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Synthesis and characterization of metallodendritic palladium-biscarbene complexes derived from 1,1'-methylenebis(1,2,4-triazole)[†]

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The syntheses of first generation dendritic compounds bearing

1,1'-alkane-1,1-diylbis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide on the periphery are described. The metallabiscarbene moieties have also been studied separately from the dendrimer. These compounds display a non-symmetric boat-to-boat conformational equilibrium that has axial and equatorial arrangements. The predominance of the axial conformer in the equilibrium is supported by DFT calculations. The X-ray solid state structures of axial conformers of 3-hydroxy- and 3-mesyloxy-1,1'-propane-1,1-diylbis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide are reported. These complexes display modest catalytic activity in the Heck reaction with activated aryl bromides and the dendritic catalysts were more active than the corresponding non-dendritic mononuclear species, a finding indicative of a cooperative effect.

Introduction

The chemistry of stable *N*-heterocyclic carbenes (NHCs) has experienced remarkable growth since their initial synthesis as transition metal complexes by Wanzlick¹ and Öfele² and as freecarbenes by Arduengo.³ The synthesis of NHCs has contributed to the development of new organometallic complexes that have mainly been employed as powerful catalysts. Within this topic, the tunability of NHCs gives rise to a wide variety of ligands, comparable to the range shown by phosphines.⁴ NHCs derived from imidazole are the most widely studied carbenes although some NHC systems derived from 1,2,4-triazole have been prepared and used as catalysts.^{5,6}

Recovery and re-use of the catalysts are amongst the main goals in organometallic chemistry due to the increased interest in the design of efficient and environmentally benign synthetic methods, which is one of the main principles of Green Chemistry.⁷

Immobilization of the catalysts onto polymers has commonly been used as a method to recover the catalysts. However, very few examples of immobilized catalysts based on NHCs have been described. The main strategy that has been reported in the literature concerns NHCs that are linked to a polymer or silica.⁸ On the other hand, dendritic macromolecules can be separated from the reaction media by precipitation or ultra-centrifugation because of their large size. Since the work published by van Koten in 1994,9 where nickel pincer complexes were present on the periphery of a carbosilane dendrimer, an increase in research in this area has taken place and very useful reviews were published.¹⁰ Metallodendrimers combine advantages from homogeneous and heterogeneous catalysis. On the homogeneous side, the fact that they are macromolecules with a very low polydispersity (1.0 or near to 1.0) facilitates the study of their role in reaction mechanisms.^{10a} These complexes show activity and selectivity similar to those of conventional homogeneous catalysts. Moreover, tuning the complex periphery through a rational synthetic design can affect the properties of the metal centre. On the heterogeneous side, recovery and recyclability are very likely to be successful on using the aforementioned techniques. However, examples of dendrimers bearing NHCs in the core are scarce.¹¹ Some NHCs complexes were non-covalently attached to dendrimers by either ionic or hydrophobic interactions.¹² Complexes bound to the periphery of a dendrimer through a ligand in the organometallic complex other than the NHC system have also been described.¹³ Our group reported an NHC system covalently attached to a dendritic structure that is able to chelate three palladium atoms (Fig. 1).¹⁴ The significant electrophilic character of the benzyl methyne makes the synthesis of 1 difficult as the loss of triazole rings is observed.15

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Fig. 1 Dendritic G0 palladabiscarbene complex.

In this paper, we report the synthesis and catalytic activity in a standard Heck reaction of dendritic palladabiscarbene complexes bearing chelating NHCs derived from 1,1'-methylenebistriazole.

Results and discussion

Mononuclear dicarbene structures

In an effort to synthesize dendrimers bearing N-heterocyclic carbene complexes on the periphery, we focused our attention on 1,1'-alkane-1,1-divlbis(4-butyl-4,5-dihydro-1H-1,2,4triazol-5-ylidene)palladium(II) diiodide and dibromides 4-7 (Scheme 1). These compounds were previously synthesized by our group¹⁶ and have a structure that allows them to be incorporated within different dendritic architectures. We proposed that the palladium atoms have square-planar geometries and that the metallacycles show a boat-to-boat inversion at room temperature. NMR studies showed two conformers for these systems in a 10:1 ratio and, based on bibliographical data, we proposed that the main conformers are those in which the alkyl chains are placed in the axial position and the minor ones in the equatorial. Before embarking on the synthesis of the dendritic molecules, we wished to gain an insight into the structure and the catalytic activity of these non-dendritic complexes. In order to increase our knowledge of these compounds, we report here the solid-state structure of the axial conformers of compounds 4 and 7, as determined by X-ray diffraction. Monocrystals were grown from solutions in dichloromethane/diethyl ether. ORTEP diagrams are shown in Fig. 2 and selected bond lengths and angles are shown in Table 1. The figure shows disorder in one of the butyl substituents as well as in the OH group of 4 and in one of the butyl groups of 7. However, the correlation factors are good and the structures were determined unequivocally. In both compounds two carbene carbons are bound to one palladium atom, which has a quasi square planar geometry with the twocarbene carbons in cis positions and two bromine atoms in the other two positions. Both complexes contain a six-membered metallacycle, which adopts boat-like conformations with the alkyl chain in the axial position. The main distortion is detected in

