Continuous Shape Measures as a Stereochemical Tool in Organometallic Chemistry

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The continuous shape measures of homoleptic organometallic compounds of the transition elements relative to the classical coordination polyhedra offer a tool for their accurate stereochemical description, including geometries along polyhedral interconversion pathways. The use of the centroid of π-bonded carbon atoms to define a coordination position allows us to show that polyhedral continuous shape measures may serve as excellent stereochemical descriptors for complexes with such ligands as olefins, alkynes, and allyls. Such an approach can be extended to treat π-bonded diolefins as bidentate ligands, defining their bite and establishing comparisons with classical chelating ligands such as diamines, carboxylates, and diketonates. The adequacy of considering the η^5-coordinated cyclopentadienide ligand as occupying one or three coordination positions in the piano-stool [M(η^5-Cp)L_3] complexes is also discussed.

Following the proposal of Avnir and co-workers to define molecular symmetry or shape as continuous structural properties,[1,2] we have been exploring the application of such a concept and the associated methodology to the stereochemical description of transition-metal compounds. So far, we have reported systematic studies for tetra-,[3] penta-,[4] hexa-,[5] hepta-,[6] and octacoordinate[7] metals, although such studies have been restricted to systems with ligands having well-defined, localized metal−ligand bonds.

In this paper we summarize the stereochemical behavior of σ-bonded homoleptic organometallic complexes as compared to that of the Werner complexes (those having hard bases as ligands, typically with N−, O−, or Cl donor atoms) and explore the possibility of applying such a methodology to compounds with π-bonded ligands such as olefins, alkynes, allyls, diolefins, and η^5-cyclopentadienide. Can we describe the coordination sphere of an olefin complex as if this ligand were a monodentate one? Are the resulting coordination polyhedra similar to those obtained with η^1 ligands? Can diolefins be considered as bidentate ligands? Also, how do their bites compare to those of classic chelating agents? Are the piano-stool complexes of formula [M(η^5-Cp)L_3] best described as tetrahedra, considering the Cp ring as occupying a single coordination site or as an octahedron in which that ring occupies three coordination positions? These are some of the questions we try to answer here.

Continuous Shape Measures: Methodology

A continuous shape measure (abbreviated from here on as CShM) of a molecular fragment is defined as its *distance* to an ideal shape, independent of size and orientation. For molecules or molecular fragments that can be approximately described by a polyhedron (eventually including a central atom, as in coordination compounds), the coordinates of the N atoms are given by their position vectors $\vec{Q}_k$ (k = 1, 2, ..., N), whereas the coordinates for the perfect polyhedron closest in size and orientation are given by the vectors $\vec{P}_k$ (k = 1, 2, ..., N). The *distance* of the molecular structure Q to the perfect polyhedron P is then defined as[8]

$$S_Q(P) = \min \frac{\sum_{k=1}^{N} |\vec{Q}_k - \vec{P}_k|^2}{\sum_{k=1}^{N} |\vec{Q}_k - \vec{Q}_0|^2} \times 100 \qquad (1)$$

where $\vec{Q}_0$ is the coordinate vector of the geometrical center of the investigated structure and the expression is minimized with respect to rotations and isotropic scaling of the reference polyhedron. With such definitions, it has been shown that the bounds for any shape measure are $0 \le S_Q(P) \le 100$. The lower limit corresponds to structures that exactly match the shape of polyhedron P, and increasing values result for increasingly distorted structures. A very useful property of the shape measures is that they allow us to compare on the

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same scale the proximity of different molecules to the same polyhedron or of the same molecule to different ideal polyhedra. One can also calibrate on the same scale different distortions from a particular ideal structure.

From our experience in the continuous shape studies of transition-metal compounds, we can get some rules of thumb about the meaning of the CShM values. Thus, shape measures of less than 1.0 usually indicate minor distortions from the reference shape; values of up to 3.0 units indicate important distortions, while the reference shape provides still a good stereochemical description. We have also observed that CShM's are much less affected by bond length than by angular distortions,[4] a fact that is related to the much wider variation found in bond and torsion angles compared to those in bond distances.

We have also recently described an analytical expression for the minimal distortion interconversion path between two polyhedra in terms of shape measures.[9] It is thus seen that structures that are severely distorted from all ideal polyhedra can in many instances be correctly described as being intermediate between two of them. We have further described the path deviation function $\Delta_Q(P,T)$, which quantifies how much the structure Q deviates from the interconversion path between polyhedra P and T. In the way Δ_Q is defined, a value of, for example, 0.10 indicates that the deviation of the analyzed structure from the path is 10% of the total distance between the two extremes of the path.

Homoleptic Alkyl and Aryl Complexes

The CShM's provide an efficient and quantitative way of describing the polyhedral shape of the metal coordination sphere in the homoleptic [MR$_n$] organometallic complexes analyzed, as seen in Table 1 for R = Me, Ph. The general picture we obtain from that table is that of nearly perfect shapes among compounds with coordination numbers between 3 and 8, providing examples of 9 different geometries. However, a few particular cases deserve some comment.

