Percent buried volume for phosphine and *N*-heterocyclic carbene ligands: steric properties in organometallic chemistry

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Electronic and steric ligand effects both play major roles in organometallic chemistry and consequently in metal-mediated catalysis. Quantifying such parameters is of interest to better understand not only the parameters governing catalyst performance but also reaction mechanisms. Nowadays, ligand molecular architectures are becoming significantly more elaborate and existing models describing ligand sterics prove lacking. This review presents the development of a more general method to determine the steric parameter of organometallic ligands. Two case studies are presented: the tertiary phosphines and the *N*-heterocyclic carbenes.

1. Introduction

Homogenous catalysis using metal complexes continues to be widely studied and used by both academic and industrial communities.[1] This has led to the understanding of unprecedented reactivities and product selectivities, which in turn revolutionized polymerization chemistry and resulted in significant progresses in asymmetric catalysis. The development of organometallic catalysts is certainly the main reason behind major advances in homogenous catalysis. Comprehensive studies of the stereo-electronic parameters associated with ligands surrounding the metal center are fundamental and have assisted in rationalising and improving catalyst performances. Following the pioneering work of Bigorgne and Strohmeier,[2] Tolman, in his seminal reports, suggested an experimental measure of electronic parameter ν by using the fundamental CO stretching frequency A_1 of $[Ni(CO)_3(L)]$ complexes, thereby quantifying the electronic effect of L on the electronics around the metal.[3] Since electronic and steric effects are intimately related and difficult to separate, the geometry around the nickel center allows for minimal steric influence in the determination of ν.

Several attempts have been undertaken to define a reliable steric parameter paired to an electronic parameter. Tolman proposed to measure the size of a ligand by the cone angle θ defined with the metal at the vertex and the atoms at the

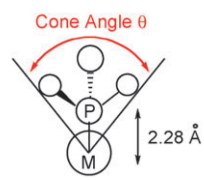

Fig. 1 The Tolman cone angle θ.

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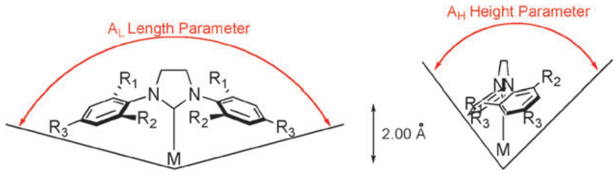


Fig. 2 Early model for steric parameter determination of NHCs.

perimeter of the cone (Fig. 1).[3] CPK models can be used with a metal to phosphorus distance of 2.28 Å, the standard Ni–P bond length in $[Ni(CO)_3(L)]$ complexes. Tertiary phosphine ligands are commonly classified using this parameter, but the method could be applied in theory to any ligand. With the recent development of more structurally elaborate ligands such as biarylphosphines (Buchwald ligands), bidentate ligands and *N*-heterocyclic carbenes (NHCs), steric parameter calculations using the Tolman model have proven difficult and sometimes meaningless.

In order to measure the steric bulk of NHCs, an early phosphine-like model was proposed by Nolan based on crystallographic data.[4] The two views of NHC-M presented in Fig. 2 depict the model to extract the length parameter A_L and the height parameter A_H. The original M-carbene bond length was 2.105 Å, but 2.00 Å can be considered as the average bond distance. To validate this steric model, a steric *versus* enthalpic relationship was examined and provided a fair correlation. However, this first simple model highlighted the need for an improved metric parameter for steric bulk for this ligand family.

In order to better define the steric pressure brought about by the use of NHC ligands, Nolan and Cavallo proposed an alternate model to measure the NHC steric bulk; "percent buried volume" ($\%V_{bur}$) defined as the percent of the total volume of a sphere occupied by a ligand (Fig. 3). The sphere has a defined radius and has the metal center at the core.[5,6] $\%V_{bur}$ is calculated using crystallographic data. The volume of this sphere represents the potential coordination sphere space around the metal occupied by a ligand/ligand fragment. The spatial occupation value of the ligands are obtained using the Samb*V*ca (**Sa**lerno **m**olecular **b**uried **v**olume **ca**lculation) software developed by Cavallo and co-workers that is now available on-line as a very user-friendly tool.[7] Originally developed to be applied to NHC ligands with examples of ruthenium-,[5] iridium-,[8] palladium-,[9] rhodium-,[10] nickel-,[11] gold-,[12] and silver–NHC complexes,[13] the "percent buried volume" model can be extended to numerous other types of coordination chemistry ligands.

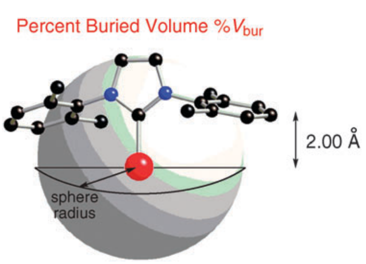


Fig. 3 Percent buried volume $\%V_{bur}$.

Alternatively, Gusev has recently used DFT calculations to determine steric and electronic properties of numerous NHC ligands.[14] He has used a different descriptor **r** (repulsiveness) which is a measure of direct repulsive interactions between the NHC and carbonyl ligands of $[(NHC)Ni(CO)_3]$. Gusev established a stereoelectronic relationship of the type $\Delta H = 86.35 - 0.06741\text{TEP} + 21.63d(\text{Ni–C})$, where $d(\text{Ni–C})$ is the distance between the Ni center and the C of the NHC *N*-substituent adjacent to the N. Thus, $d(\text{Ni–C}) = -4.075 + 0.003172\text{TEP} + 0.0446\Delta H$. IDM (see, Fig. 6) with $d(\text{Ni–C}) = 3.493$ Å was chosen as a reference and consequently its $\mathbf{r} = 0.0$; then **r** is the variation from this value; $\mathbf{r} = 10 \times (3.493 - d(\text{Ni–C}))$. The descriptor **r** showed a good correlation with the percent buried volume, however its calculation seems restricted to $[(L)Ni(CO)_3]$ complexes.

In this contribution, we provide a clear overview of the steric properties of various phosphorus-based ligands and NHCs using the Samb*V*ca software. We first investigated the possibility of a correlation between cone angle and percent buried volume. Parameters such as other ligands borne on the metal center, the nature of the metal itself and the geometry of the resulting complexes and indeed all parameters that could affect the $\%V_{bur}$, were examined. We also inspected the steric congestion for biaryl and bidentate phosphines. The calculations of percent buried volume were made using literature crystallographic data. Importantly, we considered only CIF with an R factor less than 7%. Moreover, when a number of molecules were found existing in the unit cell or when in a single complex two ligands or more bind the metal center, the average buried volume was calculated. *It is worth highlighting the parameters used for SambVca calculations: (1) for $\%V_{bur}$ calculations: 3.50 Å was selected as the value for the sphere radius, (2) both 2.00 and 2.28 Å were considered as distances for the metal–ligand bond, (3) usually irrelevant in crystallography hydrogen atoms were omitted and (4) scaled Bondi radii were used as recommended by Cavallo.*[7]

2. Correlation cone angle–buried volume

Our first aim was to probe the percent buried volume model in looking for a correlation between the Tolman cone angle and $\%V_{bur}$. We planned to use the crystal structures of $[Ni(CO)_3(PR_3)]$ complexes as Tolman did, unfortunately, in searching crystallographic data bases, we were only able to retrieve the cif file of $[Ni(CO)_3(P^tBu_3)]$.[15] Since only the atomic coordinates of elements belonging to the ligand are required to use Samb*V*ca, we thought we could simply use the crystal structures of phosphines themselves. A wide range of phosphines and one phosphite were selected in this manner to perform the analysis and allowed us to compute $\%V_{bur}$ with fictive metal–phosphorus bond distances of 2.00 and 2.28 Å. Results are compiled in Table 1. The values of cone angle are plotted *versus* $\%V_{bur}$ and the relationship is presented in Fig. 4. In view of the linear correlation present ($R^2 = 0.96$), there is good evidence that a relationship between cone angle and buried volume does exist. The regression analysis presented in Fig. 4 was calculated for M–P bond distance of 2.28 Å, however a similar trend was obtained for a bond length of 2.00 Å. Note that the phosphite $P(OPh)_3$, which obviously does not fit the correlation, was excluded from the final calculation (*vide infra*).

Table 1 Cone angle and $\% V_{bur}$ for selected tertiary phosphines

Entry	Phosphine PR_3	Reference	Cone angle $\theta/°$	$\% V_{bur}$ for M–P length at 2.00 Å	2.28 Å
1	PMe_3	16	118	26.1	22.2
2	PEt_3	16	132	32.7	27.8
3	$P\textit{n}Pr_3$	17	132	30.6	26.0
4	$P\textit{n}Bu_3$	18	132	30.4	25.9
5	PPh_3	19	145	34.5	29.6
6	$P(\textit{p}\text{-Tol})_3$	20	145	33.0	28.2
7	$P\textit{i}Pr_3$	17	160	37.6	32.3
8	PCy_3	21	170	37.1	31.8
9	$P(^tBu)_3$	18	182	42.4	26.7
10	$P(C_6F_5)_3$	22	184	42.6	37.3
11	$P(\textit{o}\text{-Tol})_3$	23	194	46.7	41.4
12	$PMes_3$	24	212	53.1	47.6
13	$P(OPh)_3$	25	128	35.4	30.7

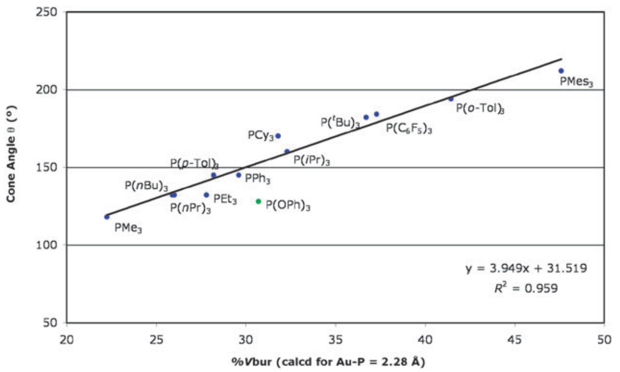


Fig. 4 Correlation of the Tolman steric parameter θ with the percent buried volume ($\% V_{bur}$) calculated for M–P bond distance of 2.28 Å.

