

## Reaction Path Analysis. 2. The Nine-Atom Family

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**Abstract:** "Points on a Sphere" repulsion calculations incisively identify the  $D_{3h}$  tricapped trigonal prism as the most favorable polytopal form for an  $ML_9$  coordination complex. For reasonable values of 4 to 6 for the exponential in the Born term, the  $D_{3h}$  model is a deep minimum in the potential energy surface. The most plausible alternative polytopal form is the  $C_{4v}$  monocapped square antiprism which is generated from the  $D_{3h}$  form by a relatively minor stretching mode. This  $C_{4v}$  form lies well above the minimum for  $D_{3h}$  with no evidence of a minimum. Fully consistent with these calculations are the crystallographic structural data for  $ML_9$  and  $M_9$  complexes. All discrete  $ML_9$  complexes and boron and metal  $M_9$  clusters are explicitly  $D_{3h}$  or very close to  $D_{3h}$ . Even in extended chains of  $ML_9$  coordination complexes where there is polyhedral edge sharing, the departure of  $ML_9$  aggregates from  $D_{3h}$  is usually quite small; in only three complexes are the departures clearly in the direction of  $C_{4v}$ . Structural and calculational data identify as the lowest energy intramolecular rearrangement pathway the  $D_{3h} \rightleftharpoons C_{4v}$  interconversion. Calculations suggest a very low barrier for the rearrangement process in an  $ML_9$  complex but the available structural data point to a higher barrier.

Delineation of the *geometric* features of intra- or intermolecular reactions has been an almost ephemeral quest except for very simple gas phase reactions where theoretical calculations and experiments can provide a reasonable geometric outline. Rarely can spectroscopic techniques, even NMR buttressed with permutational analysis, yield a differentiation between two or more plausible physical mechanisms. However, evidence is accumulating that careful selection and assessment of crystallographic data can provide a geometric outline of reaction mechanism for relatively complex molecules. In fact, we believe that this approach is the most important new development in the study of reaction mechanisms. This point was convincingly presented for the lowest energy pathway in five-coordinate  $ML_5$  intramolecular rearrangements in our first paper<sup>2</sup> in this series. In a most impressive fashion, Bürgi<sup>3</sup> has effectively used this approach for the definition of the geometric features in reaction paths for inter- and intramolecular reactions. We describe herein an attempt to assay reaction paths for intramolecular rearrangements in the nine-atom family of coordination complexes and clusters.

Available structural data for the nine-atom family clearly show even from casual examination of data that the  $D_{3h}$ -sym. tricapped trigonal prism is the favored polytopal form.<sup>4</sup> Exceptions may be found especially among coordination compounds with chelate ligands, and usually these variances bring the coordination polyhedron close to the idealized  $C_{4v}$  monocapped square antiprism.<sup>4,5</sup> This alternative is readily generated from the  $D_{3h}$  model by a polyhedral edge (4,7) stretching motion (see Figure 1).<sup>4,6,7</sup> Since this stretching motion represents a bending mode for coordination compounds and a stretching mode in clusters, activation energies for intramolecular rearrangements in the nine-atom family via the  $D_{3h} \rightleftharpoons C_{4v}$  interconversion should be substantially higher in clusters than in coordination compounds as noted before for all general cases.<sup>6,7</sup> This appears to be the prevailing situation for this family.<sup>6,7</sup>

An alternative physical rearrangement process comprises stretching polyhedral edges (5,6) and (4,7) of the  $D_{3h}$  model whereby a  $C_{2v}$  transition state or intermediate is generated (Figure 2a). Another alternative process depicted in Figure 2b involves stretching polyhedral edges (4,7) and (5,8) to achieve a  $C_{2v}$  intermediate (in a concerted process, this stretching mode cannot lead to permutation of labeled vertices). Reaction paths in Figure 1 and 2b maintain  $C_{2v}$  symmetry whereas the path in Figure 2a has maximal  $C_s$  symmetry. The  $C_{2v}$  intermediates in Figures 2a and 2b are the same except in

a labeled sense; the origin of the atom on the  $C_2$  axis is from the 6-atom set in 2a and the 3-atom set in 2b. Of these three mechanisms,<sup>8</sup> the  $D_{3h} \rightleftharpoons C_{4v}$  traverse seems intuitively most favorable but there are no theoretical or experimental data that relate to reaction paths in the nine-atom system.

