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The Nature of Seat-ligand Fitting in Coordination Space.
Part 2. Seat and Geometrical Frame – Pre-bonding Molecular Structures

LI XING FU*, SHEN TIAN-GI, GUO AO-LING, SHUN GUANG-LI and SUN PENG-NIAN

Application Department, The Institute of High Energy Physics, Academia Sinica, Beijing P.O. Box 2732, China

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Abstract

With the ligands packed around the central ion at the non-bonding contact distances, the geometries calculated according to the 'Seat-ligand Least Fitting Method' are found to be in close agreement with the actual molecular structure geometries, providing distinct evidence that steric packing plays a dominant role in molecular structure. Distortions of the geometrical frame caused by bonding and other interactions are discussed.

Introduction

Structural chemistry has, in the past, been discussed in terms of sphere packing for ionic lattices, of electron pair repulsion for compounds of main group elements, and of crystal field stabilization energy for transition metal coordination compounds. It has also been discussed generally in terms of topological analysis [1] and of repulsion of electron clouds [2]. The ligand sizes have been neglected in all the above treatments.

Based on the quantitative description of coordination space [3] our application to structural chemistry is planned as a two-step approach. The first step is aimed at the 'geometrical frame' before bonding. This refers to the way the ligands arrange themselves in the space around the central ion according to their sizes and shapes. For this purpose the metal–ligand distance is estimated as the sum of their Van der Waal's radii. The bond angle is then estimated by Seat-ligand Least Fitting Method. The results are called 'pre-bonding molecular structures' (see Fig. 3). In the second step bonding and other interactions will shorten the non-bonding distances and distort the molecular geometries until the equilibrium between bonding effects and non-bonding repulsions is reached. The actual molecular structures are considered as the reflection of the equilibrium in the second step. Since all the ligands are either spheres and sphere combinations, their seats should also be spheres or sphere combinations. In the first approximation, if we consider only the directly coordinating atoms, the sphere seat could be simplified as the cone seats or cone seat combinations. The former represents monodentate ligands such as cyclopentadienyl whereas the latter represents multidentate ligands. In the present paper only the cone seats are discussed.

In molecular structures, the centres of bonding can be classified into three groups. In the first class, the central ion has lost its valence shell electrons completely, for example Na^+, Mg^{2+}, Sc^{3+}, Ti^{4+}. In the second class, the electron configuration of the central atom or ion is $[I]d^n$ or $[I]p^n$ where [I] refers to the electron configuration of an inert gas. In the third class, the electron configuration of the central atoms are close to that of the next inert gas, for example the oxygen atom in water. The valence shell electron pair repulsion applies well to the third class of bond centres, and the crystal field theory is successful with the second one. Neither model applies to the first class of central ion, for which steric factors become dominant. Because of the weak CFSE, the ions of f-block elements also belong to the first class.

The purpose of the present paper is to introduce the concept of 'Pre-bonding Molecular Structure'. In order to simplify and clarify the discussion, central ions of the first class only are dealt with here. The number of ligands packed around one centre are limited mainly for four ligand packing because distortions of the pre-bonding molecular structures due to other factors are easier to locate.

1. Calculation of the Ligand Sizes

The geometrical frame of a molecular structure is calculated directly according to the sizes and numbers of the ligands present. There are two types of ligands which can be equated to cones. One of the two types consists of ball-like ligands (e.g. F^-, Cl^-, Br^-) and ligands which do not strongly exert a secondary steric effect, such as thiocyanates. Another type of ligand is dish-like (e.g. $C_5H_5^-$, $C_5Me_5^-$, $C_8H_8^{2-}$).

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*Author to whom correspondence should be addressed.

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The fan angle of the unbonded ball-like ligands is derived according to eqn. (1.1) if the ligands are anions (Fig. 1)

$$\theta = \sin^{-1}\left(\frac{r_{X^-}}{R_{M^{n+}} + R_{X^-}}\right) \tag{1.1}$$

where $R_{M^{n+}}$ is the ionic radius of the central ion. For simplicity, corrections for the coordination numbers are not considered. R_{X^-} and r_{X^-} are the ionic and the Van der Waal's radii respectively of the anion.

In the direction of bonding ionic radii are used instead of the Van der Waal's radii. This is only meaningful in our following work when we wish to correct the ionic radii for bridging anions, which have coordination numbers greater than one. In the present paper the difference between the ionic radii and the Van der Waal's radii is not significant.

If the coordinated ligands are not simple anions, the Van der Waal's radius is used through the following equation:

$$\theta = \sin^{-1}\left(\frac{r_X}{R_{M^{n+}} + r_X}\right) \tag{1.2}$$

Equation (1.2) applies both to anionic and to neutral ligands. In neutral ligands X refers to the coordinated atoms.

