Electronic Supplementary Material (ESI) for ChemComm.


# Quantifying and understanding the steric properties of *N*-heterocyclic carbenes

Adrián Gómez-Suárez,[a] David J. Nelson,[b] and Steven P. Nolan[c]

[a]*Organic Chemistry Institute, WWU Münster, Corrensstrasse 40, 48149 Münster, Germany.*

[b]*WestCHEM Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK.*

[c]*Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 – S3, 9000 Gent, Belgium.*

**Table S1.** Buried volumes calculated for IMes-containing complexes from the CCDC; each reference is listed, plus the buried volume (%$V_{bur}$) determined at metal-carbon bond lengths of 2.00 and 2.28 Å.[a]

| Reference | | 2.00 Å | 2.28 Å | | 2.00 Å | 2.28 Å | | 2.00 Å | 2.28 Å | | 2.00 Å | 2.28 Å | Error (2.00 Å) | Error (2.28 Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BIGYEV | **In1** | 34.4 | 29.82 | **In2** | 34.0 | 28.8 | | | | | | | 0.4 | 0.4 |
| BOGQOF | **Ni1** | 33.6 | 28.6 | **Ni2** | 33.7 | 28.7 | | | | | | | 0.1 | 0.1 |
| CAJFOK | **W1** | 33.6 | 28.5 | **W2** | 32.2 | 27.2 | | | | | | | 1.4 | 1.3 |
| COMVOK | **Ir1** | 32.1 | 27.2 | **Ir2** | 32.4 | 27.5 | | | | | | | 0.3 | 0.3 |
| COMVUX | **Ir1** | 31.6 | 26.8 | **Ir2** | 31.8 | 26.9 | | | | | | | 0.2 | 0.1 |
| DEJJAE | **Fe1** | 31.1 | 26.2 | **Fe2** | 31.1 | 26.1 | **Fe3** | 31.2 | 26.2 | **Fe4** | 31.3 | 26.4 | 0.2 | 0.3 |
| EFUXAF | **Pd1** | 34.5 | 29.6 | **Pd2** | 34.8 | 29.9 | | | | | | | 0.3 | 0.3 |
| HOVTOC | **Sn1** | 34.4 | 29.2 | **Sn2** | 34.0 | 28.9 | | | | | | | 0.4 | 0.3 |
| JUPVAT | **Ga1** | 35.3 | 30.0 | **Ga2** | 34.3 | 29.1 | | | | | | | 1.0 | 0.9 |
| LOMPUZ | **Fe1** | 31.2 | 26.3 | **Fe2** | 31.9 | 27.0 | | | | | | | 0.7 | 0.7 |
| LUFWIS | **In1** | 34.2 | 29.0 | **In2** | 34.1 | 28.9 | | | | | | | 0.1 | 0.1 |
| MAJBAC | **Pt1** | 34.1 | 29.1 | **Pt2** | 34.1 | 29.0 | | | | | | | 0.0 | 0.1 |
| MIVGEF | **Fe1** | 33.1 | 28.0 | **Fe2** | 33.5 | 28.3 | | | | | | | 0.4 | 0.3 |
| NAPQOM | **Ni1** | 34.6 | 29.4 | **Ni2** | 33.9 | 28.9 | | | | | | | 0.7 | 0.5 |
| NEHBAE[b] | **Ag1** | 34.8 | 29.7 | **Ag1'** | 35.5 | 30.4 | **Ag2** | 35.5 | 30.4 | **Ag2'** | 35.9 | 30.8 | | |
| | **Ag3** | 35.8 | 30.7 | **Ag3'** | 35.6 | 30.4 | | | | | | | 1.1 | 1.1 |
| NEHBOS | **Rh1** | 33.4 | 28.3 | **Rh2** | 32.9 | 27.9 | | | | | | | 0.5 | 0.4 |
| NISJIJ | **Os1** | 31.0 | 26.0 | **Os2** | 33.4 | 28.3 | | | | | | | 2.4 | 2.3 |
| OLUQIW01 | **Au1** | 35.0 | 29.8 | **Au2** | 34.7 | 29.5 | | | | | | | 0.3 | 0.3 |
| PUNLEQ[b] | **Ru1** | 32.0 | 27.0 | **Ru1'** | 31.9 | 26.8 | **Ru2** | 32.2 | 27.1 | **Ru2'** | 31.5 | 26.4 | 0.7 | 0.7 |
| QIWPES | **Ir1** | 32.9 | 27.9 | **Ir2** | 33.1 | 28.1 | | | | | | | 0.2 | 0.2 |
| REHXIM | **Pd1** | 34.3 | 29.2 | **Pd2** | 34.1 | 29.0 | | | | | | | 0.2 | 0.2 |
| RINHOL | **Tl1** | 34.7 | 29.4 | **Tl2** | 34.4 | 29.2 | | | | | | | 0.3 | 0.2 |
| SONGEJ | **Pt1** | 35.1 | 29.8 | **Pt2** | 34.5 | 29.3 | | | | | | | 0.6 | 0.5 |
| SONGUZ | **Pt1** | 35.9 | 30.8 | **Pt2** | 36.5 | 31.4 | | | | | | | 0.6 | 0.6 |
| TUCRUF | **Pd1** | 33.9 | 28.7 | **Pd2** | 34.7 | 29.6 | | | | | | | 0.8 | 0.9 |
| TUTSIK[b] | **Ru1** | 31.4 | 26.4 | **Ru1'** | 32.1 | 27.1 | **Ru2** | 31.7 | 26.7 | **Ru2'** | 31.4 | 26.4 | 0.7 | 0.7 |
| WEZDIQ | **Mn1** | 31.9 | 26.9 | **Mn2** | 31.7 | 26.7 | **Mn3** | 32.0 | 27.0 | **Mn4** | 31.6 | 26.7 | 0.4 | 0.3 |