There is a further motivation for analysis of rearrangements in the nine-atom family. We have discerned no substantive differences between the extent of polyhedral edge stretching required for stylized rearrangements in the eight ( $D_{2d} \rightleftharpoons D_{4d}$ ) and nine ( $D_{3h} \rightleftharpoons C_{4v}$ ) atom families. This appears to be consonant with the limited data on intramolecular rearrangements in coordination compounds but not in boron clusters.<sup>10,11</sup> The larger barrier in  $B_9$  clusters relative to  $B_8$  clusters has been ascribed to the degeneracy of  $C_{4v} - B_9H_9^{2-}$ ,<sup>7,11</sup> but it seemed that a further examination of this cluster from another point of view was warranted, especially a view in which alternative (to  $D_{3h} \rightleftharpoons C_{4v}$ ) reaction paths were critically assessed.

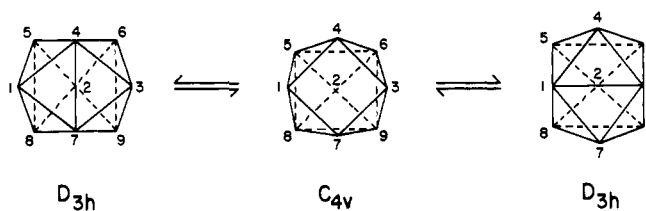


Figure 1. Low energy  $D_{3h} \rightleftharpoons C_{4v}$  nine-coordinate rearrangement process.

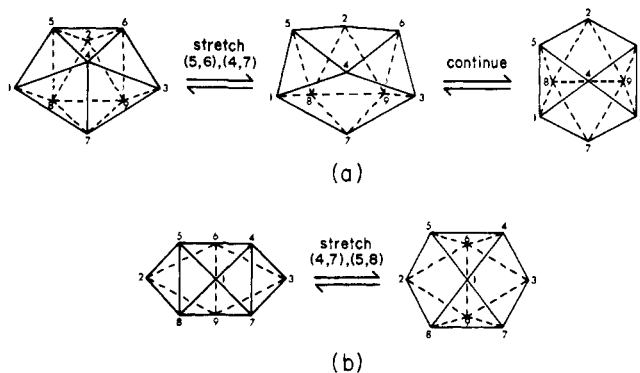


Figure 2. Alternative rearrangement processes considered for  $ML_9$  and  $M_9$  complexes each of which produce a  $C_{2v}$  form (differentiated only by labels). The process partially shown in (b) cannot permute vertex (ligand) labels if the process is concerted.

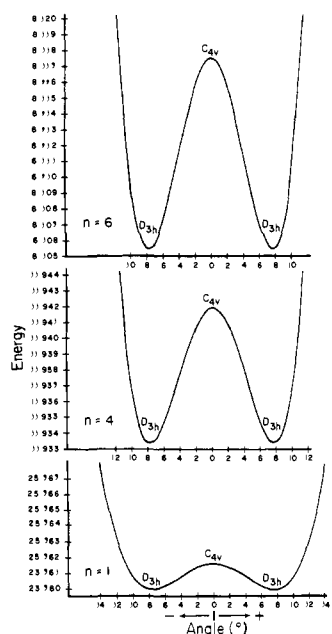
**Table I.** Energies and Edge Lengths for  $D_{3h}$  and  $C_{4v}$  Polyhedra

	Exponent	Energies <sup>a</sup>	
		$D_{3h}$	$C_{4v}$
	1	25.7600	25.7616
	2	19.2529	19.2568
	3	14.9341	14.9404
	4	11.9334	11.9419
	5	9.7536	9.7640
	6	8.1055	8.1175