The fan angle of the unbonded dish-like ligands (e.g. $C_5H_5^-$) is derived according to the following equation:

$$\theta_{Cp} = \tan^{-1}(L/b)$$

where b is the non-bonding distance between the metal centre and the ring centre of the ligand $C_5H_5^-$, and L is the radius of the cyclopentadienyl dish, where $L = L_1 + L_2 + L_3$ (L_1 is the distance between the carbon atom and ring centre, $L_1 = 1.395$ Å/ 2 sin 36° = 1.187 Å, L_2 is the standard bond length between the carbon and the hydrogen atom in aromatic compounds (1.084 Å [4]), and L_3 is the Van der Waal's radius of the hydrogen atom). The radius of the cyclopentadienyl dish was thus calculated to be 3.471 Å. The distance b between the metal centre and the ring centre is derived according to the equation (Fig. 2)

$$b = [(R_{M^{n+}} + r_c)^2 - L_1{}^2]^{1/2} \tag{1.3}$$

For the non-bonding fan angles of ligands, the seats and the geometrical frames were calculated using the SEATANALYS program designed according to the Seat-ligand Least Fitting Method.

2. The Seat-ligand Fitting

The apex of the rigid cones coincides with the apex of a group of seats. Each ligand takes its seat according to the Seat-ligand Least Fitting Method, namely that big cones take large seats and small cones take small seats. The fitting principle can be quantitatively expressed as the minimum of the seat function $F(S)$:

$$F(S) = \sum_{i=1}^{m} K_i(S_i - \theta_i)^2 \tag{2.1}$$

where S_i is the fan angle of ith seat and θ_i is the fan angle of the ith ligand. K_i is the coefficient. When $S_i \geqslant \theta_i$, $K_i = 1$, and when $S_i \leqslant \theta_i$, $K_i = 5$. This is easy to understand because of incompressibility of the rigid cones. m refers to the number of ligands.

According to eqn. (2.1) the calculation deviations are the same both for the large and the small seats. Another expression for the seat function is

$$F'(S) = \sum_{i=1}^{m} K_i(S_i - \theta_i)^2/\theta_i{}^2 \tag{2.2}$$

which gives results with relative deviations, but in practice the results are very similar. Therefore, unless otherwise indicated, all the results given here were calculated according to eqn. (2.1).

Pre-bonding geometrical frame can be calculated using the compound $TiCp_2Cl_2$ as an example ($R_{Ti^{4+}}$ = 0.68 Å). The fan angle of Cp^- is 57.2° and the fan angle of the chloride ion is 46.3°, derived according to the above equation. The seats for the cyclopentadienyl ligand and the chloride ion are calculated to be

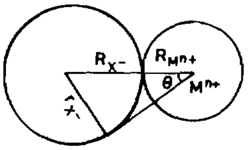


Fig. 1. Calculation of fan angle of a ball-like ligand (Cl^-).

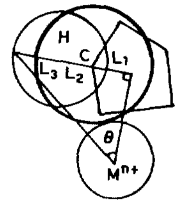


Fig. 2. Calculation of fan angle of a dish-like ligand ($C_5H_5^-$).

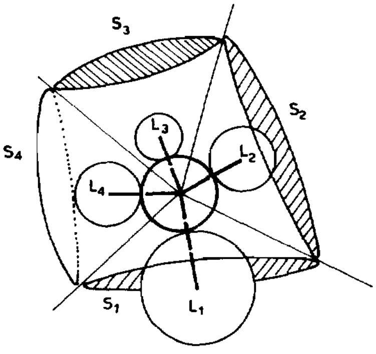


Fig. 3. Pre-bonding molecular structure, each ligand takes its seat according to the Seat-ligand Least Fitting Method.

TABLE I. Ionic and Van der Waals Radii Adopted for Calculation[a]

Ionic radii of the elements										
Ti^{4+}	Zr^{4+}	Hf^{4+}	Th^{4+}	U^{4+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Gd^{3+}	
0.68	0.79	0.78	1.02	0.97	1.061	1.034	1.013	0.995	0.938	
Dy^{3+}	Yb^{3+}	Lu^{3+}	Sc^{3+}	Y^{3+}	Br^-	Cl^-	F^-	H^-	I^-	
0.908	0.858	0.85	0.732	0.893	1.96	1.81	1.33	1.54	2.20	
O^{2-}	S^{2-}									
1.32	1.84									
Van der Waals' radii (Å)										
C^b	N	O	H	F	Cl	Br	I	S	P	CH_3
1.85	1.5	1.4	1.2	1.35	1.80	1.95	2.15	1.85	1.9	2.0
Bond lengths in C_5H_5		Bond lengths in C_5Me_5								
C⋯C(in aromatic compounds)	1.395	C⋯C(in aromatic compounds)	1.395							
C–H (aromatic in C_6H_6)	1.084	C–C (shortening of single bond of aromatic ring)	1.53							

[a] All data except [b] from ref. 4. [b] Ref. 64.

S_{Cp^-} = 60.2° and S_{Cl^-} = 48.9° using the least fitting method. The ligand–metal– ligand packing angles based on the seat interlocking are: Cp–$\widehat{Ti}$–Cp = $2S_{Cp^-}$ = 120.4°, Cp–$\widehat{Ti}$–Cl = $S_{Cp^-} + S_{Cl^-}$ = 109.1° and Cl–$\widehat{Ti}$–Cl = $2S_{Cl^-}$ = 97.8° (Table I). The influences of bonding should decrease further if the metal–ligand distances are greater than the contact distances. Thus the geometrical frame is also calculated on the assumed ion radius $R_{Ti^{4+}} > 0.68$ Å (Fig. 4).

