

An improved method for the computation of ligand steric effects based on solid angles

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An improved algorithm has been designed to characterize ligand interactions in organometallic and coordination complexes in terms of the percentage of the metal coordination sphere shielded by a given ligand. The computations for ligand solid angles are performed numerically and employ introduced atomic radii that are larger than covalent but smaller than van der Waals radii. This approach enables facile evaluation of steric congestion in the metal coordination sphere, quantification of unfavorable interligand contacts, and in some cases prediction of the complex composition or ligand coordination on purely geometrical grounds.

Introduction

Numerous measurements of ligand steric parameters^{1,2} have been pursued with the intention of establishing quantitative relationships between ligand bulk and reaction rate and equilibrium constants and/or chemical and physical properties of organic and organometallic systems. Such data may supply chemists with predictive power, enable them to better understand experimental data and modify reaction conditions appropriately.

The most commonly employed steric and stereoelectronic parameters for ligand characterization include Tolman cone angle θ ,³ solid angle Ω , ligand repulsive energies E_R ,⁴ Taft–Dubois E_s steric parameters,^{5,6} and QALE.^{7,8} Herein we will be concerned with steric effects only. “Steric effect” of a ligand reflects not only its size, which can be measured by its volume, but also its shape and conformation that are dependent on the coordination center and other ligands present in the system. In solid-state structures the ligand conformation also depends on the intermolecular interactions with adjacent molecules and/or ions.

Most published studies target the behavior of individual ligands in certain systems without simultaneous consideration of all interligand steric effects in a given molecule, with the exception of those reported by Coville *et al.*^{9–12} and Fischer and Li.¹³ Qualitative considerations of ligand congestion within a metal coordination sphere are ubiquitous; however there is one report that proposes quantification of ligand–ligand interactions by use of solid angles¹⁴ in organometallic compounds. Having explored the applications of solid angle computations to complexes in organic^{15–17} and organometallic^{2,9,10,13,14,18,19} chemistry, we have expanded the solid angle approach to metal complexes to encompass its ligands with any composition, hapticity, shape, and conformation. We also propose a geometrical method of quantifying unfavorable ligand–ligand interactions within metal complex.

In all literature studies to date van der Waals radii²⁰ of the elements have been used for quantitative calculations of solid and cone angles. Herein we define an alternative choice of the

element radii to be used in solid angle Ω calculations, propose a new measure of ligand steric requirement (called G-parameter), and discuss examples in the application of this parameter to predict compositions of and ligand coordination in organometallic complexes.

There is no commercial computational program available for calculating cone and solid angles in a facile fashion. Programs Omegas90¹⁵ and Steric¹⁹ have been cited, and the latter is available on the web; yet the analytical algorithm employed in Steric has left room for improvement.²¹ Therefore, we designed and wrote a PC program “Solid-G” that numerically calculates ligand steric parameters in organometallic compounds in a reliable fashion. The computations presented herein have been performed with Solid-G; this program and the algorithms implemented in it are described elsewhere.^{22,23}

The choice of radii for steric parameter calculations

There is a significant body of literature work addressing cone and solid angle computations. To describe non-bonded interactions authors most often utilize van der Waals (vdW) radii for 19 elements by Bondi²⁰ in 1964. Frequently, the calculations have been performed in order to explain the dependency of a reaction rate on ligand bulkiness, with the cone and solid angles being determined for a series of individual ligands that were to react with the complex of interest. In a few publications the steric parameters of all ligands within one complex have been considered simultaneously to describe the steric crowdedness in the metal coordination sphere.^{9,10} Such computations executed with vdW radii would not be very meaningful (*vide infra*); nonetheless, it would be beneficial and informative to design a means to quantify steric congestion among the ligands. In 1997 Taverner *et al.*¹⁴ published the first attempt to quantify ligand–ligand interactions in terms of solid angles; however, the authors noticed for iodine that its covalent radius was too small and its vdW radius was too large for accessing steric effects in their system. This salient observation reveals an intrinsic flaw that can be generalized to the entire periodic table.

Brown⁴ reasoned that a ligand steric effect is a consequence of non-bonded repulsion between substituents. Interatomic

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interactions become the most attractive when the distance between two atoms corresponds to r_{\min} in Fig. 1. As r decreases the repulsive forces increase rapidly and become predominant at $V(r) = 0$ when the potential energy curve crosses the abscissa at r_z ($Z =$ zero energy point).

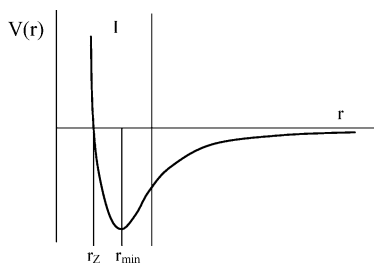


Fig. 1 Typical interatomic potential with regions to scale. I—the Morse potential region. $r_{\min} = \sum_i R_{\min}$, $r_z = \sum_i R_z$.

The non-bonded interactions between two atoms in region I can be well described with a Morse potential,²⁴ [eqn (1)],²⁵

$$E_M = \sqrt{E_1^{\text{vdW}} E_2^{\text{vdW}}} e^{\epsilon_{12} - b_{12} r} (e^{\epsilon_{12} - b_{12} r} - 2)$$

$$b_{12} = \frac{1}{2}(s_1 + s_2)$$

$$c_{12} = \frac{1}{2}(s_1 r_1 + s_2 r_2) \quad (1)$$

where E_i^{vdW} —non-bonded energy for each atom, r —distance between atoms, r_i —non-bonded diameter of each atom, s_i —non-bonded scaling for each atom.²⁶

We propose in our model to use atomic radii R_z corresponding to $V(r) = 0$ for all atoms for computing steric parameters. As defined above, the zero point energy radii most closely correspond to the radii of atomic “hard spheres”.