Expt	$D_{3h}$ Polyhedron		Edge Lengths <sup>b</sup>		$C_{4v}$ Polyhedron		
	4-7	5-6	1-5	5-6	1-5	2-5	1-4
1	1.4076	1.2304	1.1356	1.3182	1.1829	1.1294	1.1195
2	1.4090	1.2292	1.1359	1.3184	1.1815	1.1298	1.1211
3	1.4117	1.2269	1.1365	1.3186	1.1798	1.1300	1.1234
4	1.4148	1.2243	1.1372	1.3187	1.1780	1.1303	1.1257
5	1.4182	1.2213	1.1379	1.3189	1.1763	1.1305	1.1279
6	1.4217	1.2182	1.1387	1.3191	1.1746	1.1309	1.1300

<sup>a</sup> Energies in arbitrary units. <sup>b</sup> Edges referenced to metal–ligand distances of 1 (unit sphere). The atom labeling is identified in Figure 1.



**Figure 3.** Energy profiles of the  $D_{3h} \rightleftharpoons C_{4v}$  rearrangement for exponents of 1, 4, and 6. The angles on the abscissa are for the 4-center-7 angle with the zero taken at the  $C_{4v}$  position.

For the analysis of geometric reaction path in the nine-atom family we have (1) surveyed repulsive interactions for nine “points on a sphere” and (2) carefully analyzed all crystallographic data for  $ML_9$  (all ligands equivalent) and  $M_9$  complexes.

### Repulsion Model Calculations

Favored polytopal forms in  $x$ -atom families are consistently identified from calculations in which only repulsive interactions among polyhedral vertices are taken into account.<sup>5,12–14</sup> This is a reasonable calculational approach for clusters even though polyhedral vertex interactions are bonding in this class.<sup>6</sup> Basic conclusions derived from such calculations are the same for both classes of compounds; however, the fine details, e.g., ratios of polyhedral edge lengths, may differ (vide infra).

Our calculations for the nine-atom family focused on the coordination class. Preliminary analysis of structural data for  $ML_9$  complexes showed that an equal bond distance assumption was realistic. The differences between metal ligand dis-

tances, in the  $D_{3h}$  model, for those in the horizontal mirror plane (3 set) and those on the trigonal prismatic vertices (6 set) were generally small. Most importantly, the 3-atom sets were just as often the shorter set as the longer set and this ambivalence was extant within crystalline  $K_2ReH_9$  for two independent crystallographic  $ReH_9^{2-}$  polyhedra. These structural data logically led to a “points on a sphere” calculation model which gave substantial computational flexibility. Repulsive energy was minimized in the following form:

$$E = \sum r_{ij}^{-n} \quad (n = 1, 2, \dots, 6; \quad i \neq j)$$

as in earlier studies of seven-coordination by Thompson and Bartell<sup>13</sup> and by Claxton and Benson<sup>14a</sup> wherein the algorithms of Claxton and Benson<sup>14a</sup> were used. The essential calculational feature is a steepest descents approach wherein the points are moved on the surface of a sphere until the tangential force on each point is zero. Our results show the two high symmetry forms,  $C_{4v}$  and  $D_{3h}$ , converge nicely but all  $C_{2v}$ ,  $C_2$ , and  $C_s$  forms (vide infra) have flat energy minima where the precise end point depends somewhat on the starting point. Results are tabulated in Table I in terms of energies and symmetry independent edge lengths as a function of six different exponents.

Since  $C_{2v}$  is a subgroup of  $D_{3h}$ , there are  $C_{2v}$  models close to the favored  $D_{3h}$  model; the interesting question arises as to whether preferred  $C_{2v}$  models occur on either side of  $D_{3h}$  and how such models compare energetically with  $D_{3h}$ . These  $C_{2v}$  models are generated by increasing or decreasing the 4-center-7 angle; increasing takes the polyhedron toward the  $C_{4v}$  model. Accordingly, energy was minimized as a function of the 4-center-7 angle (or equivalently the 4–7 edge length); this was accomplished by fixing the colatitude spherical coordinates for the 4 and 7 positions while varying the spherical coordinates for all other positions. These data are plotted in Figure 3 for  $n = 1, 4, \text{ and } 6$ . For simplicity, the zero angle in Figure 3 is taken at the  $C_{4v}$  points; the actual magnitude of the angles at the zero positions vary slightly for the different exponents (Table I). Positive deviations from zero correspond to decreasing the 4-center-7 angle (or 4–7 edge length). There is no single repulsion exponent appropriate for all cases. The repulsions, and hence the exponents, in a given case will be affected by stereochemically active lone pairs, the number and nature of bonding pairs, and regular nonbonding ligand interactions.<sup>13</sup> Obviously, the ligand atoms in coordination complexes cannot be spherical as are the anions in “ionic”