The pre-bonding geometrical frame of several coordination and organometallic compounds of lanthanides, actinides and some group IVB elements have been calculated and the results are given in Tables II–VI. Because of the limited precision of the Van der Waal's radii for the coordinated atoms, the resemblance of the pre-bonding geometrical frames and the experimentally determined molecular structures provide clear evidence that the molecular structures are predominantly decided by the steric packing of the ligands. Bonding only causes distortions from the ideal geometry in the pre-bonding structures. Such a phenomenon is particularly well marked in the molecular structures of the first class ions as the centre of bonding. In previous papers [5–7] we have adopted a CONPACKS computing program which adopted the Minimum Sum of Gap Square Principle. In the present paper the SEATANALYS program was used. The feed-in steric parameters are no longer the empirical FA_L, however the results are very similar giving further evidences of the steric factors.

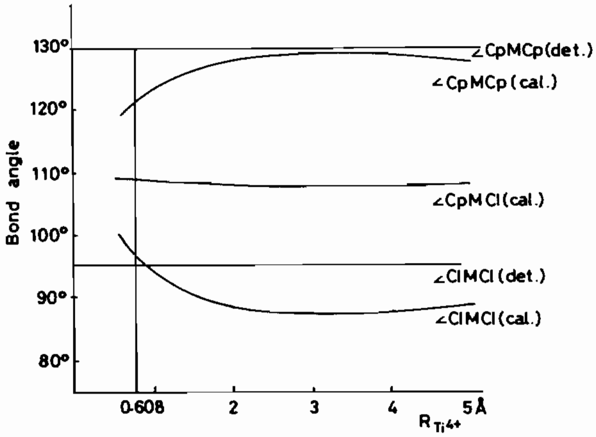


Fig. 4. Pre-bonding geometrical frame of $TiCp_2Cl_2$. The bond angles are calculated with the assumed Ti(IV) radius, increasing from 0.68 to 5 Å. Comparisons are made at 0.68 Å.

The geometrical frame could be regarded as the most probable packing, whereas bonding, static repulsion, the Van der Waal's effect and other interactions will induce systematic distortions from the original geometrical frames. The quantitative treatment of distortions is not the aim of our present paper. We only wish to discuss a few important factors qualitatively.

1. Static Effects

Distortions caused by static effects are due to unequal charge distribution among the ligands. For example, in the tetrahedral structures of UCp_3X (Table II) if all the ligands are equally charged and if the geometrical factor was not considered, a normal tetrahedral structure should result. When both steric packing and static repulsion are considered, the actual molecular structure should be in between the normal tetrahedral structure and the calculated geometrical frames. We can see that the X-ray determined structures are very close to the geometrical frames (Fig. 5 and Table II), nevertheless they are distorted somewhat towards the normal tetrahedron. Moreover, the direction and the extent of the distortion are closely

TABLE II. Calculated Geometrical Frames of MCp_3X and $MCpX_3$ in Comparison with the Actual Bond Angles

Structure	Ligand	θ	Seat	Bond angle	Geometrical frame	Reported angle	Reference
UCp_3F	C_5H_5	53.61	59.0	Cp–U–Cp	118.0	117.2	12
	F	35.94	39.20	Cp–U–F	98.20	99.70	
UCp_3Cl	C_5H_5	53.61	58.0	Cp–U–Cp	116.0	116.7	13
	Cl	40.35	43.69	Cp–U–Cl	101.7	101.0	
UCl	Cp′	53.61	58.0	Cp–U–Cp	116.0	117.1	14
$(C_5H_4CH_2C_6H_5)_3$	Cl	40.35	43.69	Cp′–U–Cl	101.7	100.0	
$UCp_3[CH_3C(CH_2)_2]$	C_5H_5	53.61	57.90	Cp–U–Cp	115.8	115–119	15
	$CH_3C(CH_2)_2$	41.00	44.09	Cp–U–C	101.99	97.5–102	
$UCp_3C{\equiv}CPh$	C_5H_5	53.61	57.90	Cp–U–Cp	115.8	116–119.0	16
	$C{\equiv}CPh$	41.00	44.09	Cp–U–C	101.99	100	
$UCp_3(n\text{-}C_4H_9)$	C_5H_5	53.61	57.90	Cp–U–Cp	115.8	115.8–118.1	17
	$n\text{-}C_4H_9$	41.00	44.09	Cp–U–C	101.99	98.2–102.3	
UCp_3	C_5H_5	53.61	57.90	Cp–U–Cp	115.8	115.6–120.6	17
$(p\text{-}CH_3C_6H_4CH_2)$	$p\text{-}CH_3C_6H_4CH_2$	41.00	44.09	Cp–U–C	101.99	99.4–99.8	
$UCp_3(C{\equiv}CH)$	C_5H_5	53.61	57.90	Cp–U–Cp	115.8	116–121	18
	$C{\equiv}CH$	41.00	44.09	Cp–U–C	101.99	94–99.0	
$ZrCp_3H$	Cp	55.81	59.90	Cp–Zr–Cp	119.8	118.5–120.2	19
	H	31.0	32.67	Cp–Zr–H	92.57	94.7–97.2	
$Cp_3Zr(\sigma\text{-}C_5H_5)$	Cp	55.81	57.4	Cp–Zr–Cp	114.8	117.0	20
	$\sigma\text{-}C_5H_5$	44.49	46.0	Cp–Zr–C	103.4	99.3	
$TiCpCl_3$	Cp	57.23	63.32	Cp–Ti–Cl	115.02	114.3–117.2	21
	Cl	46.29	51.70	Cl–Ti–Cl	103.4	102.2–104.1	
$Lu(Me_5C_5)(CH_3)_3$	Cp′	62.79	69.76	C–Lu–C	98.48	90–110	22
	CH_3	43.25	49.24	Cp′–Lu–C	119.0	112–120	

