two molecules are virtually identical, implying the structure found is a true energy minimum. In the solid state, $(C_5H_5)Co(B_9H_9NH)$ possesses a molecular mirror plane through Co(1), N(2), B(3), B(8), and B(9). The cobalt, however, is not over the idealized C_2 axis of the azaborane, being slightly closer to N(2) than to B(3). This asymmetry is also seen in the Co(1)–B(4,7) bond lengths when compared to the Co(1)–B(5,6) bond lengths, being slightly shorter in the latter.

Upon coordination of the $(C_5H_5)Co^{2+}$ group to the azaborane, several bond changes occur as compared to the case for B_9H_{11}-$NH{\cdot}CN(C_6H_{11})$. The nitrogen-basal boron length increases, but the N(2)–B(4,7) bond lengths stay the same. The B(3)–B(5,6) bond lengths decrease nearly 0.1 Å. These two changes are probably interrelated since the cobalt would rather share electrons with the negatively charged nitrogen[28,29] than with the electron-withdrawing B(3). Loss of electron density from the cage due to nitrogen electron density delocalization should be balanced by decreasing the B(3)–B(5,6) bond lengths and increasing the sharing of electrons. Molecular orbital studies are needed to investigate the bonding in this complex.

$(C_5H_5)Co(B_9H_9NH)$, Related Compounds, and Their NMR Spectra. The synthesis of $(C_5H_5)Co(B_9H_9NCH_3)$ is analogous to the synthesis of $B_9H_9NCH_3$ from B_9H_9NH. In both cases, NaH is used to remove the acidic hydrogen, forming H_2. Methyl iodide is then added to form the corresponding methylated derivative. The COSY 2-D spectra of $(C_5H_5)Co(B_9H_9NH)$ and (C_5H_5)-$Co(B_9H_9NCH_3)$ have been obtained and the results listed in Table II. The ^{14}N NMR chemical shifts can be found in Table III. The ^{14}N chemical shift of $(C_5H_5)Co(B_9H_9NH)$, −401 ppm, represents the most upfield shift of any nitrogen–boron compound, and its nitrogen is one of the most shielded nitrogens presently known (screening constant of gaseous NH_3 is −399.9 ± 0.2 ppm).[19a] The significance of this physical property is not yet apparent. The ^{11}B NMR spectrum of $(C_5H_5)Co(B_9H_9NH)$ is very similar to that of the isoelectronic $(C_5H_5)Co(B_9H_9CNH_3)$[25] (Table I), and the structural assignments for the metallocarborane can easily be made (Table II). As was observed with several of the other azaboranes, $(C_5H_5)Co(B_9H_9NH)$ exhibits no cross peak between the resonances of B(8) and B(4,7). Further studies of this and other closo metallaazaboranes are planned. It should also be noted that several of the closo 11-atom cyclopentadienyl first-row metallaheteroboranes are blue or violet.[25-27] The significance of this physical property is not yet apparent.

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Supplementary Material Available: Tables containing complete atomic coordinates with isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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Alkoxides of the Hexanuclear Niobium and Tantalum Cluster Units $[M_6X_{12}](OMe)_2{\cdot}4MeOH$ and $M'_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$ (M = Nb, Ta; X = Cl, Br; M′ = Alkali Metal)

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In an inert atmosphere, the diamagnetic, mixed halide–methoxide clusters of the composition $[M_6X_{12}](OCH_3)_2{\cdot}4CH_3OH$ (M = Nb, Ta; X = Cl, Br) are prepared by the exchange reaction of the terminal halides in the clusters $[M_6X_{12}]X_2{\cdot}8H_2O$ by methoxide groups. The mixed halide–methoxide clusters are not soluble in methanol, but from suspensions in this solvent they dissolve slowly with further addition of alkali-metal methoxides. From concentrated alkaline solution in an oxygen-containing atmosphere a series of diamagnetic compounds $M'_2[Ta_6Cl_{12}](OCH_3)_6{\cdot}6CH_3OH$ (M′ = alkali metal) having all six terminal positions of the cluster units occupied by methoxide groups are isolated and their properties described.

