Inorg. Chem. **1996,** *35,* 2097−2099

Bent's Rule and the Structure of Transition Metal Compounds

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Received October 30, 1995[⊗]

The equilibrium geometries of Me_2XCl_2 for X = C, Si, Ge, Sn, Pb, Ti, Zr, and Hf are calculated at the HF and MP2 levels of theory using valence basis sets of DZ+P quality. The calculated geometries are in good agreement with experimental gas-phase values. The Cl−X−Cl angle is always smaller than the C−X−C angle when X is a main group element C−Pb. This is in agreement with Bent's rule. The opposite relationship is predicted for the transition metal compounds. The calculated Cl−X−Cl angle is significantly larger than the C−X−C angle for X = Ti, Zr, and Hf. The different order of the Cl−X−Cl and C−X−C angles between the main group and the transition metal compounds is explained by the energy levels of the valence orbitals of the central atom X. The transition metals have mainly sd^x-hybridized bonds, while the main group elements have sp^x-hybridized bonds. The valence s orbital of the main group elements is always below the p valence orbitals, but the valence s orbital of the transition metals is above the valence d orbitals. The energetically lower lying valence orbital concentrates in bonds toward the more electropositive methyl substituents yielding bond angles C−X−C > Cl−X−Cl when X is a main group element and C−X−C < Cl−X−Cl when X is a transition metal. It is suggested that Bent's rule should be formulated in a more general way: *"The energetically lower lying valence orbital concentrates in bonds directed toward electropositive substituents"*.

Introduction

Bent's rule states that *"Atomic s character concentrates in orbitals directed toward electropositive substituents"*.[1] The rule was derived from a systematic comparison of the physical properties of molecules and a correlation with qualitative models such as valence bond structures and bond hybridization.[1] Because of the good correlation between hybridization and molecular structure, Bent's rule has been very helpful to explain qualitatively molecular geometries and to predict the changes of a structure when an atom or group is substituted. For example, the Cl−C−Cl bond angle in Me_2CCl_2 is smaller (108.3°) than the C−C−C angle (113.0°), because the C−Cl bonds have a higher p character at the central carbon atom than the C−C bonds.[2a] Although Bent's rule was suggested for compounds of the first full row of the periodic table, it seems to hold for molecules containing heavier main group elements as well.[1] The Cl−Si−Cl angle in Me_2SiCl_2 is smaller (107.2°) than the C−Si−C angle (114.7°).[2b] Even for transition metal compounds it has been shown that Bent's rule appears to be valid.[3]

We studied recently the performance of different theoretical methods for calculating the geometries of the titanium compounds Me_nTiCl_{4-n}.[4] At all levels of theory it was found that for Me_2TiCl_2 the calculated Cl−Ti−Cl bond angle is *larger* than the C−Ti−C bond angle.[5] This is opposite to what is known about compounds Me_2XCl_2 of main group elements X. At that time the experimental geometry of Me_2TiCl_2 was not known. We have recently been informed about electron diffraction studies of this molecule.[6] The results indicate that the Cl−Ti−Cl bond angle is 116.7° and the C−Ti−C angle is 106.2°, which is in good agreement with the theoretically predicted values. The apparent contradiction between the theoretical[4] and experimental results[6] of the geometry of Me_2TiCl_2 and what is predicted by Bent's rule[1] prompted us to study the equilibrium geometries of the main group compounds Me_2XCl_2 (X = C, Si, Ge, Sn, Pb) and the transition metal compounds Me_2XCl_2 (X = Ti, Zr, Hf). The results are reported in this paper. The trends for the Cl−X−Cl and C−X−C bond angles are compared and the results are discussed in terms of the X−C(Me) and X−Cl natural bond orbital (NBO) hybridization.[7]

Methods

The geometries of the molecules were optimized at the Hartree−Fock (HF) and MP2 (Møller−Plesset perturbation theory terminated at second order)[8] levels of theory using a 6-31G(d) basis set[9] for H, C, Si, and Cl. For Ge, Sn, and Pb an effective core potential (ECP) with a (31/31/1) valence basis set was employed.[10] An ECP has also been used for Ti, Zr, and Hf with a (441/2111/*N*1) (*N* = 4 for Ti, 3 for Zr, 2 for Hf) valence basis set.[11] This basis set combination is denoted basis set II.[12] The optimized geometries are minima on the potential energy surface, which was verified by calculating the Hessian matrix