connected to the electronegativity of the anions. Thus the distortion is more serious when $X = F^-$ than when $X = Cl^-$, simply because the negative charge located on the fluoride anion produces stronger repulsion than does that on the chloride. The bond angle between the fluoride and the cyclopentadienyl group therefore increases and the bond angle between the two cyclopentadienyl groups decreases as compared with the geometrical frame. It is interesting that the bond angles of UCp_3Cl are almost identical with those of the corresponding geometrical frame, whereas the bond angles of UCp_3R have distorted in the opposite direction. This might be explained on the basis that the σ-bonded carbon atom is less negative than the cyclopentadienyls. When the metal centres are lanthanide ions, the bond angle based on the ideal static effect of the three cyclopentadienyl groups should be Cp–Ln–Cp = 120° and Cp–Ln–thf = 90°, when steric packing is not considered. However, because of the secondary steric effect of tetrahydrofuran and also because of the negative charge localised on the oxygen atom, the actual structures are closer to the geometrical frames rather than to the geometry expected by the static repulsion (Table III).

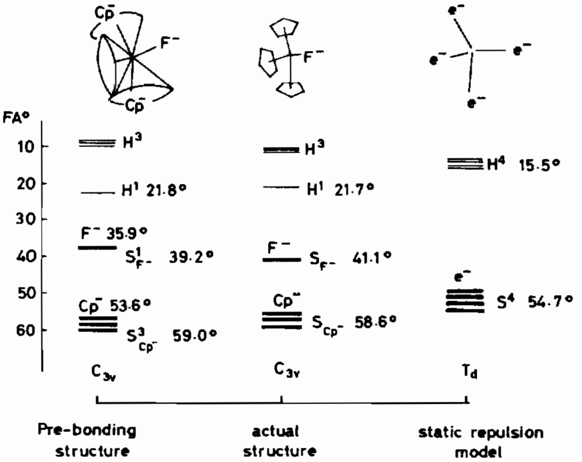


Fig. 5. Distortion of the geometrical frame of UCp_3F caused by static repulsion.

2. *Polarization Effects*

Distortion caused by polarization is essential in the structures of the group IVB elements. The molecular structure of $TiOCl_4^{2-}$ is a good illustration of such distortion. When the ligands are at the non-bonding distances, the cone formed by the oxygen atom is

TABLE III. Calculated Geometrical Frames of MCp_3L in Comparison with the Actual Bond Angles

Structure	Ligand	θ	Seat	Bond angle	Geometrical frame	Reported angle	Reference
YCp_3thf	Cp	54.53	58.80	Cp–Y–Cp	117.6	117.4	23
	thf	37.63	40.20	Cp–Y–thf	99.0	99.1	
$LaCp_3thf$	Cp	52.56	59.20	Cp–La–Cp	118.4	117.7	23
	thf	34.67	38.12	Cp–La–thf	97.30	99.50	
$PrCp_3thf$	Cp	53.11	59.10	Cp–Pr–Cp	118.2	117.6	24
	thf	35.45	38.67	Cp–Pr–thf	97.77	99.0	
$NdCp_3thf$	Cp	53.32	59.0	Cp–Nd–Cp	118.0	117.0	24
	thf	35.77	39.20	Cp–Nd–thf	98.20	100.2	
$GdCp_3thf$	Cp	53.99	58.90	Cp–Gd–Cp	117.8	117.5	25
	thf	36.78	39.71	Cp–Gd–thf	98.61	99.20	
$(YbCp_3)_2Py_2$	Cp	54.96	58.40	Cp–Yb–Cp	116.8	115.6–120	26
	Py	39.50	42.03	Cp–Yb–Py	100.43	94.6–102.5	
$PrCp_3CNC_6H_{11}$	Cp	53.11	58.80	Cp–Pr–Cp	117.6	118.9	27
	CNC_6H_{11}	36.65	40.20	Cp–Pr–N	99.0	96.2	
$LuCp_3thf$	Cp	55.06	58.70	Cp–Lu–Cp	117.4	114.3–120.3	28
	thf	38.48	40.68	Cp–Lu–thf	99.38	97.4–100.0	
UCp_3thf	Cp	54.02	59.60	Cp–U–Cp	119.2	110.4–122.4	29
	thf	33.29	35.56	Cp–U–thf	95.16	90.2–106.0	

TABLE IV. Calculated Geometrical Frames of MCp_2X_2 in Comparison with the Actual Bond Angles