Neon was selected as a probe for computing the R_z radii for all atoms (Table 1). The R_z values in Table 1 were obtained as follows. The zero point energy radius of neon $R_z(\text{Ne})$ was determined from eqn (2), which is the solution of eqn (1) for $E_M(r) = 0$

$$r = \frac{c_{12} - \ln 2}{b_{12}} \quad (2)$$

For each element the distance r corresponding to $E_M(r) = 0$ for the element’s interaction with neon was calculated from eqn (2), and the atomic radius was then determined as

$$R_z(\text{element}) = r_z - R_z(\text{Ne}) \quad (3)$$

The success of the method depends on the choice of the atomic radii. Rarely have the authors of papers dealing with algorithms mentioned the specific values of the radii chosen. In the majority of the cone and solid angle studies the van der Waals radii selected are not explicitly listed; most authors used the values tabulated by Bondi, whose approach was recently criticized.²⁷ For each atom there seem to exist a range of vdW radii measured experimentally, calculated theoretically, or derived otherwise, and there is no one comprehensive set of radii for each of the crystal, theoretical, or gas-kinetic group of data, not to mention the absence of a universal system. The choice of the radii is not trivial and can be discussed at length. Here, however, we use zero energy point R_z radii calculated

as described above. The only exception is the hydrogen atom for which the computed radius was 1.426 Å, too large for our purposes. A quote from Allinger reflected our assessment: “It was felt that an important conclusion reached concerned the van der Waals radius of hydrogen needed for successful application of the method”.²⁸ A broad array of hydrogen vdW radii ranging from 0.47²⁹ to 1.78³⁰ Å has been identified. Atomic vdW radii vary depending on the environment of the atom, and especially on the electronegativity of the atoms it is bound to. Polar flattening results in an anisotropic character of the atomic vdW shape, therefore assigning a *radius* to the hydrogen vdW *sphere* is our deliberate compromise. The smallest reported hydrogen vdW radii are ~1.03 Å [neutron diffraction structures of 23 carbohydrates with O–H...O–H...O hydrogen bonds³¹], 1.02 Å [our average of DFT data for seven linear di- and triatomic molecules³²], 1.0 Å [neutron diffraction studies³³], 1.0(1) Å [structural data for “free base”-HX (X = halide) complexes³⁴ combined with theoretical results²⁹], 0.98 Å [theoretical value for H₂ obtained with questionable assumptions³⁵], and 0.47 Å [theoretical studies of complexes formed by HF²⁹]. Thus, instead of the calculated $R_z(\text{H})$ we decided to use the smallest hydrogen vdW radius of 1.0 Å appropriate to the type of our computations.

The vdW radii computed by Bondi for 19 elements are on average 6% larger than the corresponding atomic R_z radii from Table 1. The R_z radii are ~16% larger than the corresponding RFF1 vdW radii from Table 1 (RFF1: a first-generation reaction force field, ref. 24). From Table 1 it is estimated that in order to move, for example, two carbon atoms from the r_{\min} distance (3.65 Å) to the distance equal to the sum of their R_z radii (3.078 Å) an energy of approximately 0.13 kcal mol⁻¹ is required; similarly, in order to reposition two chlorine atoms in a similar fashion from 3.8 to 3.2 Å an energy of 0.43 kcal mol⁻¹ is necessary. For two hydrogen atoms the corresponding energy (from 3.35 to 2.0 Å) is 0.72 kcal mol⁻¹. These numbers provide an energetic estimate of magnitude for unfavorable non-bonded interactions.

Definition of θ , Ω , and G

The geometrical definition of the solid angle Ω is shown in Fig. 2. The Tolman cone angle θ , measured in degrees, was not designed to be and is not an adequate measure of steric congestion in a molecule if adjacent groups can mesh to relieve steric strain.²

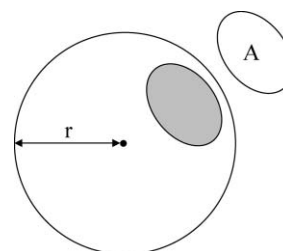


Fig. 2 Definitions of the geometrical solid angle $\Omega = \frac{A}{r^2}$.

The angle that includes a given area on the surface of that sphere is denoted as the solid angle Ω . The solid angle can be visualized as follows: the central metal of an organometallic complex is replaced with a light source, and each ligand casts a shadow on a sphere surrounding the molecule (Fig. 3). The value of the solid angle is

Table 1 Morse potential-equation parameters²⁴ for each of the elements, van der Waals (R_{\min}), and R_z radii, calculated from eqn (3)

