Table II. d-Orbital Populations (e) for Complexes from ab Initio Hartree-Fock Calculations

compd	sym	$x^2 - y^2, z^2$ [a]	xy	xz	yz	total	rel energy, kcal/mol
ScH_2^+	C_{2v}	0.9426	1.0391	0.0769	0.0490	2.1076	0.0
	$D_{\infty h}$	1.5695	0.0000	0.0000	0.0000	1.5695	70.4
ScH_3	C_{3v}	0.6779	0.3587	0.5131	0.5131	2.0628	0.0
	D_{3h}	1.3329	0.6746	0.0000	0.0000	2.0075	12.8
$ScCl_3$	D_{3h}	0.9918	0.4732	0.1523	0.1523	1.7696	
ScF_3	D_{3h}	0.8075	0.3523	0.1445	0.1445	1.4488	
TiH_3^+	C_{3v}	0.0069	0.3376	0.6726	0.6726	1.6900	0.0
	D_{3h}	0.7179	0.7514	0.0000	0.0000	1.4690	8.4
$TiCl_3^+$	D_{3h}	0.3078	0.5485	0.2558	0.2558	1.3679	
TiF_3^+	D_{3h}	0.1929	0.3820	0.1922	0.1922	0.9593	
$Ti(CH_3)_3^+$	nonplanar[b]	0.1602	0.5285	0.3789	0.3789	1.4465	0.0
	planar[c]	0.5387	0.7186	0.0492	0.0492	1.3557	7.5
TiH_4	T_d	−0.3736	0.5936	0.5936	0.5936	1.0654	
$Cl_2TiCH_3^+$	nonplanar	0.2846	0.5723	0.4290	0.1889	1.4748	0.0
	planar	0.7118	0.0887	0.3805	0.2316	1.4126	3.0

[a] Calculated by summing the x^2, y^2, and z^2 components of the Mulliken population and subtracting 2 from the result. This removes the two electrons present in the implicit 3s function. Similar d-orbital populations are found by using the PRDDO method.[14] PRDDO employs five linearly independent d functions and qualitatively reproduces the geometries and inversion barriers found at the ab initio level. [b] C_{3v} symmetry. [c] Refers to the plane containing the titanium and carbons only.

both cases, the planar structures have one imaginary frequency and are thus true transition states for the inversion mode, while the C_{3v} structures are true minima. The energies of ScH_3 and TiH_3^+ were also evaluated at the MP2 level by using GRADSCF. A slightly smaller basis set was employed for the hydrogens in these calculations, specifically a 4-31G*[16] basis.

Discussion

The bond distances and angles for the ground-state structures are shown in Table I. The geometry optimizations revealed ScH_2^+ to be bent ($\theta = 114°$), with a ground-state structure 70.4 kcal/mol lower than the linear form. Our prediction of a bent structure for ScH_2^+ is in qualitative agreement[7] with the MCSCF calculations of Harrison et al. ($\theta = 106.7°$); however, the very large energy of linearization clearly points to the need for correlated wave functions in the linear form. ScH_3, TiH_3^+, and $Ti(CH_3)_3^+$ were determined to be nonplanar molecules in the ground state, with inversion barriers of 12.8, 8.4, and 7.5 kcal/mol, respectively. The addition of MP2 corrections for ScH_3 and TiH_3^+ gives inversion barriers of 8.9 and 10.3 kcal/mol, respectively. Including correlation in these calculations, therefore, does not change the general trends observed in the ab initio calculations. FSGO calculations[8] have previously predicted a planar structure for ScH_3, with an Sc-H bond length of 2.00 Å. In contrast, our geometry optimizatons show the structure of ScH_3 to be nonplanar with a bond angle of 95.4° and a bond length of 1.60 Å. The equilibrium geometry of TiH_4 was found to be tetrahedral. Conversely, $ScCl_3$, ScF_3, $TiCl_3^+$, and TiF_3^+ were found to be planar. The equilibrium structure for $Cl_2TiCH_3^+$ was found to be nonplanar and lies 2.99 kcal/mol below the planar structure.[10]