Table 2 Percent of buried volume of silicon-containing phosphines

Entry	Phosphine PR_3	Reference	$\% V_{bur}$ for M–P length at 2.00 Å	2.28 Å
1	$P(SiMe_3)_3$	18	37.9	34.0
2	$P(Si\textit{i}Pr_3)_3$	26	82.6	78.4
3	$P(SiMe_3)_2(SiPh_3)$	27	46.7	41.1
4	$P(SiMe_2Ph_3)$	28	44.6	38.7
5	$P(SiMe_2{}^tBu)_3$	29	63.9	58.7

We decided to continue the calculations with non-coordinated molecules with the example of silicon-containing phosphines, which have been sparingly utilized in coordination chemistry. The values obtained are presented in Table 2 and were impressively large, with in particular 82.6% with 2.00 Å M–P distance for $P(Si\textit{i}Pr_3)_3$ (entry 2) and 63.9% for $P(SiMe_2{}^tBu)_3$ (entry 5). Therefore, to the best of our knowledge, with the exception of $P(SiMe_3)_3$, the other phosphines shown have not given rise to metal-based complexes. Such steric congestion might preclude coordination to a metal center already bearing ligands. Buried volume values for $P(SiMe_3)_3$ in different metal centered complexes were calculated and compiled in Table 3. Except for the indium-based complex (entry 1), the $P(SiMe_3)_3$ $\% V_{bur}$ values are very similar (entries 2–6) and comparable to those of the free ligand (Table 2, entry 1).

Table 3 $\% V_{bur}$ of $P(SiMe_3)_3$-containing complexes

Entry	Complexes	Reference	$\% V_{bur}$ for M–P length at 2.00 Å	2.28 Å
1	$P(SiMe_3)_3InI_3$	30	42.4	36.7
2	$P(SiMe_3)_3AlEt_3$	31	39.2	33.5
3	$P(SiMe_3)_3AlPh_3$	32	38.8	33.2
4	$P(SiMe_3)_3Fe(CO)_4$	33	38.8	33.2
5	$P(SiMe_3)_3Mo(CO)_5$	34	38.2	32.6
6	$P(SiMe_3)_3W(CO)_5$	34	38.1	32.4

We then aimed to find a good metal-based model to quantify the steric parameter of phosphines by Samb*V*ca calculations. In order to minimise the steric influence of spectator ligands around the metal center, complexes such as those of coinage metals with an oxidation state of +1, possessing a linear geometry caught our attention. Crystallographic structure determination of a limited number of copper(I) and silver(I) complexes have been reported with most of them being dimeric or tetrameric. Of note, recently Glorius calculated the $\% V_{bur}$ of IBiox NHC using silver(I) bromide complex.[13] In addition to being electron rich[35] these NHC ligands are also extremely sterically demanding. On the other hand, a large number of phosphine-containing gold(I) crystal structures have been reported and the recent interest in gold-catalyzed transformations[36] has translated into the publication of numerous structural characterisations.

First, we focused on $[(PR_3)AuCl]$ complexes and calculated the $\% V_{bur}$ of several phosphine ligands for which cone angle values are known. Results are compiled in Table 4. When plotted (Fig. 5) the ensuing linear regression presented a good correlation factor (R^2 = 0.98) meaning that as expected, a relationship between the Tolman cone angle and percent buried volume exists in this system. Phosphorus-based ligands such as TPA (1,3,5-triaza-7-phosphaadamantane) or *tris*(dimethylamino)phosphine ($P(NMe_2)_3$) (respectively, entries 1 and 5) fit the correlation.

Once again $\% V_{bur}$ values of triphenyl- and trimethylphosphite were found significantly higher than expected based on their cone angle (entries 14 and 15). Considering that the same trend was observed with calculations on the phosphines themselves, it seems reasonable to state that

Table 4 Cone angle and $\%V_{bur}$ for various phosphines in [PR_3AuCl] complexes

Entry	Complex	Reference	Cone angle θ/°	$\%V_{bur}$ for M–P length at 2.00 Å	2.28 Å
1	(TPA)AuCl	37	102	26.0	22.1
2	PMe_3AuCl	38	118	27.3	23.3
3	$PMe_2PhAuCl$	39	122	30.5	26.2
4	PEt_3AuCl	40	132	31.7	27.1
5	PPh_3AuCl	41	145	34.8	29.9
6	P(*p*-Tol)$_3$AuCl	42	145	34.2	29.3
7	$P(NMe_2)_3AuCl$	43	157	36.9	31.9
8	P*i*Pr$_3$AuCl	38	160	39.1	24.0
9	PCy_3AuCl	44	170	38.8	33.4
10	$P(^tBu)_3AuCl$	45	182	43.9	38.1
11	$P(C_6F_5)_3AuCl$	46	184	42.6	37.3
12	P(*o*-Tol)$_3$AuCl	47	194	44.8	39.4
13	$PMes_3AuCl$	48	212	50.5	45.0
14	$P(OMe)_3AuCl$	49	107	30.8	26.4
15	$P(OPh)_3AuCl$	50	128	36.5	31.9

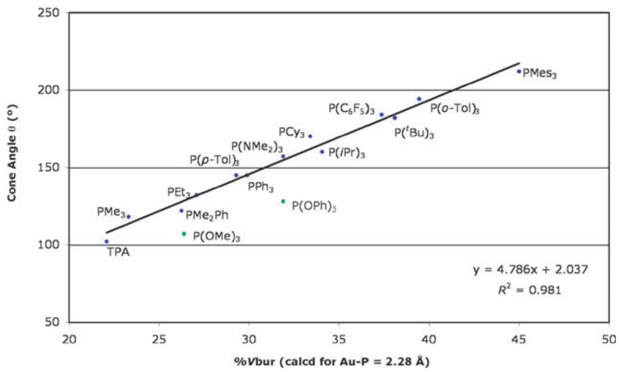


Fig. 5 Correlation of the Tolman steric parameter θ with the percent buried volume in [PR_3AuCl] with Au–P bond distance of 2.28 Å.

the simple molecular model treatment of Tolman might have underestimated the steric parameters associated with the more flexible phosphite ligands. Of note, $P(OMe)_3$ and $P(OPh)_3$ data were excluded from the linear regression depicted in Fig. 5. According to the linear regression equation, the cone angles for these phosphites should be 128 and 155°, respectively, instead of the 107 and 128° values usually employed.

3. Scope and limitations of the gold(I) model

We then examined the gold(I) model with parameters in mind such as the influence of the anionic ligand X in [PPh_3AuX], bis- and *tris*-coordinated triphenylphosphine Au^I and gold(III) complexes. We also provide a comparison between [(P^tBu_3)AuCl] and other P^tBu_3M complexes.

As presented above, we observed an excellent correlation between steric properties quantified by the Tolman cone angle and the buried volume values calculated from gold(I)chloride crystal structures. In order to validate the choice of a linear geometry complex such as gold(I), assuming that the effect of other ligands binding to the metal center are negligible, $\%V_{bur}$ values have been calculated for PPh_3 as a function of X in various [(PPh_3)AuX] complexes. Values of percent buried volume are shown in Table 5. All $\%V_{bur}$ values are within a narrow 2% range (between 29.3 and 31.2%) for calculations using a P–M distance of 2.28 Å (respectively entries 12 and 17). The average $\%V_{bur}$ for triphenylphosphine in gold(I) complexes is 30.3 and varied little since the standard deviation found is only 0.6. Consequently, we believe buried volume calculations performed from crystallographic data of various [(L)Au(I)X] complexes are capable of providing an accurate determination of the steric properties of the ligand L.

Calculations for PPh_3 have been extended to other gold complexes such as $[(L)_nAu(I)X]$ and [(L)Au(III)X]. These $\%V_{bur}$ values are presented in Table 6. Compared to [(PPh_3)Au(I)Cl] (entry 1), bis-coordinated triphenylphosphine complexes do not lead to steric property variation of the phosphine ligand (entries 2 and 3). However, in the tri-coordinated [$(PPh_3)_3Au(I)Cl$], PPh_3 steric bulk was found to be significantly smaller (entry 4). Of note, these variations are certainly small due to the relatively low steric hindrance of PPh_3 compared to other phosphorus based ligands. The PPh_3 $\%V_{bur}$ values were also compared to gold(I) and gold(III) (entries 1 and 5–9). PPh_3 appears to be sterically larger in gold(III) complexes, nevertheless these results have to be taken with care since differences are minor.

In order to support the choice of gold(I) as a model for $\%V_{bur}$ determination, we compared this system with other metal complexes bearing the more bulky P^tBu_3 (Table 7). This time, the spread was found wider with values in a range greater than 5% (34.2% entry 22 and 39.5 entry 7) with a standard deviation of 1.4 for an average $\%V_{bur}$ of 36.5. The steric hindrance of P^tBu_3 appears directly related to the number and the size of ligands borne by the metal center and to the coordination geometry of the complex used.

For instance two- and three-coordinate metals or hydride complexes presented buried volume for tri-*tert*-butyl-phosphine greater than 37% for a distance P–M = 2.28 Å (entries 1–7 and 18), whereas tetra-coordinated complexes and a higher coordination number give a P^tBu_3 $\%V_{bur}$ smaller than 37% (entries 8, 15–17 and 19–23). As a result, steric bulk of P^tBu_3 can be varied as a function of the space available around the metal center showing the slight steric flexibility of this ligand.