[a] Criteria for inclusion: $R < 0.05$ and $Z' \geq 2$. [b] Contains multiple structures, each with two NHCs in the same environment. Due to symmetry, these are treated as multiple measures of the conformation (and steric impact) of the IMes ligand.

Table 1. Buried volumes calculated for IPr-containing complexes from the CCDC; each reference is listed, plus the buried volume (%Vbur) determined at metal-carbon bond lengths of 2.00 and 2.28 Å.a

| Reference | | 2.00 Å | 2.28 Å | | 2.00 Å | 2.28 Å | | 2.00 Å | 2.28 Å | | 2.00 Å | 2.28 Å | Error (2.00 Å) | Error (2.28 Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ASICUB | **Au1** | 47.7 | 42.1 | **Au2** | 45.4 | 39.8 | | | | | | | 2.3 | 2.3 |
| BAQSOC | **Pd1** | 32.4 | 27.3 | **Pd2** | 32.2 | 27.2 | | | | | | | 0.2 | 0.1 |
| BEHXET | **Ge1** | 35.8 | 30.6 | **Ge2** | 36.6 | 31.3 | | | | | | | 0.8 | 0.7 |
| CESZUX01 | **Fe1** | 37.3 | 31.8 | **Fe2** | 37.8 | 32.4 | | | | | | | 0.5 | 0.6 |
| CODGUZ | **Cu1** | 44.5 | 39.0 | **Cu2** | 46.2 | 40.5 | | | | | | | 1.7 | 1.5 |
| DIMWIH | **Pd1** | 34.2 | 29.1 | **Pd2** | 37.8 | 32.9 | | | | | | | 3.6 | 2.8 |
| DOZHAC | **Au1** | 44.6 | 38.9 | **Au2** | 45.3 | 39.7 | | | | | | | 0.7 | 0.8 |
| EFUNOK | **Au1** | 43.9 | 38.4 | **Au2** | 46.3 | 40.7 | | | | | | | 2.4 | 2.3 |
| FUPKUY | **Au1** | 33.5 | 28.4 | **Au2** | 37.3 | 32.3 | | | | | | | 3.8 | 3.9 |
| GILKIX | **Au1** | 37.0 | 32.0 | **Au2** | 36.3 | 31.3 | | | | | | | 0.7 | 0.7 |
| GUVQIZ | **Rh1** | 38.0 | 33.3 | **Rh2** | 36.5 | 31.6 | | | | | | | 1.5 | 1.7 |
| HOBPAR | **Cu1** | 46.9 | 41.3 | **Cu2** | 46.8 | 41.2 | | | | | | | 0.1 | 0.1 |
| HOXZOK | **Pt1** | 39.5 | 34.1 | **Pt2** | 42.8 | 37.3 | | | | | | | 3.3 | 3.2 |
| INOXEP | **Au1** | 45.3 | 39.7 | **Au2** | 42.8 | 37.4 | | | | | | | 2.5 | 2.3 |
| JOLFIB[b] | **Ni1** | 34.6 | 29.6 | **Ni1'** | 36.0 | 30.9 | **Ni2** | 33.9 | 28.8 | **Ni2'** | 34.5 | 29.4 | 2.1 | 2.1 |
| KOKZAN | **Zn1** | 37.7 | 32.2 | **Zn2** | 39.3 | 33.8 | | | | | | | 1.6 | 1.6 |
| KOTYUP | **Au1** | 44.6 | 39.0 | **Au2** | 45.6 | 40.1 | | | | | | | 1.0 | 1.1 |
| MADYUN | **Ir1** | 34.4 | 29.6 | **Ir2** | 34.0 | 29.0 | | | | | | | 0.4 | 0.6 |
| NEZCIG | **Pd1** | 40.5 | 35.1 | **Pd2** | 38.2 | 32.8 | | | | | | | 2.3 | 2.3 |
| NICWIG | **Au1** | 34.2 | 29.1 | **Au2** | 34.3 | 29.1 | | | | | | | 0.1 | 0.0 |
| NIPLUV | **Sn1** | 35.5 | 30.3 | **Sn2** | 34.6 | 29.4 | **Sn3** | 35.0 | 29.8 | | | | 0.9 | 0.5 |
| OZIBOP | **Au1** | 44.6 | 39.1 | **Au2** | 43.6 | 38.1 | | | | | | | 1.0 | 1.0 |