Introduction

The outer halogen atoms (X^a) of the cluster units $[M_6X^i_{12}]^{n+}X^a_nL_{6-n}$, where M = Nb or Ta, X = Cl or Br, n = 2–4, i = inner, and a = outer, are easily replaceable by other halogens[1-5] or anions such as BF_4^- or OH^-.[1-3,6] A series of mixed-ligand clusters of the type $[M_6X^i_{12}]X^a_2$ (X^i = Cl, Br; X^a = Cl, Br, I, OH) has been described,[5,7] and the members have been classified into five structural groups according to their X-ray diffraction patterns. Only another halogen could be introduced into the inner (X^i) positions of the $[M_6X^i_{12}]^{n+}$ cluster units without destruction of the whole cluster unit.[8] Transition-metal alkoxides have been studied extensively and their relation to metal oxide systems discussed.[9,10] Cluster alkoxides of molybdenum and tungsten having two to six metal atoms in one cluster unit and having various bond orders between metal atoms have been widely investigated from preparative, structural, and theoretical points of view.[11,12] Although the cluster alkoxides of the molybdenum hexanuclear cluster units, namely, $Na_2[Mo_6X_8](OR)_6$, with X = Cl or Br and R = Me or Et, and $Na_2[Mo_6(OMe)_8](OMe)_6$, were prepared as early as two decades ago,[13] and their crystal structures solved more recently,[14] so far no results have been reported for

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reactions of $[M_6X_{12}]^{n+}$ cluster units with alkoxide groups. As a part of our work on the investigations of the hexanuclear cluster systems[15] we report here the synthesis and properties of the cluster alkoxides having $[M_6X_{12}]^{2+}$ (M = Nb, Ta) and $[Ta_6Cl_{12}]^{4+}$ cluster units.

Experimental Section

Materials. Commercially available methanol (water content 0.01%) was dried over 3-Å activated molecular sieves and distilled on a vacuum line before each titration. Alkali-metal alkoxides were freshly prepared before each titration by dissolving the weighed amount of alkali metal in an appropriate amount of dried methanol. The cluster compounds $[M_6X_{12}]X_2{\cdot}8H_2O$ (M = Nb, Ta; X = Cl, Br) were prepared as previously described[16] and dissolved in dry methanol, and the solutions were evaporated to dryness on a vacuum line at 35 °C. By this process the amount of water in the starting clusters was considerably reduced. However, completely anhydrous clusters, $[M_6X_{12}]X_2{\cdot}6CH_3OH$, are not desired, as they are not soluble in methanol.[17]

General Information. All cluster methoxides described here are moisture sensitive (the clusters $[M_6X_{12}](OMe)_2{\cdot}4MeOH$ are also oxygen sensitive), and all operations were carried out under dry oxygen-free nitrogen for the $[M_6X_{12}](OCH_3)_2{\cdot}4CH_3OH$ series and an oxygen atmosphere for $M'_2[Ta_6Cl_{12}](OCH_3)_6{\cdot}6CH_3OH$.

Preparation of $[M_6X_{12}](OMe)_2{\cdot}4MeOH$ (M = Nb, Ta; X = Cl, Br). All compounds were prepared in a common manner and obtained in ca. 60% yield. The preparation of the niobium chloride derivative is given as a typical procedure.

A suspension of 0.6 g (0.47 mmol) of $[Nb_6Cl_{12}]Cl_2{\cdot}nCH_3OH{\cdot}(8-n)H_2O$ in 25 mL of dried methanol was dissolved by mixing and heating at 35 °C for 15 min. After cooling, the solution was filtered (G-4 frit) in a drybox under nitrogen in order to remove the evident traces of hydrated niobium(V) oxide. Under nitrogen atmosphere the solution was titrated potentiometrically with sodium methoxide (0.1 mol dm^{-3}) until 2 equiv/cluster was added. The velocity of adding sodium methoxide was 0.1 mL/3 min. At the 2-equiv point the titrated suspension was allowed to settle for 1 h before the precipitated cluster methoxide was filtered off in a drybox under nitrogen atmosphere, washed with methanol (2 mL), and dried in an evacuated tube overnight. Anal. Calcd for $[Nb_6Cl_{12}](OMe)_2{\cdot}4MeOH$: Nb, 47.52; Cl, 36.26; C, 6.14; H, 1.89. Found: Nb, 47.45; Cl, 36.17; C, 6.04; H, 1.90. Calcd for $[Nb_6Br_{12}](OMe)_2{\cdot}4MeOH$: Nb, 32.66; Br, 56.19; C, 4.22; H, 1.30. Found: Nb, 32.48; Br, 56.21; C, 4.12; H, 1.30. Calcd for $[Ta_6Cl_{12}](OMe)_2{\cdot}4MeOH$: Ta, 63.81; Cl, 25.00; C, 4.23; H, 1.30. Found: Ta, 63.60; Cl, 25.02; C, 4.17; H, 1.24. Calcd for $[Ta_6Br_{12}](OMe)_2{\cdot}4MeOH$: Ta, 48.58; Br, 42.91; C, 3.22; H, 0.99. Found: Ta, 48.38; Br, 42.83; C, 3.11; H, 0.95.

