is very surprising is the extraordinarily large dihedral angle between the ring planes, Φ, of 161.6° observed in (η^5-C_5Me_4Et)(η^5-C_5H_5)ReH (**2′**). While such large values of Φ have been observed in other rhenocene species (Table IV), they would not be predicted for a neutral bent metallocene.

It is tempting to invoke a steric interaction to explain this result. However, a plot of the metallocene unit as seen from the side shows no significant distortion of the alkyl groups at the back of the wedge, as would be expected if a strong steric interaction were occurring. In addition, a van der Waals plot of the back of the metallocene wedge shows no significant interaction between the ring units. The absence of any significant slippage, i.e., distance between the ring normal and the ring centroid, or tilt of the rings, i.e., an observed difference between the metal–ring centroid vector and the metal–ring normal vector,[33] also implies the lack of a strong steric effect.

As there appears to be no steric reason for the observed rhenocene hydride structure, it is then necessary to invoke an electronic factor. A general theoretical treatment of the structure and chemistry of bent metallocene complexes has been published by Lauher and Hoffmann.[34] In the molecular orbital analysis carried out for Cp_2ReH, at $\Phi = 135°$, the H^- ligand interacts predominantly with the empty $2a_1$ orbital on the bent metallocene fragment. In this model, as the metallocene dihedral angle, Φ, is increased, the metal fragment orbital drops in energy, yielding a smaller energy difference and correspondingly better bonding. This orbital, however, also rehybridizes and does not extend out as far with increasing Φ; therefore, overlap between the orbitals decreases. The effects compete. In the case of the rhenocene hydrides, the small, spherical H^- ligand is apparently still able to achieve good overlap with the metal center.

This model assumes a symmetric structure with the Re–H bond centered in the metallocene wedge. An unsymmetrical structure, with the hydride ligand out of the central position in the wedge plane, is predicted to be highly unfavorable for a d^4 molecule, as the b_2 orbital increases very quickly in energy upon assuming such a geometry. While it is clear that the position of metal hydride ligands cannot be accurately determined by X-ray analysis,[35] an apparently anomalous position for the hydride ligand is obtained for (η^5-C_5Me_4Et)(η^5-C_5H_5)ReH (**2′**). A more exact determination of the position of this ligand has been thwarted by the empirical absorption correction used and the close vicinity of the rhenium atom. We believe, however, that a neutron structure is warranted and are presently attempting to obtain sufficiently large crystals.

In light of the observed structural parameters, electronic and not steric factors appear to predominate in the structure of Cp*CpReH. In the absence of a rigorous calculation and structures of the normal ring and permethyl complexes, the discussion above remains only a qualitative rationalization of the observed structure. However, an increased bending angle, for example, in Cp_2ReH would still be consistent with the photoelectron spectra observed, i.e., two bands at 6.3 and 6.9 eV for the highest occupied metal-centered orbitals.[36]

We point out that a related system, the isoelectronic complex (η^5-C_5Me_5)ReCl(η^5-(*E*,*E*)-3,4-diphenylhexa-2,4-diene-6-yl) (**3**), has recently been structurally characterized in our research group and possesses a significantly distorted structure in which the five carbon atoms of the 2,4-pentadienyl skeleton do not define a plane. This ligand can best be described as an allyl/alkene system.[37] The distorted structure of the halide species **3** suggests a rationalization for the observed instability of the rhenocene halide complexes (see below).

We are beginning to explore the chemistry of these mixed-ring rhenocene hydride complexes and have already observed significant reactivity differences from those observed for Cp_2ReH. For example, the pentamethylcyclopentadienyl group, as would be expected, increases the basicity of the metal center. Consequently, initial attempts at deprotonation of the metal center by *n*-BuLi and *t*-BuLi under conditions that yield Cp_2ReLi·(base) have not been successful.[38] We are presently attempting to prepare halide derivatives such as Cp*CpReCl.[39] However, we have found these to be unstable during workup, i.e., clean conversion can be observed by ^1H NMR spectroscopy; however, decomposition occurs upon solvent removal. We are also attempting to isolate some of the proposed intermediate borohydride complexes, either from the reaction mixture itself or by independent synthesis.

