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SambVca: A Web Application for the Calculation of the Buried Volume of N-Heterocyclic Carbene Ligands

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We present a free web application for the calculation of the buried volume (% V_{Bur}) of NHC ligands. The web application provides a graphic and user-friendly interface to the SambVca program, developed for the calculation of % V_{Bur} values not only of NHC ligands but also of other classic organometallic ligands such as, for example, phosphanes and cyclopentadienyl-based ligands. To provide a reliable procedure for the calculation of % V_{Bur} values we tested our approach in the interpretation of the binding energies of NHC ligands in Cp*Ru(NHC)Cl complexes in terms of steric and electronic parameters.

Introduction

It is a common and useful procedure to interpret the chemical behaviour of strictly related transition metal complexes in terms of the steric and electronic properties of the various ligands coordinated to the same metal centre. This separation allows the property of interest to be broken down according to Equation (1),

$$\text{Property} = a + b \cdot S + c \cdot E \qquad (1)$$

in which S and E are measures of the steric and electronic characteristics, respectively, of a given ligand, whereas a, b and c are constants that should be fitted to reproduce a given set of training data.[1]

This approach requires that accurate and meaningful steric and electronic (S and E) parameters are available. In the case of the electronic parameter E, which represents the result of changes in molecular properties arising from transmission along chemical bonds,[1] the procedure originally suggested by Tolman was to relate it to the frequency of the A_1 carbonyl mode of $Ni(CO)_3L$ complexes. Other electronic parameters have been proposed and used,[2–8] but because this paper is focused on the steric parameter S we do not discuss the electronic parameter E any further.

The steric parameter S, which represents the result of changes in molecular properties caused by repulsive forces (usually of the van der Waals type) between parts of a molecule, has commonly been measured in terms of the concepts of the cone angle,[1] solid angle,[9–15] deformation coordinates defined from the angles at the coordinated phosphane P,[16,17] the repulsive energy[18–20] and, more recently, methods based on the molecular electrostatic potential.[15,21] In almost all cases the ligands examined were phosphanes, phosphites or related ligands. For these ligands the Tolman cone angle is a very logical and natural choice as a steric parameter, even in cases of unsymmetrical phosphanes, due to their evident almost conical shapes. Indeed, the Tolman cone angle, despite some corrections in the originally reported values[22] and some conceptual criticisms over the years,[22] has offered the chemical community an extraordinarily useful tool. (Incidentally, the solid angle was a very reasonable alternative to the Tolman cone angle,[9–12] but it was a slightly less intuitive parameter and did not offer significant and clear-cut advantages over the cone angle, so it never acquired a prominent role in the description of steric parameters in phosphanes and related ligands.)

Although the Tolman cone angle has proved to be extremely effective in the case of phosphanes, it was similarly evident that it was not the natural choice to describe the steric properties of the emerging class of N-heterocyclic carbene (NHC below) ligands, because of their almost C_2-symmetric shapes (see Scheme 1). NHC ligands have found increasing use in recent decades as a very effective alternatives to the classic phosphanes. In many cases, use of NHC ligands results in smoother reaction conditions and new reactivity. The most noticeable examples are in the fields of Ru-catalysed olefin metathesis,[23–29] Ir-catalysed hydrogenation[30–32] or Pd-catalysed C–C coupling reactions,[33–35] and/or have led to unexpected reactivity, as in the case of Au-catalysed reactions.[36,37] Further, the skeletons of satu-

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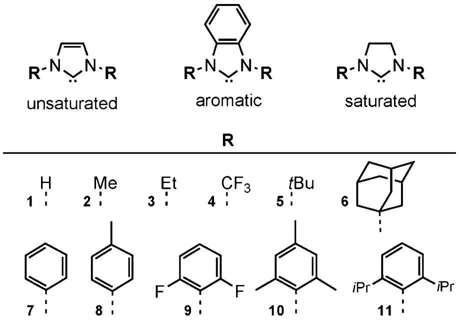
rated NHCs are key structural features for the introduction of asymmetry in the NHC ring, which opens the door to the use of chiral NHCs in asymmetric synthesis.[26,38–41]



Scheme 1.