Preparation of $M'_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$ (M' = Li, Na, K, Rb). These alkali-metal salts were prepared by using the same general procedure in ca. 70% yield after recrystallization from dried methanol. The detailed procedure is given for the lithium salt.

The weighed amount (1 g, 0.56 mmol) of $[Ta_6Cl_{12}]Cl_2{\cdot}nCH_3OH{\cdot}(8-n)H_2O$ was dissolved in 40 mL of dried methanol at room temperature. After filtration (G-4 frit) in the drybox of the emerald green solution, a freshly prepared solution of lithium methoxide was added dropwise under an oxygen atmosphere until 6–8 equiv/cluster (15 mL of 0.1 mol dm^{-3}) was added (pH = 10.5). During the addition of lithium methoxide the solution changed color from dark green to olive green and finally to dark red within approximately 10 min. The solution was left in oxygen at ambient temperature for another 30 min to ensure complete oxidation, then evaporated on a vacuum line until a volume of ~5 mL was reached, and left under vacuum to crystallize. Alternatively, the oxidized solution could be transferred to a desiccator and left to evaporate at room temperature over P_2O_5 in a carbon dioxide free atmosphere. The dark red crystals that appeared in both cases within a 1-week period were separated and recrystallized from dried methanol by using the same procedure. The deuteriated compounds $[Ta_6Cl_{12}](OCD_3)_2{\cdot}4CD_3OD$ and $Na_2[Ta_6Cl_{12}](OCD_3)_6{\cdot}6CD_3OD$ were prepared by using the same general procedure and deuteriated methanol. Anal. Calcd for $Li_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$: Li, 0.73; Ta, 57.04; Cl, 22.35; C, 7.57; H, 2.22. Found: Li, 0.67; Ta, 56.89; Cl, 22.28; C, 7.43; H, 2.17. Calcd for $Na_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$: Na, 2.37; Ta, 56.09; Cl, 21.98; C, 7.45; H, 2.19. Found: Na, 2.30; Ta, 55.91; Cl, 21.92; C, 7.33; H, 2.11. Calcd for $K_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$: K, 3.97; Ta, 55.17; Cl, 21.62; C, 7.32; H, 2.15. Found: K, 3.88; Ta, 55.05; Cl, 21.55; C, 7.21; H, 2.07. Calcd for $Rb_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$: Rb, 8.29; Ta, 52.69; Cl, 20.65; C, 6.99; H, 2.05. Found: Rb, 8.19; Ta, 52.49; Cl, 20.51; C, 6.90; H, 1.96.

Analysis. In the compounds $[M_6X_{12}](OMe)_2{\cdot}4MeOH$, niobium and tantalum were determined by the "H-tube" method.[18] The precipitation of tantalum as the tannic acid complex was applied for $M'_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$, as previously described.[19] In the filtrates after removal of tantalum the alkali metals were determined as sulfates (confirmed spectrometrically). Halogens were determined by potentiometric titration with standard silver nitrate solution after decomposition of the clusters with KOH and H_2O_2. Carbon and hydrogen analyses were performed by the Rudjer Bošković Institute Analytical Service.

