ORGANOMETALLICS
Note
pubs.acs.org/Organometallics

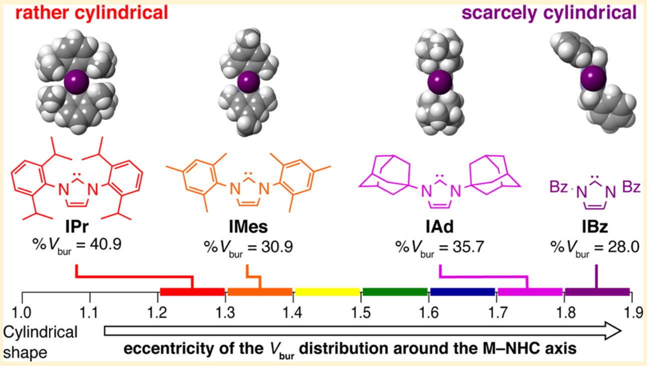
Learning about Steric Effects in NHC Complexes from a 1D Silver Coordination Polymer with Fréchet Dendrons

Alba M. Ortiz, Pilar Gómez-Sal, Juan C. Flores,* and Ernesto de Jesús*

Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá, 28871 Alcalá de Henares, Spain

Supporting Information

ABSTRACT: The complex (NHC)AgBr, which bears G1 poly(benzyl ether) dendritic substituents in the NHC ligand, forms a 1D coordination polymer based on unusual zigzag −Ag−halide− chains. The asymmetric distribution of the volume buried by the NHC ligand in the Ag coordination sphere is important to explain the formation of this structure. A V_{bur} eccentricity parameter has been introduced and used in conjunction with the $\%V_{\text{bur}}$ descriptor to analyze the X-ray structures of 100 (NHC)AgX complexes.

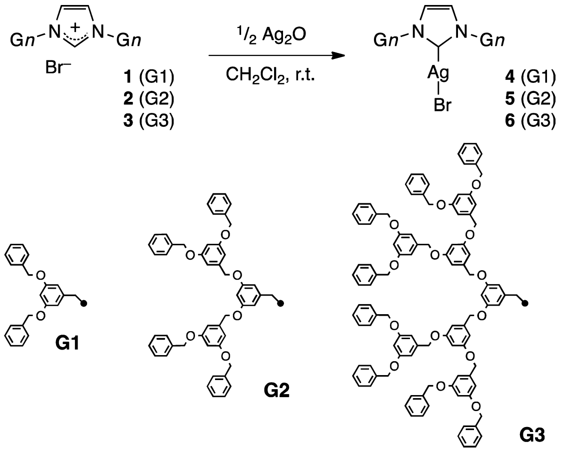


An extensive array of structural topologies in which the metal displays a wide range of coordination numbers and geometries are known for silver(I) complexes.[1] This coordinative flexibility is in part due to the lack of stereochemical preference arising from the d^{10} configuration and weak nature of the bond between this soft acceptor and most donors.[2] The plasticity of Ag(I) is of interest for crystal engineering and subsequent potential applications[3] because weak interactions acquire a greater influence, and factors such as small ligand variations can drastically modify the supramolecular assembly process.[4] In this regard, N-heterocyclic carbene ligands (NHC) are appealing due to their versatile functionalization and the synthetic availability and air and water stability of their Ag(I) complexes. This has led to a plethora of silver NHC complexes[5−7] with a wide diversity of supramolecular motifs, ranging from discrete arrangements to extended staircase structures, aesthetic cages, or cubane-type clusters.[8]

As a consequence of our interest in the structural chemistry of metallodendrimers,[9,10] this report describes the unusual zigzag −Ag−halide− chain formed in the solid state by the (NHC)AgBr dendritic complex **4**. The importance of the asymmetric distribution of the volume buried by the NHC ligand will be outlined, leading to the introduction of a V_{bur} eccentricity parameter that might be a useful addition to the $\%V_{\text{bur}}$ descriptor.

Silver(I) NHC complexes **4**−**6**, which have previously been utilized as "non-isolated" intermediates for carbene transmetalation to Rh(I),[11] were obtained using Lin's standard procedure (Scheme 1).[12] Preparation of the imidazolium precursors **1**−**3** was also optimized using a stepwise protocol that simplified the purification steps and significantly increased the overall yields. Full synthetic and characterization details are given in the Supporting Information.