Table 5 $\%V_{bur}$ for PPh_3 as a function X in $[PPh_3AuX]$ complexes

			$\%V_{bur}$ for M–P length at	
Entry	Complex	Reference	2.00 Å	2.28 Å
1	PPh_3AuCl	41	34.8	29.9
2	PPh_3AuBr	51	34.9	29.9
3	PPh_3AuI	52	35.1	30.1
4	PPh_3AuOAc	53	34.9	30.0
5	PPh_3AuOTf	54	35.6	30.6
6	PPh_3AuCN	55	34.8	29.8
7	PPh_3AuN_3	56	35.7	30.8
8	PPh_3AuONO_2	57	34.5	29.5
9	PPh_3AuNCO	58	35.0	30.1
10	PPh_3AuCNO	58	35.3	30.3
11	PPh_3AuSCN	59	35.4	30.4
12	PPh_3AuMe	60	34.3	29.3
13	PPh_3AuCF_3	61	35.2	30.2
14	PPh_3AuPh	62	35.0	30.0
15	PPh_3AuMes	63	34.7	29.8
16	$[PPh_3Au]NTf_2$	64	36.9	32.0
17	$[PPh_3Au]NMs_2$	65	36.1	31.2
18	$[PPh_3Au]N(SiMe_3)_2$	66	35.6	30.7
19	$[PPh_3Au(MeCn)]SbF_6$	67	35.6	30.6
20	$[PPh_3AuNMe_3]ClO_4$	68	35.5	30.6
21	$[PPh_3AuPy]BF_4$	69	35.2	30.2
22	$[PPh_3Au(2,6\text{-}Me\text{-}Py)]ClO_4$	70	36.4	31.5

Table 6 PPh_3 $\%V_{bur}$ comparison in $[(PPh_3)_nAuX]$ and $[PPh_3AuX_3]$ complexes

			$\%V_{bur}$ for M–P length at	
Entry	Complex	Reference	2.00 Å	2.28 Å
1	PPh_3AuCl	41	34.8	29.9
2	$(PPh_3)_2AuCl$	71	34.9	30.0
3	$[(PPh_3)_2Au]BF_4$	72	35.1	30.2
4	$(PPh_3)_3AuCl$	73	33.8	28.9
5	PPh_3AuCl_3	74	35.5	30.5
6	PPh_3AuBr	51	34.9	29.9
7	PPh_3AuBr_3	75	35.1	30.1
8	PPh_3AuMe	60	34.3	29.3
9	PPh_3AuMe_3	76	34.7	29.7

Having established the gold(I) model as meaningful for $\%V_{bur}$ determination, we extended calculations to other phosphorus-based ligands for data found in crystallography data bases and determined their cone angles using the linear regression obtained in Fig. 5 (Table 8). Whereas most of the ligands examined present a buried volume in a middle range 30–35% some were found particularly sterically hindered, for example the tri-(2,4,6-trimethoxyphenyl)phosphine (43.6%, entry 4), the *tris*(diphenylmethyleneamino)phosphine (43.3%, entry 13) and the benzhydryl(mesityl)(methyl)phosphine (41.1%, entry 18). For *tris*(2-cyanoethyl)phosphine, the value obtained is higher than expected (40.5%, entry 12)—it should be similar to PEt_3 (27.1%, Table 4, entry 4; see also Table 1, entries 2–4). According to the X-ray structure, this can be explained by secondary interactions between the nitrile function and the gold center. Other phosphorus ligands presented a low $\%V_{bur}$: methylphenylphosphine (21.8%, entry 26), difluorophosphines (24.1 and 24.8%, entries 29 and 30), and dichlorophenylphosphine (26.7%, entry 31). Small atoms (H, F, Cl) binding to the phosphorus allow for considerable reduction of the congestion around the metal center as illustrated by entries 28 and 29, replacing a tri-*tert*-butylphenyl group by a hydrogen lead to a decrease in the $\%V_{bur}$ of 4.4%. Comparison between phosphites (Table 4, entries 14 and 15) and thiophosphites (Table 8, entries 15 and 16) revealed that thiophosphites are generally more sterically demanding. Nevertheless, the difference found was small for methyl-containing ligands whereas it was considerable for phenyl-bearing congeners.

Table 7 P^tBu_3 $\%V_{bur}$ in various $[(P^tBu_3)_nM]$ complexes

			$\%V_{bur}$ for M–P length at	
Entry	Complex	Reference	2.00 Å	2.28 Å
1	P^tBu_3AuCl	45	43.9	38.1
2	$(P^tBu_3)_2AuCl$	77	44.1	38.3
3	$[P^tBu_3CuCl]_4$	78	42.9	37.1
4	$P^tBu_3CuOSiPh_3$	79	43.5	37.7
5	$P^tBu_3AlH_3$	80	43.4	37.6
6	$P^tBu_3GaH_3$	80	43.6	37.8
7	$P^tBu_3Hg(OAc)_2$	81	45.3	39.5
8	$P^tBu_3NiBr_3$	82	41.9	36.3
9	$(P^tBu_3)_2Pd$	83	42.5	36.8
10	$(P^tBu_3)_2PdClH$	84	42.0	36.3
11	$(P^tBu_3)_2PdBrPh$	85	43.2	37.4
12	$[P^tBu_3PdBr]_2$	86	42.9	37.2
13	$P^tBu_3Pt(dvtms)$	87	40.7	35.1
14	$P^tBu_3PtH_2$	88	41.9	36.2
15	$(P^tBu_3)_2PhCl(CO)$	89	41.1	35.4
16	$P^tBu_3IrCl(CO)_2$	15	41.7	36.0
17	$P^tBu_3Fe(CO)_4$	90	40.7	35.1
18	$[P^tBu_3FeS]_4$	91	42.9	37.2
19	$[P^tBu_3RuBr(CO)_2]_2$	92	40.9	35.2
20	$[P^tBu_3RuOAc(CO)_2]_2$	93	40.9	35.2
21	$[P^tBu_3OsCO)_3[Os(CO)_4]$	94	40.2	34.6
22	$P^tBu_3Re(CO)_4[Re(CO)_5]$	95	40.0	34.3
23	$P^tBu_3W(CO)_5$	96	40.6	34.9

4. Steric properties of bidentate phosphine ligands

Following Tolman's work, we then focused on bidentate phosphines and calculated their buried volume for half bidentate phosphines (steric hindrance around one phosphorus atom).

Table 8 $\%V_{bur}$ for various phosphines in $[(PR_3)AuCl]$ complexes, cone angle calculation

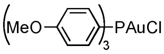
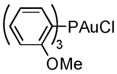
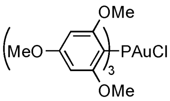
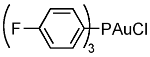
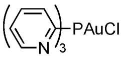
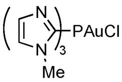
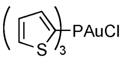
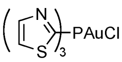
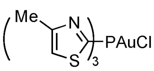
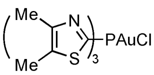
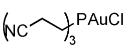
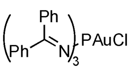
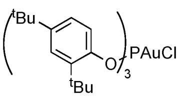
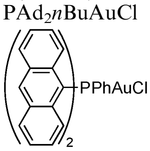
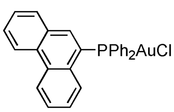
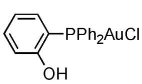
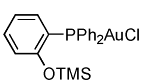
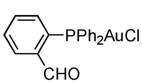
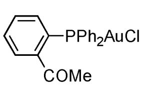
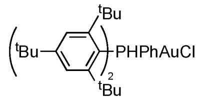
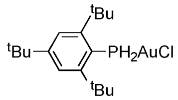
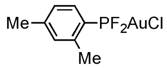
Entry	Complex	Reference	$\%V_{bur}$ for M–P length at 2.00 Å	2.28 Å	Cone angle $\theta/^{\circ a}$
1	$P(m\text{-Tol})_3AuCl$	97	34.5	29.5	143
2		98	35.8	30.8	150
3		99	40.7	35.4	171
4		100	48.7	43.6	211
5		60	34.7	29.8	145
6		101	34.2	29.3	142
7		102	37.2	32.1	156
8		103	35.8	30.8	149
9		102	35.0	30.2	147
10		102	37.5	33.2	161
11		103	34.0	29.1	141
12		104	45.3	40.5	196
13		105	48.1	43.3	209
14		106	37.8	32.4	157
15	$P(SMe)_3AuCl$	49	32.6	27.8	135
16	$P(SPh)_3AuCl$	49	45.0	40.3	195
17	$PCy_2PhAuCl$	107	38.0	32.7	159
18	$P(CHPh_2)MeMesAuCl$	108	46.2	41.1	199
19	PAd_2nBuAuCl	109	41.9	36.3	176
20		110	44.3	38.9	188
21		111	38.1	33.0	160
22		112	37.5	32.5	158
23		112	39.7	34.6	168
24		113	40.1	34.9	169
25		114	41.2	36.1	175

Table 8 (*continued*)

Entry	Complex	Reference	$\%V_{bur}$ for M–P length at 2.00 Å	2.28 Å	Cone angle $\theta/^{\circ a}$
26	PHMePhAuCl	115	25.5	21.8	106
27		116	37.9	33.2	161
28		117	32.8	28.8	140
29		118	27.9	24.1	117
30	$PF_2(NMe_2)AuCl$	118	28.5	24.8	121
31	$PCl_2PhAuCl$	119	31.0	26.7	130

[a] Calculated by linear regression.