**Table II.** Dihedral Angles in Nine-Coordination for Idealized and Real Complexes<sup>a</sup>

Type of faces	Position	Face 1	Face 2	Angle (deg)
Idealized $D_{3h}$ Polyhedron				
(a) Opposed ( $\perp$ )	$\perp$ threefold	(4,6,5)	(7,8,9)	180.0
(b) Opposed ( $\parallel$ )	$\parallel$ threefold	(1,7,4)	(2,6,9)	3 at 146.4
(c) Vicinal ( $\parallel$ )	$\parallel$ threefold	(1,7,4)	(3,4,7)	3 at 26.4
Idealized $C_{4v}$ Polyhedron				
(a) Opposed (type 1)	1 vertex on sq. face	(1,5,8)	(3,9,6)	2 at 163.5
(b) Opposed (type 2)	2 vertices on sq. face	(1,4,5)	(3,7,9)	2 at 138.2
(c) Vicinal ( $\perp$ )	$\perp$ fourfold	(1,3,4)	(1,7,3)	0.0

<sup>a</sup> Idealized angles based on models with exponent of 6. See Figure 1 for plane identifications.

compounds which have periodic lattices. We assume that an exponent in the range of 3–6 is realistic for ligand atoms like fluorine or oxygen with hydrogen at the low end of this range. Nevertheless, a number of salient features are evident from direct inspection of the three curves. In no exponential case is there evidence of a minimum at  $C_{4v}$ . Even at the unrealistically small value of 1 for  $n$ , there is no evidence of a  $C_{2v}$  minimum to either side of  $D_{3h}$  although the minimum is relatively flat. For more realistic values of  $n$ , 4–6, the  $D_{3h}$  minimum deepens dramatically and the  $D_{3h}$  to  $C_{4v}$  energy separation increases. The model calculations predict that few  $ML_9$  (or  $M_9$ ) molecules or molecular ions will have the idealized  $C_{4v}$  structure although such a variance might be found for  $ML_9$  or  $M_9$  ions in the solid state where cation–anion interactions are significant.

Our repulsive energies cannot be converted directly to energy units so it is difficult to estimate the actual magnitude of the  $D_{3h} \rightleftharpoons C_{4v}$  energy barrier. In all cases, the calculated barrier is less than 0.1% of the total energy of either form. Blight and Kepert<sup>15</sup> found an analogous situation for ligand–ligand repulsion energies in eight-coordinate complexes and they predicted essentially no barrier for the  $D_{2d} \rightleftharpoons D_{4d}$  process (0.1–1 kcal/mol). In the nine-atom case, we feel that the barrier is significant, albeit small, because all discrete  $ML_9$  structures have  $D_{3h}$  symmetry (vide infra). We have also examined the rearrangement processes outlined in Figure 2, and find the barriers in these cases are an order of magnitude or more larger than the  $D_{3h} \rightleftharpoons C_{4v}$  process.

### Analysis of Crystallographic Data

Analysis of crystallographic data for coordination complexes was limited to those nine-coordinate species in which all ligating atoms or groups are equivalent. Chelate complexes were excluded because chelate bite might largely be structure determining. However, the calculational data, vide supra, may be used to predict to a first approximation chelate structures by matching ligand bites with the edge lengths in the idealized  $C_{4v}$  and  $D_{3h}$  models for  $n = 4$  and 6. These lengths are listed in Table I (note that the arbitrary bond length is 1.0000).