Structure	Ligand	θ	Seat	Bond angle	Geometrical frame	Reported angle	Reference
$Yb(Me_5C_5)_2Py_2$	Cp′	61.94	66.25	Cp′–Yb–Cp′	133	136.3	30
	Py	38.12	41.35	Cp′–Yb–Py	107.6	108	
				Py–Yb–Py	82.7	82.5	
$(AsPh_4)[Nd\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2Cl_2]$	Cp′	53.32	61.80	Cp′-Nd-Cp′	123.6	126.3	31
	Cl	39.92	47.0	Cp′–Nd–Cl	108.8		
				Cl–Nd–Cl	94.0	99.3	
$(C_5H_5)_2Ti(NCO)_2$	Cp	57.23	61.7	Cp–Ti–Cp	123.4		32
	NCO	43.48	47.12	Cp–Ti–N	108.82		
				N–Ti–N	94.24	94.7	
$(C_5H_5)_2Ti(NCS)_2$	Cp	57.23	61.7	Cp–Ti–Cp	123.4	133.7	33
	NCS	43.48	47.12	Cp–Ti–N	108.82		
				N–Ti–N	94.24	93.9	
$TiCp_2Cl_2$	Cp	57.23	60.2	Cp–Ti–Cp	120.4	129.4	34
	Cl	46.29	48.88	Cp–Ti–Cl	109.1		
				Cl–Ti–Cl	97.8	95.2	
$ZrCp_2Cl_2$	Cp	55.81	60.85	Cp–Zr–Cp	121.7		35
	Cl	43.81	48.12	Cp–Zr–Cl	109.0		
				Cl–Zr–Cl	96.25	97.1	
$ZrCp_2F_2$	Cp	55.81	63.1	Cp–Zr–Cp	126.2	127.8	36
	F	39.55	45.42	Cp–Zr–F	108.52		
				F–Zr–F	90.83	96.2	
$ZrCp_2I_2$	Cp	55.81	59.7	Cp–Zr–Cp	119.4	126.3	36
	I	45.98	49.45	Cp–Zr–I	109.15		
				I–Zr–I	98.90	96.20	
$Cp_2Ti(N_3)_2$	Cp	57.23	61.7	Cp–Ti–Cp	123.4	132.2	37
	N_3	43.48	47.12	Cp–Ti–N	108.82	106.1	
				N–Ti–N	94.24	94.1	
$Ti(Me_5C_5)_2Cl_2$	Cp′	64.65	63.3	Cp′–Ti–Cp′	126.6	137.4	38
	Cl	46.29	45.17	Cp′–Ti–Cl	108.47	104.5	
				Cl–Ti–Cl	90.34	92.94	

(continued)

TABLE IV. *(continued)*

Structure	Ligand	θ	Seat	Bond angle	Geometrical frame	Reported angle	Reference
$Ti(CH_3C_5H_4)_2Cl_2$	Cp′	57.23	60.2	Cp′–Ti–Cp′	120.4	130.2	39
	Cl	46.29	48.88	Cp′–Ti–Cl	109.08	106.8	
				Cl–Ti–Cl	97.75	93.15	
$[Yb(Me_5C_5)_2I_2]Li(ether)_2$	Cp′	62.71	63.3	Cp′–Yb–Cp′	126.6	135–140	40
	I	44.67	45.17	Cp′–Yb–I	108.5		
				I–Yb–I	90.3	86.1	
$[Yb(C_5H_4SiPh_2Me)_2Cl_2]Li(ether)_2$	Cp′	54.96	61.2	Cp′–Yb–Cp′	122.4	135–140	40
	Cl	42.43	47.71	Cp′–Yb–Cl	108.9		
				Cl–Yb–Cl	95.4	87.14	
$U(Me_5C_5)_2Cl_2$	Cp′	61.53	65.0	Cp′–U–Cp′	130		41
	Cl	40.35	43.0	Cp′–U–Cl	108		
				Cl–U–Cl	86	95.3	
$Th(Me_5C_5)_2(CH_2SiMe_3)_2$	Cp′	61.01	64.90	Cp′–Th–Cp′	129.8	134.9	42
	C	40.14	43.13	Cp′–Th–C	108.0	104.5	
				C–Th–C	86.3	96.8	
$HfCp_2(CH_3)_2$	Cp	55.93	60.5	Cp–Hf–Cp	121	132.1	43
	C	44.70	48.6	Cp–Hf–C	109.1	105.9–106	
				C–Hf–C	97.2	94.8	
$Hf(\eta\text{-}C_5H_5)_2[(CO)_9Co_3CO]_2$	Cp	55.93	61.97	Cp–Hf–Cp	123.94	129.5	44
	O	41.81	46.8	Cp–Hf–O	108.77		
				O–Hf–O	93.6	96.1	
$Ti(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2$	$\eta^1\text{-}C_5H_5$	46.99	49.33	C–Ti–C	98.66	86.3	45
	$\eta^5\text{-}C_5H_5$	57.23	59.8	C–Ti–Cp	109.13	108.1	
				Cp–Ti–Cp	119.6	129.9	
$TiCp_2(\eta^1\text{-}NC_4H_4)_2$	N	43.48	47.12	N–Ti–N	94.24	90.4	
	Cp	57.23	61.7	N–Ti–Cp	108.82	106.5–109.1	46
				Cp–Ti–Cp	123.4	128.5	
$ZrCp_2(\eta^1\text{-}NC_4H_4)_2$	N	40.92	46.3	N–Zr–N	92.6	95.68	46
	Cp	55.81	62.38	N–Zr–Cp	108.68	105–108.4	
				Cp–Zr–Cp	124.76	128.5	
$Zr(\eta\text{-}C_5H_5)_2(CO)_9Co_3CO_2$	Cp	55.81	62.95	Cp–Zr–Cp	125.9	129.3	44
	O	39.74	45.60	Cp–Zr–O	108.55		
				O–Zr–O	91.2	96.1	
$Cp_2Zr(CH_2SiMe_3)_2$	Cp	55.81	60.50	Cp–Zr–Cp	121	129.9	47
	C	44.49	48.53	Cp–Zr–C	109.3	105.6–106.5	
				C–Zr–C	97.06	97.80	