Similarly to phosphanes, NHCs are extremely flexible structures that can be modified almost at will, which is the key to fine-tuning of steric and electronic properties. This has spurred a series of studies directed towards appropriate characterization and classification of different NHC ligands both experimentally and theoretically. Excellent reviews have been written on this topic.[42–50] In the realm of these studies, to quantify the differences in steric bulk of different NHC ligands we introduced the concept of the buried volume ($\% V_{Bur}$), which gives a measure of the space occupied by the NHC ligand in the first coordination sphere of the metal centre (see Figure 1).

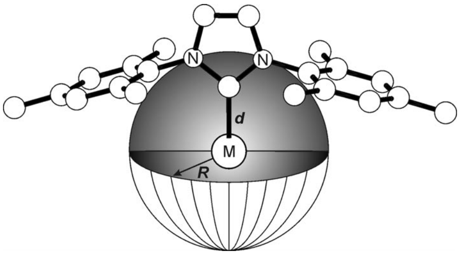


Figure 1. Graphical representation of the sphere used to calculate $\% V_{Bur}$ values.

In the beginning, we used $\% V_{Bur}$ values for qualitative explanation of trends in the experimentally measured bond disruption enthalpies (BDEs) in a series of Cp*Ru(NHC)Cl complexes.[51] In these first calculations we evaluated $\% V_{Bur}$ values for a few NHC ligands whose geometries were obtained through DFT optimizations of the free NHC ligand. These geometries were performed with the ADF program.[52,53] Similar calculations were also used to estimate the DFT binding energies of the same NHC ligands in the corresponding Cp*Ru(NHC)Cl complexes. The experimentally measured BDEs and the DFT binding energies, with inclusion of solvent effects through use of the COSMO model,[54] were shown to correlate qualitatively with the $\% V_{Bur}$ values of the various NHC ligands.[45,51]

Since the binding energies of the various NHC ligands had been corrected for solvent effects with the COSMO model,[55] the most natural choice for the calculation of the $\% V_{Bur}$ values was to use the same atomic radii as we had used in the DFT calculations (labelled as "old set" in Table 1), while we set the radius of the sphere as 3.0 Å, a reasonable value to describe the first coordination sphere around the metal, and set the distance between the centre of the sphere and the NHC ligand as 2.00 Å. For the sake of consistency, we used this set of data in almost all the following studies, in which $\% V_{Bur}$ values were used almost systematically to classify a large series of NHC ligands, and even to compare NHC ligands with classical phosphanes.[45,56–60] The only exception was in the interpretation of the stabilities of $(NHC)Ni(CO)_n$ complexes, in which we also tested the M–NHC distance of 2.28 Å,[57] the value suggested by Tolman for calculation of the cone angles of phosphanes in $(PR_3)Ni(CO)_3$ complexes.[1]

Table 1. Old set, Bondi and scaled Bondi radii (Å) used to calculate $\% V_{Bur}$ values.

Atom	Old set	Bondi	Bondi*1.17
H	1.16	1.20	1.40
C (sp^2)	1.76	1.70	1.99
C (sp^3)	1.87		
N (sp^2)	1.65	1.55	1.81
N (sp^3)	1.87		
O	1.70	1.52	1.78
F	1.60	1.47	1.72
P	1.90	1.80	2.11

However, this old set of radii was not quantitatively validated towards a test set of experimental and/or computational data. Furthermore, they have the disadvantage that atoms are assigned different radii according to their hybridization states (see Table 1), which typically requires some tedious and error-prone input handling to label all the atoms properly. Nevertheless, it is clear that a larger set of radii, which also reflects the hybridization state of a given atom, gives more flexibility to the whole procedure.

We recently tested the atomic and sphere radii used in the breaking down of the DFT dimerization energies of a series of NHC ligands (E_{Dim}) into steric and electronic contributions.[61] The fairly large and consistent set of DFT binding energies (E_{DFT}) was fitted by use of Equation (2),

$$E_{Fit} = a + b\% V_{Bur} + c\cdot E_{ST} \quad (2)$$

in which E_{ST}, the singlet–triplet splitting of the isolated NHC, was assumed as the electronic parameter E of 1.[62–64] As in the case of the $\% V_{Bur}$ values, we decided to use an aseptic estimate from NHC geometries in prototype $(NHC)Ir(CO)_2Cl$ complexes, which in the case of the Tolman cone angle calculations should in principle mimic the $(PR_3)Ni(CO)_3$ prototype complex. For the atomic radii we used the Bondi radii of Table 1, a well accepted set commonly used in the literature,[65] and we found that the DFT dimerization energies were better reproduced ($R^2 = 0.93$) if the radius of the sphere (R) was set equal to 4.0 Å.[61] However, even if this application validates $\% V_{Bur}$ values as steric descriptors of potential utility for interpretation of chemical behaviour in organic chemistry, NHC dimers cannot be considered typical organometallic complexes.