As in the past we have found the dihedral angles ( $\delta$ 's) useful in making quantitative assessments of geometric excursions from idealized polyhedra.<sup>2</sup> Dihedral angles are always taken between plane normals directed out from the polyhedral center. To make symmetry distinctions in nine-coordination it is most expeditious to examine opposite triangular faces and measure their deviation from planarity ( $\delta = 180^\circ$  for the planar case). Opposite faces form a trigonal prism and the deviation of  $\delta$  from  $180^\circ$  represents the deviation from a right trigonal prism. When there is one right trigonal prism the polyhedron is clearly  $D_{3h}$ . The clue to a  $C_{4v}$  model is the absence of a  $\delta$  of  $180^\circ$  and the presence of two orthogonal trigonal prisms with  $\delta$ 's larger

than  $160^\circ$ . The  $C_4$  axis is then normal to the two trigonal prisms, or more precisely, the bisector of the two  $\delta$ 's coincides with the  $C_4$  axis. In the idealized  $C_{4v}$  polyhedron, two of the triangular planes with normals in the  $C_4$  direction become square ( $\delta$  of  $0^\circ$  for vicinal triangular planes).

The dihedral angle criteria for idealized nine-coordinate structures are listed in Table II. The dihedral angles of 180 and  $0^\circ$  for pairs of faces perpendicular to the three- and fourfold axes, respectively, are fixed by symmetry, i.e., independent of exponent. The exponent dependence of the remaining angles is small as evidenced by the small edge changes in Table I. Table III summarizes the data found for real complexes close to the  $D_{3h}$  limit. Included also in Table III are the  $v/h$  ratios which describe the elongation (or compression) of the rectangular prismatic faces ( $v$  is the vertical edge length and  $h$  is the horizontal edge length). Included are ions which are not discrete and which share edges. Not included in Table III are x-ray structures of some nine-coordinate metal–halogen complexes, because in these cases halogen atom positions were not precisely determined. These structures were nevertheless examined and the following  $v/h$  ratios were calculated (all six have  $D_{3h}$  point symmetry).

	$v/h$		$v/h$
$U_2F_9$ <sup>16</sup>	1.07	$\beta_1$ - $K_2UF_6$ <sup>17</sup>	1.52
$NaTh_2F_9$ <sup>16</sup>	0.98	$\beta_2$ - $Na_2ThF_6$ <sup>17</sup>	1.48
$UCl_3$ <sup>17</sup>	1.23	$Y(OH)_3$ <sup>18</sup>	1.24

Also included in Table III are the nine-atom clusters  $Rb_2B_9H_9$ ,  $B_7H_7C_2(CH_3)_2$ , and  $Bi_9^{5+}$  but not  $B_9Cl_9$  for which the atomic coordinates are not published, but which clearly has  $D_{3h}$  symmetry.<sup>19</sup>  $HoD_3$ <sup>20</sup> was examined but is best described as a ten-coordinate complex. In all cases, published atomic coordinates were used to calculate interatomic distances, dihedral angles, and construct precision models so that geometric excursions from the idealized  $D_{3h}$  model could be conveniently examined from all perspectives.

Most of the  $ML_9$  and all of the boron and metal clusters have  $D_{3h}$  symmetrically tricapped trigonal prismatic form within experimental error.<sup>21</sup> There are three  $ML_9$  complexes which depart significantly from  $D_{3h}$  and give a distribution of  $\delta$ 's which puts them closer to the  $C_{4v}$  limit (Table IV). All three have extensive internal constraints in the form of polyhedral edge and/or face sharing. In these cases the severe internal constraints could easily be structure determining. The surprise, to us at least, was that there were not more structures at or close to the  $C_{4v}$  limit. Hence we see in the full group of crystallographic data—although the sample is perhaps not sufficiently large to literally “sample” a potential energy (reaction path) surface in  $ML_9$  as a function of shape parameters—rather convincing evidence that the tricapped trigonal prism is the most favored polytopal form in  $ML_9$  and  $M_9$  species.