Table 1Bond lengths (Å) and angles (deg) for 4 and 7

Bond	4	Bond	7	
Pd(1)-C(1)	1.972(4)	Pd(1)–C(2)	1.975(4)	
Pd(1) - C(5)	1.989(5)	Pd(1)-C(5)	1.983(4)	
N(1) - C(1)	1.353(6)	N(3) - C(2)	1.344(5)	
N(3) - C(1)	1.338(5)	N(1) - C(2)	1.336(5)	
N(4) - C(5)	1.322(6)	N(4) - C(5)	1.333(5)	
N(6)–C(5)	1.355(6)	N(6)-C(5)	1.357(5)	
Angles	4	Angles	7	
C(1)-Pd(1)-C(5)	84.25(18)	C(2) - Pd(1) - C(5)	84.52(15)	
C(5) - Pd(1) - Br(1)	169.60(14)	C(5) - Pd(1) - Br(1)	172.06(11)	
C(1)-Pd(1)-Br(2)	176.83(13)	C(2)-Pd(1)-Br(2)	175.87(11)	



Fig. 2 ORTEP diagrams of 4 and 7. Hydrogen atoms have been omitted for clarity.

the angles between the two carbenes and the palladium atoms, 84.25° for **4** and 84.52° for **7**. These angles are less than 90° due to a chelate effect. These values are comparable to those of related imidazole-derived compounds.17 The Pd-C bonds are slightly shorter than those in a similar iodide complex,⁶ thus reflecting the lower trans influence of bromide versus iodide, and are comparable with related dibromo-biscarbene palladium complexes derived from 1,1'-methylenebis(imidazole).^{17b} Endocyclic nitrogen-carbene carbon bonds are similar to those in other related iodide complexes^{5a} and they are of the same order or slightly larger than the distances observed in unsubstituted 1H-1,2,4-triazole,¹⁸ showing an NCN delocalization. These complexes are reminiscent of the heteroscorpionates derived from pyrazole.¹⁹ It is very likely that metals other than palladium that display an octahedral geometry could show a similar arrangement to heteroscorpionates.



Scheme 1 *i*) *n*-BuOTs, 100 °C, 24 h. *ii*) Pd(OAc)₂, KBr, THF, DMSO, r. t. 1 h. *iii*) Pd(OAc)₂, KI, THF, 0 °C, 24 h. *iv*) CBr₄, PPh₃, CH₃CN, r. t. 14 h. *v*)MsCl, Et₃N, CH₂Cl₂, r. t. 2 h.