Scheme 1. Synthesis of the NHC Silver Complexes



We were only able to obtain suitable crystals for X-ray diffraction studies in the case of the G1 complex (**4**). The difficulties associated with the growth of single crystals from large dendrimers is well known and, therefore, it is not surprising that the few X-ray structures reported for metal complexes containing Fréchet dendrons correspond to generations G1[11,13] and G2.[10] Complex **4** crystallizes as 1D zigzag chains which are formed by the assembly of (NHC)AgBr units by halide bridges to give a planar three-coordinate silver environment (Figure 1). The C_2 axis defined by the Ag−C_{NHC} bond renders the $-(\text{AgBr})_n-$ chain symmetric, with identical Ag−Br distances (2.662 Å) and Br−Ag−Br and Ag−Br−Ag angles (106.5°). The monomers are

Received: October 31, 2013
Published: January 10, 2014

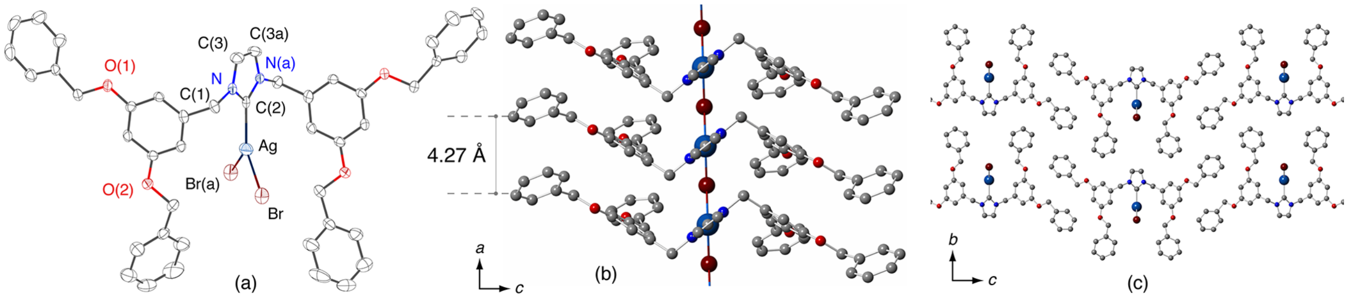


Figure 1. (a) ORTEP diagram showing the silver coordination environment in **4** (H atoms omitted for clarity). (b) View of a single 1D chain along the crystallographic *b* axis. (c) View along the *a* axis. Selected bond lengths (Å) and angles (deg): Ag−Br, 2.662(1); Ag−Br(a), 2.662(1); Ag−C(2), 2.152(6); N−C(2), 1.372(5); N−C(1), 1.500(5); C(3)−C(3a), 1.350(10); C(2)−Ag−Br, 126.75(2); Br−Ag−Br(a), 106.50(3); Ag−Br−Ag(a), 106.50(3); Ag−C(2)−N, 128.0(2); N−C(2)−N(a), 104.1(5); C(2)−N−C(1), 122.5(4).

propagated along the crystallographic *a* axis at a constant distance of 4.27 Å. This dense stacking of NHC ligands is sterically possible because the dendrons are fully extended (Ph−C−O−Ar torsion angles of 174−175°) and the NHC rings are rotated around the perpendicular to the propagating axis *a* (N−C(2)−Ag−Br torsion angle of 52.9°).[10,14] The Ag−C_{NHC} distance of 2.15 Å is longer than that observed in $[(IBz)AgBr]_2$ (2.10 Å)[15] and in most (NHC)Ag(halide) complexes (usually 2.08−2.10 Å).[5] The Ag−Br distance (2.662 Å) is also longer than in [(NHC)AgBr] monomers (2.40−2.43 Å)[16] and intermediate between the short (2.4−2.5 Å) and long Ag−Br distances (2.8−3.1 Å) found in $[(NHC)Ag(\mu\text{-Br})]_2$ dimers.[15,16]

Although single-stranded Ag(I) coordination polymers are common, they are typically accessible by means of bidentate ligands bridging the metal atoms,[1] whereas those exclusively enchained by halide bridges are rare.[17] Indeed, the complex (phen)AgCl is the only precedent in the Cambridge Structural Database (CSD) of an unsupported zigzag $-(Ag(halide))_n-$ chain.[18] Both polymeric structures display π-stacked aromatic rings (phen or Bz) in a parallel-displaced disposition of close geometric parameters. These parameters are compared in Table 1 with those reported by Janiak on the basis of the most frequent values found in the CSD database for π-stacked pyridine complexes[19,20] and with those determined by Sinnokrot et al. based on ab initio calculations on benzene dimers.[21] The distances between ring centroids within the chains (4.3 Å) are imposed by the geometry of the halide bridges, whereas ligand rotation with respect to the perpendicular to the chain axis results in short interplanar distances (3.4−3.8 Å) and large parallel displacements between rings in the stacks (1.9−2.6 Å). The temptation to assign a determinant role in the solid-state organization of **4** to π−π interactions must be resisted. First, the large slippage moves the C_6 rings away from the distances more favorable for attractive interactions between aromatic rings. Second, and more importantly, interactions between small π rings are not necessarily stronger than those between saturated fragments of the same number of C atoms.[22,23] In other words, the geometrical existence of stacked aromatic rings does not necessarily involve an abnormal added stabilization that will inevitably force a given structural arrangement.