| PIKLOL | **Ga1** | 37.0 | 31.6 | **Ga2** | 37.5 | 32.0 | | | | | | | 0.5 | 0.4 |
| PIYNOC | **Au1** | 42.5 | 37.0 | **Au2** | 41.2 | 35.8 | **Au3** | 41.2 | 35.8 | **Au4** | 42.6 | 37.2 | 1.4 | 1.4 |
| PIYVIE[b] | **Ni1** | 33.7 | 28.6 | **Ni2** | 34.6 | 29.6 | **Ni3** | 35.5 | 30.4 | **Ni4** | 34.4 | 29.2 | 1.8 | 1.8 |
| POJPAG | **Pd1** | 46.4 | 41.0 | **Pd2** | 47.7 | 42.2 | | | | | | | 1.3 | 1.2 |
| POJPIO | **Pd1** | 36.3 | 31.1 | **Pd2** | 37.2 | 32.2 | | | | | | | 0.9 | 1.1 |
| QIGBOZ | **Cu1** | 39.6 | 34.6 | **Cu2** | 40.4 | 35.5 | | | | | | | 0.8 | 0.9 |
| QIWMAL | **Ir1** | 36.0 | 31.1 | **Ir2** | 33.9 | 28.9 | | | | | | | 2.1 | 2.2 |
| QOCRUX | **Ni1** | 35.0 | 29.7 | **Ni2** | 35.9 | 30.6 | | | | | | | 0.9 | 0.9 |
| QOSHUC | **Pd1** | 37.8 | 32.9 | **Pd2** | 39.7 | 34.9 | | | | | | | 1.9 | 2.0 |
| SICKIA | **Au1** | 42.2 | 36.9 | **Au2** | 41.9 | 36.4 | | | | | | | 0.3 | 0.5 |
| SOCFAT | **Au1** | 42.7 | 37.1 | **Au2** | 45.0 | 39.4 | | | | | | | 2.3 | 2.3 |
| SOPZUU[b] | **Pd1** | 36.7 | 31.9 | **Pd2** | 33.1 | 27.9 | **Pd3** | 34.6 | 29.7 | **Pd4** | 33.6 | 28.6 | 3.6 | 4.0 |
| SOQPUL | **Ir1** | 36.5 | 31.4 | **Ir2** | 35.0 | 29.9 | | | | | | | 1.5 | 1.5 |
| TEGZOV | **Pd1** | 36.7 | 31.5 | **Pd2** | 35.8 | 30.6 | | | | | | | 0.9 | 0.9 |
| UBIFES | **Rh1** | 35.7 | 31.0 | **Rh2** | 36.2 | 31.6 | | | | | | | 0.5 | 0.6 |
| VEBJUJ | **Co1** | 34.6 | 29.3 | **Co2** | 37.0 | 31.8 | | | | | | | 2.4 | 2.5 |
| VUCRUI | **Pd1** | 36.0 | 30.8 | **Pd2** | 38.5 | 33.4 | **Pd3** | 36.1 | 30.9 | | | | 2.5 | 2.6 |
| XONMET | **Ni1** | 40.7 | 35.2 | **Ni2** | 41.2 | 35.6 | | | | | | | 0.5 | 0.4 |
| YOWXUF | **Os1** | 31.2 | 26.5 | **Os2** | 31.4 | 26.7 | | | | | | | 0.2 | 0.2 |
| YUGTEA | **Ge1** | 37.8 | 32.4 | **Ge2** | 38.1 | 32.6 | | | | | | | 0.3 | 0.2 |
| ZEXMUM[c] | **Au1** | 40.9 | 35.4 | **Au2** | 41.3 | 35.8 | | | | | | | 0.4 | 0.4 |
| | **Au1'** | 39.9 | 34.4 | **Au2'** | 41.1 | 35.7 | | | | | | | 1.2 | 1.3 |
| ZIHPAJ | **Au1** | 36.4 | 31.5 | **Au2** | 37.6 | 32.7 | | | | | | | 1.2 | 1.2 |
| ZUWGIJ | **Co1** | 34.7 | 29.4 | **Co2** | 32.5 | 27.3 | | | | | | | 2.2 | 2.1 |

[a)] Criteria for inclusion: $R < 0.05$ and $Z' \geq 2$. Structures with significant disorder at the ligand were excluded. [b)] Contains multiple structures, each with two NHCs in the same environment. Due to symmetry, these are treated as multiple measures of the conformation (and steric impact) of the IPr ligand. [c)] Contains two structures, each with two Au atoms in different environments.