Regardless, the entire ligand was included in the calculations and values depicted in Table 9 are the average $\%V_{bur}$ obtained for both P atoms. Since various bidentate phosphine-containing gold chloride complexes are reported in the literature with an accompanying crystal structure determination, the same model as described above was employed. Concerning the $(CH_2)_n$ chain length between the P atoms (entries 1–6), surprisingly, the trend observed was not found in accordance to Tolman's report (θ increases with the length). Here, the $(CH_2)_n$ bridge length leads to important variations on $\%V_{bur}$ values. When $n = 1$ or 3 (dppm and dppp, entries 1 and 3), larger $\%V_{bur}$ were obtained whereas for $n = 2$ or 4 (dppe and dppb, entries 2 and 4), the $\%V_{bur}$ was found significantly smaller. This might be due to special molecular interactions as is the case for $[(dppm)(AuCl)_2]$ where some interactions between one phenyl ring and the non-adjacent gold center exist. Of note, for $n > 3$, $\%V_{bur}$ values are comparable and the bridge length effect is minor (entries 4–6). Replacing the hydrogens of dppm by fluorine atoms allows for decreasing the buried volume (entries 1 and 7). On the other hand, introducing some strain in the linker does not lead to $\%V_{bur}$ variations (entries 2 and 8). Apparently in this case, $\%V_{bur}$ cannot be related to bite angle, thus Xantphos and dbfphos $\%V_{bur}$ are notably different for a similar bite angle (respectively 111 and 109°) (entries 11 and 12); bite angle of DPEphos is 102° for $\%V_{bur}$ of 41.3 (entry 10). As expected the other substituents of the P atoms play a critical role on the steric hindrance. Thus replacing phenyl by a *p*-tolyl group in BINAP increases the congestion (entries 14 and 15), or phenyl by *iso*-propyl in dppf also raises the $\%V_{bur}$ (entries 17 and 18). The largest bidentate phosphines are the ones containing a biaryl moiety (BINAP and Segphos, entries 14–16). This class of ligands will be developed in detail in section 5.

While Tolman took into consideration only half of the chelate for cone angle determination, assuming the P–M–P in $M[R_2P–(CH_2)_n–PR_2]$ of 74, 85, 90° for $n = 1$, 2, or 3, the Samb*V*ca software allowed for determining the steric bulk of the entire ligand. It is relevant to have access to both values of

Table 9 $\%V_{bur}$ for half of the bidentate phosphines in $[(AuCl)R_2P\text{-}X\text{-}PR_2(AuCl)]$ complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–P length at 2.00 Å	2.28 Å
1	$(dppm)(AuCl)_2$	120	44.2	39.9
2	$(dppe)(AuCl)_2$	121	34.2	29.2
3	$(dppp)(AuCl)_2$	122	41.2	36.8
4	$(dppb)(AuCl)_2$	123	35.8	30.9
5	$(dpppent)(AuCl)_2$	123	33.3	28.4
6	$(dpph)(AuCl)_2$	124	35.6	30.7
7	$ClAuPh_2PCF_2PPh_2AuCl$	125	38.8	33.4
8	$ClAuPh_2PCH{=}CHPPh_2AuCl$	126	33.8	29.1
9	$(dpp\text{-}benzene)(AuCl)_2$	127	44.7	39.9
10	$(DPEphos)(AuCl)_2$	128	45.3	41.3
11	$(Xantphos)(AuCl)_2$	128	46.8	42.5
12	$(dbfphos)(AuCl)_2$	128	44.3	39.9
13	$(dppn)(AuCl)_2$	129	34.6	29.7
14	$(BINAP)(AuCl)_2$	130	57.9	54.6
15	(BINAP-*p*-Tol)$(AuCl)_2$	131	61.9	58.5
16	$(Cy\text{-}Segphos)(AuCl)_2$	132	60.4	56.6
17	$(dppf)(AuCl)_2$	133	38.7	33.5
18	(d*i*prpf)$(AuCl)_2$	134	44.1	38.8

Table 10 $\%V_{bur}$ for bidentate phosphines in $[PdCl_2(X(PR_2)_2)]$ complexes

Entry	Complex	Reference	$\%V_{bur}$
1	(dppm)$PdCl_2$	135	47.0
2	(dppe)$PdCl_2$	136	51.4
3	(dppp)$PdCl_2$	135	52.2
4	(dppb)$PdCl_2$	137	53.8
5	(dcpe)$PdCl_2$	138	53.9
6	(d(Mes)pe)$PdCl_2$	139	62.0
7	(d(DIPP)pe)$PdCl_2$	139	64.6
8	(=$CHPPh_2)_2PdCl_2$	140	49.3
9	(dppx)$PdCl_2$	141	56.3
10	(1,8-dpmn)$PdCl_2$	142	54.5
11	(TRANSphos)$PdCl_2$	143	59.8
12	(dpbp)$PdCl_2$	144	54.6
13	(BINAP)$PdCl_2$	145	55.6
14	(BINAP-Cy)$PdCl_2$	146	55.0
15	(Segphos)$PdCl_2$	147	54.7
16	(Xantphos)$PdCl_2$	148	54.4
17	(DIOP)$PdCl_2$	149	51.6
18	(TADDOL)$PdCl_2$	150	55.4
19	(Duphos-Me)$PdCl_2$	151	48.0
20	(Me-FerroLANE)$PdCl_2$	152	53.1
21	(dppf)$PdCl_2$	153	55.5
22	(dmpf)$PdCl_2$	154	46.7
23	(d*i*Prpf)$PdCl_2$	155	56.5
24	(dcpf)$PdCl_2$	156	57.5
25	(d*t*Bupf)$PdCl_2$	157	60.9
26	(dppr)$PdCl_2$	158	54.7
27	(dppo)$PdCl_2$	159	55.5

half and the entire ligand, since bidentate ligands have a very specific activity compared to monodentate phosphines.

Nevertheless, to determine $\%V_{bur}$ for the entire bidentate ligand, a system where both phosphorus atoms are linked to the same metal center had to be selected. Because numerous X-ray structures are readily accessible, we have calculated $\%V_{bur}$ based on $[(L_2)Au_2Cl_2]$ crystallographic data. Moreover, we had to adapt the manner in which the calculation was performed. We considered the metal as the origin (M is the atom coordinated at the center of the sphere with distance from sphere center = 0 Å) and the two P for axis definition. Thus, the distance of the M–L bond is no longer considered a fixed parameter. With the values obtained and shown in Table 10, we observed a match with Tolman's results. The $\%V_{bur}$ increases according to the $(CH_2)_n$ bridge length (entries 1–4), therefore in the case of bidentate phosphines, we believe this model to be more meaningful. The steric hindrance of the entire ligand is also directly related to the bulk of the other P-substituents (entries 1, 5–7 and 21–25), the 2,6-di-*iso*-propylphenyl moiety giving the most important steric hindrance (entry 7). Entry 8 shows that introducing strain in the bridge leads to a reduction in steric crowding (compared to entry 2). Ligands with a large bite angle such as TRANSphos present larger $\%V_{bur}$ (59.8%, entry 11 *vs.* entries 9–12 and 16). Ferrocene-, ruthenocene- or osmocene-based ligand showed a buried volume that is independent of the metallocene used (entries 21, 26 and 27).

5. Buried volume of biarylphosphine ligands

Over the last decade, biaryldialkyl phosphines, namely those developed by the Buchwald group such as SPhos and XPhos, have attracted much attention for their efficiency in Pd-based systems mediating C–C, C–N and C–O bond formations.[160] These particular ligands are recognized to be electron-rich and bulky phosphines, but to the best of our knowledge no quantification of the steric parameter of these versatile ligands has been reported to date. Empirically, from single crystal structures, it seems that the biphenyl pattern interacts with the metal center *via* π-interactions and sterically protects it, but through a simple rotation of the ligand, the metal can be rendered accessible to permit reactions. Several structures of AuCl complexes bearing biaryl phosphines have been reported in the literature and consequently their buried volumes were determined (Table 11). In this case again, the nature of the dialkyl P-substituents shapes the steric bulk; JohnPhos with *tert*-butyl groups is 4.0% bigger than Cy-JohnPhos (entries 2 and 3). The PCy_2Ph is an analogue of the biaryldialkyl phosphine family where the biaryl moiety has been replaced by a phenyl. Thus considering this ligand as the reference, we evaluated the steric influence of the biphenyl group. This moiety leads to a 14% increase in the $\%V_{bur}$ (entries 1 and 3). We believe that this difference of at least 14% permits easier substrate approach in catalytic reactions. Then, the buried volume increases as a function of the biaryl substitution (entries 3–6) to reach the impressive value of 53.1% and a cone angle of 256° for XPhos (entry 6 based on the linear regression previously obtained. Despite using the $[Au(MeCN)]SbF_6$ structure instead of the [AuCl] one, *t*BuXPhos $\%V_{bur}$ was determined to be even larger (entry 8). BINAP and Segphos, possessing the biphenyl moiety, could also be included in this series of ligands with $\%V_{bur}$ even more impressive (entries 8 and 9). This is in good agreement with the effect of biaryl substitution.

In order to confirm such values, we decided to perform calculations on other metal-based complexes (Table 12). Copper and silver complexes bearing, respectively, JohnPhos and Cy-John (entries 1 and 2) gave the same $\%V_{bur}$ values as those using the AuCl system (Table 11, entries 2 and 3). Examination of ruthenium(II) complexes with DavePhos proved also that biaryl phosphines are flexible and their steric bulk can change as a function of the congestion around the metal center. Replacing chlorines by methyl groups diminishes the $\%V_{bur}$ and introduction of more hindered PMe_3 and PPh_3 ligands also leads to reducing the size of DavePhos (entries 3–7). Calculations carried out on Pd complexes allow for the corroboration of the value range and the metal crowding effect (entries 7–9).

6. Buried volume of *N*-heterocyclic carbenes

Since the first report of *N*-heterocyclic carbenes in the early sixties, and later the seminal discoveries of (NHC)–transition metal complexes, the development and applications of NHCs has seen great activity, to reach now a status of "privileged" ligands in organometallic chemistry.[167] The study of NHC electronic properties have shown them to be more donating than the best donating phosphines, but this difference is small.[8] Steric properties are another matter as NHC ligands are sterically very demanding yet these parameters for NHCs require better quantification.

