The Dy^{3+} and Yb^{3+} ratios are slightly larger, and we do indeed observe a small downshift in the peak OD frequency (Table I). Furthermore, the higher coordination number for the lanthanide ions probably also contributes to suppress the effect of the higher valency.

An eye-catching feature of the lanthanide spectra is the different intensities of the cation bands. The two lighter ions, La^{3+} and Nd^{3+}, display intensities similar to those of the divalent transition-metal ions, whereas the heavier Dy^{3+} and Yb^{3+} are much more intense (Table I). We would like to emphasize that the parameters given in Table I indicate that the band-fit procedure works satisfactorily and gives reliable results; the perchlorate band parameters, which should be invariable, are almost the same for the different solutions. Furthermore, a difference in the cation OD band intensity is not necessarily coupled to a difference in hydration number. This is illustrated by a previous ab initio calculation on the $Zn^{2+}\cdot H_2O$ and $Mg^{2+}\cdot H_2O$ complexes.[30] The calculation showed that the experimentally obtained difference in OD band intensities for these two hexacoordinated ions in aqueous solution[31] could be explained in terms of a 3d-σ orbital overlap for the transition-metal complex.[30] It is also important to stress that the hydration numbers obtained from the double-difference method is derived from band shapes rather than band intensities,[4] and there is no controversy in the fact that large intensity differences are obtained between the lanthanide ions although our results indicate that there is no significant difference in hydration number.

To further analyze this intensity difference, we reevaluated the OD band intensities for fixed lanthanide hydration numbers of 9 for the light and 8 for the heavy ions. This resulted in an intensity decrease for the heavy ions of ~6% and an increase for the light ions of ~10%. The intensity difference between the two groups thus becomes smaller, but is still substantial; it originally amounted to ~40% (Table I). If we believe these hydration numbers to be true, which has been suggested from several authors,[21–23,26–29] it is reasonable to expect an intensity increase for the heavier lanthanide ions. The heavier ions are smaller, and stronger bonds are probably formed to the neighboring water molecules, especially if the primary hydration shell consists of 8 water molecules, in which case they can come closer to the cation than in the case of 9. The reported $R(\mathrm{M}\cdots\mathrm{O})$ distances are 2.58 Å (La), 2.51 Å (Nd), 2.39 Å (Dy), and 2.33 Å (Yb).[21b,27,28] We thus expect a larger dipole moment derivative in the vibrations of the hydrating water molecules for the heavier lanthanide ions.

It thus seems clear that in terms of intensities a grouping in two categories, the light and the heavy lanthanide ions, is established. Due to the fact that the heavy lanthanide OD bands are shifted somewhat downward in frequency (Table I), an increase intensity is expected, in line with the well-known increase in molar absorptivity with decreasing wavenumber.[32] However, this cannot at all account for the very large increase of intensity. Further studies in relation to this issue are needed to reach a better understanding of the phenomenon. An ab initio calculation on lanthanide–water complexes, similar to the one mentioned above for Zn^{2+} and Mg^{2+},[30] could probably give more information. It would then be necessary to take into account all the electrons of the ions, in order to clarify for example the influence of the inner f-orbitals.

Conclusions

The Mn^{2+}, Fe^{2+}, and Co^{2+} transition-metal ions have a similar effect on the coordinated water molecules, giving rise to OD stretching bands at 2427 (2) cm^{-1}. The obtained hydration numbers are 6.5 (5), 7.3 (5), and 6.5 (5), respectively.

Water molecules neighboring the La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} ions give rise to OD bands similar to the transition-metal ion bands. Single OD bands are assigned to cation-perturbed water molecules, at frequencies ranging from 2414 to 2421 cm^{-1}. This means that there is no perturbation of water molecules beyond the primary cation hydration sphere. The double-difference method allows no significant differences in terms of hydration numbers to be detected between the light (7.8 (6) (La) and 8.0 (6) (Nd)) and the heavy (8.7 (6) (Dy) and 8.8 (6) (Yb)) lanthanide ions. However, a significantly increased OD hydration band intensity is observed for the heavy lanthanide ions compared to the light, and a grouping in two categories can be made.

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Registry No. Mn^{2+}, 16397-91-4; Fe^{2+}, 15438-31-0; Co^{2+}, 22541-53-3; La^{3+}, 16096-89-2; Nd^{3+}, 14913-52-1; Dy^{3+}, 22541-21-5; Yb^{3+}, 22537-40-2.