For these reasons, here we present a careful validation of the procedure used to calculate the $\% V_{\mathrm{Bur}}$ values of NHC ligands. To this end we tested a variety of parameters for the best reproduction of the DFT binding energies (E_{DFT}) of the NHC ligands shown in Scheme 1 in the Cp*Ru(NHC)Cl complexes, calculated according to Equation (3), by use of the generic expression of Equation (2).

$$4\mathrm{NHC} + (\mathrm{Cp^*RuCl})_4 \rightarrow 4\mathrm{Cp^*Ru(NHC)Cl} + E_{\mathrm{DFT}} \qquad (3)$$

This strategy allows better validation of the quantitative usage of $\% V_{\mathrm{Bur}}$ values in the interpretation of the behaviour of NHC ligands. Beside a procedure that could represent a standard for the calculation of $\% V_{\mathrm{Bur}}$ values of other NHC ligands and also of different ligands used in organometallic chemistry, we also present the algorithm we implemented in the Samb*V*ca program (Salerno at the MoLNaC Buried Volume Calculation), which is the program we developed to evaluate the $\% V_{\mathrm{Bur}}$ value for a given ligand.

Finally, because $\% V_{\mathrm{Bur}}$ values seem to be rather useful molecular descriptors, we decided to implement a web application for $\% V_{\mathrm{Bur}}$ calculation as a free service to the chemical community. For this reason, in the last section of this manuscript we describe the web interface to use the Samb*V*ca program, which can be found at http://www.molnac.unisa.it/OMtools.php.

Computational Details

All the DFT calculations were performed at the GGA level with the BP86 functional[66–68] as implemented in the Gaussian03 program.[69] Ahlrichs' triple-ζ plus one polarization function basis set, TZVP, was used for main group atoms,[70] while the relativistic Stuttgart–Dresden ECP in combination with a triple-ζ basis set was used for the Ru and Ir atoms.[71–73]

Results and Discussion

Calculation of % V_{Bur} Values

Calculation of $\% V_{\mathrm{Bur}}$ values requires the definition of the metal centre (M) to which the ligand is coordinated. If the structure to be examined is a transition metal complex, it might be natural to use the coordinates of the metal centre as in the structure. In contrast, if the structure of the ligand alone is available, a putative metal centre (M below) to which the NHC ligand is coordinated through the carbene C atom (see Figure 1) must be defined. Similarly, in the case of phosphanes it is the P atom that is coordinated to the putative metal centre. Incidentally, the $\% V_{\mathrm{Bur}}$ value for a classical η^5-coordinated Cp-based ligand can also be estimated; in this case it is the centroid of the Cp ring that is coordinated to the putative metal centre. In all the cases we decided to place the M centre on the line passing through the point to be coordinated (C or P in NHC or PR_3, respectively) and the centre of mass either of the two N atoms of the heterocyclic ring in NHCs, or of the three C (H) atoms bonded to the P atom in phosphanes (X_N and X_C, respectively; see Figure 2). The distance between the M centre and the coordinating centre of the ligand (*d* below) is also shown in Figure 2.

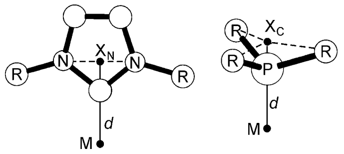


Figure 2. Geometrical positioning of putative M atoms in NHC and PR_3 ligands.