Atom	$r_{\min}/\text{\AA}$	$E_{\text{vdw}}/\text{kcal mol}^{-1}$	s_{vdw}	$R_{\min}/\text{\AA}$	$R_z/\text{\AA}$	Atom	$r_{\min}/\text{\AA}$	$E_{\text{vdw}}/\text{kcal mol}^{-1}$	s_{vdw}	$R_{\min}/\text{\AA}$	$R_z/\text{\AA}$
H	3.35	0.02	1.44	1.675	1.000	I	4.582	0.724	1.348	2.291	1.941
He	2.97	0.022	2.016	1.485	1.311	Xe	4.52	0.659	1.383	2.260	1.928
Li	4.15	0.92	0.944	2.075	1.599	Cs	6.729	1.105	0.802	3.365	2.336
Be	3.999	0.416	1.101	2.000	1.606	Ba	5.846	3.399	0.928	2.923	2.174
B	3.847	0.195	1.239	1.924	1.592	La	4.4	0.745	0.954	2.200	1.691
C	3.65	0.095	1.35	1.825	1.539	Ce	4.4	0.694	0.958	2.200	1.693
N	3.545	0.089	1.476	1.773	1.521	Pr	4.401	0.65	0.963	2.201	1.695
O	3.394	0.084	1.581	1.697	1.470	Nd	4.402	0.61	0.968	2.201	1.698
F	3.242	0.084	1.679	1.621	1.413	Pm	4.403	0.573	0.972	2.202	1.701
Ne	3.091	0.084	1.773	1.546	1.350	Sm	4.404	0.54	0.977	2.202	1.703
Na	4.9	0.8	0.922	2.450	1.845	Eu	4.405	0.51	0.981	2.203	1.706
Mg	4.737	0.489	1.049	2.369	1.862	Gd	4.406	0.481	0.986	2.203	1.708
Al	4.573	0.353	1.163	2.287	1.856	Tb	4.407	0.455	0.99	2.204	1.711
Si	4.41	0.303	1.266	2.205	1.834	Dy	4.408	0.431	0.995	2.204	1.714
P	4.247	0.288	1.361	2.124	1.801	Ho	4.41	0.408	0.999	2.205	1.716
S	4.083	0.285	1.451	2.042	1.757	Er	4.412	0.387	1.004	2.206	1.719
Cl	3.8	0.285	1.335	1.900	1.599	Tm	4.413	0.368	1.008	2.207	1.722
Ar	3.757	0.285	1.614	1.879	1.649	Yb	4.303	0.408	1.039	2.152	1.696
K	5.429	1.364	0.847	2.715	1.968	Lu	4.235	0.371	1.06	2.118	1.680
Ca	4.672	3.823	1.005	2.336	1.814	Hf	4.172	0.336	1.082	2.086	1.665
Sc	3.54	0.652	1.042	1.770	1.415	Ta	4.112	0.311	1.102	2.056	1.650
Ti	3.575	0.483	1.052	1.788	1.430	W	4.056	0.29	1.123	2.028	1.636
V	3.61	0.368	1.063	1.805	1.447	Re	4.003	0.274	1.143	2.002	1.623
Cr	3.645	0.288	1.073	1.823	1.463	Os	3.953	0.259	1.163	1.977	1.610
Mn	3.678	0.226	1.084	1.839	1.478	Ir	3.906	0.246	1.182	1.953	1.598
Fe	3.713	0.179	1.094	1.857	1.495	Pt	3.862	0.235	1.201	1.931	1.586
Co	3.746	0.144	1.104	1.873	1.510	Au	3.773	0.243	1.235	1.887	1.560
Ni	3.779	0.117	1.114	1.890	1.526	Hg	4.632	1.494	1.314	2.316	1.948
Cu	3.812	0.096	1.124	1.906	1.542	Tl	6.082	0.346	1.005	3.041	2.324
Zn	3.675	0.104	1.186	1.838	1.507	Pb	5.756	0.403	1.067	2.878	2.254
Ga	4.65	0.722	1.24	2.325	1.922	Bi	5.482	0.437	1.125	2.741	2.191
Ge	4.54	0.611	1.291	2.270	1.899	Po	5.248	0.53	1.181	2.624	2.134
As	4.446	0.5	1.34	2.223	1.879	At	5.044	0.594	1.234	2.522	2.081
Se	4.364	0.488	1.388	2.182	1.861	Rn	4.866	0.636	1.284	2.433	2.033
Br	4.291	0.441	1.434	2.146	1.845	Fr	7.258	0.895	0.772	3.629	2.460
Kr	4.228	0.386	1.478	2.114	1.831	Ra	6.04	3.705	0.934	3.020	2.246
Rb	6.046	1.069	0.831	3.023	2.152	Ac	6.15	3.108	0.925	3.075	2.276
Sr	5.252	3.132	0.97	2.626	2.000	Th	6.133	2.974	0.934	3.067	2.278
Y	3.835	0.691	1.037	1.918	1.522	Pa	6.116	2.855	0.944	3.058	2.282
Zr	3.822	0.561	1.055	1.911	1.523	U	6.1	2.743	0.954	3.050	2.285
Nb	3.81	0.468	1.073	1.905	1.525	Np	6.086	2.64	0.963	3.043	2.288
Mo	3.799	0.397	1.09	1.900	1.526	Pu	6.072	2.544	0.972	3.036	2.292
Tc	3.79	0.343	1.108	1.895	1.529	Am	6.058	2.456	0.982	3.029	2.295
Ru	3.782	0.297	1.125	1.891	1.531	Cm	6.046	2.369	0.991	3.023	2.299
Rh	3.775	0.26	1.141	1.888	1.533	Bk	6.035	2.288	1	3.018	2.303
Pd	3.769	0.23	1.158	1.885	1.536	Cf	6.024	2.213	1.009	3.012	2.306
Ag	3.948	0.154	1.119	1.974	1.593	Es	6.014	2.14	1.018	3.007	2.310
Cd	3.856	0.158	1.161	1.928	1.571	Fm	6.004	2.071	1.027	3.002	2.314
In	4.906	1.003	1.201	2.453	2.008	Md	5.995	2.007	1.035	2.998	2.318
Sn	4.811	0.896	1.239	2.406	1.988	No	5.986	1.946	1.044	2.993	2.322
Sb	4.727	0.772	1.276	2.364	1.971	Lr	5.979	1.924	1.053	2.990	2.327
Te	4.651	0.773	1.313	2.326	1.955						

numerically equal to the size of that shadowed area divided by the square of the radius of the sphere [eqn (4)].

$$\Omega = \frac{A}{r^2} \quad (4)$$

The standard unit of a solid angle is the (mathematically unitless) Steradian (sr), and the maximum solid angle is 4π . The non-linear relationship between the cone and solid angle is shown in Fig. 4.

The new entity, parameter G (or G -parameter) that we propose to use for description of ligand steric effects is defined as a

percentage of the metal coordination sphere shielded by the ligand [eqn (5)],

$$G = 100 \frac{\Omega}{4\pi} \quad (5)$$

This G -parameter is entropic in nature and measures the probability of an incoming reagent *not* accessing the metal center. For instance, if a ligand shields 30% of a metal's coordination sphere, there is only a 70% chance that another reagent will reach the metal center. The G -parameter values are calculated based upon atomic coordinates available either from experimental single-crystal X-ray diffraction analysis, parameter G^X (X denotes

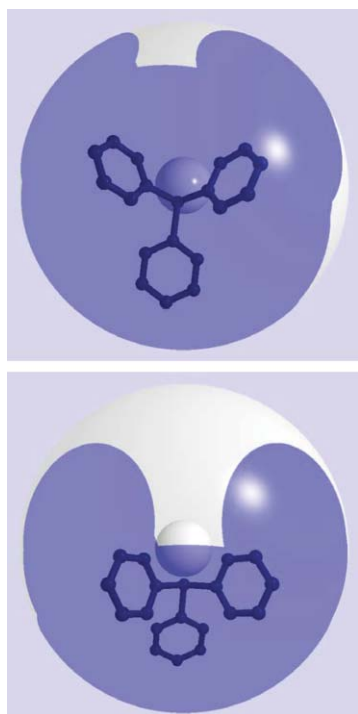


Fig. 3 Two views of projections of a PPh₃ ligands onto a sphere of an arbitrary radius of 13 Å. The metal is shown as a large white sphere of an arbitrary radius for easy visualization. The ligand solid angle can be considered as the area of the ligand projection shadow divided by the square of the sphere radius, $\Omega = \frac{A}{r^2}$. A ligand *G*-parameter is the percentage of the sphere shielded by the ligand, $G = 100 \frac{\Omega}{4\pi}$.