In both cases the axial conformers were crystallized and, although this is consistent with the proposal that the main conformers in the equilibria have axial arrangements, we can not unequivocally rule out the possibility that the minor conformers are the axial ones and they were obtained in the solid state due to crystal packing effects. In order to ascertain whether the axial conformers are the main compounds in the equilibria, we estimated the energy differences between these two conformations by DFT²⁰ calculations. The non-dendritic mononuclear compounds 4-7 were used as models to provide an explanation for the location of the alkyl chain. The two possible conformers **a** (axial) and **b** (equatorial) were located at the B3LYP/6-31G*&LANL2DZ²¹⁻²³ level of theory using the GAUSSIAN 03 programme.²⁴ First of all, compounds 4a and 4b were fully optimized. Structural simplifications were also introduced with the aim of minimizing the computational cost of the calculations; *i.e.* the two butyl groups (compounds 4a and 4b) were changed to methyl groups (compounds 4'a and 4'b). The main geometrical features of the compounds are depicted in Fig. 3. The outcomes showed that the geometrical parameters are quite similar in each pair of compounds (4a/4'a and 4b/4'b) and we therefore optimized the rest of the carbene complexes with two methyl groups instead of butyl groups (compounds 5', 6' and 7', Fig. 4). Geometrical data and formation energies of the complexes are collected in Table 2. The formation energy differences between equatorial and axial conformers were determined by taking away the formation energy of the axial conformers from that of the equatorial ones. It can be seen that the axial conformers are more stable (1.34–2.73 kcal mol⁻¹) than the equatorial ones and therefore in the boat-to-boat equilibrium the axial conformers must be the major compounds. In order to understand the origin of these energy differences, we analysed the optimized geometry of these compounds. We noticed that three critical distances could be responsible for possible steric interactions: firstly, the distances between Pd and H(10) in the axial conformers, secondly the distances between Pd and H(3) in the equatorial conformers and finally the distances between N(2)/N(5) and C(10) in both axial and equatorial conformers. The first and second distances are similar to each other and larger than the sum of the van der Waals radii-therefore these steric interactions are negligible and they can not be responsible for the difference in the energy values. On the other hand, in the third case, the distances between N(2) and C(10) or N(5) and C(10) are in the order of 3.40 Å in the axial conformers, which is around 0.60 Å larger than in the equatorial conformers (2.80 Å). In addition, the sums of the van der Waals radii are shorter than the distances in the axial conformers (N(2)/N(5)-C(10)) and larger than the same distance in the equatorial conformers. These analyses led us to conclude that the steric interactions between N(2)/N(5) and C(10)in the equatorial compounds have to be greater than in the axial ones. These interactions are reminiscent of the allylic 1,3-strain²⁵ between the C(3)–H(3) bond and sp^2 orbitals of N(5) and N(2), which are minimized in the axial conformers. In our opinion, all of these steric repulsions are likely to be responsible for the higher energy level of the equatorial isomers and, as a consequence, the axial conformers should be the main products in the boat-to-boat equilibrium.

A main drawback within the dendrimer synthesis concerns the time-consuming process and low yields associated with the synthesis of a multicarbenic dendrimeric entity. For this reason,

Table 2Calculated main distances (Å) and energy differences (kcal mol⁻¹)

Comp.	N(5)-C(10) ^{a,c}	$Pd-H(10)^d$	Comp.	N(5)-C(10) ^{a,c}	$Pd-H(3)^d$	ΔE^{b}
4a	3.40	2.92	4b	2.81	3.02	2.64
4'a	3.42	2.92	4'b	2.80	3.03	1.90
5'a	3.43	2.85	5'b	2.84	3.02	1.34
6'a	3.40	2.90	6'b	2.81	2.99	1.72
7'a	3.41	2.86	7'b	2.80	3.09	2.73

^{*a*} Distances N(5)–C(10) and N(2)–C(10) are identical. ^{*b*} ΔE = (formation energy of conformer **b**) – (formation energy of conformer **a**). ^{*c*} Sum of the van der Waals radii [N–C] = 3.25 Å. ^{*d*} Sum of the van der Waals radii [Pd–H] = 2.83 Å.



Fig. 3 Fully optimized compounds **4a**, **4b**, **4'a** and **4'b** calculated at the B3LYP/6-31G*&LANL2DZ level.



Fig. 4 Non-dendritic mononuclear theoretical models.

it is highly desirable to study the catalytic performance of the compounds that have a palladium-diiodide or palladiumdibromide moiety, focusing on the right choice of palladium derivative to incorporate within the dendritic framework. We selected a standard Heck reaction as the appropriate tool to study the catalytic activity because of our previous experience with this C–C coupling. We used compounds **4** and **5** to catalyze the coupling of 4-bromobenzaldehyde and *n*-butyl acrylate. This reaction is appropriate for the determination of the activity in the Heck reaction and it was the subject of catalytic studies performed by Herrmann *et al.*²⁶ We previously used this methodology to elucidate the catalytic activity of **1**¹⁴ and other related palladiumpincer complexes.²⁷ We used 1.40 equiv. of butyl acrylate per mol of

онс-	✓ Br + <	CBu ⁿ Cat., TBAB, NaOAc DMA, 125 ℃	онс—	OBu"
Entry	Cat. (0.5% mol)	TBAB (% mol)	<i>t</i> (h)	Conversion (%) ^a
1	4	0	6	50
2	4	0	20	67
3	4	100	2	77
4	4	100	8	99 ^b
5	5	0	6	19
6	5	0	20	22
7	5	100	6	50
8	5	100	20	69

 Table 3
 Heck reaction between 4-bromobenzaldehyde and *n*-butyl acrylate using compounds 4 and 5 as catalysts

^{*a*} Conversions of the reactions were estimated by ¹H NMR. ^{*b*} Isolated product yield was higher than 90%.

p-bromobenzaldehyde, 1.10 equiv. of sodium acetate, 0.5 mol% of catalyst and tetrabutylammonium bromide (TBAB).²⁸ The results are shown in Table 3. Conversions of the reactions were estimated by ¹H NMR spectroscopy because starting materials and final products were the only materials detected by this technique.²⁶ However, in order to verify the suitability of this method to evaluate the conversions, on several occasions we isolated the final product obtained under the best conditions described in entry 4.