Table 1. Comparison of Geometric Parameters (Å) for the Parallel-Displaced π Stacking of Aromatic Rings

	$d_{cent-cent}$[a]	$d_{interplanar}$[b]	d_{slip}[c]
4	4.27	3.41−3.82	1.91−2.57
(phen)AgCl[18]	4.28	3.37	2.64
CSD database[d]	3.8	3.6	1.3
ab initio calc[e]	3.6	3.2	1.6

[a] Distance between centroids of adjacent rings in the π stack. [b] Distance between the ring planes. [c] Ring slippage. [d] Most frequent parameters found in structures containing almost parallel pyridine rings after searches in the CSD database.[19] [e] Equilibrium distances in benzene dimers in parallel-displaced configurations, as determined by ab initio calculations.[21]

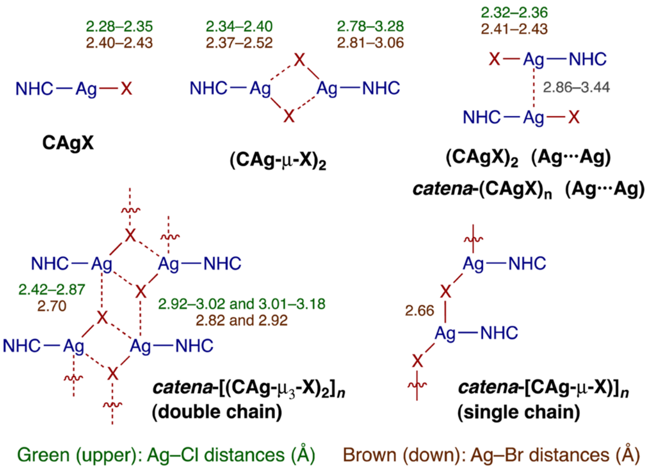


Figure 2. Structural arrangements of (NHC)Ag(halide) units in the solid state. Halide-bridged dimers are usually asymmetric. Double chains are constituted of dimers stacked by formation of a third X bridge. The single-chain structure corresponds to **4**.

Consequently, we focused our attention on the silver coordination sphere. Figure 2 shows a structural classification of (NHC)Ag(halide) complexes that is mostly based on the reviews of Garrison[5] and Lin,[6] omitting the cases in which $(NHC)_2Ag^+$ ions are formed. To analyze more exactly at which point steric effects and structural types are linked, we calculated the percent buried volume ($\%V_{bur}$)[24,25] for the NHC ligands in around 100 reported X-ray structures containing monodentate NHC ligands. The resulting distribution of $\%V_{bur}$, which is represented in Figure 3, outlines the limits imposed by the steric crowding of the NHC ligand on the tendency of the AgX moieties to condense by formation of halide bridges or argentophilic interactions. In this context, the combination of a very high $\%V_{bur}$ (42.2) with a chain structure in **4** is unusual. Indeed, this is possible because the distribution of the NHC-buried volume around the metal center is highly polarized in two of the three spatial dimensions (corresponding to the crystallo-

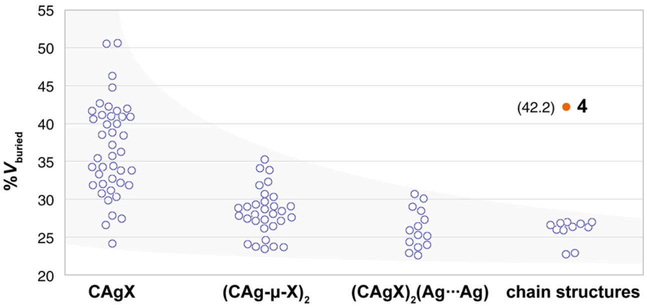


Figure 3. Distribution of percent buried volumes for NHC ligands by structural type of the (NHC)Ag(halide) complex. $\%V_{bur}$ values were calculated at an M−NHC distance of 2.28 Å.