Once the position of the M centre is defined, a sphere of radius *R*, centred on M, is built. This sphere is sectioned by a regular 3D cubic mesh of spacing *s*, which defines cubic voxels v_{xyz} of volume s^3. The distance between the centre of each voxel with all the atoms in the ligand is tested to check whether any of the atoms is within a van der Waals distance from the centre of the examined voxel. If no atom is within a van der Waals distance, the volume s^3 of the examined voxel is assigned to the free volume V_{Free}. Conversely, if a single atom is within a van der Waals distance, the volume s^3 of the examined voxel is assigned to the buried volume V_{Bur}. With this description, Equation (4) holds:

$$\mathrm{V_{Sphere}} = \Sigma v_{xyz} = V_{\mathrm{free}} + V_{\mathrm{Bur}} = \Sigma v_{xyz}(\mathrm{free}) + \Sigma v_{xyz}(\mathrm{buried}) \qquad (4)$$

While the V_{Bur} value already indicates the amount of the coordination sphere that is occupied by the considered ligand, we prefer the more intuitive $\% V_{\mathrm{Bur}}$ descriptor of Equation (5), which is simply:

$$\% V_{\mathrm{Bur}} = 100 \cdot V_{\mathrm{Bur}}/\mathrm{V_{Sphere}} \qquad (5)$$

Choice of NHC Geometries for the Calculation of the % V_{Bur} Value

The first point to solve is the NHC geometry that should be used in the $\% V_{\mathrm{Bur}}$ calculations. In our first estimates of $\% V_{\mathrm{Bur}}$ values we used the DFT-optimized geometries of the uncoordinated NHC ligands. However, this choice has some disadvantages. In many instances we found that the structures of free NHC ligands with aromatic N-substituents are biased towards geometries with the N-substituents coplanar with the NHC rings. Of course, this geometry is scarcely representative of the same NHC in the large majority of organometallic complexes, in which the planes of aromatic N-substituents are classically orthogonal to the NHC mean planes.

Another possibility that we discarded is represented by $\mathrm{(NHC)Ni(CO)_3}$ complexes. Although attractive, because $\mathrm{(PR_3)Ni(CO)_3}$ complexes are the standards in the calculation of Tolman cone angles, they are probably not the best choice in the case of NHC ligands because $\mathrm{(NHC)Ni(CO)_3}$ complexes are known not to be stable with particularly bulky NHC ligands.[57] Still another possibility that we discarded is represented by the easy accessible (NHC)AgCl complexes,[74] for the opposite reason. In fact, in these complexes the Cl ligand is *trans* to the NHC ligand, which results in a scarcely hindered and thus poorly representative complex. As a final choice, then, we decided to adopt (NHC)Ir(CO)$_2$Cl complexes as the model system to obtain the NHC geometries to be used in the %V_{Bur} calculations. In such a complex the coordination geometry around the Ir centre is square-planar, with one Cl *trans* to the NHC ligand.[59] The (NHC)Ir(CO)$_2$Cl complexes also have the advantage that they are experimentally accessible and have indeed already been used to investigate the steric and electronic properties of NHC ligands.[59]

Because of this choice, all the %V_{Bur} values reported below have been obtained from NHC geometries extracted from the DFT-optimized geometries of (NHC)Ir(CO)$_2$Cl complexes. Because the average Ir–(NHC) distances in these complexes are usually slightly shorter than 2.1 Å,[59] we decided to use a value of $d = 2.10$ Å in all the %V_{Bur} values reported below.

Choice of Atom Radii and of Sphere Radii

The set of atomic radii and the radii of the spheres around the putative M atoms were validated for the best reproduction of the DFT binding energies (E_{DFT}) of the NHC ligands shown in Scheme 1 in Cp*Ru(NHC)Cl complexes according to Equation (2). The a–c parameters of Equation (2) were varied to minimize the quadratic deviation (χ^2) of the E_{Fit} value from the E_{DFT} value, as shown in Equation (6).

$$\chi^2 = \sum_{\substack{\text{NHCs}\\ \text{of Scheme 1}}} (E_{DFT} - E_{Fit})^2 \tag{6}$$

The plot shown in Figure 3 reports the E_{Fit} versus the E_{DFT} values with the %V_{Bur} values calculated with use of the Bondi radii, for three values of the radius of the sphere around the metal (R = 3.0, 3.5 and 4.0 Å). The best correlation, $R^2 = 0.87$, is found for R = 3.5 Å, whereas slightly worse correlations, $R^2 = 0.79$ and 0.80, are found for sphere radii R = 3.0 and 4.0 Å, respectively.