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Notes

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Disproportionation of Alkoxyborohydrides: A ^{11}B NMR Study of the Reaction between Sodium Borohydride and Fluorinated Alcohols and Phenols. The Preparation of Tris(fluoroalkoxy)- and Tris(fluorophenoxy)borohydrides

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^{11}B NMR studies have shown that alkoxyborohydrides, when formed in THF solution at 0 °C from sodium borohydride and methanol or fluoroalcohols, disproportionate over time to yield tetraalkoxyborohydride and BH_4^- ions. In contrast to alkoxyborohydrides, triphenoxy and tris(pentafluorophenoxy)borohydrides appear to be stable at 0 °C toward disproportionation. Consequently, modification of $NaBH_4$ with various fluoro alcohols and fluorophenols will yield a class of reducing agents that may be very promising in designing selective and asymmetric reductions.

Modification of alkali metal borohydrides with alkoxy groups has been reported to afford trialkoxyborohydrides which give reductions with high chemo- and stereoselectivity.[1,2] These trialkoxyborohydrides are usually prepared via a Lewis acid/base reaction from the corresponding trialkoxyborane and a metal hydride and stored over excess metal hydride to prevent any disproportionation reaction.[3,4] Direct reactions of alcohols with

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Table I. Summary of the ^{11}B NMR Data[a]

ROH	$NaBH_3OR$	$NaBH_2(OR)_2$	$NaBH(OR)_3$	$NaB(OR)_4$
methanol	−7.0 (q) $J = 88$ Hz	b	+9.5 (d) $J = 115$ Hz	+5.1 (s)
trifluoroethanol	−5.9 (q) $J = 87$ Hz	b	+9.8 (d) $J = 124$ Hz	+5.4 (s)
hexafluoro-2-propanol	b	b	+11.9 (d) $J = 128$ Hz	b
phenol	b	b	+5.4 (br s)	b
pentafluorophenol	b	b	+5.8 (d) $J = 120$ Hz	b

[a] With reference to $Et_2O{\cdot}BF_3$ in ppm. Negative sign indicates chemical shift upfield from the reference. [b] Not observed.

alkali metal borohydrides have never been pursued as a route to these valuable trialkoxyborohydrides. In large part, this is due to the marked inertness of most of the alcohols toward reaction with these borohydrides.[5a] We report here our results on the synthesis of (fluoroalkoxy)- and (fluorophenoxy)borohydrides directly from sodium borohydride.

Results and Discussion

We speculated that fluoro alcohols, due to their enhanced acidity, may react readily with sodium borohydride to yield the fully substituted borate as well as useful intermediates,[5b] such as tris(fluoroalkoxy)borohydride. Accordingly, we undertook a ^{11}B NMR study of the reaction between sodium borohydride and various fluoroalcohols. Recently, it has been reported that the reactivity and selectivity of alkali metal borohydrides can be enhanced through the use of mixed solvents such as methanol–tetrahydrofuran (THF).[6-8] Consequently, we included the reaction of sodium borohydride with methanol in our study in order to detect the formation of any of the methoxyborohydrides postulated frequently as reactive intermediates from the alkali metal borohydrides in mixed solvents containing methanol.[9,10]

A standard procedure was usually followed: sodium borohydride (4 mmol) was suspended in THF (4 mL) and was treated with appropriate alcohols (neat, 12 mmol) at 0 °C. Gas evolution was measured by using a gas buret.[11] After the gas evolution, a sample was analyzed by ^{11}B NMR spectroscopy. The reaction mixture was maintained at 0 °C for an additional 12 h and the ^{11}B NMR spectrum was redetermined (Table I).

When sodium borohydride reacts with 3 equiv of trifluoroethanol, 2 molar equiv of hydride react rapidly and the third more slowly. However, ^{11}B NMR spectral analyses showed the existence of BH_4^- ions in large amounts in the THF solution through the disproportionation of the initially formed bis(trifluoroethoxy)borohydride. After 12 h at 0 °C, the ^{11}B NMR spectrum of the reaction mixture confirmed the product to be a mixture of (fluoroalkoxy)borohydrides of which tris(trifluoroethoxy)borohydride was the major product. Similarly, 3 equiv of hexafluoroisopropyl alcohol react with $NaBH_4$ to liberate essentially 3 equiv of hydrogen gas over a period of 12 h at 0 °C. The ^{11}B NMR spectral analyses indicated the presence of essentially pure tris(hexafluoroisopropoxy)borohydride. The results summarized in Table I suggest that the initially formed alkoxyborohydrides participate in a series of disproportionation equilibria such as those shown in eqs 1–3. The relative stability of tris(hexafluoroisopropoxy)borohydride ion toward disproportionation, compared to the tris(trifluoroethoxy)borohydride ion, is attributed to an unfavorable equilibrium possibly arising from the steric congestion in the highly branched tetrakis(hexafluoroisopropoxy)borate ions.