Physical Measurements. A Perkin-Elmer 580 B spectrophotometer was used to measure the infrared spectra. Electronic spectra were recorded on a Cary 17 spectrophotometer using 0.1-cm quartz cells. ^1H NMR spectra were measured on a JEOL 290 FT NMR spectrophotometer in methanol-d_4 with Me_4Si as the internal reference. Magnetic susceptibilities were measured by the Gouy method at 22 °C for the starting substances and all complexes. Thermogravimetric measurements were carried out on a Cahn RG microanalytical balance with a heating rate of 2 °C/min. The X-ray diffraction patterns were recorded on a Philips X-ray diffractometer using graphite-monochromatized Cu Kα radiation. Potentiometric titrations were performed with a Metrohm Potentiograph Model E 436 at 25 °C. Electrolytic conductance measurements were obtained for 10^{-3} mol dm^{-3} solutions at 25 °C in methanol and water by using a Tacussel Electronique conductivity bridge.

Results and Discussion

Clusters of the Type $[M_6X_{12}](OMe)_2{\cdot}4MeOH$ (M = Nb, Ta; X = Cl, Br). These emerald green substances are prepared in good yields by reaction of the clusters $[M_6X_{12}]X_2{\cdot}nCH_3OH{\cdot}(8-n)H_2O$ with 2 equiv of alkali-metal alkoxide in dried methanol. The reactions must be performed in oxygen-free atmosphere in order to prevent oxidation of the cluster units. The isolated compounds also must be handled in a nitrogen atmosphere. They are poorly soluble in aliphatic alcohols but are soluble in dimethyl sulfoxide and *N*,*N'*-dimethylformamide. Because of the low solubilities in deuteriated methanol, it was not possible to observe the OMe signal in ^1H NMR spectra. Neither the chloro nor bromo derivatives could be classified in any of the six structural groups[5,7] found earlier within the crystalline derivatives of the $[M_6X_{12}]^{2+}$ cluster units. The substances are diamagnetic, as expected for $[M_6X_{12}]^{2+}$ clusters.[4]

These cluster methoxides also display most of the physical and chemical properties typical of metal alkoxides.[9] They are sensitive to moisture, and exposure to air leads to hydrolysis of the methoxide groups. This process is nicely observable for $[Nb_6Cl_{12}](OMe)_2{\cdot}4MeOH$, where hydrolysis of the methoxide groups results in formation of the cluster hydroxide $[Nb_6Cl_{12}](OH)_2{\cdot}8H_2O$ according to the IR spectra and X-ray powder diffraction patterns. The process of air oxidation of $[Ta_6Cl_{12}]^{2+}$ to $[Ta_6Cl_{12}]^{4+}$ observed for $[Ta_6Cl_{12}](OMe)_2{\cdot}4MeOH$ stabilizes the coodinated methoxide groups, making the salts of $[Ta_6Cl_{12}](OMe)_6{}^{2-}$ less sensitive to moisture in comparison to the other cluster methoxides described here. An attempt to prepare the analogous ethoxide clusters failed; there was no precipitate upon addition of 2 equiv of alkali-metal ethoxides to the ethanolic solutions of the starting substances. If such a solution was allowed to stand for several days at room temperature, complete destruction of the cluster units was accompanied by formation of hydrated niobium(V) or tantalum(V) oxide.

The presence of both methoxide groups and methanol molecules, all of which are expected to be coordinated, results in the appearance of several absorption bands in the region 1100–900 cm^{-1}, shown in Figure 1. The splitting of the C–O stretching absorption is apparent in all cases, although it is smaller in the spectra of the chloro clusters. For comparison, in the spectra of $[M(OMe)_5]_2$ (M = Nb, Ta), which have both bridging and terminal methoxide groups,[20] the C–O absorptions are also split and are found at higher wavenumbers in the region 1200–1000 cm^{-1}, with main absorption at 1100 and 1113 cm^{-1} for M = Nb and M = Ta, respectively.