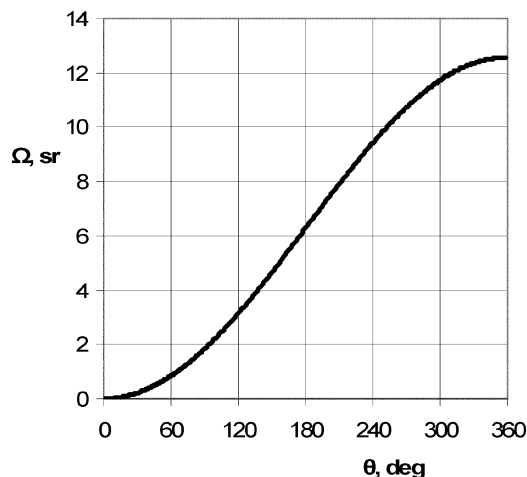


Fig. 4 Non-linear relationship between the cone angle and the solid angle. $\Omega = 2\pi \left(1 - \cos \frac{\theta}{2}\right)$, where θ is the Tolman cone angle.

X-ray data), or from theoretical molecular mechanics calculations, parameter G^T (T denotes theoretical data). In the latter case when a conformational analysis for a certain ligand has been performed, the population-weighted average *G*-parameter is called G^P (P = population-weighted). The *G*-parameters presented in this work were calculated based on experimental crystallographic data for complexes reported to the Cambridge Structural Database

(CSD);³⁶ although they should be designated G^X for brevity we will refer to them simply as *G*.

Methodology

Hirota *et al.*¹⁶ suggested using Ω_s for hydrocarbons, [eqn (6)], as an entropic steric substituent constant that is reasonably well applicable to systems of varying nature and that represents local steric hindrance about the reaction center.¹⁷ Ω_s is calculated as a population-weighted sum of Ω_s of all conformers of a given substituent in molecular mechanics optimizations.¹⁵

$$\Omega = \frac{\text{Area of the shadow}}{\text{Total surface area of the sphere}} = \sum_i p_i \Omega_{s_i} \quad (6)$$

¹⁴ where *i* is the conformer index.

It has been shown that Ω_s works as well or better than Dubai's constants E_s' for a series of organic reactions.¹⁵ In our nomenclature solid angle Ω_s is directly proportional to parameter G^P , [eqn (3) and (7)], representing the percentage of a metal's coordination sphere shielded by a ligand or a number of ligands.

$$G^P = 100 \frac{\Omega}{4\pi} = 25 \frac{\Omega}{\pi} = 100 \Omega \quad (7)$$

This work expands the findings of Hirota *et al.*^{15–17} and Taverner *et al.*^{18,38} and we expect *G*-parameters to be applicable to a wide variety of organic and organometallic systems.

It is imperative to point out the following aspects.

(1) Parameter *G* is expressed in percent, a common unit that can be readily understood. It is more straightforward to visualize that five ligands with a *G*-parameter of 20% can theoretically fit around one metal center, than to decide whether five ligands with identical cone angles of 106.26° can do the same. Using cone angles may be appropriate for individual ligands; however, an intrinsic problem with cone angles is that their use is complicated for estimating the crowdedness of the metal coordination environment when several ligands are considered at the same time. The maximum cone angle is 360°; is this value equivalent to 360 one-degree cone angles or four 90° cone angles? Will the central metal be shielded to the same extent in all of these cases? The solid angle Ω does not suffer from this ambiguity, yet most of us are not used to thinking in (unitless) steradians. In addition, certain classes of ligands such as porphyrins and phthalocyanines cannot be characterized with a meaningful cone angle but are readily parameterized with Ω and *G*-parameter values.

(2) Parameter *G* is independent of the ligand size, shape, symmetry, or, importantly, hapticity.

(3) Parameter *G* can be calculated either for an individual ligand or for a metal complex as an entity, if one is interested in the total shielding of the central metal.

(4) We use atomic R_z radii rather than vdW radii for all *G*-parameter calculations. This is an important distinction from the previously published work of others.

Several authors have indicated that a single value characterizing a ligand's steric parameter is preferable to a range; however, there are no reports of tables with values providing standard deviations for the calculated parameters Ω , θ , E_R or E_S , and only several reports mention observed ranges. *G*-parameter effectively shows how well the ligand shields the metal that it is ligated to (“ligand shielding”). We will report standard deviations for each value

of G because it encompasses a range of ligand conformations, ligand environments, metal centers, lattice packing effects, and experimental temperatures that are obtained from mining of crystallographic data.

The methodology proposed herein is equally applicable to structures based on theoretical studies. In the latter case it is advisable to perform conformational analysis of the ligand of interest in order to obtain a plausible range of its G value (G^p) and its estimated standard deviation. In the present work all calculations were performed with program Solid-G²² that is available from the authors and will be described in a forthcoming publication.

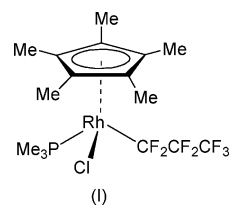
Notation for steric parameter G

To enrich the plethora of parameters designed to characterize ligand steric properties we utilize the following notations for parameter G (Table 2): $G_M(\text{moiety})$, where M denotes the central metal of the system, which is important to specify since metal–ligand distances (and G values) are dependent on it, and moiety is a ligand or an entire complex. In the latter case the G value will reveal how shielded the central metal is when all ligands are treated as one cumulative ligand. Thus, $G_{\text{Rh}}(\text{PMe}_3)$ represents the percentage of the sphere about Rh shielded by a trimethylphosphine ligand. In order to sensibly compare the same ligands observed in different systems, we also calculate $G_{2.28}(\text{moiety})$, the value of $G_M(\text{moiety})$ “normalized” to the $M-L$ distance of 2.28 Å. This normalization is straightforward for monodentate ligands; for bidentate ligands it is the distance between the metal and the center of the line connecting the ligating atoms, while for tri- and higher-dentate ligands it is the distance between the metal and the center of the polygon defined by the coordinated atoms. Apparently, this normalization approach can work well for rigid systems such as bidentate pyrazoles or cyclopentadienyl derivatives, but becomes less meaningful for systems such as bidentate diphosphines, tridentate scorpionates, or porphyrines.