$$2NaBH_3(OR) \rightarrow NaBH_2(OR)_2 + NaBH_4 \quad (1)$$

$$2NaBH_2(OR)_2 \rightarrow NaBH_3(OR) + NaBH(OR)_3 \quad (2)$$

$$4NaBH(OR)_3 \rightarrow 3NaB(OR)_4 + NaBH_4 \quad (3)$$

In comparison to these fluorinated alcohols, 3 equiv of methanol react only slowly with $NaBH_4$ in THF at 0 °C causing the solubilization of $NaBH_4$ with the liberation of 1 equiv of hydrogen gas over a period of 12 h. However, the ^{11}B NMR spectrum of the reaction mixture diplayed major peaks due to BH_4^- and $B(OMe)_4^-$ ions and minor peaks due to the elusive $BH_3(OMe)^-$ and $BH(OMe)_3^-$ ions. No NMR evidence of $BH_2(OMe)_2^-$ was seen. Apparently, initially formed methoxyborohydrides undergo rapid disproportionation as well as contribute to the solubilization of the otherwise insoluble sodium borohydride in THF.

Contrary to these results obtained from aliphatic alcohols, 3 equiv of pentafluorophenol react rapidly with sodium borohydride in THF at 0 °C to liberate 3 equiv of hydrogen gas rapidly. The ^{11}B NMR spectrum of the reaction mixture showed the clean formation of tris(pentafluorophenoxy)borohydride, which is stable toward any disproportionation (eq 4).

$$NaBH_4 + 3C_6F_5OH \xrightarrow[3\ h]{THF,\ 0\ °C} NaBH(OC_6F_5)_3 + 3H_2\uparrow \quad (4)$$

Similarly, 3 equiv of phenol react with sodium borohydride at 0 °C to liberate 3 equiv of hydrogen over a period of 12 h and afford triphenoxyborohydride. Thus, the results from this study confirm the ready disproportionation reaction of alkoxyborohydrides and the relative stability of the phenoxyborohydrides. Unlike the alkoxyborohydrides, the phenoxyborohydrides are stable without having to have present an equilibrium concentration of metal hydrides.[4] In the present study we describe, for the first time, the preparation of (fluoroalkoxy)borohydrides starting from sodium borohydride. Sterically demanding (fluoroalkoxy)borohydrides are also relatively more stable than the alkoxyborohydrides. We characterized these borohydrides in solution by hydrogen evolution measurements and ^{11}B NMR spectroscopy. The last three entries in the Table I show a ^{11}B NMR signal attributable to a single-boron containing compound, confirming the clean preparation of the corresponding monohydridoborohydrides.

These reagents are for solution reactions; therefore, it is important to characterize these substituted borohydrides in solutions rather than as solids. For example, sodium trimethoxyborohydride is a stable, white solid. However it rapidly disproportionates in solution to sodium borohydride. We not only give the first spectroscopic evidence for the above disproportionation but also provide spectroscopic evidence for the presence of the highly elusive $BH_3(OMe)^-$ ions in the THF solution of sodium trimethoxyborohydride and in the THF–MeOH solution of sodium borohydride. It is probable that this $BH_3(OMe)^-$ ion is responsible for the enhanced reactivity of sodium borohydride in mixed solvents containing methanol. We are actively exploring the reactions of fluoroalcohols and fluorophenols with alkali metal borohydrides with a view to designing selective and asymmetric reducing agents.

Experimental Section

All operations were carried out under a nitrogen atmosphere. All glassware, syringes, and needles were oven-dried and cooled under nitrogen gas before use. THF was freshly distilled from sodium benzophenone ketyl. Anhydrous ether was used directly. Sodium borohydride and all of the fluorinated alcohols and phenols were commercial products and used without further purification. ^{11}B NMR spectra were obtained at 300 MHz, and the chemical shifts are in δ units relative to $Et_2O{\cdot}BF_3$ with chemical shifts downfield from $Et_2O{:}BF_3$ assigned as positive.