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Table I. Physical and Spectral Data for the Compounds

cluster no.	compd	dec pt, °C	λ_M,[a] S cm^{-2}: CH$_3$OH (H$_2$O)	$10^6\chi_g$(295 K), cm^3 g^{-1}	electronic spectra in CH$_3$OH,[b] 10^3 cm^{-1}
1	$[Nb_6Cl_{12}](OMe)_2 \cdot 4MeOH$	32		−0.12	
2	$[Nb_6Br_{12}](OMe)_2 \cdot 4MeOH$	27		−0.19	
3	$[Ta_6Cl_{12}](OMe)_2 \cdot 4MeOH$	32		−0.02	
4	$[Ta_6Br_{12}](OMe)_2 \cdot 4MeOH$	27		−0.16	
5	$Li_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$	30	132 (127)	−0.03	9.4 m, 17.7 sh, 20.4 sh, 27.2 m, 34.3 sh, 43.3 m
6	$Na_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$	28	134 (129)	−0.08	9.4 m, 17.2 sh, 20.2 sh, 27.2 m, 34.4 sh, 42.9 m
7	$K_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$	30	132 (130)	−0.04	9.4 m, 17.2 sh, 20.2 sh, 27.2 m, 34.4 sh, 43.1 m
8	$Rb_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$	35	132 (130)	−0.11	9.5 m, 17.2 sh, 20.2 sh, 27.2 m, 34.3 sh, 43.1 m

[a] For 10^{-3} mol dm^{-3} solution at 25 °C. [b] m = maximum; sh = shoulder.

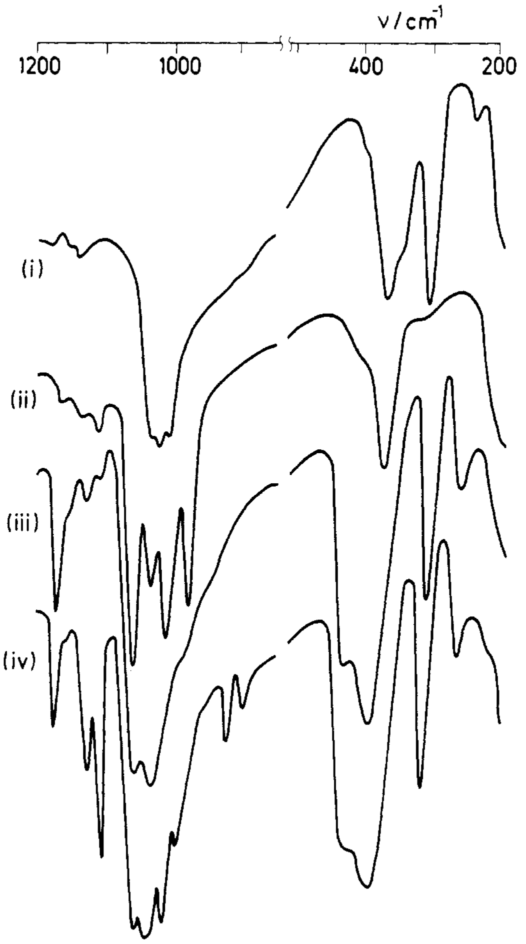

Figure 1. Infrared spectra of (i) $[Ta_6Cl_{12}](OMe)_2 \cdot 4MeOH$, (ii) $[Ta_6Br_{12}](OMe)_2 \cdot 4MeOH$, (iii) $Na_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$, and (iv) $Na_2[Ta_6Cl_{12}](OCD_3)_6 \cdot 6CD_3OH$.

The position of the C–O absorption band of methoxide in these hexanuclear cluster systems is very comparable to that observed at 1050 cm^{-1} in the spectra[13] of $Na_2[Mo_6Cl_8](OMe)_6$, where only terminal methoxide groups are present.[14] A single, strong C–O absorption band is observed at 995 cm^{-1} in the spectrum of each of the bromides $[M_6Br_{12}]Br_2(MeOH)_6$ (M = Nb, Ta), where methanol molecules are coordinated to the M_6 octahedron.[17] Consequently, the low-wavenumber absorption bands in the C–O absorption region for the present complexes must originate from the C–O stretching vibrations of coordinated methanol molecules. For the compounds listed in Table I, two absorptions are present in the M–O region of the spectra, namely, at 361, 340 and 410 (sh), 376 cm^{-1} for clusters 1 and 2 and at 385, 365 (sh) and 415 (sh), 380 cm^{-1} for clusters 3 and 4, respectively. Similar to the above conclusion about the position of C–O stretching frequencies, the absorptions at higher wavenumbers in this region probably originate from the M–O stretching of methoxide groups and those at lower wavenumbers from M–O stretching of coordinated methanol molecules. The positions of the absorption bands arising from the M–X stretching of the bridging halogen atoms are not affected by the presence of methoxide groups or methanol molecules and are observed nearly at the same position as for the starting complexes.[21,22]