The estimated standard deviation of the normalized ligand G -parameter serves as a measure of the ligand’s conformational flexibility. By means of example we compare the G -parameters obtained with the use of program Solid-G for two common ligands, namely $G_{2.28}(\text{PMe}_3) = 20.4(3)\%$ and $G_{2.28}(\text{PEt}_3) = 24.3(6)\%$

computed for selected Pt complexes from the CSD. From the magnitudes of the G -parameters we conclude that PEt_3 shields the coordinated metal to a higher degree (24.3 vs. 20.4%), and from the standard deviations that PEt_3 is slightly more flexible than PMe_3 (0.6 vs. 0.3%). Not all Et substituents adopt a conformation that minimizes shielding,³ hence an increase relative to the $G(\text{PMe}_3)$ value.

To illustrate the use of G and $G_{2.28}$ let us consider complex $[\text{Rh}(\text{Cp}^*)(\text{PMe}_3)(\text{CF}_2\text{CF}_2\text{CF}_3)\text{Cl}]^{37}$ (**1**), Scheme 1. The Rh–P distance in **1** is 2.2971(13) Å and $G_{\text{Rh}}(\text{PMe}_3)$ is 20.1%; the normalized $G_{2.28}(\text{PMe}_3)$ is 20.3%, which is expectedly larger than $G_{\text{Rh}}(\text{PMe}_3)$ because the reference distance of 2.28 Å is shorter than that of the metal–ligand bond. The Rh– $\text{CF}_2\text{CF}_2\text{CF}_3$ distance is 2.073(5) Å and the $G_{\text{Rh}}(\text{CF}_2\text{CF}_2\text{CF}_3)$ is 21.3%; the corresponding $G_{2.28}(\text{CF}_2\text{CF}_2\text{CF}_3)$ is 18.6%, a value noticeably smaller because the Rh–C distance is substantially shorter than 2.28 Å. Similarly, the normalized values for the other two ligands are smaller than the observed G values: Rh–Cl distance is 2.252(4) Å, $G_{\text{Rh}}(\text{Cl}) = 12.8\%$, $G_{2.28}(\text{Cl}) = 14.4\%$; Rh–centroid(Cp^*) distance is 1.875(4) Å, $G_{\text{Rh}}(\text{Cp}^*) = 38.5\%$, $G_{2.28}(\text{Cp}^*) = 32.2\%$. Note that while the normalized G percentage for heptafluoropropyl ligand is smaller than that for PMe_3 , in complex **1** the heptafluoropropyl shields the central metal to a higher extent than the PMe_3 ligand. This illustrates a logical, but not an obvious fact that ligands with larger $G_{2.28}$ values can have smaller G_M parameters than ligands with smaller $G_{2.28}$ parameters in the same metal complex, if the metal–ligand distance to the ligand with the larger $G_{2.28}$ value is appreciably longer than the metal–ligand distance to the ligand with the smaller $G_{2.28}$ parameter. If all four ligands in complex **1**



Scheme 1

Table 2 Summary of the designated G -parameters utilized to characterize ligand steric behavior *via* the use of atomic R_Z radii

$G_M(\text{L})$ (%)	“Ligand shielding”, percentage of the metal M coordination sphere shielded by ligand L .
$G_{2.28}(\text{L})$ (%)	“Normalized ligand shielding”, percentage of the metal coordination sphere shielded by ligand L for the metal– L distance of 2.28 Å.
$G_M(\text{complex})$ (%)	Percentage of the metal M coordination sphere shielded by all ligands.
$G_i(\text{complex})$ (%)	Percentage of the metal coordination sphere shielded by more than one ligand, “ligand shadow overlap”.
$G_U(\text{L}_1\text{–L}_2)$ (%)	Percentage of the metal coordination sphere shielded by the region of an unfavorable ligand–ligand $\text{L}_1\text{–L}_2$ contact.
$G_U(\text{complex})$ (%)	Percentage of the metal coordination sphere shielded by all regions of unfavorable ligand–ligand contacts.
$V_G(\text{L}_1\text{–L}_2)/\text{Å}^3$	Volume of the interpenetration region (disc) of the atomic spheres of the atoms in ligands L_1 and L_2 that give rise to unfavorable close contacts.
$V_G(\text{complex})/\text{Å}^3$	Volume of all interpenetration regions (discs) of the atomic R_Z spheres of the atoms belonging to different ligands participating in unfavorable close contacts.
G^x	Calculated G value based on crystallographic data.
G^t	Calculated G value for a molecule with a theoretically optimized geometry.
G^p	Population-weighted G value calculated for a ligand with a theoretically optimized geometry that has been subjected to conformational analysis.
StdDev(G)	Standard deviation of the G -parameter indicating a measure of ligand conformational flexibility. The larger the value, the more flexible the ligand is.

are treated as one cumulative ligand the total percentage of sphere shielded from the central metal is expressed by $G_{\text{Rh}}(\mathbf{1}) = 91.0\%$.

There is one caveat in the area of normalized distances. There is a mathematical formula [eqn (8)] that allows one to calculate the ligand solid angle for any distance between a metal and a ligand if the ligand solid angle for a certain distance is known. In our case the distance is 2.28 Å since this is the length chosen by Tolman in his studies. One can imagine calculating a solid angle for a ligand at any certain distance and then creating a plot of the solid angle value against the distance based on eqn (8) to encompass all possibilities. But eqn (8) is accurate only when the contour of the ligand (the shape of the area for which the solid angle is calculated) remains unchanged when the metal–ligand distance is altered. If the ligand is a sphere (single atom or linear carbonyl) the formula holds. For more complex ligands that is not necessarily so because other atoms may change the ligand profile, Fig. 5.

$$\Omega_2 = 2\pi \left(1 - \sqrt{1 - \left(\frac{d_1}{d_2} \right)^2 \left(1 - \left(1 - \frac{\Omega_1}{2\pi} \right)^2 \right)} \right) \quad (8)$$

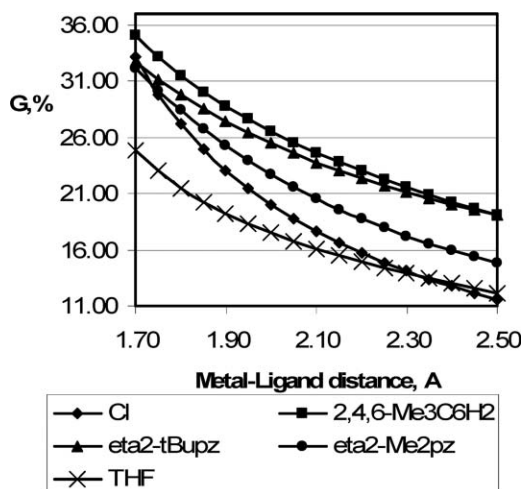


Fig. 5 G -parameter dependence on the metal–ligand separation for five ligands. The steepest change below 2 Å is observed for the spherical ligand.