(1) The [TiMe$_5$]$^-$ anion presents two crystallographically independent molecules which are close to a square pyramid and a trigonal bipyramid, respectively.

(2) In practically all cases in which the shape measure indicates a significant deviation from the ideal polyhedron, we can see from the path deviation functions that the distortion is along the well-established polyhedral interconversion paths: (i) the spread distortion of the square toward the tetrahedron in [MnMe$_4$]$^-$, (ii) the Berry pseudorotation in the nearly square-pyramidal and trigonal-bipyramidal molecules of [TiMe$_5$]$^-$, and (iii) the Bailar twist of some octahedra (Cr^{III}, Rh^{III}, and Ir^{III} compounds) and trigonal prisms (Zr^{IV} and Ta^V compounds). The exception is [FePh$_4$]$^{4-}$, which appears to be strongly distorted from a regular square through a scissoring mode (C−Fe−C bond angles of 61°) rather than toward a tetrahedron.

(3) The small distortion of the d^0 hexacoordinate compounds from the ideal trigonal prism to C_{3v} structures[10] is clearly indicated in the small but non-negligible values of the corresponding shape measures.

Table 1. Continuous Shape Measures of Homoleptic Methyl and Phenyl Transition-Metal Complexes, Relative to Their Closest Polyhedron, and Path Deviation Functions for Those Cases with Significant Distortion from the Chosen Polyhedron[a]

compd	refcode	shape	CShM	Δ(path)
[CdMe$_3$]$^-$	RAWTAK	equilateral triangle	0.02	
[ZnPh$_3$]$^-$	JAFZUL	equilateral triangle	0.04	
[OsPh$_4$]	FEFTOZ	tetrahedron	0.03	
[MnMe$_4$]$^{2-}$	GINZAE	tetrahedron	0.04	
[ZnMe$_4$]$^{2-}$	LTMEZN	tetrahedron	0.14	
[AuMe$_4$]$^-$	WEMGOQ	regular square	0.02	
[AuPh$_4$]$^-$	DEYBUE	regular square	0.06	
[CrPh$_4$]$^{2-}$	VEWXOK	regular square	0.10	
[CrMe$_4$]$^{2-}$	VUGKAJ	regular square	0.11	
[MnMe$_4$]$^-$	KISDEV	regular square (tetrahedron)	2.64	0.00
[FePh$_4$]$^{4-}$	BUJWOS	regular square	6.33	
[MoMe$_5$]	DOSBIW	square pyramid	0.33, 0.66	
[CrPh$_5$]$^{2-}$	SPHENC	square pyramid	0.91	
[TiMe$_5$]$^-$	KELQIB	trigonal bipyramid (SP)	0.47	0.07
		square pyramid (TBP)	1.07	0.06
[MnMe$_6$]$^{2-}$	GINZEI	octahedron	0.19	
[CrMe$_6$]$^{3-}$	MCRLDX	octahedron (trigonal prism)	1.03	0.00
[RhMe$_6$]$^{3-}$	KAWVAF	octahedron (trigonal prism)	1.63	0.01
[IrMe$_6$]$^{3-}$	KAWVEJ	octahedron (trigonal prism)	1.94	0.01
[ReMe$_6$]	ZOSXEL	trigonal prism	0.07	
[TaMe$_6$]$^-$	POZHUH	trigonal prism	0.31	
[NbMe$_6$]$^-$	POZJAP	trigonal prism	0.35	
[MoMe$_6$]	LOJDIX	trigonal prism	0.91, 0.93	
[WMe$_6$]	ZOSXEK01	trigonal prism	0.67, 0.74	
[ZrMe$_6$]$^{2-}$	JAMWOJ	trigonal prism (octahedron)	0.88	0.05
[TaPh$_6$]$^-$	REZBAZ	trigonal prism (octahedron)	1.36	0.03
[WMe$_7$]$^-$	RETNIN	capped octahedron	0.28	
[WMe$_7$]$^-$	RETNEJ	capped octahedron	0.36	
[MoMe$_7$]$^-$	LOJDOD	capped octahedron	0.42	
[ReMe$_8$]$^{2-}$	RETMUY	square antiprism	0.21	

[a] The alternative polyhedron for the interconversion path is indicated in parentheses.

(4) The tetracoordinate complexes collected in Table 1, as well as a number of homoleptic aryl analogues (aryl = C_6Cl_5, C_6F_5, MePh) reported by the groups of Wilkinson, Fackler, Forniés, and Laguna, obey the following stereochemical preferences, in agreement with the general behavior of tetracoordinate complexes:[3] metals with d^1, d^2, d^3, and d^{10} electron configurations appear in the tetrahedral geometry, those with d^7 or d^8 configurations are square planar, and d^4 ions can be either tetrahedral or square planar.