graphic b and c axes, Figure 1c), thereby leaving free space for propagation of the chain in the a direction.[26]

To overcome the limitations of $\%V_{bur}$ as an average property, 2D contour maps are becoming popular as a powerful tool for detailed analysis of the impact of V_{bur} asymmetry on limited sets of complexes.[27] However, the simplicity of a single parameter for measuring the steric asymmetry, especially that originating around the metal−C_{NHC} bond, might be practical for understanding structural or chemical trends in large sets of complexes. As such, herein we propose a definition for such a parameter based on the well-established $\%V_{bur}$ and conveniently calculated using the SambVca application.[25] This parameter is especially pertinent for NHC ligands because of their noncylindrical (planar) core, although the methodology is also applicable to phosphanes and other common ligands. We start by considering an ellipsoid with three independent dimensions (a, b, and c) and a spheroid, which represents a special case of an ellipsoid with symmetry around the c axis ($a = b$, Figure 4). When an ellipsoid is rotated around the c axis, the overlap between the original and rotated ellipsoids is determined by the relative length of the semiprincipal axes a and b. The overlap coefficient is $S = 1$ for a spheroid S and decreases as the eccentricity of the ellipsoid increases. Considering the ellipsoid as an acceptable analogy, we calculated the buried volume overlap for NHC ligands in (NHC)AgX complexes by considering the metal−NHC bond as the axis for the 90° rotation (see the Supporting Information for details). The results for a selection of NHC ligands are given in Figure 5 in the form of a/b values, calculated using the formula shown in Figure 4, as this gives a more workable scale of values than the direct use of S.[28]

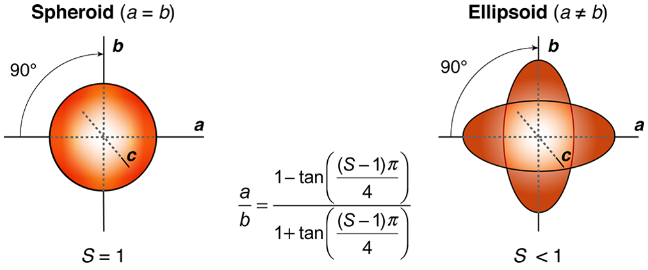


Figure 4. Overlap ratio (S) between an ellipsoid and the same ellipsoid rotated by 90° around the c axis. This value is equal to 1 for a spheroid and decreases with the asymmetry of the a and b dimensions, in accordance with the displayed formula.

When the structures of (NHC)AgX complexes with symmetrically substituted NHC ligands are placed in a 2D map of percent buried volume and eccentricity values, a borderline above which steric factors prevent the formation of condensed structures appears at the top (Figure 6).[29] The positive slope of the borderline means that condensed structures are compatible with ligands of low steric demand or with ligands of higher steric demand when this demand is directionally focused (as for **4**). Condensed structures prevail below the borderline, but crystal packing or other weak forces can determine the formation of monomers due to the stereochemical nonrigidity of silver(I).

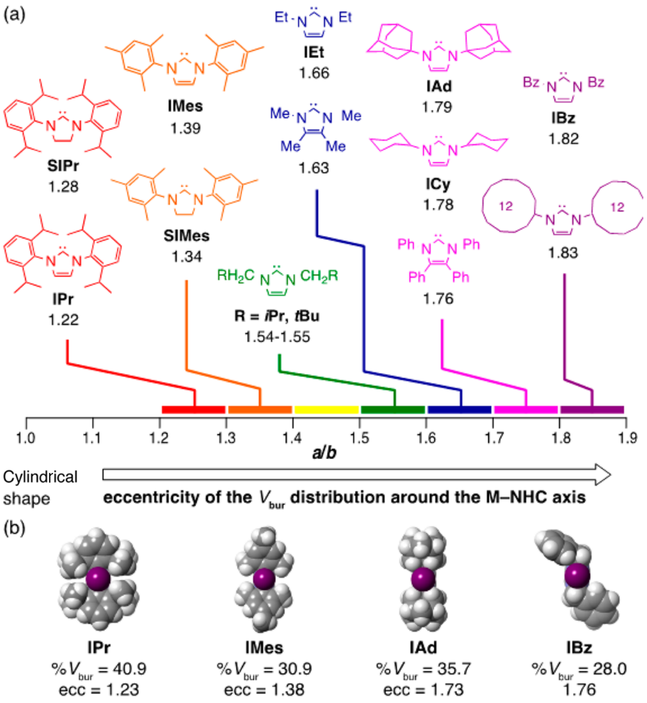


Figure 5. (a) Buried volume eccentricities for a set of representative NHC ligands, determined as described in the text. (b) Space-filling representation of selected NHC ligands.