Thus, if one knows the ligand solid angle at 2.28 Å and wishes to calculate the solid angle for a different distance eqn (8) can serve as a source of a crude preliminary estimate only. The correct approach implemented in Solid-G for computing the normalized $G_{2.28}$ values is to reposition each ligand at 2.28 Å from the metal and perform the complete solid angle calculation anew rather than utilize eqn (8).

Sometimes different ligands in a system can shield the same regions of the surrounding sphere (Fig. 6). Taverner *et al.*¹⁴ suggested using value Γ [eqn (9)] as a measure of steric congestion between ligands

$$\Gamma = (\Omega_A + \Omega_B) - \Omega_{AB} \quad (9)$$

Similarly, we define a $G_\gamma(\text{complex})$ (γ denotes resemblance to Taverner's Γ) value for all areas shielded simultaneously by several ligands to quantify the ligand shadow overlap:

$$G_\gamma(\text{complex}) = \sum_i G_M(L_i) - G_M(\text{complex}) \quad (10)$$

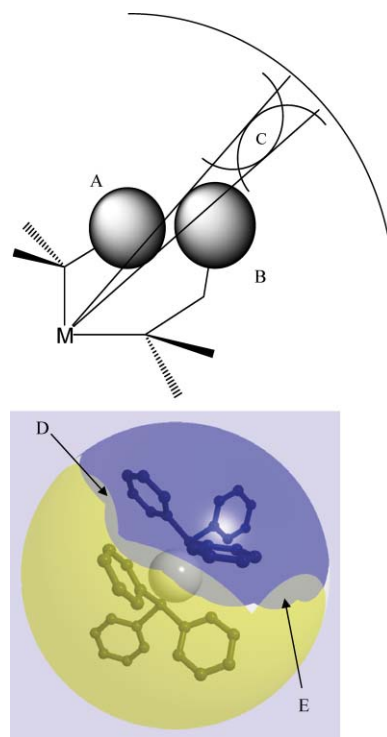


Fig. 6 Overlap of ligand shadows of two PPh_3 ligands, A and B, on the reference sphere: (top) percentage of the sphere shielded simultaneously by ligands A and B is the overlap area C characterized by G_γ ; (bottom) the shape of the ligand overlap area may be complex and consist of several fragments. Here, parameter $G_\gamma(\text{PPh}_3\text{--PPh}_3)$ is equal to the sum of G values for darkened areas D and E.

This G_γ value is collective and is the sum of any and all ligand shadow overlaps in a given system. Parameter G_γ does not quantify interligand interactions but is used to parameterize ligand spatial arrangement and total congestion within a system. Compact ligands of similar shape and size will exhibit small G_γ values since they do not substantially mesh. Ligands with extended alkyl chains such as tri-*n*-octylphosphine oxide may produce large G_γ values.

In the case of **1** the appropriate overlap value is

$$\begin{aligned} G_\gamma(\text{Rh}(\text{Cp}^*)(\text{PMe}_3)(\text{CF}_2\text{CF}_2\text{CF}_3)\text{Cl}) \\ = G_{\text{Rh}}(\text{Cp}^*) + G_{\text{Rh}}(\text{PMe}_3) + G_{\text{Rh}}(\text{CF}_2\text{CF}_2\text{CF}_3) \\ + G_{\text{Rh}}(\text{Cl}) - G_{\text{Rh}}((\text{Cp}^*)(\text{PMe}_3)(\text{CF}_2\text{CF}_2\text{CF}_3)\text{Cl}) \\ = 20.1 + 12.8 + 38.5 + 21.3 - 91.0 = 1.7\% \end{aligned}$$

This value G_γ , similarly to Γ , does not differentiate between ligand and shadow overlaps and unfavorable ligand–ligand interactions, and an improvement is desirable.

In our model all non-coordinated atoms are considered to be spheres with appropriate R_z radii. If two atoms belonging to two different ligands are situated closer than the sum of their R_z radii, an unfavorable interligand interaction is presumed to be present (Fig. 7). The area of interpenetration of the two atomic spheres can be characterized by a corresponding G -parameter value, G_U (U = unfavorable), and the sum of all unfavorable pair-wise interatomic interactions between two ligands is designated $G_U(L_1\text{--}L_2)$. The sum of all $G_U(L_X\text{--}L_Y)$ (subscripts X and Y designate different ligands) values for a given complex is the total value of all unfavorable interactions in the complex, $G_U(\text{complex})$. By definition, a non-zero value of G_U will result in a non-zero value of