Table 11 $\%V_{bur}$ and cone angle calculation for biaryl phosphines in $[PR_3Au^I]$ complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–P length at 2.00 Å	2.28 Å	Cone angle $\theta/°^a$
1	$PCy_2PhAuCl$	107	38.0	32.7	159
2	(JohnPhos)AuCl	67	55.5	50.9	246
3	(Cy-JohnPhos)AuCl	67	51.0	46.7	226
4	(MePhos)AuCl	161	53.6	49.3	238
5	(SPhos)AuCl	67	53.7	49.7	240
6	(XPhos)AuCl	161	57.4	53.1	256
7	$[(JohnPhos)Au(MeCN)]SbF_6$	67	57.2	52.2	—
8	$[(t\text{Bu-XPhos})Au(MeCN)]SbF_6$	67	59.2	54.8	—
9	$(BINAP)(AuCl)_2$	130	57.9	54.6	263
10	$(Cy\text{-}Segphos)(AuCl)_2$	132	64.0	56.6	273

[a] Calculated by linear regression.

Table 12 $\%V_{bur}$ for biarylphosphines in other metal complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–P length at 2.00 Å	2.28 Å
1	$[(JohnPhos)CuBr]_2$	162	57.3	52.8
2	$[[Cy\text{-}JohnPhos]Ag(thf)]SbF_6$	163	53.7	49.8
3	$(DavePhos)RuCl_2$	164	65.9	63.1
4	$(DavePhos)RuMe_2$	164	65.0	61.9
5	$[(DavePhos)RuCl(PMe_3)]SbF_6$	164	62.2	59.0
6	$[(DavePhose)RuCl(PPh_3)]SbF_6$	164	59.0	55.7
7	$(Cy\text{-}JohnPhos)_2Pd$	165	47.3	42.5
8	$(SPhos)_2Pd$	166	45.9	40.9
9	$(SPhos)_2PdCl_2$	166	38.1	32.7

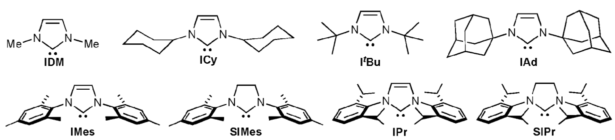


Fig. 6 The most frequently encountered NHCs.

The structures of the most frequently encountered NHC ligands are shown in Fig. 6.

The gold(I) chloride model, which gave good results for phosphine ligands, was used to calculate the percent buried volumes of various NHCs. Values are compiled in Table 13. As anticipated, the smallest NHCs are those possessing methyl as *N*-substituents (entries 1 and 2). $\%V_{bur}$ increases as a function of the *N*-substituents bulk (entries 1–1). Nonetheless the influence is limited to the close area around the nitrogen. Thus *iso*-propyl groups give a similar $\%V_{bur}$ value as cyclohexyl (entries 3 and 6) showing that only the first 2 or 3 atoms connected to the nitrogen atom influence the buried volume of the NHC. According to these values, IPr and SIPr are significantly bigger than IAd (entries 9–11), this could explain why such NHCs usually lead to good results in transition metal catalysis. These results also support literature statements mentioning that the nature ((un)saturation and substitution) of the NHC backbone has a minor impact on its steric properties (entries 1–5).[9b,12] However, in the case of *iso*-propyl-containing carbenes, two methyl groups on the backbone lead to a movement of the *iso*-propyl groups near the gold center and to an increase of the $\%V_{bur}$ value. In the context of backbone saturation/unsaturation, the difference in terms of sterics is small. In the case of mesityl-based NHCs as for 2,6-di*iso*propyl phenyl, the variation is much more pronounced (entries 7–10). Furthermore, we were able to determine the $\%V_{bur}$ of cyclic (alkyl)(amino)carbenes (entries 16–18). This special class of NHCs appears to be particularly interesting in order to modulate steric properties since these are very small (23.5%, entry 16) yet high steric congestion can also be attained (51.2%, entry 18).

Whereas copper and silver based complexes bearing phosphines give frequent rise to dimeric or tetrameric structures, NHC-containing analogues are most often monomeric. Therefore, determination and comparison of NHC $\%V_{bur}$ for coinage metal complexes presenting a linear geometry (Table 14) is possible. In a general manner, there is a good match between values calculated for coinage metals. This suggests that NHC buried volume values can be accurately calculated from [(NHC)AgCl], [(NHC)CuCl] as well as [(NHC)AuCl] crystal structures. A significant difference was found in the case of SIPr/IPr. The SIPr ligand is bigger than IPr in the case of gold chloride complexes whereas with silver and copper the trend is reversed (entries 3 and 4), at this point we do not have an acceptable explanation for this trend reversal.

Since the synthesis of $[(NHC)Ag^ICl]$ complexes is particularly straightforward using the procedure developed by Lin,[183] numerous complexes and X-ray structures are reported in the literature. The $\%V_{bur}$ calculated from [(NHC)AgCl] are presented in Table 15. In general, the same trend as that observed for [(NHC)AuCl] complexes is found with identical features such as a higher $\%V_{bur}$ for the NHC incorporating *iso*-propyl

Table 13 $\%V_{bur}$ for *N*-heterocyclic carbenes in [(NHC)AuCl] complexes

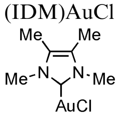
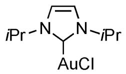
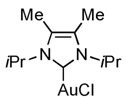
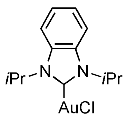
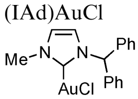
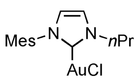
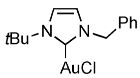
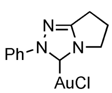
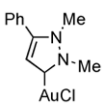
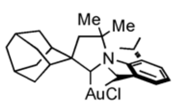
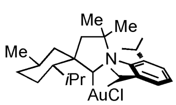
Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at 2.00 Å	2.28 Å
1	(IDM)AuCl	168	26.3	22.7
2		169	26.1	22.6
3		170	27.4	23.5
4		169	38.4	33.9
5		171	27.9	23.9
6	(ICy)AuCl	169	27.4	23.5
7	(IMes)AuCl	169	36.5	31.2
8	(SIMes)AuCl	169	36.9	31.7
9	(IPr)AuCl	172	44.5	39.0
10	(SIPr)AuCl	169	47.0	41.5
11	(IAd)AuCl	169	39.8	35.4
12		173	27.7	23.7
13		174	33.3	28.6
14		175	33.0	28.8
15		169	29.7	24.3
16		176	23.5	20.3
17		177	48.5	43.4
18		178	51.2	45.8

Table 14 Comparison of $\%V_{bur}$ values in [(NHC)CuCl], [(NHC)AgCl] and [(NHC)AuCl] complexes (M–NHC length = 2 Å)

Entry	NHC	$\%V_{bur}$ (Cu)	Ref.	$\%V_{bur}$ (Ag)	Ref.	$\%V_{bur}$ (Au)	Ref.
1	ICy	28.8	78	27.7	181	27.4	169
2	SIMes	36.9	78	36.1	181	36.9	169
3	IPr	47.6	179	46.5	182	44.5	172
4	SIPr	46.4	180	44.5	182	47.0	169

on nitrogen atoms and methyl on the backbone (entry 16) or (S)IPr being more sterically bulky than IAd (entries 8–10). Of note, increasing the ring size from cyclohexyl to cyclododecyl connected to the N atoms involves an increase of the NHC steric hindrance (entries 4 and 5), but the bismacrocyclic NHC (entry 11) showed a bulk similar to the one calculated for SIMes (entry 7). Whereas it could appear as sterically hindered, the tetrasubstituted phenyl NHC showed a moderate $\%V_{bur}$ value (entry 17). An efficient way to enhance NHC congestion is to expand the NHC ring size from 5 to 6-membered cycles (entries 7 and 19). In spite of their unique structures and good donating properties, naphthoquinone-based NHCs and annulated bis-NHCs show standard $\%V_{bur}$ values (entries 21 and 22). We established that the ligand X or the metal (Cu^{I}, Ag^{I}, or Au^{I}) have little effect on the $\%V_{bur}$ values. Thus we can conclude that the IBiox-menthyl NHC, for which $\%V_{bur}$ calculations are performed using [(NHC)AgBr] X-ray data, is the most sterically demanding NHC ligand reported to date.[13]

We further investigated NHC steric properties focused on several commonly used *N*-heterocyclic carbenes varying from small to large NHCs. $\%V_{bur}$ of IDM has been calculated for various metallic compounds including mono-, bis-, and tri-coordinated complexes (Table 16). Calculations were performed with a M–NHC bond distance of 2.00 and 2.28 Å, albeit the average bond length in NHC-containing complexes is 2.00 Å. At this distance, all $\%V_{bur}$ values for IDM are included in a narrow range 24.5–26.3% (respectively entries 4 and 1) with a low standard deviation of 0.4 for an average $\%V_{bur}$ of 25.7. The steric properties of IDM appear independent of the metal and of the crowding generated by other ligands around the metal.

In the case of the cyclohexyl *N*-substituted NHC ICy, $\%V_{bur}$ ranges from 26.3 to 29.4% (Table 17, entries 5 and 15) and was found slightly more disperse with a standard deviation of 0.8. The average $\%V_{bur}$ of 27.4 agrees with the value obtained with the gold(I) chloride complex (entry 1).

To complete the *N*-alkyl NHC investigation, I^{t}Bu (Table 18) was examined. The average $\%V_{bur}$ value was found to be 37.7% with a standard deviation of 1.3. Since I^{t}Bu is considerably bigger than IDM and ICy, it was expected that a more pronounced variation of the $\%V_{bur}$ values would be observed. The range spans from 35.7 to 39.2% (entries 2, 5 and 9). Steric properties of I^{t}Bu are moderately influenced by the metal and its environment. Its core geometry renders it relatively rigid and no large variations in NHC $\%V_{bur}$ are observed. As an example, removing a chloride in the [(I^{t}Bu)Pd(allyl)Cl] complex leading to the cationic species [(I^{t}Bu)Pd(allyl)]BF_4 should free space around the palladium center, however the I^{t}Bu $\%V_{bur}$ increases by only 1% (entries 10 and 11) when doing this halide abstraction at Pd. In [(I^{t}Bu)M(allyl)Cl] compounds with M = Ni or Pd, the I^{t}Bu $\%V_{bur}$ has the same value (entries 8 and 11).