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Supplementary Material Available: Listings of bond lengths, bond angles, positional parameters, selected least-squares planes (and distances of atoms from those planes), thermal parameters, and all crystal data and refinement parameters, stereodrawings of the molecule and unit cell, and Schakal plots of **2′** as seen from the side and top and with van der Waals radii (17 pages); a listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of Texas at Arlington,
Arlington, Texas 76019-0065

Ground-State Geometries and Inversion Barriers for Simple Complexes of Early Transition Metals

Cynthia A. Jolly and Dennis S. Marynick*

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The electronic and molecular structures of transition-metal hydrides and halides have long been of interest to inorganic and theoretical chemists.[1] A recent report by Zerner and co-workers[2] on the equilibrium geometry of TiH_6^{2-} is a prime example. Crystal and ligand field theories predict the complex to be octahedral. Extended Hückel calculations, however, predict a bicapped tetrahedron of C_{2v} symmetry.[3] Further investigation[2] using more accurate ab initio calculations with large basis sets revealed the ground-state geometry to be octahedral. The addition of electron correlation, however, has been shown to reverse this result; in fact, calculations at the MP2 and MP4 levels of theory predict TiH_6^{2-} to be trigonal prismatic in the ground state.[4]

Many other theoretical studies on simple transition-metal complexes have been performed by various researchers. Schaefer

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and co-workers[5] have studied the electronic structures of transition-metal hydrides including the tetrahydrides of Ti, V, Cr, Mn, Fe, Co, and Ni as well as the dihydrides of Ti, Mn, and Ni. Yates and Pitzer[18] studied the ground-state structures of transition-metal trifluorides for Sc through Ni. Pietro et al.[6] calculated equilibrium geometries for a number of transition-metal fluorides and chlorides using ab initio theory. MCSCF and CI studies on ScH^+ and ScH_2^+ have been performed by Harrison and co-workers.[7] The FSGO method has been used to study complexes such as ScH_3, TiH_4, VH_3, and CrH_2.[8] A theoretical study on a related compound, $Cl_2TiCH_3^+$, using ab initio theory was reported by Fujimoto et al.,[9] but no geometry was published for this complex.

The simplest transition-metal complexes of interest for studying geometrical preferences are those containing d^0 early transition metals, where the complicating effects of introducing a manifold of partially occupied d orbitals are avoided. Naively, one would expect that pure σ-bonded complexes of this type would be planar, since this would minimize Coulombic repulsions. A group-theoretical analysis of these systems, however, reveals that they would most likely be nonplanar. For example, in the D_{3h} form of ScH_3 the ligand orbitals transform as a_1' and e', while the metal d orbitals transform as $a_1' + e' + e''$. Therefore, only three of the five d orbitals are of the correct symmetry for bonding with the ligands. In C_{3v} symmetry, however, the ligand orbitals transform as a_1 and e and all five d orbitals are of the correct symmetry. An analogous result is obtained for linear systems. This leads to the obvious possibility that the equilibrium geometries of early transition-metal hydrides and alkyls may be nonplanar, since more low-lying d orbitals can be utilized in bonding. This same argument, however, will not hold for the complexes containing π-bonding ligands, where the π overlap is expected to be the largest in the planar (or linear) form. In addition, the high electronegativity of π-donating ligands will result in a strong component of ionic bonding, which will also favor a planar structure in which the ligands are as far apart as possible.

Previous work[10] in our theoretical laboratories on the model Ziegler–Natta initiator $Cl_2TiCH_3^+$ revealed its structure to be nonplanar. This enticed us to perform a study of the geometries and inversion barriers of these simple transition-metal systems. In order to minimize the number of complicating factors introduced by partially occupied d orbitals and present a more unified body of work, we chose to look at a series of d^0 early-transition-metal compounds. In particular, we report here the structures and inversion barriers of several hydrides, halides, and related complexes of Ti and Sc.