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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0020-1669/96/1335-2097$12.00/0

Table 1. Calculated and Experimental Bond Lengths (Å) and Bond Angles (deg) of Me_2XCl_2 Molecules

struct	method	X−Cl	X−C	C−X−C	Cl−X−Cl
Me_2CCl_2	HF/II	1.798	1.521	113.0	108.3
	MP2/II	1.793	1.516	113.1	108.7
	expt[a]	1.799	1.523	113.0(±0.4)	108.3(±0.3)
Me_2SiCl_2	HF/II	2.069	1.867	114.5	107.8
	MP2/II	2.061	1.860	114.2	108.2
	expt[b]	2.055	1.845	114.7(±0.3)	107.2(±0.3)
Me_2GeCl_2	HF/II	2.184	1.949	118.6	106.2
	MP2/II	2.183	1.954	118.3	106.6
	expt[c]	2.155	1.926	121.7(±1.4)	106.1(±0.6)
Me_2SnCl_2	HF/II	2.379	2.159	122.1	105.4
	MP2/II	2.380	2.161	122.0	105.9
	expt[d]	2.327	2.109	110.1(±9.1)	107.5(±3.9)
Me_2PbCl_2	HF/II	2.466	2.218	128.6	104.7
	MP2/II	2.470	2.227	128.9	105.1
Me_2TiCl_2	HF/II	2.230	2.037	100.4	122.6
	MP2/II	2.185	2.046	102.7	120.1
	expt[e]	2.196	2.048	106.2(±2.0)	116.7(±0.5)
Me_2ZrCl_2	HF/II	2.402	2.225	104.4	118.2
	MP2/II	2.372	2.207	105.0	117.6
Me_2HfCl_2	HF/II	2.370	2.205	105.0	116.4
	MP2/II	2.344	2.183	104.9	116.5

[a] Reference 2a. [b] Reference 2b. [c] Reference 2c. [d] Reference 2d. [e] Reference 6.

(only positive eigenvalues). The calculations were carried out using the program packages Turbomole[13a] and Gaussian 92.[13b]

Results and Discussion

Table 1 shows the theoretically predicted and experimentally observed geometries of the molecules. The calculations predict that the Cl−X−Cl angle for X = C−Pb is always smaller than the C−X−C angle (Table 1). This is in agreement with the experimental data and with Bent's rule. The calculations predict also that the Cl−X−Cl angle decreases and the C−X−C angle increases continuously from X = C to X = Pb. The reported value for the Cl−Sn−Cl angle is larger than for Cl−Ge−Cl, but the experimental value for Me_2SnCl_2 has a rather high error margin.[2c] We tend to believe that the calculated trend of the Cl−X−Cl bond angles is correct. It should be noted that for all molecules the bond angles calculated at HF/II and MP2/II are not very different from each other. Recent ab initio calculations at the CISD/DZ(d) level of theory of the geometries of Me_2SiCl_2 and Me_2GeCl_2 gave bond angles which are very similar to our results.[19]

The opposite order of the Cl−X−Cl and C−X−C bond angles is calculated for the transition metal compounds. The Cl−X−Cl angle is always clearly larger than the C−X−C angle for X = Ti−Hf. This is also opposite to the prediction due to Bent's rule. The calculated geometry at MP2/II of Me_2TiCl_2 is in good agreement with the experimental gas-phase values.[6] There are no experimental values for Me_2ZrCl_2 and Me_2HfCl_2 known to us. We expect that the theoretically predicted geometries at the MP2/II level of theory for the two compounds should be rather accurate. This means that the Cl−X−Cl angle should decrease with the order Ti > Zr > Hf.

Table 2. Results of the NBO Analysis at MP2/II[a]

	X−C				X−Cl			
	% X	% s(X)	% p(X)	% d(X)	% X	% s(X)	% p(X)	% d(X)
Me_2CCl_2	52.5	31.4	68.5	0.1	46.1	18.6	81.1	0.2
Me_2SiCl_2	26.4	29.3	69.2	1.5	22.8	20.7	76.8	2.6
Me_2GeCl_2	29.1	30.7	68.8	0.5	22.3	19.3	79.4	1.3
Me_2PbCl_2	31.2	31.8	68.2	0.0	18.6	18.2	81.6	0.2
Me_2TiCl_2	29.5	22.7	0.1	77.2	16.6	27.1	0.3	72.6
Me_2ZrCl_2	21.4	24.2	0.2	75.7	12.5	25.7	0.5	73.8
Me_2HfCl_2	15.6	25.5	5.4	69.1	9.8	24.4	11.0	64.6

[a] % X gives the central atom part of the X−C and X−Cl bonds; % s(X), % p(X), and % d(X) give the hybridization of the X−C and X−Cl bonds at the central atom X.