As alluded to earlier, the complexes containing no π-bonding ligands, such as the hydrides and alkyls, would be expected to be nonplanar since in this form all of the formally vacant d orbitals can be utilized in bonding, whereas in the planar geometry only three d orbitals of the proper symmetry type are available. The d orbital populations for the complexes shown in Table II reflect this phenomenon. The complexes that show large energy differences between the planar (or linear) and nonplanar (or bent) forms also show significant differences in the d-orbital populations. In all these cases, the calculated ground-state geometry has a larger total d-orbital population. The importance of ligand to metal π-bonding in the halide complexes is also apparent in Table II.

Conclusions

We have calculated the ground-state geometries for a series of d^0 titanium and scandium complexes. The hydrides, as well as $Ti(CH_3)_3^+$, were found to be nonplanar (or bent), while the halides had planar structures. These results, along with the d-orbital populations for the complexes, show that when no π-bonding ligands are present, simple d^0 complexes adopt geometries in which the maximum amount of d-orbital participation to bonding is possible. However, when π-bonding ligands are available, such as in the fluorides and chlorides, the complexes will adopt the planar geometries.

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Metastable AlCl as a Solid and in Solution

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Among the low-valent chlorides of group III elements InCl and TlCl are well-known stable solids. Low-valent chlorides in the solid state are also known for the homologues Ga and B: $Ga^I(Ga^{III}Cl_4)$[1,2] and the molecular clusters B_xCl_x ($x = 4, 8, 9$).[3] On the other hand, AlCl as a molecule is thermodynamically stable at high temperatures and low pressure only.[4]

In earlier papers, we reported the synthesis of molecular AlCl at high temperatures and its isolation in solid noble gases.[5] The reactivity of AlCl was demonstrated by some matrix reactions that have been investigated by spectroscopic methods.[6]

In this paper, we present our results on the characterization (a) of solid AlCl at low temperatures by IR spectroscopy and (b)

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of AlCl in solution at room temperature by IR and ^{27}Al NMR spectroscopy. First results concerning the reactivity of AlCl in solution are reported as well.

The synthesis of AlCl(g) is carried out in the following way:

$$\mathrm{Al(l) + HCl(g) \xrightarrow[\text{yield} > 90\%]{1200\ K,\ p\ <\ 0.2\ mbar} AlCl(g) + \tfrac{1}{2}H_2(g)}$$

Condensation of about 1 mg of AlCl(g) on the cold surface (77 K) of an optical cryostat gives dark red, solid AlCl. The IR spectrum shows a broad absorption with a maximum at 320 cm^{-1} and a half-width of about 100 cm^{-1}. The significant decrease of the frequency compared with the gas-phase value of 477 cm^{-1} [7] and the broad shape of the band agree with the vitreous structure of this compound. When the vitreous film of AlCl is allowed to warm up, its color changes to black at about 180 K, since disproportionation occurs according to[8]

$$\mathrm{3AlCl(s) \xrightarrow{180\ K} AlCl_3(s) + 2Al(s)}$$

Therefore, AlCl(s) can be kept for a long time only below 77 K. Under these conditions the disproportionation reaction, which is thermodynamically favored, is prevented.

In a previous paper, we demonstrated that the synthesis described is also useful for the preparation of AlCl(s) on a larger scale.[9] The cryochemical reaction of AlCl with butyne-2, cocondensed in a pentane matrix at 77 K, leads to dimeric 1,4-dialuminacyclohexadiene via a carbene analogue [2 + 1]-cycloaddition. The product obtained is the first example of a compound containing aluminum–olefin π-bonds, as determined by X-ray structure analysis.