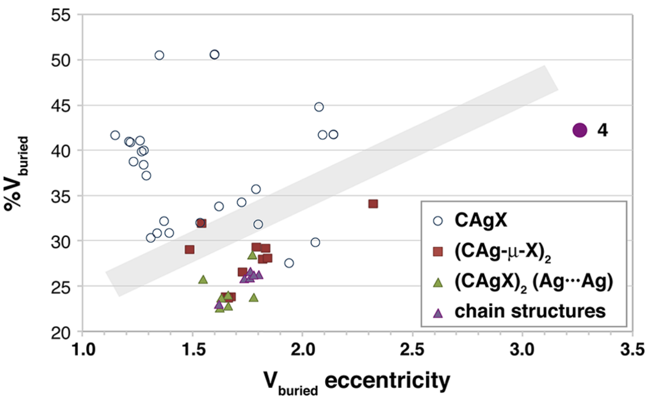


Figure 6. Distribution of the structures reported for (NHC)AgX complexes with symmetrically substituted NHC ligands in the 2D map of percent buried volumes and eccentricities.

In summary, the singular zigzag-chain arrangement found in **4** can be understood in steric terms when the asymmetry of the ligand is considered. The combined use of $\%V_{bur}$ and the eccentricity parameter proposed herein is useful for understanding the solid-state structures of silver NHC complexes. This approach can be convenient in other contexts in which the shape and orientation of the NHC N substituents are considered to be determining factors. The V_{bur} eccentricity is sensitive to them and complements the %V_{bur} value. For instance, the IAd ligand has a %V_{bur} value intermediate between those of bulky IMes and IPr ligands (Figure 5b) but its V_{bur} eccentricity is much higher. This is in agreement with the differences found in the reactivity of their metal complexes, which arise from localization of the most hindered region around the adamantyl group.[30]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and a CIF file giving general and synthetic procedures, characterization data, crystallographic data for **4**, calculations and V_{bur} eccentricity values for (NHC)Ag(halide) structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ernesto.dejesus@uah.es (E.d.J.); juanc.flores@uah.es (J.C.F.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ministerio de Economía y Competitividad (Projects CTQ2011-24096 and CSD2006-00015). A.M.O. is grateful to the Ministerio de Educación for a FPU Fellowship. Dedicated to Professor A. Laguna on the occasion of his 65th birthday.

■ REFERENCES

(1) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. *Coord. Chem. Rev.* **2001**, *222*, 155−192.

(2) Young, A. G.; Hanton, L. R. *Coord. Chem. Rev.* **2008**, *252*, 1346−1386.

(3) Lu, X.; Zhang, W.; Wang, C.; Wen, T.-C.; Wei, Y. *Prog. Polym. Sci.* **2011**, *36*, 671−712. Constable, E. C. In *Supramolecular Chemistry: From Molecules to Nanomaterials*; Steed, J. W., Gale, P. A., Eds.; Wiley: Hoboken, NJ, 2012; Vol. 6, pp 3073−3086. Haj, M. A.; Aakeröy, C. B.; Desper, J. *New J. Chem.* **2013**, *37*, 204−211.

(4) Hutchinson, D. J.; Cameron, S. A.; Hanton, L. R.; Moratti, S. C. *Inorg. Chem.* **2012**, *51*, 5070−5081. Akhbari, K.; Morsali, A. *Inorg. Chem.* **2013**, *52*, 2787−2789.

(5) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978−4008.

(6) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642−670.

(7) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561−3598.

(8) Li, Q.; Li, X.; Yang, J.; Song, H.-B.; Tang, L.-F. *Polyhedron* **2013**, *59*, 29−37. Ahamed, B. N.; Dutta, R.; Ghosh, P. *Inorg. Chem.* **2013**, *52*, 4269−4276. Clark, W. D.; Tyson, G. E.; Hollis, T. K.; Valle, H. U.; Valente, E. J.; Oliver, A. G.; Dukes, M. P. *Dalton Trans.* **2013**, *42*, 7338−7344.

(9) Sánchez-Mendez, A.; Benito, J. M.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R.; Gómez-Sal, P. *Dalton Trans.* **2006**, 5379−5389.