smaller than the cones of each of the chloride anions (Fig. 6). The seat occupied by the oxygen atom should therefore be smaller than those taken by chlorides. According to the Seat-ligand Fitting Method, one might expect the structure of $TiOCl_4^{2-}$ to be similar to that of BrF_5, with the metal centre lying out of the square pyramid. However, because the largest seat located opposite the pyramidal oxygen in $TiOCl_4^{2-}$ is empty, according to the Isomer Criterion [8], such a structure is not stable (in BrF_5, the largest seat is taken by the lone pair electrons). In fact, in forming the molecular structure, the bond length between the metal and the chloride ions has decreased much less than that between the metal and the oxygen ions, so that the seat taken by the oxygen becomes the largest one, while the vacant seat, originally expected to be the largest, has decreased in size to become the minor one. The inversion of seat

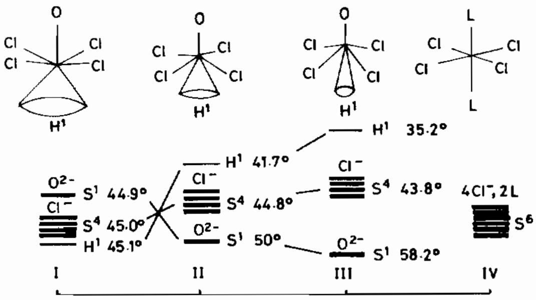


Fig. 6. Distortion of the geometrical frame of $TiOCl_4^{2-}$. I, geometrical frame calculated based on the contact distance; II, the great shortening of Ti–O distance in forming the bond had pushed the O–Ti–Cl bond angle greater than 90°; III, the actual molecular structure of $TiOCl_4^{2-}$ the strong static repulsion made the Cl–Ti–O bond angle even greater; IV, the vacant seat H^1 tends to accommodate additional ligands to form an octahedral structure.

TABLE V. Calculation Deviation due to Uncorrected Van der Waals and Ionic Radii

Structure	Ligand	Seat	Bond angle	Geometrical frame	Reported angle	Deviation	Reference
$Yb(Me_5C_5)_2AlCl_4$	Cp'	64.40	Cp'–Yb–Cp'	128.8	135–140		48
	Cl	43.78	Cp'–Yb–Cl	108.18			
			Cl–Yb–Cl	87.56	73.36	+14.2	
$[Yb\{\eta^5\text{-}\{C_5H_3SiMe_3]_2\}_2Cl]_2$	Cp'	61.2	Cp'–Yb–Cp'	122.4	130.0		49
	Cl	47.71	Cp'–Yb–Cl	108.91	100		
			Cl–Yb–Cl	95.42	80	+15.42	
$[Yb(CH_3C_5H_4)_2Cl]_2$	Cp'	61.2	Cp'–Yb–Cp'	122.4	126.7		50
	Cl	47.71	Cp'–Yb–Cl	108.9	109.7		
			Cl–Yb–Cl	95.42	82.1	+13.32	
$[Nd\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2(\mu\text{-}Cl)]_2Li(thf)_2$	Cp'	61.8	Cp'–Nd–Cp'	123.6			51
	Cl	47.00	Cp'–Nd–Cl	108.8			
			Cl–Nd–Cl	94	82.1	+11.9	
$[Pr\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl]_2$	Cp'	61.9	Cp'–Pr–Cp'	123.8	130		49
	Cl	46.88	Cp'–Pr–Cl	108.78	102		
			Cl–Pr–Cl	93.76	78	+15.76	
$[Sc\{\eta^5\text{-}\{C_5H_3(SiMe_3)_2]\}_2Cl]_2$	Cp'	60.5	Cp'-Sc–Cp'	121	131		49
	Cl	48.53	Cp'–Sc–Cl	109.03	101		
			Cl–Sc–Cl	97.06	79	+18.06	
$[ScCp_2Cl]_2$	Cp	60.5	Cp–Sc–Cp	121			52
	Cl	48.53	Cp–Sc–Cl	109.3			
			Cl–Sc–Cl	97.06	81.8	+15.26	
$[Yb(C_5H_5)_2CH_3]_2$	Cp	60.8	Cp–Yb–Cp	121.6	128.2		53
	CH_3	48.18	Cp–Yb–C	108.98	105.9–110		
			C–Yb–C	96.36	93.4	+2.96	
$[YbCp_2(\mu\text{-}CH_3)_2Al(CH_3)_2]$	Cp	60.8	Cp–Yb–Cp	121.6	133.1		54
	CH_3	48.18	Cp–Yb–C	108.98	104.5–107.8		
			C–Yb–C	96.36	87.1	+9.26	
$[YCp_2(CH_3)]_2$	Cp	61.0	Cp–Y–Cp	122	128.9		53
	CH_3	47.95	Cp–Y–C	109.0	105–110		
			C–Y–C	95.9	92.3	+3.6	
$[ErCp_2(C{=}C{-}CMe_3)]_2$	Cp	61.0	Cp–Er–Cp	122	130.2		55
	C	47.95	Cp–Er–C	108.95	108.3		
			C–Er–C	95.9	83.4	+12.5	
$Cp_2Ti(CO)_2$	Cp	59.8	Cp–Ti–Cp	119.6	138.6		56
	CO	49.53	Cp–Ti–C	109.13	105		
			C–Ti–C	98.66	87.5	+11.16	
$Cp_2Hf(CO)_2$	Cp	60.5	Cp–Hf–Cp	121	141		57
	C	48.6	Cp–Hf–C	109.1	103.5		
			C–Hf–C	97.2	89.3	+7.9	

