The composition of the reaction mixture was determined from the characteristic shifts of the Cp and Nb-H signals, which are summarized below, and their intensities relative to the toluene methyl signal; the precision of such determinations is ± 5%.

NMR parameters: Cp_2NbH_3 (7): Cp, 5.17; Nb-H, 12.6, 13.5 (1:2 ratio). $Cp_2NbH(CO)$ (7): Cp, 5.42; Nb-H, 16.5. $Cp_2NbH(PMePh_2)$: Cp, 5.58 (double doublet, J_{PH} = 2.0 Hz; J_{HH} = 0.4 Hz); Me, 8.33 (doublet, J_{PH} = 6.0 Hz); Nb-H, 17.70 (broad doublet, J_{PH} = 29 Hz). $Cp_2NbH_2AlH_2$ (<u>II</u>), Cp, 5.15; Nb-H-Al, 19.8; $Cp_2NbH_2AlEt_2$ (<u>III</u>), Cp, 5.37; Nb-H-Al, 21.4. $Cp_2NbH_3 \cdot AlHEt_2$ (<u>IV</u>), Cp, 5.12; Nb-H, 14.5; Nb-H-Al, 15.0. $Cp_2NbH_2Al(OCH_2CH_2OCH_3)_2$, Cp, 5.40; Nb-H-Al, 20.2 τ. All of the above spectra were determined in benzene solution; the niobium hydride signals are all very broad (presumably because of interaction with quadrupolar Nb and/or weak coupling to the Cp protons; the latter could be measured for $Cp_2NbH(PMePh_2)$ as 0.4 Hz) and have the correct intensity relative to the Cp signal to within experimental uncertainty.

<u>$Cp_2NbH_2AlH_2$</u>. The reaction mixture of Cp_2NbCl_2 plus excess $LiAlH_4$ in THF (see above) was evaporated to dryness <u>in vacuo</u>, extracted with several portions of benzene, filtered and concentrated. Recrystallization from hexane gave an orange, microcrystalline solid. The solid (and its solutions) is extremely air-sensitive, darkening within seconds of exposure to air. It also is thermally unstable, gradually darkening over several days at room temperature under argon; C, H analytical data on a compound sent out for analysis were not satisfactory, but analysis for Al (as the 8-hydroxyquinolinate (17)) on a freshly prepared sample gave: Calcd., 10.62; Found, 11.35%. The mass spectrum does not show a parent peak; the highest mass fragment detected has m/e = 225, assigned as $Cp_2NbH_2^+$, with peaks corresponding to loss of hydrogen at 224 and 223. Peaks at 29, 28 and 27 are also present; these are assigned as resulting from the remaining fragment, AlH_2^+, and

hydrogen loss therefrom. NMR parameters are given above; the infrared spectrum (THF solution) shows a very broad, intense band with a number of shoulders, centered at about 1680 cm^{-1}, assigned to metal-hydrogen stretching vibrations.

Cp_2NbH_3 by hydrolysis. Benzene solutions containing niobium hydridoaluminate complexes were treated with equal volumes of degassed, distilled water. After agitation, the benzene layer was drawn off by syringe and filtered through a bed of anhydrous sodium sulfate. The filtrate contained, in all cases, only Cp_2NbH_3, obtained essentially quantitatively from the precursor.

Labelling studies. These were carried out exactly as above, using $LiAlD_4$ for $LiAlH_4$ and D_2O for H_2O, and incorporation of deuterium monitored by NMR.

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