(10) Sánchez-Méndez, A.; de Jesús, E.; Flores, J. C.; Gómez-Sal, P. *Inorg. Chem.* **2007**, *46*, 4793−4795.

(11) Fujihara, T.; Obora, Y.; Tokunaga, M.; Sato, H.; Tsuji, Y. *Chem. Commun.* **2005**, 4526−4528.

(12) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

(13) Catalano, V. J.; Parodi, N. *Inorg. Chem.* **1997**, *36*, 537−541. Schenning, A. P. H. J.; Arndt, J.-D.; Ito, M.; Stoddart, A.; Schreiber, M.; Siemsen, P.; Martin, R. E.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Gramlich, V.; Diederich, F. *Helv. Chim. Acta* **2001**, *84*, 296−334. Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S.; Scherer, L. J. *Dalton Trans.* **2004**, 2635−2642. Pawlica, D.; Marszalek, M.; Mynarczuk, G.; Sieron, L.; Eilmes, J. *New J. Chem.* **2004**, *28*, 1615−1621. Shen, L.; Shi, M.; Li, F.; Zhang, D.; Li, X.; Shi, E.; Yi, T.; Du, Y.; Huang, C. *Inorg. Chem.* **2006**, *45*, 6188−6197. Yang, H.-B.; Hawkridge, A. M.; Huang, S. D.; Das, N.; Bunge, S. D.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 2120−2129. Fujihara, T.; Obora, Y.; Tokunaga, M.; Tsuji, Y. *Dalton Trans.* **2007**, 1567−1569. Chen, W.-Z.; Fanwick, P. E.; Ren, T. *Inorg. Chem.* **2007**, *46*, 3429−3431. Forrest, W. P.; Cao, Z.; Chen, W.-Z.; Hassell, K. M.; Kharlamova, A.; Jakstonyte, G.; Ren, T. *Inorg. Chem.* **2011**, *50*, 9345−9353.

(14) For a study on the structural features of Fréchet-type dendrons in single crystals, see: Stadler, A.-M. *Cryst. Growth Des.* **2010**, *10*, 5050−5065.

(15) Berding, J.; Kooijman, H.; Spek, A. L.; Bouwman, E. *J. Organomet. Chem.* **2009**, *694*, 2217−2221.

(16) See the Supporting Information for references.

(17) Healy, P.; Kildea, J.; White, A. *Aust. J. Chem.* **1988**, *41*, 417−418. Wölper, C.; Polo Bastardés, M. D.; Dix, I.; Kratzert, D.; Jones, P. G. *Z. Naturforsch., B: Chem. Sci.* **2010**, *65*, 647−673.

(18) Odoko, M.; Wang, Y.; Okabe, N. *Acta Crystallogr., Sect. E* **2004**, *60*, m1522−m1524.

(19) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885−3896.

(20) We obtained values similar to those reported by Janiak in CSD searches for structures with benzyl groups either not substituted or substituted with oxygen at the meta ring positions (as for the aryl rings of the dendron in **4**; see the Supporting Information for details).

(21) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2006**, *110*, 10656−10668.

(22) The term "$\pi-\pi$ stacking" should be used as a geometrical descriptor of the interaction mode in unsaturated molecules and to understand $\pi-\pi$ interactions as a special type of electron correlation (dispersion) effect that can only act in large unsaturated systems when they are in the stacked orientation: Grimme, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3430−3434. See also: Wheeler, S. E. *Acc. Chem. Res.* **2012**, *46*, 1029−1038.

(23) The results of both types of argumentations are quite different in the case of the larger 1,10-phenanthroline ring.

(24) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407−5413. Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322−4326. Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841−861.

(25) Percent buried volumes were calculated using the SambVca web application (www.molnac.unisa.it/OMtools.php): Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 1759−1766.

(26) It is interesting to note here that the long-range influence of the dendritic substituent in **4** helps to efficiently block the Ag−C_{NHC} bond axis direction, thus preventing the formation of double-chain structures.

(27) Ragone, F.; Poater, A.; Cavallo, L. *J. Am. Chem. Soc.* **2010**, *132*, 4249−4258.

(28) This has to be exclusively considered as an analogy. NHC ligands are not ellipsoids, and a/b values have no direct physical meaning.

(29) The borderline is logically less well defined when asymmetrically substituted ligands are considered, but the general behavior remains unchanged (see Figure S11 in the Supporting Information).

(30) Liu, P.; Montgomery, J.; Houk, K. N. *J. Am. Chem. Soc.* **2011**, *133*, 6956−6959.