Calculations

Ab initio gradient optimizations[11,12] employing the GAMESS[11] program were used to obtain the ground-state structures for all complexes except $Ti(CH_3)_3^+$. The geometry for this complex was obtained by optimizing the bond lengths and angles manually while minimizing the ab initio energy. The methyl groups in both the planar (excluding the hydrogens) and nonplanar geometries were fixed such that the complexes had C_{3v} symmetry. To estimate the importance of free rotation about the metal–carbon bond, the methyl groups for both the planar and nonplanar structures were optimized independently by using the approximate PRDDO[13,14] method. The energies of both complexes were lowered, but the inversion barrier remained about the same (6.9 kcal/mol on the assumption of C_{3v} symmetry, 7.2 kcal/mol with no symmetry constraints at the PRDDO level, with the exception of local C_{3v} symmetry for the methyl groups).[15]

Table I. Geometries of Optimized Ground-State Structures

compd	geometrical param[a]	calcd value[b]
ScH_2^+	Sc–H	1.51 (1.80)
	H–Sc–H	114.0 (180.0)
ScH_3	Sc–H	1.60 (1.69)[c]
	H–Sc–H	95.4 (120.0)
ScF_3	Sc–F	1.70
	F–Sc–F	120.0
$ScCl_3$	Sc–Cl	2.24
	Cl–Sc–Cl	120.0
TiH_3^+	Ti–H	1.61 (1.69)[d]
	H–Ti–H	88.4 (120.0)
TiF_3^+	Ti–F	1.69
	F–Ti–F	120.0
$TiCl_3^+$	Ti–Cl	2.11
	Cl–Ti–Cl	120.0
$Ti(CH_3)_3^+$[e]	Ti–C	2.01 (2.00)
	C–Ti–C	108.9 (120.0)
TiH_4	Ti–H	1.67
	H–Ti–H	109.5
$Cl_2TiCH_3^+$	Ti–Cl	2.17 (2.17)
	Ti–C	1.99 (1.99)
	Cl–Ti–Cl	118.7 (126.3)
	Cl–Ti–C	108.3 (116.9)

[a] Distances in angstroms and angles in degrees. [b] Numbers in parentheses correspond to linear or planar form. [c] Calculated vibrational frequencies in cm^{-1} are as follows. D_{3h}: A_2'', 565.15*i*; E′, 690.48, 1104.16; A_1', 1450.40. C_{3v}: A_1, 75.14; E, 286.28, 1327.02; A_1, 1614.38. [d] Calculated vibrational frequencies in cm^{-1} are as follows. D_{3h}: A_2'', 666.16*i*; E′, 835.62, 2067.63; A_1', 2119.27. C_{3v}: E, 95.57; A_1, 230.93; E, 2075.36; A_1, 2169.88. [e] C_{3v} symmetry.

All of the complexes in this study were optimized in both the planar (or linear) and nonplanar (or bent) forms. All bond lengths and angles were optimized except for the methyl group parameters, which included the methyl C–H bond lengths and H–C–H angles, fixed at 1.08 Å and 109.5°, respectively. Ab initio Hartree–Fock calculations were performed with a large basis set, specifically a 4-31G*[16] basis plus diffuse sp functions[17] on all the ligands with the exception of the methyl hydrogens, which were represented by a 4-31G basis.[16a,18] The metal basis set was triple-ζ in the 3d space, double-ζ in the 4s and 4p space, and single-ζ for the inner shells.[19] This corresponds to basis set A in ref 19 with the following Slater exponents: for scandium, 3s/3d 7.792, 3.550, and 1.588, 4s/4p 1.464 and 0.902; for titanium, 3s/3d 8.041, 3.770, and 1.752, 4s/4p 2.215 and 1.355. Diffuse s and p functions were included on the atoms directly attached to the metals to account for the potential anionic character of ligands coordinated to early transition metals. For the metal basis sets the 3d functions included a sixth Cartesian d function used to represent the 3s space.[19] The metal basis sets consisted of 3G expansions on the core orbitals and 2G expansions on the valence 3d, 4s, and 4p orbitals. The convergence criterion for all gradient calculations was set at 5×10^{-4}. For ScH_3 and TiH_3^+, force constants were calculated from analytic second derivatives by using the program GRADSCF.[20] In

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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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Contribution from the Anorganisch-Chemisches Institut
der Universität Münster, Wilhelm-Klemm-Strasse 8,
D-4400 Münster, West Germany

Metastable AlCl as a Solid and in Solution

Matthias Tacke and Hansgeorg Schnöckel*

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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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