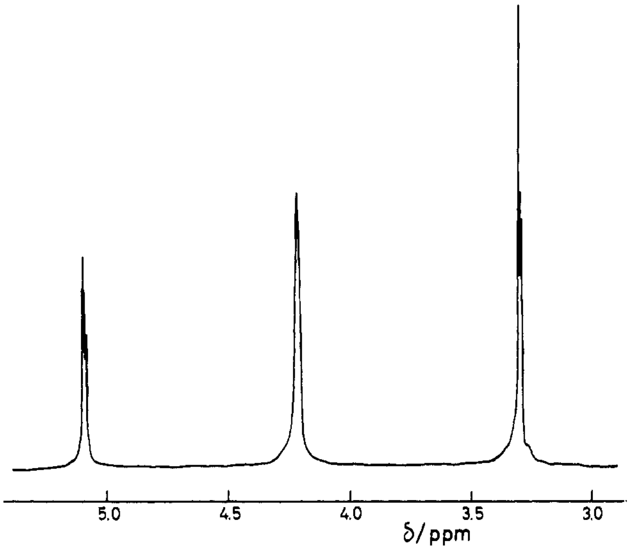

Figure 2. ^{1}H NMR spectrum of $Li_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$ in methanol-d_4.

Clusters of the Type $M'_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$ (M′ = Li, Na, K, Rb). In alkaline medium containing excess alkali-metal methoxide the cluster unit $[Ta_6Cl_{12}]^{2+}$ could be oxidized to $[Ta_6Cl_{12}]^{4+}$ by pure oxygen or by air.[19,23] The process could be nicely followed by change of color (from emerald green to olive green and finally to red) and by the change in the position of the absorption bands in the electronic spectra. The diamagnetic, highly crystalline, dark red (Table I) substances are obtained by slow evaporation of the alkaline methanol solutions of $[Ta_6Cl_{12}]^{4+}$ on a vacuum line or more slowly over phosphorus pentoxide in a carbon dioxide free atmosphere. The substances are soluble in alcohols, water, and strong oxygen donor solvents and could be recrystallized from methanol. Their sensitivity to moisture and thermal stability (Table I) are comparable to those observed for $[M_6X_{12}](OMe)_2 \cdot 4MeOH$. The X-ray powder diffraction patterns do not indicate any isomorphism among this group of compounds. Magnetic measurements and electronic spectra (Table I) confirm that these contain the $[Ta_6Cl_{12}]^{4+}$ cluster unit and are very close to those observed for $M'_2[Ta_6Cl_{12}](OH)_6 \cdot nH_2O$ compounds.[19] Conductivity values obtained in methanol and in water solutions are very comparable. This indicates that in water solutions the hydrolysis of methoxide groups is not accompanied by hydrolysis of the $[Ta_6Cl_{12}]^{4+}$ units.

The infrared spectra display absorption bands similar to those observed for $[M_6X_{12}](OMe)_2 \cdot 4MeOH$ (Figure 1) with some positional differences. The strong and complex C–O absorption band (1200–900 cm^{-1}) is present in all compounds and is shifted to higher wavenumbers in comparison to the position of the same

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absorption band in $[Ta_6Cl_{12}](OMe)_2 \cdot 4MeOH$. The same is observed for the strong doublet in the region of 400 cm^{-1} originating from Ta–O stretching (from OCH_3 groups). These shifts should be the consequence of the shortening of the Ta–OMe terminal bond distances in the compounds containing the $[Ta_6Cl_{12}]^{4+}$ unit as compared to those compounds of the $[Ta_6Cl_{12}]^{2+}$ unit. This effect was previously observed and confirmed by the crystal structure determination for $[Nb_6Cl_{12}]^{n+}$ and $[Ta_6Cl_{12}]^{n+}$ ($n = 2$–4) analogues.[15,24] The deuteriated form of $Na_2[Ta_6Cl_{12}](OMe)_6$ shows significant shifts of all CD_3 vibrations to lower wavenumbers, as expected.[25]