The plot shown in Figure 4 instead reports the E_{Fit} versus the E_{DFT} values with the %V_{Bur} values calculated with use of the Bondi radii, the old set of radii we used in the past, and the Bondi radii scaled by 1.17, which is the scaling of the original Bondi radii suggested for the evaluation of solvent effects with the COSMO model.[54] In each case the radius of the sphere around the metal is set to R = 3.5 Å. Very similar correlation – R^2 ca. 0.87 – is found independently of the specific set of atoms radii used. As a remark, we note that some of the scatter between the E_{Fit} and the E_{DFT} values shown in Figure 3 and Figure 4 could also arise from the use of E_{ST} as the electronic parameter. For this reason we also tested the HOMO energy or the chemical hardness of the isolated NHC in the singlet electronic state as the electronic parameter, but no better fitting of E_{DFT} was obtained.

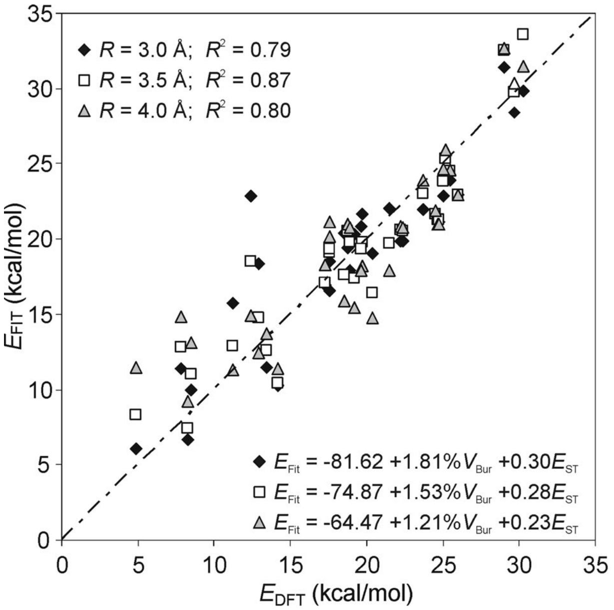


Figure 3. E_{Fit} versus E_{DFT} (kcal mol^{-1}) for the NHC ligands shown in Scheme 1; %V_{Bur} values calculated with Bondi radii and with the sphere radius at R = 3.0, 3.5 and 4.0 Å.

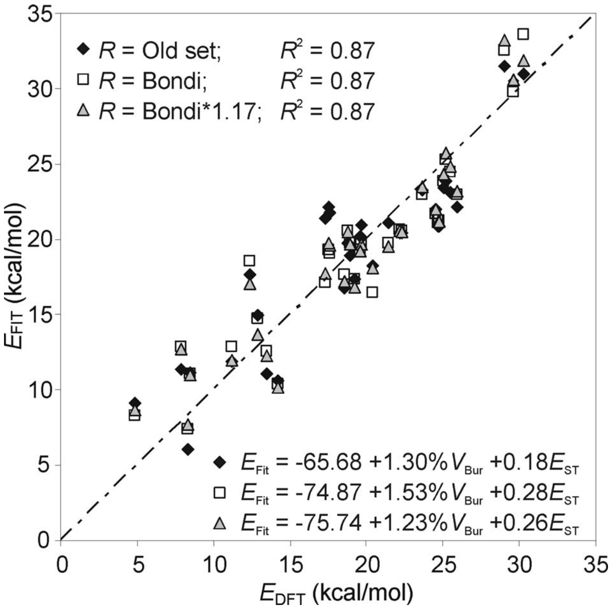


Figure 4. E_{Fit} versus E_{DFT} (kcal mol^{-1}) for the NHC ligands shown in Scheme 1; %V_{Bur} values calculated with the "old set" of radii, as well as with original and scaled (by 1.17) Bondi radii, with the sphere radius R = 3.5 Å.