The reverse order of the Cl−X−Cl and C−X−C bond angles of the Me_2XCl_2 molecules when X is a main group element or a transition metal is not a trivial result, and it is difficult to explain by qualitative models. For example, the VSEPR model of molecular geometry[16] fails to explain the observed change in the bond angle. Due to this model, the effect of higher ligand electronegativity should lead to smaller bond angles, because the space occupied by the bonding electron-pair domain in the valence shell of the central atom decreases.[17] Obviously, the prediction is wrong for the transition metal compounds Me_2XCl_2. The failure of the VSEPR model cannot be explained by additional interactions of the ligands with nonbonding d electrons, because the transition metals in Me_2XCl_2 have a d^0 electron configuration. The difference between the main group elements and the transition metals can also not be explained by the size or the electronegativity of the central atom. It is obvious that the calculated and observed change of the bond angles must be related to the differences in the covalent X−Cl and X−C(Me) bonds between X = C−Pb and X = Ti−Hf.

Table 2 shows the results of the NBO analysis at the MP2/II level of theory. The X−Cl bonds of the main group molecules Me_2XCl_2 are always polarized toward the chlorine atom. This can be expected because the electronegativity of Cl is higher than those of the atoms X. The polarization of the X−Cl bond is not very high for Me_2CCl_2 (46.1% at the carbon end), but it is much higher for X = Si−Pb (between 22.8% for Si−Cl and 18.4% for Sn−Cl; Table 2). The X−C(Me) bonds of the main group compounds with X = Si−Pb are polarized toward the carbon end. The C−C(Me) bond of Me_2CCl_2 is slightly (52.5%) polarized toward the central carbon atom. The chlorine atoms reduce the electron density at the central carbon atom of Me_2CCl_2, which leads to a higher electronegativity relative to the methyl carbon atoms. The X−Cl bonds have always a lower s character at X than the respective X−C(Me) bonds (Table 2). This is exactly what is predicted by Bent's rule.[1] We do not want to discuss in detail the small variations of the hybridization of the X−C(Me) and X−Cl bonds from X = C−Pb. It should be noted that there is no regular trend in the change of the % s character of the X−C(Me) and X−Cl bonds from X = C to X = Pb. The increase in the % s character of the X−C bond from Si to Ge and from Sn to Pb may be related to the filling of the d shell and f shell, respectively. The important point for

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this study, however, is the relative % s character of the X−Cl and X−C(Me) bonds.

The NBO analysis shows that the X−C(Me) and X−Cl bonds for X = Ti, Zr, and Hf are strongly polarized toward the carbon and chlorine end, respectively. In particular the Hf−C(Me) and Hf−Cl bonds are very ionic. The polarization of the Ti−C and Ti−Cl bonds is comparable, however, to the corresponding Sn and Pb bonds (Table 2). A qualitative difference between the main group compounds and the transition metal compounds is found for the hybridization. The transition metal bonds of Me_2TiCl_2 and Me_2ZrCl_2 are essentially sd^3 hybridized at the metal with negligible contributions by the metal p orbitals. This is in agreement with the results of photoelectron spectroscopy using variable photon energy of $MeTiCl_3$, which demonstrate clearly that Ti is sd^3 hybridized.[20] The % s character at X = Ti and Zr is always *lower*, however, for the X−C(Me) bonds than for the X−Cl bonds. This is opposite to the sp^x hybridized X−C(Me) and X−Cl bonds of the main group compounds, and it is also opposite to what is predicted by Bent's rule. In the case of Me_2HfCl_2 there is a significant amount of p character in the Hf−C(Me) and particularly in the Hf−Cl bonds (Table 2). The % s character at Hf for the Hf−C(Me) bonds is higher than for the Hf−Cl bonds, but the amount of the (energetically higher lying) metal p contribution is clearly larger in Hf−Cl than in Hf−C(Me).