^{1}H NMR Spectra. Proton magnetic resonance spectra of all $M'_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$ were recorded in highly concentrated methanol-d_4 solutions. The spectrum of the lithium compound is shown in Figure 2. Between the methyl proton signal of the methanol at 3.30 ppm and hydroxyl proton signal at 5.09 ppm there is a sharp peak at 4.21 ppm, indicating the presence of protons of the methoxide ligands. The sharpness of this peak indicates the equivalency among the six methoxide ligands present. Slow exchange of the methoxide ligands with solvent methanol leads to a decrease in intensity of the signal at 4.21 ppm, which becomes noticeable after 1 h.

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Preparation of Bis(trifluoromethyl)tellurium, Bis(trifluoromethyl)selenium, Bis(trifluoromethyl)diselenium, Tris(trifluoromethyl)antimony, Tris(trifluoromethyl)arsine, Bis(trifluoromethyl)arsenic Iodide, Tris(trifluoromethyl)phosphine, and (Trifluoromethyl)phosphorus Diiodide by Reaction of Bis(trifluoromethyl)mercury with the Group 5 and 6A (15 and 16) Halides

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The reactions between $Hg(CF_3)_2$ and representative halides of the lower elements of main groups 5 (15) and 6A (16) have been investigated. At 155 °C the reaction between $TeBr_4$ and $Hg(CF_3)_2$ affords $Te(CF_3)_2$ in 92% yield. In 4.5 h at 210 °C $SeBr_4$ and $Hg(CF_3)_2$ form $Se(CF_3)_2$ and $Se_2(CF_3)_2$ in 67% and 3% yields, respectively; in 2.5 h at 170 °C they generate $Se(CF_3)_2$ and $Se_2(CF_3)_2$ in 26% and 57% yields, respectively. At 165 °C SbI_3 and $Hg(CF_3)_2$ produce $Sb(CF_3)_3$, 63%. The interaction of AsI_3 and $Hg(CF_3)_2$ can result in either $As(CF_3)_3$, 75%, or $As(CF_3)_2I$, 54%. Similarly, exposure of PI_3 to $Hg(CF_3)_2$ can synthesize either $P(CF_3)_3$, 55%, or $P(CF_3)I_2$, 37%. In general, these reactions are more convenient than the classic route pioneered by Emeleus and his students, the interactions of trifluoromethyl iodide with the elements.

Introduction

Perfluoroalkyl derivatives of the late main-group elements, the elements of groups 5A (15) and 6A (16), are currently under examination for a variety of reasons. The central thrust of various studies ranges from detailing the differences in reactivity afforded by the "substitution" of more electronegative perfluoroalkyl groups for perhydroalkyl substitutents in ligands like thiolates, alkoxides, and phosphides, e.g., $Mo(CO)_3(Cp)SCF_3$,[1] Re(C-*t*-Bu)(NAr)$(OCMe(CF_3)_2)_2$,[2] and $Fe(CO)_2(Cp)P(CF_3)_2$,[3] to studying multiply bonded compounds of the heavier atoms, e.g., $CF_3P{=}CF_2$[4] and $CF_3As{=}CF_2$,[5] to assessing high-valent oxo acids as fuel cell electrolytes, e.g., $(CF_3)_2P(O)OH$.[6] Potential uses of perfluoroalkyl-substituted ligands include the fine tuning of the electronic properties of a metal complex by means of a judicious selection of the groups attached to, for example, a phosphine, thereby enhancing the catalytic properties of the system,[7] or the introduction of chiral centers by ligands such as $PMe(Ph)(CF_3)$.

Although a variety of alternative syntheses of the trifluoromethyl derivatives of the lower group 5 and 6A elements have been proposed, in practice the procedure almost universally employed is based upon that originally developed by Emeleus and his students during the period 1949–1958. These preparations involve the reactions of any of the elements P, As, Sb, S, and Se with CF_3I at elevated temperatures, 165–285 °C, and high pressures, ca. 50 atm.[8-12] While this type of reaction has been

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