Synthesis of (Fluoroalkoxy)- and (Fluorophenoxy)borohydrides from Sodium Borohydride. The following procedure for the preparation of sodium tris(pentafluorophenoxy)borohydride is typical. A 100-mL round-bottom flask, with a side arm, equipped with a magnetic stirring

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bar was charged with sodium borohydride (0.38 g, 10 mmol) and cooled to 0 °C. A 3.0 M THF solution of pentafluorophenol (10 mL, 30 mmol) was added slowly with constant stirring. Hydrogen evolution was rapid and was essentially complete at 3 h at 0 °C. The reaction mixture was left aside for an additional 9 h to ensure complete reaction. A 1.0-mL aliquot of the clear solution containing the product, $NaBH(OC_6F_5)_3$, gave on hydrolysis 0.96 mmol (100%) of hydrogen. A ^{11}B NMR spectrum of the clear reaction solution showed a single signal: δ 5.8 (d, J = 120 Hz). No signals attributable to the presence of $NaBH_4$ in the solution could be detected by ^{11}B NMR spectroscopy.

Registry No. MeOH, 67-56-1; C_6H_5OH, 108-95-2; C_6F_5OH, 771-61-9; $NaBH_3(OMe)$, 18253-42-4; $NaBH(OMe)_3$, 16940-17-3; $NaBH(OC_6H_5)_3$, 139494-69-2; $NaBH(OC_6F_5)_3$, 139494-70-5; $NaB(OMe)_4$, 18024-69-6; $NaBH_4$, 16940-66-2; trifluoroethanol, 75-89-8; hexafluoro-2-propanol, 920-66-1; sodium (trifluoroethoxy)borohydride, 139494-66-9; sodium tris(trifluoroethoxy)borohydride, 139494-67-0; sodium tris(hexafluoro-2-propanoxy)borohydride, 139494-68-1; sodium tetrakis(trifluoroethoxy)borohydride, 139494-71-6.

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Preparation and Reactivity of Molybdenum Hydride and Phenyldiazene Complexes

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Introduction

We are interested in studying the fundamental reaction chemistry of a class of simple nitrogen-containing molecules, the monosubstituted diazenes (NH=NR). Although NH=NR compounds are very reactive and generally decompose at low temperatures with loss of N_2,[1] the coordination chemistry of these molecules is extensive, and thermally stable aryldiazene complexes have been prepared for various metals including Pt, Fe, Ru, Os, Rh, Ir, Mn, Re, and W.[2,3] The two most general synthetic routes to M(NH=NR) complexes, 1,1-insertion of arenediazonium cations into M–H bonds and oxidation of coordinated hydrazine ligands, are complementary since the former method is limited to aryl derivatives (but ^{15}N and ^{2}H isotopic labeling is trivial),[2] while the latter method allows extension to alkyl (and even the parent, NH=NH) systems.[3] Clearly, the complexed diazenes can be studied to some degree while still attached to the metals, but we have been exploring systems where these ligands can be freed from the coordination sphere at low temperatures, allowing their study as the free molecules in solution.[4]

The discovery that bromide ions smoothly displace the NH=NPh ligand from [*trans,trans*-W(NH=NPh)$(CO)_2$(NO)$(PPh_3)_2{}^+$] at ~0 °C sparked our initial studies into the subsequent chemistry of the very reactive NH=NPh molecule.[4a,b] However, NH=NPh is only marginally stable at the temperature of the displacement reaction ($t_{1/2}$ ~ 85 min at 5 °C), and other aryl and alkyl derivatives are even more thermally sensitive.[1,5] We thus set out to prepare analogous molybdenum diazene complexes with the hope that displacement reactions from this second transition-series metal could be effected at lower temperatures than for the third-row W species. Herein we report the synthesis of a Mo(NH=NPh) complex and its reactivity with respect to displacement of the NH=NPh ligand.

Experimental Section

Dry, oxygen-free solvents and standard high-vacuum and Schlenk techniques were used throughout. [NO][$AlCl_4$] was obtained from the reaction of NOCl with $AlCl_3$.[6] *trans*-Mo($ClAlCl_3$)(NO)$(CO)_4$ (**1**) was prepared from $Mo(CO)_6$ and [NO][$AlCl_4$], and *trans,trans*-Mo(Cl)$(CO)_2$(NO)$(PPh_3)_2$ (**2a**) was prepared from **1** and PPh_3, according to literature procedures;[7] *trans,trans*-Mo(Cl)$(CO)_2$(NO)$(PCy_3)_2$ (**2b**) was analogously prepared from **1** and PCy_3 (Cy = c-C_6H_{11}).