Polyhedra with π-Bonded Ligands: Olefins, Alkynes, and Allyls

To analyze the polyhedral shapes of π-bonded ligands, we consider the centroid of the carbon−carbon double or triple bond, or the centroid of the three allylic carbons, as occupying a coordination site in the metal coordination sphere. The stereochemical behavior of the formally hexacoordinate complexes [M(olefin)L$_5$], [M(alkyne)L$_5$], [M(η^3-allyl)L$_5$], and [M(olefin)$_2$L$_4$] is summarized in the shape map shown in Figure 1, where

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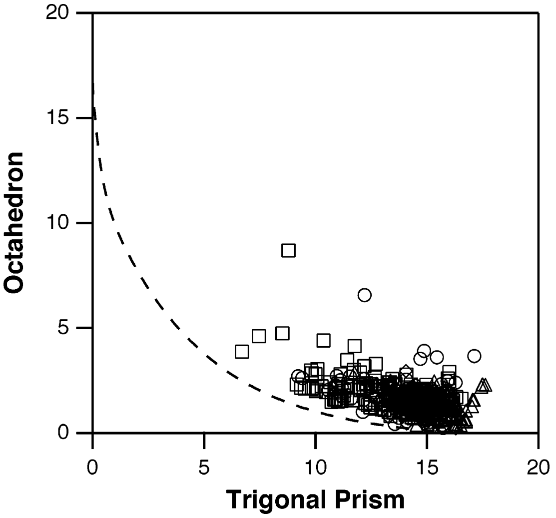

Figure 1. Map of the octahedral and trigonal-prismatic shape measures of complexes of the types [M(olefin)L_5] (circles, 160 crystallographically independent data sets), [M(alkyne)L_5] (triangles, 76 data sets), [M(allyl)L_5] (squares, 253 data sets), and [M(olefin)$_2L_4$] (rhombuses, 34 data sets). The dashed line represents the ideal Bailar path for the interconversion of an octahedron and a trigonal prism.

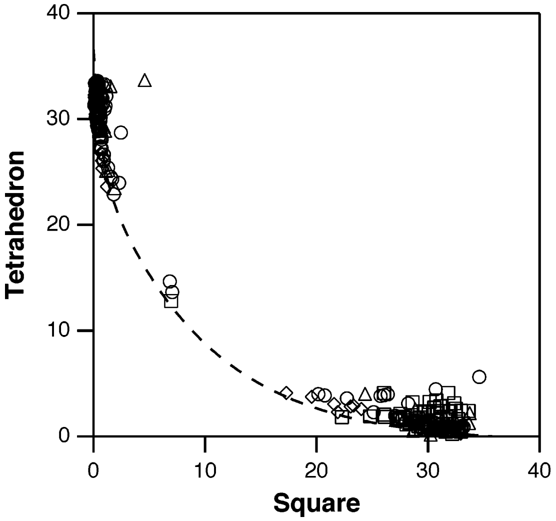

Figure 2. Map of the square-planar and tetrahedral shape measures of complexes of the types [M(olefin)L_3] (circles, 142 data sets), [M(alkyne)L_3] (triangles, 35 fragments), [M(allyl)L_3] (squares, 95 data sets), and [M(olefin)$_2L_2$] (rhombuses, 42 fragments). The dashed line represents the ideal spread path for the interconversion of a tetrahedron and a square.

we see that most of them can be described as being practically octahedral. Significant deviations from an octahedron, though, are observed in some cases in which two ligands cis to the π-bonded group are bent away, forming L−M−L bond angles of about 150°: [{$ZrBr_3(PEt_3)_2$}$_2$(μ_2-η^4-C_2H_4)] (M = Zr, Hf),[11,12] [Zr(η^3-allyl)Pr(tmbzm)$_2$] (tmbzm = bis(trimethylsilyl)benzamidinato),[13] [Mo(η^3-allyl)(dppe)(pyridinethiolato)],[14] [{Y(η^3-allyl)(dmpa)}$_2$(μ-Cl)$_2$] (dmpa = bis(((dimethylphosphino)methyl)dimethylsilyl)amido-*P*,*P*,*N*)[15] and [Mo(η^2-dimethyl maleate)$_2$(CO)$_2$(H_2NPhNH_2)].[16]

The tetracoordinate complexes analyzed (Figure 2) belong to the families [M(olefin)L_3], [M(alkyne)L_3], [M(η^3-allyl)L_3], and [M(olefin)$_2L_2$], which show a richer stereochemistry than the hexacoordinate analogues. They appear clustered around a tetrahedron and a square, and significant distortions from these two shapes fall along their interconversion path. In a few cases, the geometry is far away from both a tetrahedron and a square, as in [Ir(dmpm)Cl(η^2-OC=CPh$_2$)][17] and [Ir(CO)(S-*t*-Bu)$_2$(η^2-TCNE)]$^+$,[18] as indicated by their corresponding shape measures: $S(D_{4h})$ = 6.83, 7.05 and $S(T_d)$ = 14.64, 13.62, respectively. However, they present rather small deviations from the interconversion pathway (path deviation functions of 0.07 and 0.05, respectively). Within the wider context of a continuous shape measures analysis of pentacoordinate complexes, we have also found that [M(olefin)L_4] complexes behave in much the same way as all other pentacoordinate compounds with monocoordinate ligands.[19]