**Table III.** Dihedral Angles (deg) for Real Complexes at or Close to  $D_{3h}$  Symmetry<sup>a</sup>

Complex	Opposed ( $\perp$ threefold)	Opposed ( $\parallel$ threefold)	Vicinal ( $\parallel$ threefold)	$v/h$	Ref
Idealized	180.0	146.4, 146.4, 146.4	26.4, 26.4, 26.4	1.17	
RbTh <sub>3</sub> F <sub>13</sub> (poly 1) <sup>b</sup>	176.5	148.9, 148.6, 148.6	29.0, 29.0, 28.6	1.03	<i>b</i>
K <sub>2</sub> PaF <sub>7</sub>	169.5	148.0, 148.0, 130.8	29.8, 18.6, 18.6	1.09	<i>c</i>
NaNbF <sub>4</sub> (poly 1)	180.0	140.6, 140.6, 140.6	20.6, 20.6, 20.6	1.37	<i>d</i>
NaNbF <sub>4</sub> (poly 2)	180.0	146.2, 146.2, 146.2	26.2, 26.2, 26.2	1.28	<i>d</i>
K <sub>2</sub> ReH <sub>9</sub> (poly 1)	180.0	143.1, 143.1, 143.1	23.1, 23.1, 23.1	1.19	<i>e</i>
K <sub>2</sub> ReH <sub>9</sub> (poly 2)	180.0	153.8, 153.8, 153.8	33.8, 33.8, 33.8	1.10	<i>e</i>
Er(C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	180.0	141.1, 141.1, 141.1	21.1, 21.1, 21.1	1.15	<i>f</i>
Rb <sub>2</sub> B <sub>9</sub> H <sub>9</sub>	178.6	143.9, 143.9, 140.7	25.4, 21.6, 21.6	0.97	<i>g</i>
B <sub>7</sub> H <sub>7</sub> C <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	179.7	156.3, 150.3, 148.5	32.6, 32.3, 30.3	0.90	<i>h</i>
Bi <sub>9</sub> <sup>5+</sup>	180.0	142.2, 142.2, 142.2	22.2, 22.2, 22.2	1.15	<i>i</i>

<sup>a</sup> In cases where there are two symmetry independent polyhedra, both are listed as poly 1 and poly 2. <sup>b</sup> G. Brunton, *Acta Crystallogr., Sect. B*, **27**, 1823 (1971). <sup>c</sup> D. Brown, S. F. A. Kettle, and A. J. Smith, *J. Chem. Soc. A*, 1429 (1967); D. Brown and A. J. Smith, *Chem. Commun.*, 554 (1965). <sup>d</sup> J. H. Burns, *Inorg. Chem.*, **4**, 881 (1965). <sup>e</sup> (neutrons) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964); (x-ray) K. Knox and A. P. Ginsberg, *ibid.*, **3**, 555 (1964). <sup>f</sup> D. R. Fitzwater and R. E. Rundle, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristalchem.*, **112**, 362 (1959). <sup>g</sup> L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968). <sup>h</sup> T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1076 (1968). <sup>i</sup> R. M. Friedman and J. D. Corbett, *Inorg. Chem.*, **12**, 1134 (1973).

**Table IV.** Dihedral Angles (deg) for Real Complexes Approaching  $C_{4v}$  Symmetry

Complex	Opposed (type 1) <sup>d</sup>	Opposed (type 2) <sup>d</sup>	Vicinal ( $\perp$ fourfold)	Ref
Idealized	163.5, 163.5	138.2, 138.2	0.0	
CsU <sub>6</sub> F <sub>25</sub>	161.2, 156.8	148.0, 148.0	9.7	<i>a</i>
RbTh <sub>3</sub> F <sub>13</sub> (poly 2)	163.6, 159.3	140.2, 135.1	12.1	<i>b</i>
(NH <sub>4</sub> ) <sub>4</sub> ThF <sub>8</sub>	163.9, 159.2	144.1, 134.9	5.4	<i>c</i>

<sup>a</sup> G. Brunton, *Acta Crystallogr., Sect. B*, **27**, 245 (1971). <sup>b</sup> Reference *b* of Table III. <sup>c</sup> R. R. Ryan, R. A. Penneman, and A. Rosenzweig, *Acta Crystallogr., Sect. B*, **25**, 1958 (1969). <sup>d</sup> See Table II for plane identifications.