IMes is probably the most commonly employed NHC in coordination chemistry and X-ray structures are plentiful for this NHC. A selection of 42 complexes has been used to perform buried volume calculations (Table 19). Whereas the $\%V_{bur}$ average is, 34.3%, the standard deviation of 1.7 attests for some variability of the IMes steric properties. This indicates some flexibility in the NHC structure in order to fit with the crowding around the metal center. $\%V_{bur}$ values range from 30.7 to 38.2% (entries 10 and 9). IMes steric bulk

Table 15 $\%V_{bur}$ for *N*-heterocyclic carbenes in [(NHC)AgCl] complexes

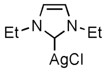
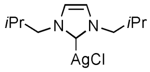
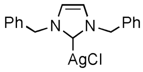
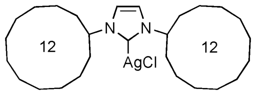
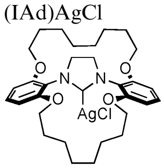
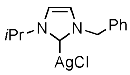
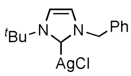
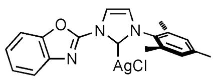
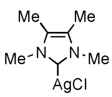
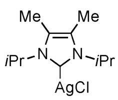
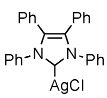
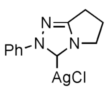
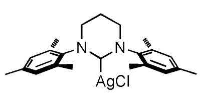
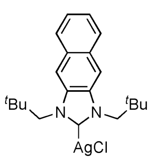
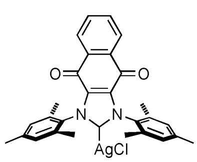
Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at	
			2.00 Å	2.28 Å
1		184	27.9	24.0
2		181	30.0	25.8
3		185	32.1	27.9
4	(ICy)AgCl	181	27.7	23.8
5		181	32.2	27.9
6	(IMes)AgCl	186	36.1	30.9
7	(SIMes)AgCl	181	36.1	30.8
8	(IPr)AgCl	182	46.5	40.9
9	(SIPr)AgCl	181	45.5	40.1
10	(IAd)AgCl	181	40.2	35.7
11		187	36.2	31.4
12		188	28.3	24.2
13		175	33.5	29.1
14		189	33.4	29.0
15		181	26.1	22.5
16		181	38.8	34.3
17		190	30.7	26.6
18		181	28.9	25.3
19		191	42.9	37.6
20		192	38.1	33.8
21		193	35.6	30.3

Table 15 (*continued*)

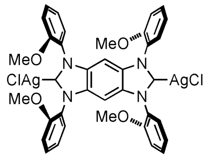
Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at 2.00 Å	2.28 Å
22		194	32.9	28.5

Table 16 IDM $\%V_{bur}$ comparison in various M(IDM) complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at 2.00 Å	2.28 Å
1	(IDM)AuCl	168	26.3	22.7
2	(IDM)Cr(CO)$_5$	195	25.3	21.8
3	(IDM)$_2$Cr(CO)$_4$	196	25.2	21.7
4	(IDM)$_2$MO(CO)$_4$-*cis*	197	24.5	21.1
5	(IDM)$_2$MO(CO)$_4$-*trans*	197	25.3	21.8
6	(IDM)MO(Cp)$_2$	198	25.8	22.2
7	(IDM)Fe(CO)$_4$	199	25.6	22.1
8	(IDM)OsCl$_2$(CO)$_3$	200	25.4	21.9
9	(IDM)RhCl(cod)	200	26.0	22.5
10	(IDM)RhBr(cod)	201	26.1	22.5
11	(IDM)RhI(cod)	201	26.0	22.5
12	(IDM)RhCl$_2$(Cp*)	202	25.4	21.9
13	(IDM)$_2$RhCl(CO)	203	26.0	22.4
14	(IDM)IrI(cod)	204	26.1	22.6
15	(IDM)Ni(Cp)I	205	26.1	22.6
16	(IDM)$_2$Ni(CO)$_2$	206	25.8	22.3
17	(IDM)$_3$Ni	207	25.8	22.2
18	(IDM)$_2$HgCl$_2$	208	26.1	22.6

Table 17 ICy $\%V_{bur}$ comparison in various M(ICy) complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at 2.00 Å	2.28 Å
1	(ICy)AuCl	169	27.4	23.5
2	(ICy)AgCl	181	27.7	23.8
3	(ICy)CuCl	78	28.8	24.8
4	(ICy)AuBr$_3$	209	27.4	23.4
5	(ICy)W(CO)$_5$	210	26.3	22.4
6	(ICy)RuCl(Cp*)	4	26.5	22.7
7	(ICy)RuCl(Cp*)(CO)	211	26.6	22.8
8	(ICy)RhCl(cod)	210	27.1	23.1
9	[(ICy)$_3$Rh(CO)]PF$_6$	212	27.2	23.3
10	(ICy)IrCl(cod)	8	27.3	23.3
11	[(ICy)IrI(cod)(Py)]PF$_6$	213	27.0	23.1
12	(ICy)IrCl(CO)$_2$	8	27.6	23.7
13	(ICy)$_2$NiCl$_2$	214	27.3	23.4
14	(ICy)$_2$Ni(CO)$_2$	215	26.8	22.9
15	(ICy)Pd(allyl)Cl	9*a*	29.4	25.4
16	(ICy)Pt(dvtms)	216	27.3	23.4

appears to be guided by the coordination number of the metal complex. Thus, in two-coordinate complexes showing a linear geometry the IMes $\%V_{bur}$ is generally greater than 36.0 (entries 1–9, 31 and 33), while for tetra- and penta-coordinated compounds, the buried volume does not exceed 33.0% (entries 10, 11, 13–18 and 20–27). However, in four-coordinate

Table 18 I^{t}Bu $\%V_{bur}$ comparison in various M(I^{t}Bu) complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at 2.00 Å	2.28 Å
1	(I^{t}Bu)AuBr$_3$	209	36.0	32.1
2	[(I^{t}Bu)Au(PPh$_3$)]PF$_6$	170	35.7	31.7
3	(I^{t}Bu)CuClCp	217	39.0	34.4
4	[(I^{t}Bu)$_2$Cu]BF$_4$	218	39.0	34.7
5	(I^{t}Bu)IrCl(cod)	8	35.7	31.6
6	(I^{t}Bu)IrCl(CO)$_2$	8	37.6	33.2
7	[(I^{t}Bu)$_2$IrH$_2$]PF$_6$	217	38.7	34.3
8	(I^{t}Bu)Ni(allyl)Cl	219	37.7	33.5
9	(I^{t}Bu)Ni(CO)$_2$	220	39.2	34.7
10	(I^{t}Bu)$_2$Ni	221	38.5	34.0
11	(I^{t}Bu)Pd(allyl)Cl	9*a*	37.8	33.4
12	[(I^{t}Bu)Pd(allyl)]BF$_4$	222	38.9	34.4
13	(I^{t}Bu)PdI$_2$PPh$_3$	223	36.7	32.5
14	(I^{t}Bu)Pt(dvtms)	216	37.7	33.2

hydride complexes, hydrogen atoms being sterically unhindered, IMes $\%V_{bur}$ reaches 35.0 (entries 38 and 40).

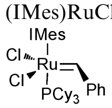
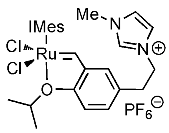
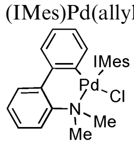
The trend observed for IMes is mirrored in the SIMes study (Table 20). The $\%V_{bur}$ average is 36.6 and the standard deviation is 1.6. The limit values were obtain for the dicoordinated [(SIMes)$_2$Cu]PF$_6$ (37.4, entry 5) and the six-coordinate complexes [(SIMes)RuCl$_2$(Py)$_3$] (30.9, entry 8). A structural flexibility of mesityl-based NHCs is somewhat surprising as torsions and rotations would appear restrained. Variations of the mesityl moiety tilt appears to explain $\%V_{bur}$ differences. This is less pronounced for alkyl *N*-substituents and the steric flexibility of aryl-containing NHCs could explain the efficiency of these ligands in catalytic reactions.

The trend observed for *N*-mesityl substituents is valid and even amplified for IPr (Table 21).

For calculations with a M–NHC distance of 2.00 Å, the $\%V_{bur}$ average is 36.6 and a substantial standard deviation of 3.9 is calculated with values ranging from 31.0 to 47.6 (entries 2 and 15). We believe the *iso*-propyl groups enhance the flexibility of the NHC and consequently steric properties can be modulated in order to reply to congestion around the metal center. As a representative example of this flexibility, the IPr buried volume in linear [(IPr)AuBr] is 45.4, whereas for the square planar gold(III) complex [(IPr)AuBr$_3$] it decreases to only 34.2% (entries 2 and 3).