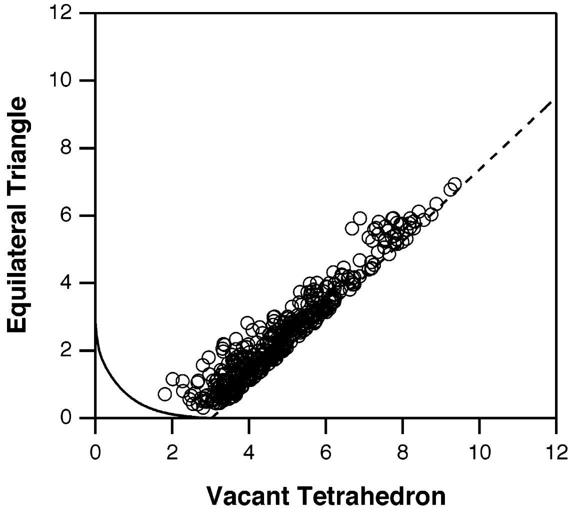

Figure 3. Shape map relative to the equilateral triangle and the vacant tetrahedron for compounds of the types [M(alkyne)L_2] (84 independent fragments) and [M(allyl)-L_2] (538 data sets). The continuous line represents the minimal distortion path between the two ideal shapes and the dashed line to the scissoring distortion of a trigonal-planar molecule.

We have analyzed a variety of tricoordinate complexes belonging to the [M(alkyne)L_2] and [M(η^3-allyl)L_2] families. In this case we represent the shape map relative to the equilateral triangle and the tetrahedron with a vacant vertex (Figure 3). In such a map, the two lines shown represent the minimal distortion path between those two shapes (continuous line) and the in-plane angular distortion (dashed line). The experimental data presented in that map clearly show that (i) many compounds can be adequately described as nearly trigonal planar, (ii) a few compounds are slightly

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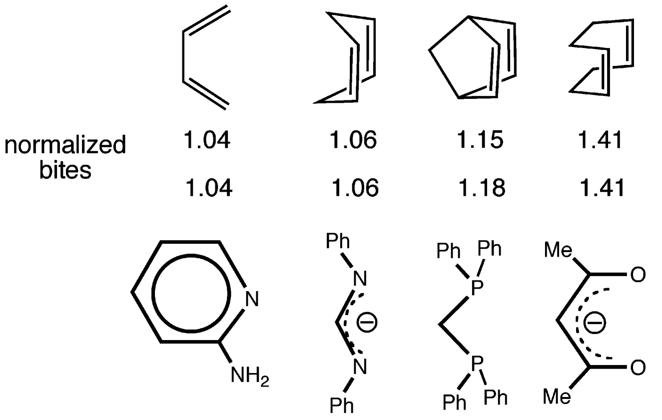
Chart 1



pyramidalized toward the vacant tetrahedron, (iii) a good number of compounds present varying degrees of in-plane scissoring distortion (with L−M−L bond angles between 112 and 72° for the allyl and between 88 and 123° for the alkyne complexes) and (iv) other compounds deviate from trigonal-planar geometries in ways that are likely to correspond to combinations of the pyramidalization and scissoring distortions. The scissoring distortions observed can alternatively be interpreted as a tendency to pseudo-square-planar geometries with the allyl group acting as a bidentate ligand. Finally, we have analyzed two-coordinate complexes of the type [M(η^3-allyl)$_2$], which are seen to be practically linear in most cases, with only a Pd complex in which the allylic groups belong to a benzosemiquinone[20] deviating slightly (linear shape measures of 0.44, average of two crystallographically independent values) from linearity.

Dienes as Bidentate Ligands

We have also analyzed compounds with butadiene, cyclohexadiene, and cyclooctadiene, which we consider as bidentate ligands bonded to metal atoms through the centers of the two C=C double bonds. A relevant characteristic of the dienes is the close distance between the two C=C double bonds, which results in rather small bite angles. These bite angles can be statistically evaluated from the structural data available in the Cambridge Structural Database and are found to be 62(4), 60(3), and 87(2)° for cyclohexadiene, butadiene, and cyclooctadiene, respectively (the numbers in parentheses are the standard deviations). These values correspond to normalized bites for first-row transition metals of 1.03(2), 1.06(3), and 1.41(3), respectively, to be compared (see Chart 1) with those of classical bidentate ligands such as carboxylates (1.01), aminopyridine (1.04), formamidinate (1.06), acetylacetonate (1.41), or propanediamine (1.42).