levels caused by polarization greatly helps to stabilize this type of structure, which is otherwise expected to be unstable according to the geometrical packing.

In Fig. 6, the seat levels diagram based on the packing of simple ions is drawn on the left side and, after inversion, the corresponding one based on the $\theta_{O^{2-}}$ and θ_{Cl^-} in the actual bond lengths is drawn next to it. The bond angle O–Ti–Cl is even greater than the calculated geometrical frame because further distortion occurs due to the stronger static repulsion between the oxygen ion and the chlorine ion than that between the two chlorine ions. A challenging question concerning the cooperative effect of steric packing and polarization arises, namely whether a structure similar to BrF_5 in the third class of metal ions, e.g. '$TiFCl_4^-$', exists, for which polarization should not be so strong. Another example of polarization effect is the structure of $UO_2Cl_4^{2-}$. The uranium(VI) and oxygen(II) interact so strongly that the chloride ions are extruded somewhat out. The distance between uranium and chlorine is even greater than the sum of the ionic radius of uranium(VI) and Van der Waal's radius of the oxygen atom.

3. Systematic Deviations due to Oversimplified Evaluation of the Ionic and Van der Waal's Radii

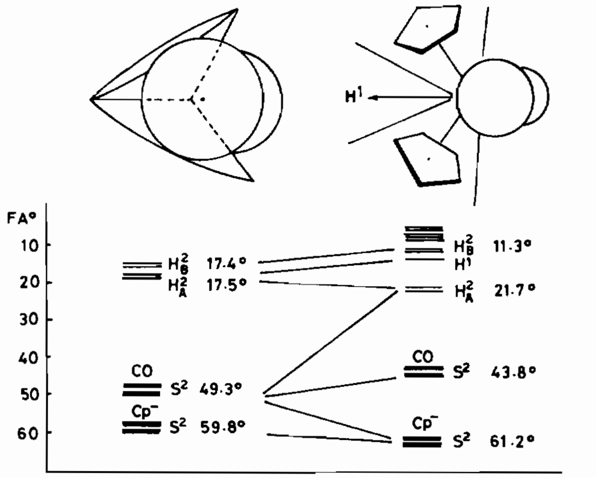
Apart from the error caused by the irregular shape of the ligands which are not standard cones, and the error caused by the inequivalence of the ball-like and

TABLE VI. Calculated Geometrical Frames of MA_2BC in Comparison with the Actual Bond Angles