This brief analysis clearly indicates that similar agreement between the E_{Fit} and the E_{DFT} values can be obtained with different choices of atom radii or of the radii of the spheres around the metal atoms. Nevertheless, we suggest that use of the Bondi radii scaled by 1.17 in conjunction with a sphere radius R = 3.5 Å is probably the most reasonable set of parameters for the calculation of %V_{Bur} values. Our preference for the scaled Bondi radii over the radii we used in the past is only for reasons of simplicity: no input handling is needed to specify the hybridization states of the atoms, so any structure obtained from a theoretical or experimental technique can be used as it is. On the other hand, use of the scaled Bondi radii seems to result in $\% V_{Bur}$ values with more chemical sense: with the unscaled Bondi radii the $\% V_{Bur}$ value for the aromatic NHC with mesityl rings (**10** in Scheme 1) is the same as that of the NHC with isopropyl groups on the aromatic ring (**11** in Scheme 1), 23.3 in both cases, which conflicts with chemical common sense. More reasonable behaviour is instead obtained with the scaled Bondi radii ($\% V_{Bur}$ values of 31.2 and 31.9 for the aromatic NHCs **10** and **11** in Scheme 1, respectively). Finally, in line with our previous calculations we did not include H atoms in the calculation of $\% V_{Bur}$ values (i.e., only heavy atoms were considered), which also allows the use of X-ray structures in which the positions of H atoms have not been determined. However, if desired, hydrogen atoms can be taken into account through the web application.

The $\% V_{Bur}$ values for the unsaturated NHC ligands reported in Scheme 1, calculated with the Bondi radii at varying sphere radius, are reported in Table 2. Surprisingly, there is no clear relationship between the sphere radius and the $\% V_{Bur}$ value. In fact, the $\% V_{Bur}$ values of the smallest NHCs, **1** and **2**, are larger with $R = 3.0$ Å, whereas for the other NHCs the larger the sphere radius, the larger the $\% V_{Bur}$ value. Rather similar trends were observed for the saturated and aromatic NHC ligands of Scheme 1. For the sake of simplicity, we do not discuss them in detail.

Table 2. $\% V_{Bur}$ values for the unsaturated NHC ligands shown in Scheme 1. Bondi radii for the atoms; radius of the sphere $R = 3.0$, 3.5 and 4.0 Å.

NHC	$R = 3.0$ Å	$R = 3.5$ Å	$R = 4.0$ Å
1	15.4	13.8	12.0
2	19.2	18.7	17.6
3	19.4	19.4	19.1
4	23.2	24.0	23.5
5	26.2	27.2	26.9
6	26.0	27.6	28.3
7	22.9	23.1	23.0
8	22.9	23.1	23.0
9	22.0	23.7	25.2
10	21.2	23.6	25.7
11	21.8	24.9	27.8

The $\% V_{Bur}$ values for the whole set of NHC ligands shown in Scheme 1, calculated with the Bondi radii scaled by 1.17 and with a sphere radius $R = 3.5$ Å, are reported in Table 3 and, incidentally, represent reference values to be used in future works. The basic behaviour expected by chemical common sense for the various NHC ligands of Scheme 1 is respected. For example, the $\% V_{Bur}$ value for **3** is only slightly larger than that for **2**, since the Et group of **3** is folded away from the substituents on the Ir atom in the $(NHC)Ir(CO)_2Cl$ complex. Similarly, the $\% V_{Bur}$ value for **8** is essentially identical to that for **7**, since the addition Me group in the *para* position of the N-bonded aromatic ring of **8** is pointing away from the Ir atom. In all cases, the larger $\% V_{Bur}$ values are calculated for the *t*Bu- and Ad-substituted NHCs **5** and **6**. Comparison between the unsaturated, aromatic and saturated NHCs indicates that, consistently with previous reports,[45,51] the $\% V_{Bur}$ values for the saturated NHCs are slightly bigger than those for the corresponding unsaturated NHCs. The presence of the fused ring in the backbones of the aromatic NHCs usually has a minor effect, with the exceptions of the NHCs **5** and **6**. In these cases the $\% V_{Bur}$ values for the aromatic NHCs are quite a lot larger than those of their unsaturated and saturated counterparts, an effect due to steric interaction between the bulky NHC backbone and the bulky *t*Bu and Ad N-substituents. This suggests that an indirect key for tuning of $\% V_{Bur}$ could be appropriate substitution on the C atoms of the NHC skeleton.

Table 3. $\% V_{Bur}$ values for the NHC ligands shown in Scheme 1. Bondi radii scaled by 1.17 for the atoms; radius of the sphere $R = 3.5$ Å.