Linear dicoordinated [(IPr)Pd(PPh$_3$)] gives an IPr $\%V_{bur}$ of 47.6 while for the trigonal peroxo analogue [(IPr)Pd(O$_2$)PPh$_3$] the value is reduced to 36.7% (entries 32 and 33). Of note for those complexes, the length of Pd–NHC bonds is approximately

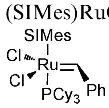
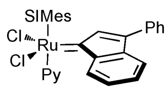
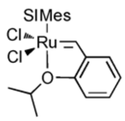
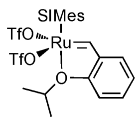
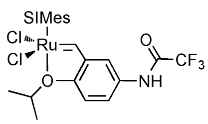
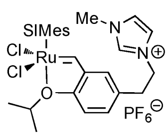
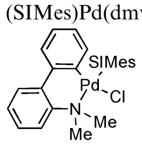
Table 19 IMes $\%V_{bur}$ comparison in various M(IMes) complexes

			$\%V_{bur}$ for M–NHC length at	
Entry	Complex	Reference	2.00 Å	2.28 Å
1	(IMes)AuCl	169	36.5	31.2
2	(IMes)$AuBr_3$	209	34.2	39.2
3	(IMes)AgCl	186	36.1	30.9
4	$(IMes)_2AgCl$	186	35.5	30.3
5	(IMes)CuBr	224	36.3	31.0
6	$[(IMes)_2Cu]PF_6$	218	37.1	31.7
7	(IMes)$CaN(SiMe_3)_2$	225	36.2	31.2
8	(IMes)$SrN(SiMe_3)_2$	225	37.1	32.1
9	(IMes)$BaN(SiMe_3)_2$	225	38.2	33.2
10	(IMes)FelCp(CO)	226	30.7	25.8
11	(IMes)$Ru(CO)_4$	227	32.5	27.4
12	(IMes)RuClCp*	228	33.3	28.3
13	(IMes)RuClCp*(CO)	229	31.2	26.3
14	(IMes)$RuH_2(CO)_2PPh_3$	230	33.0	27.9
15	(IMes)$RuClH(CO)_2PPh_3$	230	32.8	27.7
16		228	31.9	26.9
17		231	32.9	27.8
18	$(IMes)_2Ru(CO)_3$	230	31.8	26.8
19	$(IMes)_2$RuClH(CO)	230	35.2	30.2
20	(IMes)$Co(CO)_3Me$	232	32.7	27.6
21	(IMes)RhCl(cod)	233	33.5	28.5
22	(IMes)IrCl(cod)	8	33.0	28.0
23	(IMes)$IrCl(CO)_2$	8	33.8	28.7
24	[(IMes)Irl(cod)(Py)]PF_6	213	32.4	27.4
25	(IMes)NiClCp*	205	32.6	27.6
26	(IMes)$Ni(CO)_3$	11	34.0	28.9
27	$(IMes)_2Ni(CO)_2$	215	32.5	27.5
28	$(IMes)_2Ni$	234	34.6	29.4
29	(IMes)Pd(allyl)Cl	*9a*	33.9	28.8
30		235	34.9	30.1
31	$(IMes)_2Pd$	236	35.6	30.5
32	$(IMes)_2PdCl_2$	237	35.5	30.6
33	$(IMes)_2Pt$	234	35.7	30.5
34	(IMes)Pt(dvtms)	238	35.2	30.2
35	(IMes)$PtCl_2$(dmso)	239	33.5	28.6
36	(IMes)$ZnCl_2$(thf)	240	35.4	30.2
37	(IMes)$CdMe_2$	241	35.1	29.9
38	(IMes)AlH_3	242	35.2	30.0
39	(IMes)$GaCl_3$	243	34.2	29.0
40	(IMes)lnH_3	244	35.0	29.8
41	(IMes)$lnCl_3$	245	34.1	29.0
42	(IMes)UO_2Cl_2	245	34.3	29.1

the same.[272] Therefore the $\%V_{bur}$ variation cannot be caused by this parameter; only the structural organization of the NHC itself matters. In two-coordinate metal complexes, IPr buried volume can usually reach 38.0% (entries 1, 2, 4–8 and 32). Hexa-, penta- and square planar tetracoordinated complexes have an IPr $\%V_{bur}$ smaller than 35.0% (entries 9–19, 24–31, 35 and 36). For complexes showing a tetrahedral or trigonal geometry around the metal center, such as [(IPr)$Ni(CO)_3$], [(IPr)AlH_3] or $[(IPr)NiCl]_2$, the IPr $\%V_{bur}$ is intermediate to the two precedent categories (36.0–40.0%, entries 20, 22, 23, 33 and 37–39).

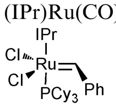
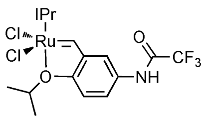
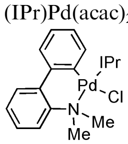
This observation raises an important point: it is clear that the [(NHC)$Ni(CO)_3$], [(NHC)$RhCl(CO)_2$], and [(NHC)$IrCl(CO)_2$] systems that have been used to quantify electronic properties of *N*-heterocyclic carbenes[8,11,277,278] are practically meaningful since with these systems NHC electronic and steric effects are very likely intimately related and cannot at this point be separated. The relatively flexible nature of IPr might also be at the origin of its very positive role as an ancillary ligand in catalysis. It is not only large but also flexible, a point that might have been underestimated so far in catalysis. In comparison to IPr, investigation of SIPr gives analogous

Table 20 SIMes $\%V_{bur}$ comparison in various M(SIMes) complexes

Entry	Complex	Reference	$\%V_{bur}$ for M–NHC length at 2.00 Å	$\%V_{bur}$ for M–NHC length at 2.28 Å
1	(SIMes)AuCl	169	36.9	31.7
2	(SIMes)AuBr$_3$	209	35.0	29.9
3	(SIMes)AgCl	186	36.1	30.8
4	(SIMes)CuCl	78	36.9	31.7
5	[(SIMes)$_2$Cu]PF$_6$	218	37.4	32.1
6	(SIMes)FeICp(CO)	226	31.6	26.6
7	(SIMes)RuCl(Cp*)	5	33.7	28.7
8	(SIMes)RuCl$_2$(Py)$_3$	246	30.9	26.0
9		247	32.8	27.8
10		248	31.7	26.6
11		249	33.7	28.6
12		250	35.3	30.1
13		251	35.0	29.9
14		231	34.7	29.5
15	(SIMes)RuCl(CO)PPh$_3$	252	36.3	31.2
16	(SIMes)IrCl(cod)	8	34.5	29.5
17	(SIMes)IrCl(CO)$_2$	8	35.0	29.8
18	[(SIMes)Irl(cod)(Py)]PF$_6$	253	33.4	28.3
19	(SIMes)NiClCp*	254	34.1	29.0
20	(SIMes)Ni(CO)$_3$	11	34.4	29.2
21	(SIMes)$_2$NiCl$_2$	255	34.9	29.8
22	(SIMes)Pd(allyl)Cl	9*a*	35.5	30.3
23	(SIMes)Pd(dmvts)	256	35.2	30.1
24		257	35.7	30.8
25	(SIMes)PtCl$_2$(dmso)	239	34.9	30.0
26	(SIMes)CdMe$_2$	241	36.4	31.1

outcomes (Table 22) with an average $\%V_{bur}$ of 38.7 and a slightly higher standard deviation: 4.1. SIPr $\%V_{bur}$ values vary from 32.8 for a metathesis catalyst to 47.0 for the gold(I) chloride (respectively, entries 7 and 1). The metal coordination number was also found determinant. The four-coordinate ruthenium [(SIPr)RuClH(CO)] shows a SIPr $\%V_{bur}$ of 35.6, whereas for 5-coordinate ruthenium [(SIPr)RuClH(CO)$_2$] this value is 33.2% (entries 9 and 10). The trend clearly indicates that the higher the metal coordination number, the smaller the percent buried volume value. Moreover, the geometry of the complex also plays a key role; in the case of tetra-coordinated metals, tetrahedral arrangement will lead to higher $\%V_{bur}$ than a square planar geometry. This demonstrates that a single model for the determination of steric properties for *N*-heterocyclic carbenes is unlikely. More importantly the steric properties ranking for NHC ligands can vary; I^{t}Bu and IAd are sterically more demanding than IPr and SIPr for complexes with a high coordination number and this tendency is reversed for low-coordinate metal complexes. This also highlights the fact that IPr and SIPr are sterically more flexible ligands.

Table 21 $\%V_{bur}$ comparison in various M(IPr) complexes

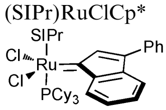
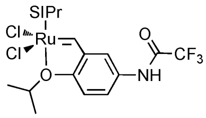
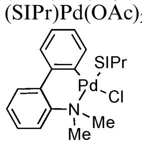
			$\%V_{bur}$ for M–NHC length at	
Entry	Complex	Reference	2.00 Å	2.28 Å
1	(IPr)AuCl	172	44.5	39.0
2	(IPr)AuBr	209	45.4	39.8
3	$(IPr)AuBr_3$	209	34.2	29.1
4	$[(IPr)AuPy]PF_6$	258	44.9	39.5
5	$[(IPr)_2Au]BF_4$	258	43.1	37.7
6	(IPr)AgCl	181	37.1	31.7
7	(IPr)CuCl	179	36.2	31.2
8	$[(IPr)_2Cu]BF_4$	259	38.0	32.6
9	$(IPr)Cr(CO)_4$	260	33.4	28.8
10	$(IPr)Ru(CO)_4$	227	34.5	29.2
11		261	32.4	27.4
12		262	34.9	29.7
13	$(IPr)_2RuH_2(CO)_2$	230	34.2	29.4
14	$(IPr)_2RuClH(CO)_2$	230	32.0	26.9
15	$(IPr)CoCpMe_2$	263	31.0	26.0
16	(IPr)RhCl(cod)	264	34.0	29.0
17	(IPr)IrCl(cod)	8	34.9	29.9
18	$(IPr)IrCl(CO)_3$	8	34.5	29.4
19	$[(IPr)Irl(cod)(Py)]PF_6$	214	35.1	30.2
20	$(IPr)Ni(CO)_3$	11	38.1	32.7
21	(IPr)Ni(allyl)Cl	265	36.9	31.8
22	(IPr)NiClCp	254	35.9	30.7
23	$[(IPr)NiCl]_2$	266	40.8	35.3
24	$(IPr)_2NiCl_2$	267	33.0	28.0
25	$(IPr)Pd(OAc)_2$	268	36.0	30.6
26	$(IPr)Pd(OAc)_2(H_2O)$	269	34.7	39.5
27	(IPr)PdCl(acac)	270	34.7	29.5
28	$(IPr)Pd(acac)_2$	270	36.6	31.6
29		235	32.3	27.2
30	(IPr)Pd(allyl)Cl	9*a*	35.2	29.9
31	$[(IPr)Pd(allyl)(MeCN)]PF_6$	271	35.4	29.5
32	$(IPr)PdPPh_3$	272	47.6	42.1
33	$(IPr)Pd(O_2)PPh_3$	272	36.7	31.6
34	$(IPr)_2Pd(dvtms)$	273	34.4	29.2
35	$(IPr)_2PdCl_2$	274	33.9	28.9
36	$(IPr)PtCl_2(octene)$	275	34.8	29.8
37	$(IPr)AlH_3$	276	40.1	34.6
38	$(IPr)GaCl_3$	243	37.2	31.8
39	$(IPr)lnBr_3$	276	37.9	32.5

7. Summary and outlook

The present study summarises results from some 700 X-ray data analyses using the percent buried volume steric model. The percent buried volumes of ligands bound to a metal center have been calculated using the Web-based Samb*V*ca software. The $\%V_{bur}$ values have to be considered with care since they are derived from solid state structures and conclusions regarding solution behavior might prove helpful but the results should not be over analysed (*caveat emptor*). Nevertheless, this model probably represents the best tool to analyse and hopefully understand ligand steric properties.