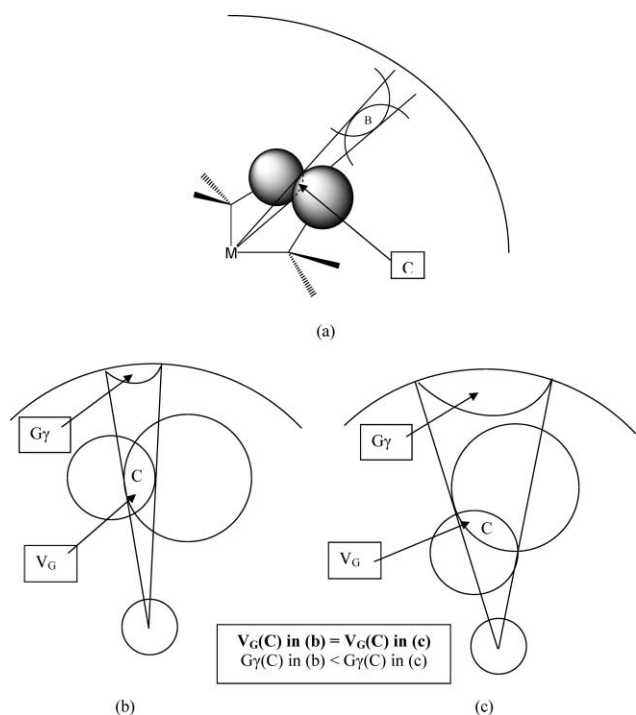


Fig. 7 Overlap of the ligand shadows on the reference sphere caused by interpenetration of the atomic spheres of radii R_Z : (a) percentage G_U of the sphere shielded by overlap area B represents unfavorable interligand interactions; (b,c) Volume V_G of solid figures C is independent of the positions of the overlapping atoms relative to the metal center M; hence, V_G is a better characteristic of this unfavorable interaction.

G_γ ; the opposite does not hold because two ligands can shield the same region on the sphere and have no unfavorable close contacts. Usually parameter G_U does not exceed a few percent. In the case of **1** the overall $G_U(\mathbf{1})$ is very small and measured only 0.2%. Taverner *et al.*¹⁴ performed similar calculations to express the total congestion within a system by summing up in-plane angles (λ) and solid angles (I) corresponding to all pair-wise overlaps between atomic vdW spheres. They ran into difficulty distinguishing between quantities that correspond to what we term G_γ and G_U ; instead, the authors used ligand radial profiles³⁸ to identify atoms causing unfavorable interactions. Our approach does not involve steric profiles but clearly identifies and quantifies unfavorable close contacts as follows.

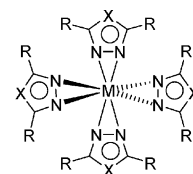
A problem arises with the use of G_U (as well as λ and I) as a means of characterization of interligand unfavorable interactions; this stems from the fact that the form of the overlap between two spheres is anisotropic in shape (lopsided disc), and the area of its projection on the reference sphere is dependent on the orientation of the disc relative to the metal center (Fig. 7). An improved way to express these interactions is by use of the volumes of the interpenetration discs formed by pairs of conflicting atomic spheres. We calculate these volumes, designated V_G (G stands for G -parameter), for all pairs of interpenetrating atomic spheres for atoms belonging to different ligands. Volumes V_G are used to characterize interactions both between separate ligands, $V_G(L_1-L_2)$, and within a complex as a whole, $V_G(\text{complex})$. In the case of **1**, the only unfavorable close contacts were $H \cdots H$ and $H \cdots F$ with the total overlap volume $V_G(\mathbf{1}) = 0.05 \text{ \AA}^3$. Note that sometimes the calculations may point out a possible hydrogen

bonding interaction in which case the overlap volume does not signify an unfavorable contact.

Complex composition

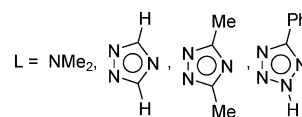
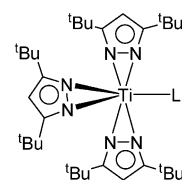
The method of evaluating of non-bonded interactions can help predict some properties of coordination and organometallic complexes such as tetrakis(2,4,6-trimethylphenyl)vanadium(IV).³⁹ In this compound, the vanadium center is covalently bound to four carbon atoms. The estimation of the $G_V(2,4,6\text{-trimethylphenyl})$ values from Fig. 5 for the V–C distance equal to the sum of their covalent radii (1.99 Å) shows that the metal center will be shielded to a degree of 106%. In order for the complex to exist there should either be some ligand overlap or an elongation of the V–C distances. From Fig. 5 the $G_V(2,4,6\text{-trimethylphenyl})$ value of 25% corresponds to the V–C distances of about 2.04 Å. In the solid state structure of this compound the metal-carbon distances average 2.079(12) Å with G_V of 96.2%, G_γ of 3.9%, and unfavorable interactions V_G of 0.05 Å³. Indeed, this is a sterically strained compound and steric considerations allowed us to predict the bond elongations about the central metal. Our data agree with the conclusions based on the use of vdW radii.⁴⁰

There is an elegant example of prediction of the pyrazolato ligand coordination mode to a titanium(IV) center. In 1997 we reported the formation of $\text{Ti}(\eta^2\text{-}3,5\text{-Me}_2\text{pz})_4$ and $\text{Ti}(\eta^2\text{-}3,5\text{-Ph}_2\text{pz})_4$ from $\text{Ti}(\text{NMe}_2)_4$ and the corresponding pyrazole,⁴¹ Scheme 2. However, a similar reaction between $\text{Ti}(\text{NMe}_2)_4$ and 3,5-^tBu₂pzhH afforded $\text{Ti}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3(\text{NMe}_2)$, Scheme 3.



X=CH, R=Me, M=Ti: $G(\text{complex})=95.2\%$, $G_\gamma=2.7\%$
 X=CH, R=Ph, M=Ti: $G(\text{complex})=97.3\%$, $G_\gamma=5.3\%$
 X=N, R=^tPr, M=Ti: $G(\text{complex})=96.5\%$, $G_\gamma=3.0\%$
 X=CH, R=^tBu, M=Ti: not formed
 X=CH, R=^tBu, M=Mo: $G(\text{complex})=95.3\%$, $G_\gamma=5.0\%$