Preparation of *trans,trans*-Mo(H)$(CO)_2$(NO)$(PPh_3)_2$ (3a). A 3.00-g (4.04-mmol) sample of *trans,trans*-Mo(Cl)$(CO)_2$(NO)$(PPh_3)_2$, 6.99 g (26.7 mmol) of triphenylphosphine, and 0.352 g (16.2 mmol) of lithium borohydride were placed in a 100-mL flask attached to a needle valve. The flask was evacuated and cooled in a −78 °C bath, and then 70 mL of THF was vacuum transferred onto the solids. The flask was placed under positive argon pressure and was slowly warmed to near reflux for 40 min, during which time the yellow mixture turned magenta in color and became homogeneous. The flask was removed from the argon manifold, and the solution was filtered through Celite. The filtrate volume was reduced to 15 mL on a rotary evaporator, and then 50 mL of hot EtOH was added to the solution dropwise to precipitate the product. The hot mixture was filtered, and the orange solids were sequentially washed with boiling EtOH (3 × 70 mL) and Et_2O (50 mL). The product was dried in vacuo to give 1.97 g (69% yield). The crude product can be conveniently recrystallized from CH_2Cl_2/petroleum ether to give a bright yellow powder; the recrystallized material was used in all subsequent reactions. Anal. Calcd for $C_{38}H_{31}NO_3P_2Mo$: C, 64.51; H, 4.42; N, 1.98. Found: C, 64.01; H, 4.52; N, 1.87.

***trans,trans*-Mo(H)$(CO)_2$(NO)$(PCy_3)_2$ (3b)** was prepared analogously from **2b** in 57% yield (using PCy_3 instead of PPh_3 in the lithium borohydride reduction).

Preparation of *trans,trans*-Mo(η^1-OSO_2CF_3)$(CO)_2$(NO)$(PPh_3)_2$ (4a). A 0.27-mL volume of triflic acid was added via syringe to a stirred CH_2Cl_2 solution of Mo(H)$(CO)_2$(NO)$(PPh_3)_2$ (2.00 g) at −78 °C. The orange solution was slowly warmed to ambient temperature with concomitant gas evolution (H_2). The resulting yellow solution was filtered, and the product was precipitated as lemon-yellow microcrystals by addition of Et_2O/petroleum ether. The product was washed with petroleum ether and dried in air to give 1.79 g (74% yield) of the triflate complex. Anal. Calcd for $C_{39}H_{30}NO_6F_3P_2SMo$: C, 54.75; H, 3.53; N. 1.64. Found: C, 54.61; H, 3.39; N. 1.78.

***trans,trans*-Mo(η^1-OSO_2CF_3)$(CO)_2$(NO)$(PCy_3)_2$ (4b)** was similarly prepared by the action of triflic acid on **3b** in 41% yield. Anal. Calcd for $C_{39}H_{66}NO_6F_3P_2SMo$: C, 52.52; H, 7.46; N, 1.57. Found: C, 53.09; H, 7.70; N, 1.89.

Preparation of [*trans,trans*-Mo(NH=NPh)$(CO)_2$(NO)$(PPh_3)_2$][PF_6] (5). A 74-mg (0.30-mmol) amount of [PhN_2][PF_6] was added to 200 mg (0.28 mmol) of **3a** in 5 mL of acetone. The yellow suspension rapidly turned homogeneous and deep red (<5 min). The solution was filtered and the volume was reduced to 2 mL, and then Et_2O was added dropwise until precipitation began. Petroleum ether (5 mL) was added to complete precipitation of the bright orange microcrystals, which were filtered off and washed with 20 mL of petroleum ether, affording 222 mg (82% yield) of product. Anal. Calcd for $C_{44}H_{36}N_3O_3F_6P_3Mo$: C, 55.19; H, 3.79; N, 4.39. Found: C, 55.39; H, 3.77; N, 4.26.

[*trans,trans*-Mo(^{15}NH=^{15}NPh)$(CO)_2$(NO)$(PPh_3)_2$][PF_6] (5-$^{15}N_2$) was prepared analogously from **3a** and [$Ph^{15}N_2$][PF_6].

Preparation of *trans,trans*-Mo(Br)$(CO)_2$(NO)$(PPh_3)_2$ (6). On a frit assembly, 5 mL of methylene chloride was transferred at −78 °C onto a mixture of 200 mg (0.234 mmol) of **4a** and 79 mg (0.25 mmol) of [*n*-Bu_4N][Br] in a 25-mL flask. The solution was warmed to ambient temperature and stirred for 5 min. Absolute ethanol (5 mL) was added by syringe to the mixture, and then the solvent volume was reduced in vacuo to precipitate the yellow product. The mixture was filtered, and

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