In summary, we have demonstrated that a simple correlation between the Tolman cone angle θ and the percent buried volume $\%V_{bur}$ exists. This relationship has been confirmed for tertiary phosphine ligands using X-ray structures of gold(I) chloride complexes and $\%V_{bur}$ calculations. Of note, phosphites do not fit this correlation, because their cone angles might have been underestimated and/or because of their variable sterics due to their more flexible nature. Further investigation into the gold(I) compounds shows that the second ligand on the metal center does not influence the buried volume of the phosphine, therefore buried volume of ligand L can be extracted from various (L)Au(I) complexes. This may

Table 22 SIPr $\%V_{bur}$ comparison in various M(SIPr) complexes

			$\%V_{bur}$ for M–NHC length at	
Entry	Complex	Reference	2.00 Å	2.28 Å
1	(SIPr)AuCl	169	47.0	41.5
2	(SIPr)$AuBr_3$	209	38.4	33.5
3	(SIPr)AgCl	181	45.5	40.1
4	(SIPr)CuCl	180	46.4	41.0
5	[$(SIPr)_2Cu$]PF_6	218	39.9	34.5
6	(SIPr)RuClCp*	5	33.9	28.7
7		279	32.8	27.6
8		262	35.7	30.5
9	(SIPr)RuClH(CO)	230	35.6	30.5
10	(SIPr)RuClH$(CO)_2$	230	33.2	28.1
11	(SIPr)Rh(acac)(CO)	280	34.6	31.4
12	(SIPr)IrCl(cod)	8	35.4	30.4
13	(SIPr)lrCl$(CO)_2$	8	37.7	32.7
14	(SIPr)Ni$(CO)_3$	11	39.0	33.6
15	(SIPr)NiClCp	254	36.9	31.7
16	[(SIPr)NiCl]$_2$	266	42.3	37.2
17	$(SIPr)_2Ni$	281	42.5	36.9
18	(SIPr)Pd(allyl)Cl	9*a*	41.1	36.3
19	(SIPr)Pd$(OAc)_2(H_2O)$	274	36.7	31.4
20		257	39.8	35.2
21	[(SIPr)$PdCl_2$]$_2$	282	38.1	33.1
22	(SIPr)Pt(dvtms)	238	38.1	34.2

also be the case for linear copper(I) complexes.[283] We have reported the $\%V_{bur}$ values of numerous phosphorus-based ligands including the very bulky biaryl phosphines introduced by the Buchwald group and calculated their cone angles by linear regression. Bidentate phosphines were also examined using X-ray structures of two different series of complexes [(AuCl)[R_2P-$(CH_2)_n$-PR_2](AuCl)] and [[R_2P-$(CH_2)_n$-PR_2]($PdCl_2$)]. On the one hand, the gold(I) system allows the determination of steric bulk of half the bidentate ligand; nevertheless these results have to be treated with caution due to specific spatial organization of the complexes. On the other hand palladium(II) system provided coherent values of steric properties for the complete ligand family.

We have also closely examined the percent buried volume of *N*-heterocyclic carbenes in order to gain insight into the steric properties of these very useful ligands in catalysis. As was the case with phosphine gold(I) chloride complexes, the NHC analyses provided rational data and $\%V_{bur}$ calculations could be extended and connected to other coinage metals: copper and silver. Investigations of some specific NHCs showed that the $\%V_{bur}$ of *N*-alkyl NHCs is almost independent of the metal complex whereas the environment of the metal center strongly influences *N*-aryl analogues. The (S)IMes and (S)IPr ligands showed that their steric properties are adjusted as a function of mainly the metal coordination number and thus demonstrate structural flexibility. As a result, the final ranking of the NHC steric hindrance is variable and related to the nature on the metal complexes. For two-coordinate metal complexes, the $\%V_{bur}$ value for I^{t}Bu is near that found for IMes and SIMes, and noticeably smaller than the one of IPr and SIPr. Alternatively for highly coordinated complexes, the buried volume decreases as follows I^{t}Bu ≈ IAd > SIPr ≈ IPr > SIMes ≈ IMes > ICy > IDM. The flexibility of NHCs possessing *N*-aryl substituents could be responsible for the excellent catalytic performances of systems containing these ligands. Thus as a function of the transition states, the NHC ligand could favor either the reactivity or the stability and facilitate the reaction in adapting/modulating its steric properties.

It is our sincere hope that the Samb*V*ca tool and this study will help to better understand late transition metal coordination chemistry, rationalise catalytic results and facilitate the rational design of even better performing catalytic systems.

Abbreviations

θ	cone angle
$\%V_{bur}$	percent buried volume
1,8-dpmn	1,8-bis((diphenylphosphino)methyl)-naphthalene
acac	acetyl acetonate
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINAP-Cy	2,2′-bis(dicyclohexylphosphino)-1,1′-binaphthyl

BINAP-*p*-Tol	2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl
BrettPhos	dicyclohexyl(2′,4′,6′-*tri*-*iso*-propyl-3,6 dimethoxybiphenyl-2-yl)phosphine
CIF	crystallographic information file
Cy-Johnphos	biphenyl-2-yldicyclohexylphosphine
Cy-Segphos	5,5′-bis(dicyclohexylphosphino)-4,4′-bibenzo-[*d*][1,3]dioxole
d(DIPP)pe	1,2-bis(bis(2,6-di-*iso*-propylphenyl)phosphino) ethane
d(Mes)pe	1,2-bis(dimesitylphosphino)ethane
DavePhos	2′-(dicyclohexylphosphino)-*N*,*N*-dimethyl-biphenyl-2-amine
dbfphos	4,6-bis(diphenylphosphino)dibenzo[*b*,*d*]furan
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dcpf	1,1′-bis(dicyclohexylphosphino)ferrocene
DIOP	(2,2-dimethyl-1,3-dioxolane-4,5-diyl)-bis(methylene)bis(diphenylphosphine)
DIPP	2,6-di-*iso*-propylphenyl
d*i*Prpf	1,1′-bis(di-*iso*-propylphosphino)ferrocene
dmpf	1,1′-bis(dimethylphosphino)ferrocene
dpbp	2,2′-bis(diphenylphosphino)biphenyl
DPEPhos	2,2′-oxybis(2,1-phenylene)bis(diphenyl-phosphine)
dppf	1,1′-bis(diphenylphosphino)ferrocene
dpp-benzene	1,2-bis(diphenylphosphino)benzene
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dpph	1,6-bis(diphenylphosphino)hexane
dppm	bis(diphenylphosphino)methane
dppn	2,7-bis(diphenylphosphino)-1,8-naphthyridine
dppo	1,1′-bis(diphenylphosphino)osmocene
dppp	1,3-bis(diphenylphosphino)propane
dppent	1,5-bis(diphenylphosphino)pentane
dppr	1,1′-bis(diphenylphosphino)ruthenocene
dppx	1,2-bis((diphenylphosphino)methyl)benzene
Duphos-Me	1,2-bis(2,5-dimethylphospholano)benzene
d*t*Bupf	1,1′-bis(di-*tert*-butylphosphino)ferrocene
dvtms	divinyltetramethylsiloxane
IAd	1,3-bisadamantylylimidazol-2-ylidene
ICy	1,3-biscyclohexylimidazol-2-ylidene
IDM	1,3-bismethylimidazol-2-ylidene
IMes	1,3-dimesitylimidazol-2-ylidene
IPr	1,3-bis(2,6-di-*iso*-propylphenyl)imidazol-2-ylidene
I^{t}Bu	1,3-bis-*tert*-butylimidazol-2-ylidene
JohnPhos	biphenyl-2-yldi-*tert*-butylphosphine
L	neutral ligand
M	metal
Me-FerroLANE	1,1′-bis(dimethylphospholano)ferrocene
MePhos	dicyclohexyl(2′-methylbiphenyl-2-yl)phosphine
NHC	*N*-heterocyclic carbene
Py	pyridine
Segphos	5,5′-bis(diphenylphosphino)-4,4′-dibenzo[*d*]-[1,3]dioxole
SIMes	1,3-dimesityl-4,5-dihydroimidazol-2-ylidene
SIPr	1,3-bis(2,6-di-*iso*-propylphenyl)-4,5dihydro imidazol-2-ylidene
SPhos	dicyclohexyl(2′,6′-dimethoxybiphenyl-2-yl) phosphine
TADDOL	(2,2-dimethyl-1,3-dioxolane-4,5-diyl)-bis(diphenyl methylene)bis(oxy)bis(diphenyl-phosphine)
*t*Bu-XPhos	di-*tert*-butyl(2′,4′,6′-triisopropylbiphenyl-2-yl) phosphine
TPA	1,3,5-triaza-7-phosphaadamantane
TRANSphos	2,11-bis((diphenylphosphino)methyl)benzo[*c*] phenanthrene
Xantphos	(9,9-dimethyl-9*H*-xanthene-4,5-diyl)-bis(diphenyl phosphine)
XPhos	dicyclohexyl(2′,4′,6′-tri-*iso*-propylbiphenyl-2-yl) phosphine

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