Thus, compounds in the [M(diene)L$_4$] family, plotted in a shape map in Figure 4, are essentially octahedral but present somewhat stronger distortions from the ideal polyhedron than the bis(olefin) analogues, mostly in the bond angle distortions that are probably induced by the small bite angle of the diene. A paradigmatic case is that of the butadiene complex [Cr(CO)$_2$(PMe$_3$)$_2$(η^4-2,4-hexadiene)],[21] shown in Figure 5, in which the angle corresponding to the positions occupied by the center of the two C=C bonds is 60°, the two trans carbonyls form a C−Cr−C bond angle of 101°, and the two cis phosphine ligands give a P−Cr−P bond angle of 152°. Quite similar values are found for other two butadiene complexes, [Cr(CO)$_3$P(OMe)$_3$(η^4-butadiene)][22] and [Ti(Me)$_2$(dmpe)$_3$(η^4-1,4-diphenylbutadiene)].[23] Such distortions are in part associated to the Bailar path that leads to a trigonal prism,[4] although significant deviations from that path can be seen in several cases (Figure 4).

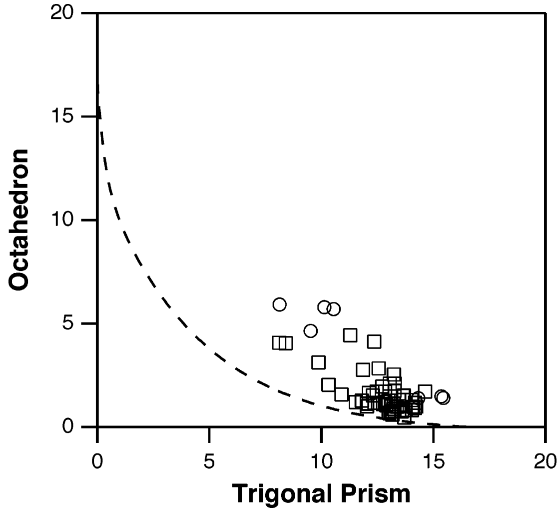


Figure 4. Map of the octahedral and trigonal-prismatic shape measures of complexes of the types [M(butadiene)L$_4$] (7 fragments) and [M(cyclooctadiene)L$_4$] (59 data sets). The ideal Bailar path for the interconversion of octahedron and trigonal prism is shown as a dashed line.

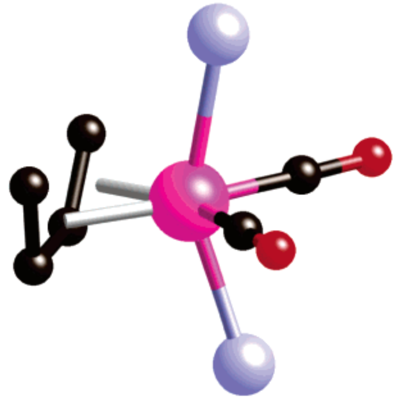


Figure 5. Distorted-octahedral coordination sphere of the metal atom in [Cr(CO)$_2$(PMe$_3$)$_2$(η^4-2,4-hexadiene)].[21]

The tetracoordinate [M(diene)L$_2$] compounds are found scattered throughout the spread pathway that connects a tetrahedron and a square. Thus, we can detect geometries that are quite distant from both ideal shapes yet are very close to the interconversion path, according to the corresponding path deviation functions $\Delta(D_{4h}, T_d)$ (Table 2).

A particularly interesting case is that of the tris(diene) complexes [Mo(2,3-Me$_2$butadiene)$_3$], [W(2,3-Me$_2$buta-

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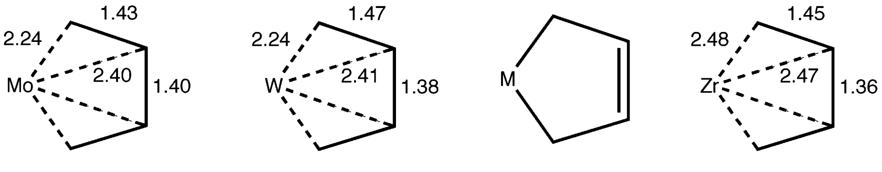
Chart 2



1 **2** **3** **4**

Table 2. Shape Measures and Path Deviation Functions for Two [M(cod)L$_2$] complexes

compd	S(SP)	S(TET)	Δ(SP,TET)	refcode
[Rh(η^4-cod)(diphosphine)]$^+$	4.66	16.28	0.03	POFXEN
[Ir(η^4-cod)(oxazoline-*N*,*P*)]$^+$	14.08	8.55	0.11	IDORUO

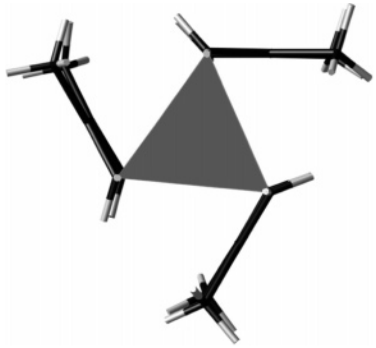
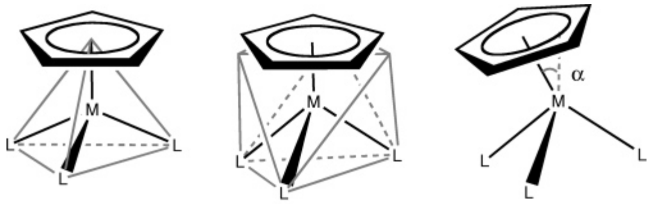


Figure 6. Projection of the molecular structure of the tris(butadiene) complex [Mo(η^4-2,3-Me$_2$-butadiene)$_3$][24,25] down the trigonal axis, showing the trigonal-prismatic coordination sphere of the Mo atom and the helical arrangement of the diolefin ligands.