There are no perfect  $C_{4v}$  structures and the three that approach  $C_{4v}$  form are explicable in terms of polyhedral edge or face sharing constraints.<sup>21</sup> All these data are fully consistent with the structural purview generated from the "points on a sphere" calculations, presented in the previous section. In fact if all observed  $D_{3h}$  dihedral angles are averaged by type in Table III, the angles generated, 178.4, 145.2, and 25.3°, are very close to the "points on a sphere" values of 180.0, 146.4, and 26.4°, respectively.

A distinctive feature of the calculation is that it predicts rectangular faces for the trigonal prismatic substructure in the  $D_{3h}$  form. The observed ratio of the vertical to horizontal trigonal prismatic edges ( $v/h$ ) falls in the range of 1.03–1.37 (average = 1.17) for coordination complexes as compared to calculated values of 1.144, 1.156, and 1.167 for exponential terms of 1, 4, and 6, respectively. In clusters, the ratio of these edges is 1.15 in Bi<sub>9</sub><sup>5+</sup>, 0.99 in B<sub>9</sub>H<sub>9</sub><sup>2-</sup>, 0.89 in B<sub>7</sub>H<sub>7</sub>C<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>, and 0.97 in B<sub>9</sub>Cl<sub>9</sub>. The substantially smaller ratio in the boron clusters is one reflection of the simple fact that the points on a sphere repulsion model is slightly flawed for such "electron deficient" clusters in which bonding (not repulsion) is the critical factor. For example, bonding considerations would tend to make the capped faces square rather than rectangular since all atoms in the capped face are of equal connexity ( $v/h$  of 0.97 found for B<sub>9</sub>H<sub>9</sub><sup>2-</sup>).<sup>22</sup> In general we expect bonding effects to reduce differences in cluster edge lengths from those calculated for ML<sub>9</sub> coordination complexes (Table I).

In summary, the dihedral angle analysis provides a viable process for quantitative assessments of polytopal form in ML<sub>9</sub> coordination complexes and M<sub>9</sub> cluster molecules as was earlier demonstrated<sup>2a</sup> for the four- through eight-atom families. Analysis of actual structural data by this technique has the potential of defining geometric reaction paths if the actual structures range between two (or more) idealized po-

lytopal forms as shown<sup>2a</sup> in the five-atom family. No reaction path could be established in the nine-atom family because most ML<sub>9</sub> and all M<sub>9</sub> complexes, structurally defined to date, have near  $D_{3h}$  tricapped trigonal prismatic form. The "points on a sphere" calculations correctly identify this  $D_{3h}$  form as the most favorable one and show the  $C_{4v}$  form to be at an energy maximum a point consistent with fact that no  $C_{4v}$  form has been reported for a discrete ML<sub>9</sub> species.

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## References and Notes

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 (22) In triangular polyhedral faces for cluster complexes, the observed and theoretically expected situations are (a) equilateral triangular faces where vertex atoms have the same connectivity, (b) isosceles triangular face with AA edge longer where vertex A has a higher connectivity than vertex B, (c) an isosceles triangular face with AA edge shorter where vertex A has a lower connectivity than vertex B, and (d) vertex positions of highest connectivity are closer to the polyhedral center than vertex positions of lower connectivity.

## Synthesis and Chemical Characterization of Platinum Carbonyl Dianions $[Pt_3(CO)_6]_n^{2-}$ ( $n = \sim 10, 6, 5, 4, 3, 2, 1$ ). A New Series of Inorganic Oligomers

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**Abstract:** Reduction of  $Na_2PtCl_6 \cdot 6H_2O$  or  $Pt(CO)_2Cl_2$  under carbon monoxide (25 °C, 1 atm) in the presence of alkali gives the dianions  $[Pt_3(CO)_6]_n^{2-}$  ( $n = \sim 10, 5, 4, 3$ ) where  $n$  depends on the alkali:Pt ratio. Other members of this series ( $n = 6, 2, 1$ ) have been obtained starting from preformed  $[Pt_3(CO)_6]_n^{2-}$  ( $n = 10, 5, 4, 3$ ) by reduction with lithium metal ( $n = 2, 1$ ) and sodium-potassium alloy ( $n = 1$ ) or by oxidation with Pt(IV) ( $n = 6$ ). These last preparations and the redistribution of metal bonds between oligomers which differ in  $n$  by to or more ( $n \leq 6, \Delta n \geq 2$ ) point out the ease with which these compounds change nuclearity. Increasing  $n$  decreases the reactivity towards electrophiles and oxidizing agents and, at the same time, the reactivity towards nucleophiles and reducing agents increases. The first example of a platinum carbonyl catalyzed hydroformylation reaction is reported. The main bonding features of these dianions, and the different stabilities of analogous nickel, palladium, and platinum carbonyl compounds, are discussed.