The apparent contradiction between the calculated % s character of the transition metal bonds and Bent's rule can be resolved when the theoretical foundation of the rule, which was originally suggested only for main group elements,[1] is examined. Covalent σ bonds of main group elements are mainly sp^x hybridized. Atomic p character concentrates in orbitals directed toward electronegative substituents, because *the valence p orbitals of a main group element are always higher in energy than the valence s orbital*. This is because the electron density can more easily be withdrawn from higher-lying orbitals than from the more tightly bound low-lying orbitals. Covalent σ bonds of transition metals are mainly sd^x hybridized. It holds, however, that *the energy levels of the valence d orbitals of transition metals are generally below the energy level of the valence s orbital*.[15] It follows that covalent bonds of transition metals with electropositive substituents should have a higher d character than transition metal bonds with electronegative elements. This is exactly what is calculated for Me_2XCl_2 (Table 2). Bent's rule should therefore be formulated in a more general way: *"The energetically lower lying valence orbital concentrates in bonds directed toward electropositive substituents"*. The lower lying valence orbital for main group elements is the s orbital, while for transition metals it is normally a d orbital.

Unfortunately, the correlation between sd^x-hybridization bonds and bond angle is not as simple as for sp^x-hybridized bonds. It has been shown that a triangular plane can be formed from sd^2-hybridized bonds and a tetrahedral arrangement may be formed from sd^3-hybridized bonds.[18] Thus, sd^2 hybridization correlates with a bond angle of 120° and sd^3 hybridization correlates with 109.5°, just like sp^2 and sp^3. Two sd hybridized bonds, however, form a 90° angle and not 180°.[18] Very recently, Landis et al. extended[21] Paulings's formulas for hybrid orbital strength functions[22] to any arbitrary combination of s, p, and d orbitals. These authors showed that a pair of sd^3 functions has *two* energy minima at 71 and 109°. A pair of sd^2 functions has an energy minimum at 90° rather than 120°.[21b] This shows that the correlation between bond angle and sd^x hybridization is not straightforward. The calculated results shown in Tables 1 and 2 indicate that for the calculated transition metal compounds a higher d character means a smaller bond angle.

Is the correlation between higher d character of a transition metal bond and smaller bond angle restricted to the Me_2XCl_2 molecules investigated here? The answer is no! There are other transition metal compounds which exhibit an order of the bond angles different from that of related main group molecules. Examples are SO_2F_2 and CrO_2F_2. In SO_2F_2, the F−S−F angle is smaller (96.0°) than the O−S−O angle (124.0°).[23a] The F−Cr−F angle of CrO_2F_2 is larger (111.9°) than the O−Cr−O angle (107.8°).[23b] Also the F−P−F angle of POF_3 is smaller (101.1°) than the F−P−O angle (116.9°),[23c] while in VOF_3 the F−V−F angle is larger (111.4°) than the F−V−O angle (107.5°).[23d]

We want to emphasize that the correlation between the hybridization and the bond angle does not mean that the hybridization *enforces* the geometry. The equilibrium geometries of the molecules Me_2XCl_2 are due to the favorable bond energies and minimal nonbonded repulsive interactions. The VSEPR model fails, because it focuses on the differences of the nonbonded repulsive interactions, while for the investigated molecules the different trend of the bond angles is caused by the different bonding interactions. For the transition metals it is energetically more favorable to have a lower % d character in the X−Cl bonds than in the X−C(Me) bonds. For the main group elements it is more favorable to have a lower % s character in the X−Cl bonds than in the X−C(Me) bonds. The structural consequences are a different order of the Cl−X−Cl and C−X−C bond angles for the two classes of compounds.

Acknowledgment. We thank Profs. Sean McGrady, Donald McKean, and Arne Haaland for informing us about their unpublished experimental work. Helpful comments by Profs. Arne Haaland and Clark Landis are gratefully acknowledged. This study was supported by the Deutsche Forschungsgemeinschaft (Grant SFB 260) and the Fonds der Chemischen Industrie. Excellent service was given by the Hochschulrechenzentrum of the Philipps-Universität Marburg. Additional computer time was provided by the HHLRZ Darmstadt and the HLRZ Jülich.

IC951397O

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