Table 3. Trigonal-Prismatic Shape Measures of the Tris(diene) Complexes, Considering the Ligands as Neutral Dienes with the Coordination Sites Occupied by the Centroids of the Double Bonds or as 2-Ene-1,3-diyl Ligands

compd	diene	diyl	ref
[Mo(2,3-Me$_2$butadiene)$_3$]	5.16	0.42	24, 25
[W(2,3-Me$_2$butadiene)$_3$]	5.25	0.37	24, 25
[Zr(η^4-naphthalene)$_3$]$^{2-}$	7.21	1.96	26

Chart 3



5 **6** **7**

diene)$_3$],[24,25] and [Zr(η^4-naphthalene)$_3$]$^{2-}$.[26] Taking the centroids of the C=C double bonds as the coordination positions, one finds that the coordination geometry around the metal atoms is neatly trigonal prismatic (Figure 6) If we count the diolefin ligands as neutral, the metal oxidation states are Mo^0, W^0, and Zr^{-II}, respectively, with a d^6 electron configuration in all cases and a total of 18 valence electrons, in agreement with the effective atomic number rule. However, we have seen that only metal atoms with d^0–d^2 electron configurations adopt trigonal-prismatic coordination spheres. A look at the structural parameters of the M(diolefin) fragments shown in **1** and **2** for Mo and W (Chart 2) reveals that these are best described as 2-butene-1,4-diyl ligands with the terminal carbon atoms coordinated in an η^1 mode, given the significantly longer M–C distances for the central carbon atoms as well as their shorter C–C bond distance and the strong pyramidalization of the terminal carbon atoms. In other words, these are metallacyclopentene complexes **3** with formal oxidation states Mo^{VI} and W^{VI}, whose d^0 electron configurations are consistent with the trigonal-prismatic coordination geometry observed. In the case of the Zr compound **4**, the Zr–C distances are quite similar but the localized double bond of the metallacyclopentene ring can be clearly identified and again a d^0 configuration for Zr^{IV} is in agreement with stereochemical rules for hexacoordinate complexes. A more detailed discussion, accompanied by quantum-chemical calculations, is given by Kaupp and co-workers[27] when discussing the similar structure of the analogous Mo complex of unsubstituted butadiene,[27] whose experimental structure is biased by the presence of disorder. An interesting point for the present shape analysis is that the metal coordination sphere, considering the terminal carbon atoms as attachment points, is much more trigonal prismatic than that in which the centroids of the diene double bonds are considered, as seen in Table 3.

The [MCpL$_3$] Piano Stools: Tetrahedral or Octahedral Coordination?

The question that arises when we consider the structure of the [M(η^5-Cp)L$_3$] piano stools is, should we consider them as tetracoordinate, with the center of the Cp ring occupying one vertex, or rather as hexacoordinate, with Cp occupying three vertices? The former situation would be reflected in a small value of the tetrahedral shape measure of the M(Cp-centroid)L$_3$ fragment (**5**; Chart 3), whereas for the octahedral option we must find the shape measure relative to the trigonal pyramid obtained by replacing one face of the octahedron by its geometrical center, in which the centroid of the Cp ring would be ideally placed (i.e., **6**, with L–M–L bond angles of 90°). An alternative for the octahedral fragment that we have also analyzed consists of comparing only the ML$_3$ legs of the piano stool with a fac-trivacant octahedron, although this approach is unable

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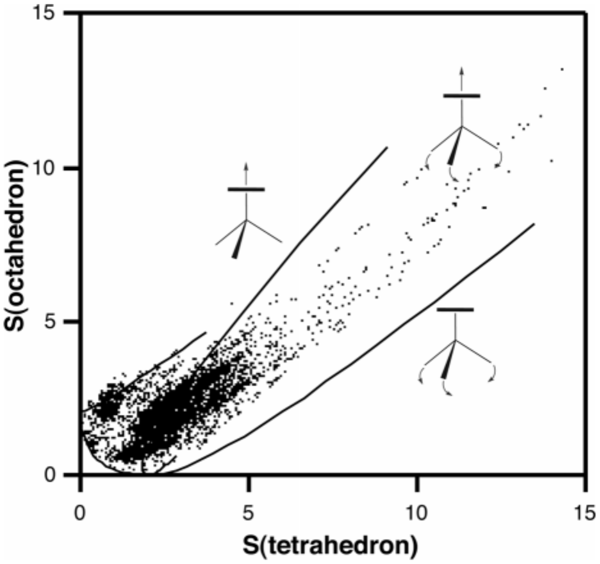

Figure 7. Map of the shape measures of complexes of the [M(η^5-Cp)L$_3$] family relative to a tetrahedron and a octahedron, considering the centroid of the Cp ring as a vertex and a trigonal face, respectively (5787 crystallographically independent structural data sets).