Structure	Ligand	θ	Seat	Bond angle	Geometrical frame	Reported angle	Reference
$TiCp_2(OC_2H_5)Cl$	Cl	46.29	50.29	Cp–Ti–Cp	122.46	130.5	58
	Cp	57.23	61.23	Cp–Ti–O	106.10	105.9–109.8	
	O	42.30	44.87	Cp–Ti–Cl	111.52	105.5–105.6	
				O–Ti–Cl	88.59	93.1	
$[CpTiCl_2]_2O_2C_2Me_4$	Cl	46.29	50.29	Cl–Ti–Cl	100.38	101.3	58
	Cp	57.23	61.23	Cp–Ti–O	106.10	118.8	
	O	42.30	44.87	Cp–Ti–Cl	111.52	114.2–115.0	
				O–Ti–Cl	95.16	102.1	
$\{TiCl(\mu\text{-}O)(\eta\text{-}C_5H_4Me)\}_4$	Cl	46.29	53.915	O–Ti–O	98.8	104.1	59
	O	42.30	49.4	Cp′–Ti–O	114.73	114.7–115.5	
	Cp′	57.23	65.33	Cp′–Ti–Cl	119.25	116.0	
				O–Ti–Cl	103.32	101.9–102.9	
$\{[Ti(H_2O)Cp_2]_2O\}(ClO_4)_2 \cdot 2H_2O$	O	42.30	46.46	Cp–Ti–Cp	124.46	134.9	60
	Cp	57.23	62.23	Cp–Ti–OH_2	108.73	101.1–104.9	
	H_2O	42.30	46.50	Cp–Ti–O	108.69	106.4–107.6	
				O–Ti–OH_2	92.96	94.3	
$[HfCp_2CH_3]_2O$	CH_3	44.70	49.70	Cp–Hf–Cp	122.06	128.5	43
	Cp	55.93	61.03	Cp–Hf–CH_3	110.73	103.7–104.0	
	O	41.81	46.04	Cp–Hf–O	107.07	108.1–110.5	
				O–Hf–CH_3	95.75	96.90	
$(CO)_9Co_3COZr(Cl)(\eta\text{-}C_5H_5)_2$	O	39.74	44.35	Cp–Zr–Cp	123.82	130.3	44
	Cl	43.81	49.21	Cp–Zr–O	106.26		
	Cp	55.81	61.91	Cp–Zr–Cl	111.12		
				O–Zr–Cl	93.56	93.8	
$(CO)_9Co_3COHf(Cl)(\eta\text{-}C_5H_5)_2$	O	41.81	46.27	Cp–Hf–Cp	122.46	128.5	44
	Cl	44.03	49.03	Cp–Hf–Cl	110.26		
	Cp	55.93	61.23	Cp–Hf–O	107.50		
				O–Hf–Cl	95.30	94.8	
$[Cp_2ZrCl]_2O$	Cl	43.81	49.21	Cp–Zr–Cp	123.82	132.0	61
	Cp	55.81	61.91	Cp–Zr–Cl	111.12	105.8–106.1	
	O	39.74	44.35	Cp–Zr–O	106.26	104.6–106.0	
				O–Zr–Cl	93.56	96.8	
$[Cp_2Zr(SC_6H_5)]_2O$	O	39.74	44.17	Cp–Zr–Cp	123.62		62
	S	44.49	49.59	Cp–Zr–O	105.98		
	Cp	55.81	61.81	Cp–Zr–S	111.40		
				O–Zr–S	93.76	98.7	
$Cp_2Lu(thf)(CH_2Si(CH_3)_3)$	Cp	55.06	62.06	Cp–Lu–Cp	124.12	130.2	63
	C	43.25	49.45	Cp–Lu–C	111.51	105.4–110.9	
	thf	38.48	43.68	Cp–Lu–thf	105.74	104.2–105.7	
				C–Lu–thf	93.13	95.8	

the dish-like ligands coordinated to the same metal ion, a major deviation in estimation of the geometrical frame is due to the oversimplified ionic and the Van der Waal's radii.

The geometrical frame calculated for the compounds containing carbon monoxide as the ligand differs very much from the actual structure. It might be a problem that all the central ions ligating to carbon monoxide are centres of the second class and they do not follow the steric considerations we have suggested. The direct reason for such deviation is attributed to the large Van der Waal's radius of carbon (1.85 Å), which we have adopted in the calculation of the geometrical frames. It is obvious, due to the greater electronegativity of oxygen relative to carbon, that electron density has moved from the carbon to the oxygen atom and the Van der Waal's radius of carbon decreases considerably in carbon monoxide (Fig. 7). The bond angle between the two carbon monoxide molecules is therefore much smaller than those calculated based on the 1.85 Å radius of the carbon atom. The same problem is encountered in that the ionic radii of neither the metal centre nor the ligand anions have been corrected for their coordination numbers [9]. The calculated bond angle between the two chlorine ions in the geometrical frame is much greater than that in the actual molecular chlorine-bridging structure (Table V).



(I) Pre-bonding structure of $TiCp_2(CO)_2$

(II) actual molecular structure of $TiCp_2(CO)_2$

Fig. 7. Seat level diagrams of pre-bonding and the actual molecular structures of $TiCp_2(CO)_2$. In (I) H^2_A: two vacant seats among Cp–Cp–CO, H^2_B: two vacant seats among Cp–CO–CO. In (II) H^2_A: the largest two vacant seats among Cp–Cp–CO, H^1: the vacant seats between Cp–Cp, H^2_B: the two vacant seats among Cp–CO–CO. There are two electrons directed to H^2_A and H^1.

4. Orbital Interactions

In spite of the inaccurate Van der Waal's radii and the simple calculation method, the good agreement between the calculated geometrical frame and the actual molecular geometry is obvious. However one can see that the bond angles in the molecular structures seem rather insensitive to the ligands' size whereas the geometrical frame is very sensitive. In the structural pattern of the series MCp_3thf, fluctuation of the actual bond angles of both Cp–Ln–Cp and Cp–Ln–thf is 1° only whereas a systematic change of 2° is expected from steric packing. Some forces seem to fix the ligands at their positions and prevent turning of the bond angles according to the metal–ligand relative sizes. Such forces could be explained by metal–ligand orbital interactions [10, 11].

The geometrical frame of Cp_2MX_2 does not seem to be in good agreement with the bond angles in the actual molecular structures, especially the bond angles Cp–M–Cp. The deviation might be explained as (a) orbital interactions distorting the frame in the direction of the normal 'sandwich'; (b) calculation error due to the approximation in projecting the dish-like cyclopentadienyl groups and the other ball-like ligands in the unit coordination sphere; or other reasons. Because of the limited precision of Van der Waal's radii, at this stage one cannot trace the error in order to correct for it. However, the fluctuation of geometrical frames is obviously greater than that in the corresponding bond angles in actual structures. We suggest that the stabilization effect is due to orbital interactions. Because the orbital interactions tend to produce the normal sandwich structures, a gap will be produced in between the two cyclopentadienyls (H^1 in Fig. 7).

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