NHC	Unsaturated	Aromatic	Saturated
1	18.8	18.9	19.0
2	24.9	25.1	25.4
3	26.0	26.4	25.9
4	31.1	30.4	31.8
5	35.5	38.9	36.2
6	36.1	40.8	36.6
7	30.5	30.2	31.6
8	30.5	30.2	32.4
9	31.3	30.9	32.3
10	31.6	31.2	32.7
11	33.6	31.9	35.7

The $\% V_{Bur}$ values for the unsaturated NHC ligands shown in Scheme 1, calculated with the Bondi radii, with the old set of radii we used in the past, and with the Bondi radii scaled by 1.17, for a sphere radius $R = 3.5$ Å, are reported in Table 4. The reported data clearly indicate that the $\% V_{Bur}$ values calculated with the old set of radii are marginally larger than those calculated with the unscaled Bondi radii, and are considerably smaller than those calculated with the scaled Bondi radii.

Table 4. $\% V_{Bur}$ values for the unsaturated NHC ligands shown in Scheme 1, calculated with the Bondi radii, with the ADF radii, and with the Bondi radii scaled by 1.17, with the sphere radius $R = 3.5$ Å.

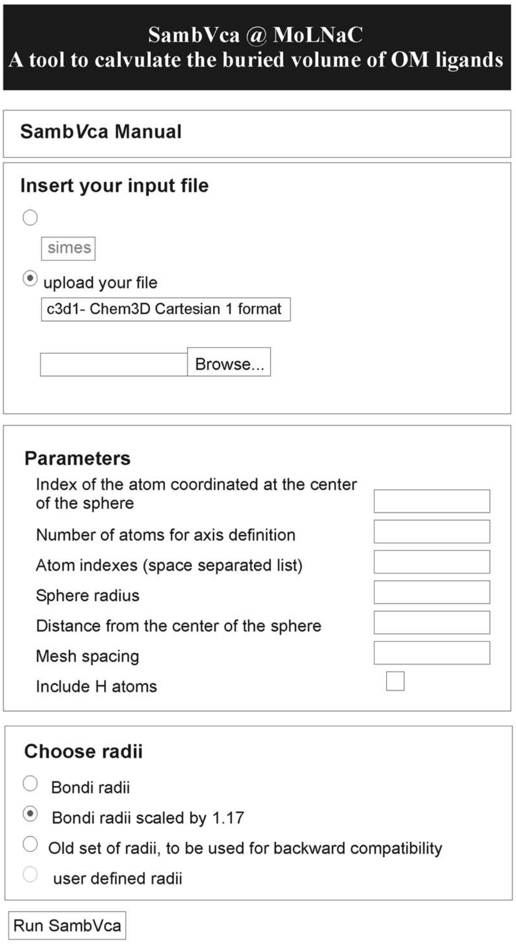
NHC	Bondi	Old set	Bondi*1.17
1	13.8	15.0	18.8
2	18.6	21.0	24.9
3	19.4	22.0	26.0
4	24.0	26.8	31.1
5	27.2	30.9	35.4
6	27.6	31.4	36.1
7	23.1	24.7	30.5
8	23.1	24.7	30.5
9	23.7	25.8	31.3
10	23.6	26.3	31.6
11	24.9	28.0	33.6

Execution Time and Mesh Spacing

The calculation of the $\% V_{Bur}$ value for any of the NHC ligands shown in Scheme 1 only requires a fraction of a second: the calculation of the $\%V_{Bur}$ value for the IMes ligand, for example, requires only 0.3 s with a 3.0-GHz Pentium®4 processor, which makes our implementation computationally very efficient. Furthermore, all the calculations reported in this work have been obtained with a mesh size $s = 0.05$ Å, which results in the breaking down of a sphere of radius 3.5 Å into roughly 1.4×10^6 voxels of volume $s^3 = 1.25 \times 10^{-4}$ Å^3. With this choice, the exact volume of a sphere of radius 3.5 Å (179.594 Å^3) is underestimated by only 0.059 Å^3, which indicates that our numerical integration procedure reproduces the exact value with an accuracy of 99.97%. Finally, we also tested the convergence of the $\%V_{Bur}$ values versus the mesh size s. As an example, the $\%V_{Bur}$ values for the IMes ligand with the Bondi radii are 23.645, 23.651 and 23.654 for s values of 0.1, 0.05 and 0.01 Å, respectively, which validates our choice of an s value of 0.05 Å.