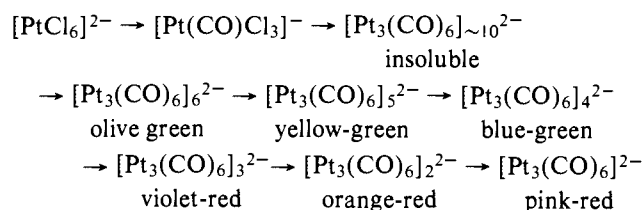
Our interest in the chemistry of the platinum(0) clusters containing tertiary phosphines and carbon monoxide as ligands<sup>2-4</sup> prompted us to investigate the nature and the reactivity of the platinumdicarbonyl,  $[Pt(CO)_2]_n$ .<sup>5</sup> This compound, which was first isolated by Booth and Chatt, has not been sufficiently characterized owing to its complete insolubility. The starting point of our research has been the observation that platinumdicarbonyl dissolves in acetone in the presence of aqueous ammonia to give dark green uncharacterized solutions.<sup>5</sup>

Although this work began in 1967,<sup>6</sup> it has only been possible to obtain the platinum carbonyl derivatives on a preparative scale some years later when we used the reductive carbonylation of platinum(IV) salts in alkaline solution, which had been successfully used for the preparation of rhodium carbonyl clusters.<sup>7</sup> Furthermore the structural characterization of the  $[Pt_3(CO)_6]_n^{2-}$  derivatives has been hampered by difficulties such as loss of crystallinity due to elimination of clathrated solvents, or crystal disorder, although these problems have been overcome recently by using bulky cations.<sup>8,9</sup>

### Results and Discussion

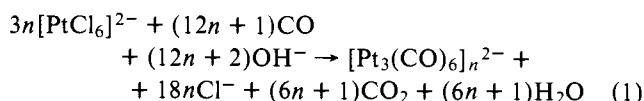
**1. Synthesis of  $[Pt_3(CO)_6]_n^{2-}$ .** The series of dianions with general formula  $[Pt_3(CO)_6]_n^{2-}$  ( $n = \sim 10, 6, 5, 4, 3, 2, 1$ ) has been synthesized from several platinum substrates ( $Na_2PtCl_6 \cdot 6H_2O$ ,  $H_2PtCl_6 \cdot xH_2O$ ,  $Na_2PtCl_4$ ,  $Pt(CO)_2Cl_2$ ) using various reducing agents (alkali hydroxides under CO,  $Fe(CO)_5$ , cobaltocene, alkali metals). Although the value of  $n$  of the final product depends greatly on the nature of the reagents as well as on the experimental conditions, by carrying out the reaction at room temperature and under carbon mon-

oxide, the reductive carbonylation proceeds following the sequence:<sup>10</sup>



Beginning from  $n = 6$ , the salts of consecutive dianions ( $\Delta n = 1$ ) have similar solubilities and their separation is always difficult and often impossible. It has therefore been necessary to find suitable experimental conditions in order to carry out selectively each step of the above sequence. The course of this reduction is conveniently monitored by infrared spectroscopy.

The most important synthetic method consists in the progressive reduction of platinum(IV) salts in the presence of alkali and carbon monoxide according to the following general stoichiometric equation:



The best platinum starting material is the sodium hexachloroplatinate because it is readily available and fairly soluble in alcoholic solvents. The most reliable experimental conditions using this route are summarized in Scheme I.<sup>11</sup>

The clear orange solution of sodium hexachloroplati-