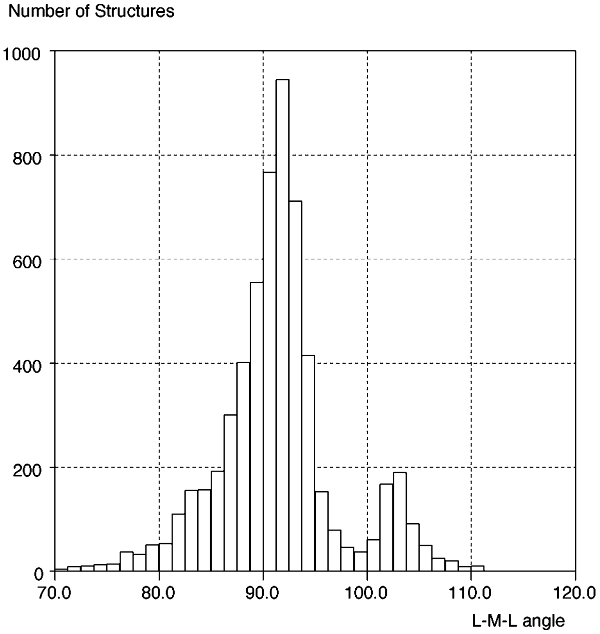

Figure 8. Distribution of the average L−M−L bond angle among the piano-stool complexes of the [M(η^5-Cp)L$_3$] family.

to detect deviations of the Cp ring from the trigonal axis of the legs, and zero shape measures would be found for a number of structures with varying degrees of off-axis distortions. Thus, we plot the available structural data in a map relative to the tetrahedral and octahedral shapes **5** and **6** (Figure 7). A large degree of stereochemical variability is revealed by such a shape map, from which the following observations can be made

(i) The two most numerous clusters of structures correspond to distorted-octahedral (**6**, in the range $2 < S(\text{tetrahedron}) < 5$) and tetrahedral (**5**, at $S(\text{tetrahedron}) < 2$) shapes, while few structures appear between these two groups.

(ii) The distorted-octahedral structures occupy the region comprised between the closing of the ML$_3$ umbrella (rightmost line in the path) and the elongation of the M−Cp distance.

(iii) A non-negligible number of structures are found to be intermediate between the pseudotetrahedral and pseudooctahedral shapes, corresponding to the curved line in the lower left corner of Figure 7.

(iv) A small number of structures that deviate from the tetrahedron[3] correspond to the spread pathway that leads to the planar square, although the square-planar geometry is never reached.

(v) The region of the shape map with large values relative to both the tetrahedral and octahedral geometries (upper right corner of the shape map) comprise both structures with small L−M−L bond angles (typically bond angles of about 80° give $S(T_d) \approx 4$ and $S(O_h) \approx 2$) and those with significant deviations of the M−Cp vector from the trigonal axis of the ML$_3$ group (**7**, with $\alpha > 5°$).

Among the most dramatic distortions from the tetrahedron, we note an Ir compound that is much closer to being square planar than tetrahedral (with $S(T_d) = 20.2$ and $S(D_{4h}) = 6.3$).[28] Closer inspection of that structure suggests that the Cp ring is coordinated in a η^3 mode, given the C−C distances, and the square-planar geometry becomes more evident when considering the centroid of the allylic portion of Cp as the coordination site ($S(D_{4h}) = 3.1$). Even if the Ir−C(Cp) distances are all similar, these may be imposed by the multidentate nature of the Cp-containing ligand. On the other hand, the compounds appearing in the high shape measures region of the map are those in which the legs are forming chelate rings and therefore present rather small L−M−L bond angles.

If we disregard the distortions related to the position of the Cp ring relative to the ML$_3$ group and focus on the differences in L−M−L bond angles, we can see that these present a bimodal distribution (Figure 8) with maxima that correspond approximately to the octahedral and tetrahedral angles, nicely reflecting the two clusters of points found in the shape map. Examination of the dependence on the periodic group of the average tetrahedricity of the centroid−ML$_3$ fragment and of the average shape measure relative to the octahedral ML$_3$ fragment (Figure 9; only compounds in which the donor atoms L are at least separated by two atoms to ensure that the structural choice is not biased by rigid chelate rings) tells us that early transition metals (groups 3−5) prefer the pseudotetrahedral geometry and there is an increasing tendency toward the pseudooctahedral shape when moving to the right of the periodic table.