Web Application Implementation

The Samb*V*ca program has been made freely available to the chemical community through a graphical interface on a web application at the URL http://www.molnac.unisa.it/OMtools.php. The application has been developed in a three-layer architecture. The user interface combines several client-side technologies such as HTML, CSS and JavaScript. The web application is PHP script running on Apache web server. Finally, the underlying program logic has been implemented in Fortran and compiled with the Intel Fortran Compiler version 10.1. The main interface is shown in Figure 5.



SambVca @ MoLNaC
A tool to calvulate the buried volume of OM ligands

Samb*V*ca Manual

Insert your input file

○ simes

● upload your file: c3d1- Chem3D Cartesian 1 format

Parameters

Index of the atom coordinated at the center of the sphere
Number of atoms for axis definition
Atom indexes (space separated list)
Sphere radius
Distance from the center of the sphere
Mesh spacing
Include H atoms ☐

Choose radii

○ Bondi radii
● Bondi radii scaled by 1.17
○ Old set of radii, to be used for backward compatibility
○ user defined radii

Figure 5. Web interface to the Samb*V*ca program.

As indicated in Figure 5, the user can upload the NHC structure as classical *xyz* format. The application also supports CIF and Chem3D Cartesian formats, which are transformed internally to *xyz* format with the Open Babel 2.1.1 program.[75,76] Of course, whatever format is used, the user needs to provide only the coordinates of the atoms of the NHC, or of any other ligand, for which the $\%V_{Bur}$ value has to be calculated. This means that in the case of an organometallic complex the coordinates of all the atoms that do not belong to the NHC ligand must be removed. After upload of the coordinates, the user needs to provide, in the mandatory input windows: 1) the sequence number of the atom that coordinates to the metal (the carbene C atom or the P atom in the cases of NHCs or PR_3, respectively), 2) the number of atoms needed to build the additional point (X_N or X_C in Figure 2) to construct the coordination axis (two in the case of the NHCs, three in the case of PR_3), and 3) the sequence numbers of the two N atoms (in the case of NHCs) or of the three C atoms bonded to the P atom (in the PR_3 case). At this point, the user can choose either to accept or to change the default settings (Bondi radii scaled by 1.17 for the atoms, $R = 3.5$ Å for the radius sphere, and $d = 2.10$ Å for the distance between the coordinated atom and the putative metal centre, $s = 0.05$ Å for the mesh spacing). Finally, if H atoms are to be included in the $\%V_{Bur}$ calculation, it is necessary to active the hydrogen atoms tick-box; by default they are omitted. After this input definition, clicking on the "Run Samb*V*ca" button executes the program for the $\%V_{Bur}$ calculation, and the output appears in a new window.

Conclusions

In conclusion, we present the details of an algorithm for the calculation of buried volume ($\%V_{Bur}$) as a molecular descriptor of the steric properties of organometallic ligands. While we have tested and validated it in the case of NHC ligands, it is clear that the same approach can also be used to calculate $\%V_{Bur}$ values for other organometallic ligands such as, for instance, phosphanes and cyclopentadienyl-based ligands. Indeed, we believe that $\%V_{Bur}$ values are good molecular descriptors for use in the comparative description of phosphanes and NHC ligands. Furthermore, we have implemented a web application interface for calculation of $\%V_{Bur}$ values as a free service to the chemical community.

As a final note, we remark that the procedure for $\%V_{Bur}$ calculation that we have described here [NHC geometries from DFT-optimized $(NHC)Ir(CO)_2Cl$ complexes, Bondi radii scaled by 1.17, sphere radius $R = 3.5$ Å, M–NHC distance d = 2.10 Å], which leads to the % V_{Bur} values given in Table 3, is slightly different from the one that we have used in the past. For this reason, the % V_{Bur} values that we have reported in previous papers cannot, unfortunately, be used in conjunction with those that we have reported in this work. However, we believe that establishing a fairly standard, easy to follow and unbiased procedure can only be a benefit.

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