If AlCl is condensed into a matrix of a nonpolar and noncoordinating solvent, like pentane, disproportionation occurs also at temperatures higher than 180 K. But if AlCl (0.04 mol) is cocondensed at 77 K with Et_2O (0.2 mol) and toluene (0.6 mol), a dark red solution of AlCl is formed by warming the mixture up to 160 K. From this solution metallic aluminum precipitates at room temperature within a few hours. Visible light[10] and heat as well as concentrating the solution accelerate this process:

$$\mathrm{3AlCl{\cdot}\mathit{x}Et_2O\ in\ toluene \rightarrow AlCl_3{\cdot}Et_2O + 2Al}$$

If the solvent is removed in vacuo and the residue is hydrolyzed, only ether and $Al(OH)_3$, but no ethanol, are formed. Therefore, oxidation of AlCl by an insertion reaction into the CO bond of the ether can be excluded.

The disproportionation process has also been investigated by IR spectroscopy of the solution. In order to eliminate noncoordinated ether, the solution was carefully concentrated at 250 K to 70% of its initial volume. The resulting solution is extremely sensitive to moisture and air. Its IR spectrum was obtained in a special cell under dry nitrogen. It shows a strong, broad band at 450 cm^{-1} that is superimposed by toluene absorptions. We assign this band to ν(AlCl) of a adduct with the formula $AlCl{\cdot}xEt_2O$. When disproportionation sets in, its intensity decreases, and two new absorptions at 545 and 415 cm^{-1} arise. They have to be attributed to ν(as, AlCl) and ν(s, AlCl) of $AlCl_3{\cdot}Et_2O$. This assignment is confirmed by the spectrum of a toluene solution of pure $AlCl_3{\cdot}Et_2O$ scanned under identical conditions.

The presence of Al^I was proved by hydrolysis of the solution and measuring the amount of hydrogen evolved:

$$\mathrm{AlCl{\cdot}\mathit{x}Et_2O \xrightarrow{H_2O} [Al(H_2O)_6]^{3+} + H_2}$$

The quantitative hydrolysis and the analytical determination of aluminum and chloride are in accordance with the formula $Al^ICl{\cdot}xEt_2O$.

Evidence for the structure of the dissolved Al^I species could be obtained from the ^{27}Al NMR spectra: At approximately 190 K, a broad signal at 15 ppm (relative to $Al(H_2O)_6^{3+}$ as standard) is observed. This precludes monomeric Al^I species to be present. Resonances of monomeric AlCl are expected at significantly higher fields.[11] Consequently, we interpret our results with the presence of ether-coordinated Al species that contain metal–metal bonds.[13] When the sample is warmed up for a few minutes to approximately 380 K, a mirrorlike layer of metallic aluminum is formed on the walls of the NMR tube. If an ^{27}Al NMR spectrum of this sample is scanned at room temperature, the resonance at 15 ppm is replaced by a new sharp signal at 101 ppm. It has to be attributed to $AlCl_3{\cdot}Et_2O$.[16]

These solutions of AlCl promise to be a source of interesting chemical reactions. The following two reactions have already been studied:[17]

$$\mathrm{AlCl{\cdot}\mathit{x}Et_2O \xrightarrow[-H_2]{MeOH} (MeO)_2AlCl}$$

IR in Nujol: ν(C–O) = 1050 cm^{-1} (st, br); ν(Al–Cl) = 600 cm^{-1} (st, br). Anal. Calcd: Al, 22.7; Cl, 28.5; C, 19.3; H, 4.9. Found: Al, 21.5; Cl, 28.3; C, 18.7; H, 5.1.

$$\mathrm{AlCl{\cdot}\mathit{x}Et_2O \xrightarrow{PhCH_2Cl} AlCl_3{\cdot}Et_2O + polybenzyl}$$

Polybenzyl, $(C_7H_6)_n$, is isolated as an red oil with a molecular weight of 585 au in $CHCl_3$. Anal. Calcd: C, 93.3; H, 6.7; Found: C, 92.1; H, 7.9. Further work is in progress.

Our results give no evidence for $AlCl_2$. The preparation of this compound has been claimed recently.[18]

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Reactions of Hydrogen Chloride and Boron Trichloride with (Trimethylsilyl)amino Groups

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B,B′,B″-Triamino-*N,N′,N″*-tris(trimethylsilyl)borazine and its telomers[1,2] provide precursors for boron nitride preceramic polymers. Due to the low-yield multistage synthesis, alternate

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