The [MCp$_2$L$_2$] Family

In this case we consider the [MCp$_2$L$_2$] groups as tetracoordinate complexes and we observe that these structures are closer to being tetrahedral than the piano-stool family, with most of the geometries having tetrahedral shape measures smaller than 2 (see Figure 10). Here we see that some structures are somewhat distorted toward the planar square, with values of the path deviation function, $\Delta(D_{4h}, T_d)$, of less than 0.04,

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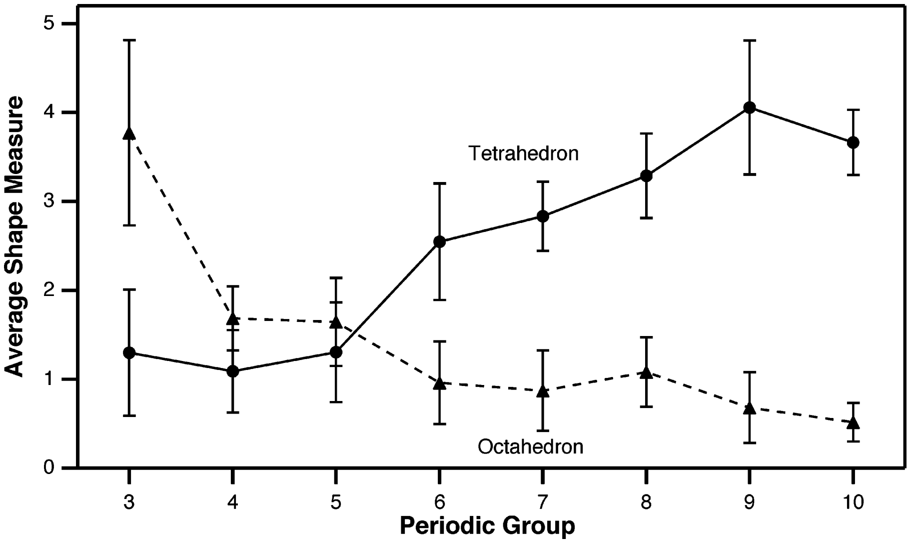

Figure 9. Evolution of the tetrahedral (circles) and fac-trivacant octahedral (triangles) shape measures of the [M(η^5-Cp)-L_3] complexes along the transition-metal series.

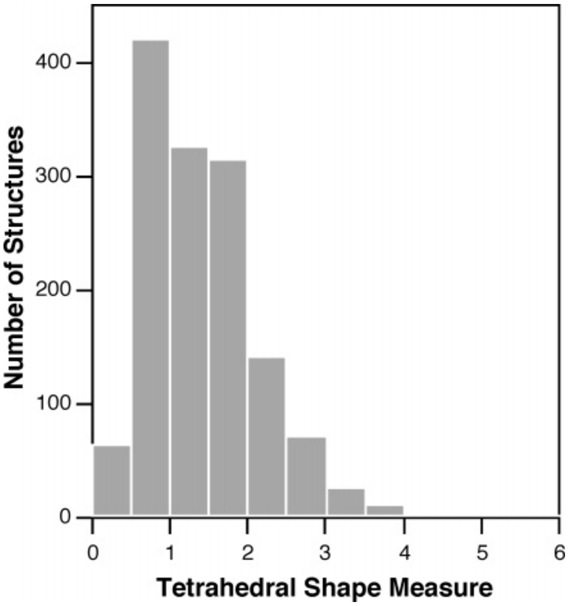

Figure 10. Distribution of the tetrahedral shape measures of [M(η^5-Cp)$_2$L$_2$] complexes (1383 structural data sets).

as in [Y(CpCH$_2$CH$_2$−O−Me)$_2$]$^+$, with $S(T_d) = 6.68$,[29] or two Zr complexes[30,31] with $S(T_d) \approx 3.3$.

Conclusions and Outlook

We have shown that the use of shape measures of coordination polyhedra for homoleptic organometallic complexes with σ-bonded ligands described in detail their stereochemistries. For π-bonded ligands, such as olefins, alkynes, and allyls, a similar polyhedral description can be obtained by considering the centroid of a π-bonded ligand as a vertex of the coordination polyhedron. A similar strategy applied to diolefin complexes allows us to classify ligands such as butadiene, cyclohexadiene, and cyclooctadiene as bidentate ligands, whose normalized bite is defined and compared to those of classical chelating ligands such as ethylenediamine and acetylacetonate. Finally, the study of η^5-coordinated cyclopentadienide ligands as ligands with a single point of attachment shows a rich and varied stereochemistry, with some [MCpL$_3$] complexes closely resembling a tetrahedron and others experiencing significant distortion from such a geometry, among which a large number are distorted toward what could be more adequately described as pseudooctahedral complexes in which the η^5-Cp ring occupies three vertices of the coordination octahedron.

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Appendix

The collection of structural data was obtained through systematic searches of the Cambridge Structural Database[32] (version 5.25). General searches for tetracoordinate transition-metal complexes were carried out, allowing single, double, or triple bonds to donor atoms from periodic groups 14−17, excluding direct bonds between donor atoms, constraining the search to non polymeric structures having no disorder, using *R* factors of at most 0.10, and excluding di- and polynuclear complexes. From all the structures retrieved, only those for which the metal oxidation state (not amenable to systematic search in the structural databases) could be unambiguously assigned were retained. The shape measures have been calculated with SHAPE (version 1.1), a program developed in our group.[33]

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