Scheme 2



Scheme 3

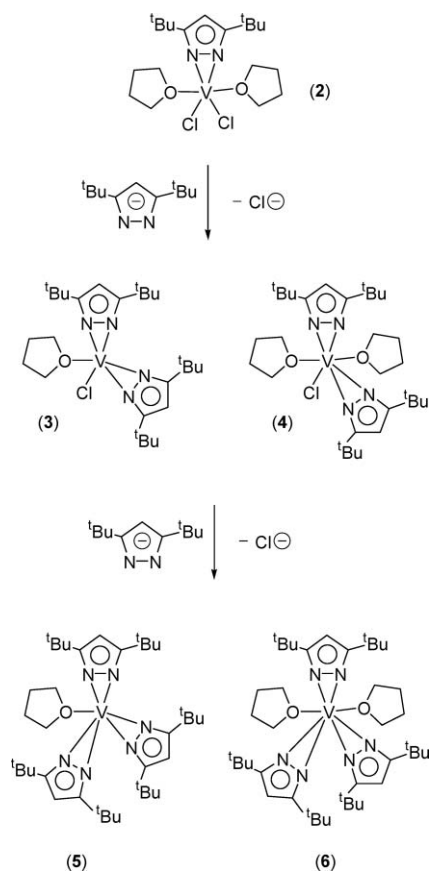
Our solid angle approach could have allowed us to predict this outcome had we known the G values for the ligands and had Fig. 5 in hand. From the graph one can see that parameter $G_{\text{Ti}}(3,5\text{-}^t\text{Bu}_2\text{pz})$ for the typical Ti-center(N–N) distance for bidentate pyrazolato ligands of 1.94 Å is close to 27%. If all four ligands bind

in the η^2 -fashion the total metal shielding will amount to 108% which can hardly be alleviated by a change in conformations of these relatively inflexible ligands. This manifests in the observation that in three structurally characterized complexes of the type $\text{Ti}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3\text{L}$ where $\text{L} = 1,2,4\text{-triazolato}$, $3,5\text{-dimethyl-}1,2,4\text{-triazolato}$, and $5\text{-phenyl-tetrazolato}$ ⁴² reported to the CSD all L ligands are N -monodentate despite the possibility of coordinating in the η^2 fashion, Scheme 3.

Apparently, the presence of three sterically demanding ligands in these complexes $G(\text{Ti}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3) = 81.5\%$ prevents incorporation of another bidentate ligand when sufficient elongation of some Ti-N bonds cannot be achieved.⁴³ Our estimation of parameter $G_{\text{Ti}}(\eta^1\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})$ based on complex $[\text{Mo}(=\text{O})(\eta^1\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})(\text{PEt}_3)_2]$ ⁴⁴ for the Ti-N distance of 2.04 Å afforded a value of 24.2%, which would theoretically allow a Ti center to bind four $3,5\text{-}^t\text{Bu}_2\text{pz}$ simultaneously, but the electronic considerations would not favor the formation of such a hypovalent complex. Changing the Ti metal center for a metal of larger radius such as $\text{Mo}(\text{IV})$ coupled with the previously observed “slipped” coordination of the $\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz}$ ligand⁴⁵ makes the formation of a homoleptic complex $\text{Mo}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_4$ possible,⁴⁶ Scheme 2. A similar cationic complex was observed for erbium.⁴⁷ We predict that such complexes with other Group IV metals Zr and Hf should exist in solid state since their covalent radii are comparable to that of molybdenum. The solid angle method allows us to evaluate the flexibility of $\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz}$ by computing the standard deviation of the ligand's G -parameter at 2.28 Å. The normalized $G_{2.28}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})$ computed for 54 ligands in 25 complexes⁴⁸ is 21.1(4)%. For the actual distances observed in the reviewed complexes the G value varied between 20.0 and 30.8%. The flexibility of this ligand as revealed by the standard deviation of 0.4% is attributed to the change in orientation of the hydrogen atoms on the methyl groups and degree of symmetry of the ligand's ligation to the metal.

Another example is shown in Scheme 4.⁴⁹ When a second $\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz}$ ligand is introduced in complex $[\text{V}(\eta^2\text{-}^t\text{Bu}_2\text{pz})\text{Cl}_2(\text{THF})_2]$ (2) two complexes may form. Using the ligand G values computed for 2, Scheme 3, one estimates parameter $G(3)$ to be $2 \times 26.9 + 16.2 + 14.6 = 84.6\%$ for the 14-e complex 3, and $G(4)$ to be $2 \times 26.9 + 2 \times 16.2 + 14.6 = 100.8\%$ for the 16-e complex 4. Since “*nature abhors vacuum*” (and a 16e species is more stable than the 14e species) one expects to isolate complex 4, which was confirmed experimentally. A subsequent substitution of another Cl^- ligand with a $\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz}^-$ ligand would similarly lead one to compute $G(5) = 96.7\%$ and $G(6) = 113.1\%$. The latter value requires a large G_r and expectedly only 5 has been isolated and structurally characterized. Note that in these calculations we have approximated the total ligand shielding, G_M , and commented on the total ligand overlap, G_r , but not the contribution or existence of unfavorable close interligand contacts described by V_G and G_U , since the latter require atomic coordinates.

Based upon similar reasoning, it is possible to realistically assume that while complex $[\text{Nd}(\eta^2\text{-}3,5\text{-Ph}_2\text{pz})_3(\text{THF})_3]$ ⁵⁰ is known, its analogue with bulkier $3,5\text{-}^t\text{Bu}_2\text{pz}$ moiety $[\text{Nd}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3(\text{THF})_3]$ will have to exhibit a substantial G_r value and overcome unfavorable interactions V_G and G_U in order to exist. To date, $[\text{Nd}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3(\text{THF})_3]$ has not been structurally characterized, but two related compounds with fewer THF ligands $[\text{Nd}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3(\text{THF})_2]$ ⁵¹ and $[\text{Er}(\eta^2\text{-}3,5\text{-}^t\text{Bu}_2\text{pz})_3(\text{THF})_2]$ ⁵² have been reported.



Scheme 4

In 1985 Fischer and Xing-Fu¹³ developed a “Solid Angle Sum Rule” and applied it to organolanthanoid compounds. Formulation of their findings in our terminology revealed that there is a preferred range of $G_M(\text{complex})$ values of $73 \pm 10\%$ when only the *first* coordination sphere of each metal was considered. Our computations of G -parameters are not restricted in such a fashion, and we have not detected explicit trends for favored G values.

Conclusions

We have developed an improved approach to characterize ligand steric requirements in metal complexes by extending previous literature work. The new method, based on ligand solid angle calculations describes each ligand by the percentage of the coordination sphere of the central atom shielded by the ligand. We have defined atomic R_z radii based on the RFF1 atomic parameters for most of the periodic table. The atomic R_z radii used for our calculations are strongly recommended for general applications involving calculations of steric ligand parameters. A manuscript describing the program for calculating parameters G is in preparation. Further studies of the application of the new approach to other classes of ligands including phosphines, cyclopentadienyl, and porphyrins, and its application to properties such as volatility, lability, and stability will be published in due course.

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