In the initial study the conversions obtained for the monouclear compounds **4** and **5** were compared. The differences between these conversion levels could be a consequence of the nature of the halogen atoms in the coordination sphere of the palladium(II). It can be seen that the presence of TBAB was essential to obtain good conversions (compare entries 1 and 3 or 4 for **4**, and 6 and 8 for **5**). The second conclusion that can be drawn is that compound **4** is a more active catalyst than **5** (compare entries 7 and 8 with entries 3 and 4). Higher conversions and shorter reaction times were observed for Pd–Br in comparison to Pd–I carbene complexes.

In the search for an explanation for the differences in the catalytic activities displayed by the mononuclear biscarbene species 4 (X = Br) and 5 (X = I), we analysed their electrochemical properties. Cyclic voltammograms are included in the Supporting Information.[†] Both compounds present an irreversible reduction peak at -1.8 and -1.0 V, respectively, versus silver wire (See Supporting Information[†]) at a scan rate of 0.1 V s⁻¹. These values are consistent with the trend reported by Jutand et al.²⁹ Compound 5 has a lower reduction potential than 4. This means that the former is electronically poorer and is more easily reduced. The UV-Visible spectra of compounds 4 and 5 lead to a similar conclusion (See Supporting Information[†]). The absorption spectra of both compounds contain two bands, with the most intense band tentatively attributed to a high-energy ligand-to-metal charge transfer transition (LMCT)³⁰⁻³² where the N-heterocyclic carbenes act as strong donor and poor π -acceptor ligands. The other band (300-400 nm) is assigned to a halogen \rightarrow Pd LMCT transition.³³ A bathochromic shift in this band was observed when iodides were present in the metal coordination sphere in comparison to the complex (NHC)₂PdBr₂. This finding indicates that the palladium atom in 5 is electronically poorer and would therefore be more easily reduced than that in 4. Despite this fact, compound 4 shows

better catalytic activity and leads to a higher reaction rate in all cases, both with and without TBAB. Therefore the reduction of compounds 4 and 5 should not be the rate-limiting step. The data are consistent with oxidative addition being the slowest step³⁴ and this depends on the nature and concentration of the catalytic species and on the nature of the halogen atom bonded to the aryl group. As halogen atoms bonded to palladium in complexes 4 and 5 are lost in the reduction step,²⁹ catalytic cycles should be identical in all cases. Therefore the observed results could be tentatively explained based on the differences in the concentration of the catalytic species.

Pd(0) nanoparticles that can be stabilized by the presence of TBAB, are often invoked to explain the Heck reaction mechanism.^{34,35} We observed that the presence of TBAB improved the results in this study. This is consistent with the formation of TBAB-stabilized nanoparticles. On the other hand, we also observed darkening of the reaction crudes; this is indicative of the formation of insoluble and less reactive palladium black in some range. Soluble palladium clusters are stable at low Pdloading, but as catalyst concentration increases, Pd black is rapidly formed.^{34,35b} As 5 is more easily reduced than 4, we propose that the former gives rise to a higher concentration of Pd(0) atoms and this could lead to formation of a higher amount of palladium black. This aggregation phenomenon is less likely to take place with compound 4 that should release Pd(0) atoms more slowly, giving rise to a higher concentration of nanoparticles and therefore leading to a higher catalytic activity.

The addition of mercury to the reaction mixture (300 eq. of metallic mercury relative to the organometallic complex) under the conditions described for entry 4 was carried out at the beginning of the reaction, at room temperature 110 and 125 °C. In all cases, the C–C coupling reaction was stopped after the addition of mercury. This reinforces the hypothesised presence of Pd nanoparticles, which are poisoned by the mercury.^{35a}

Synthesis of dendritic structures bearing palladium-biscarbene complexes

In the previous section we showed that dibromopalladium derivative 4 is more active in the C–C coupling reaction than diiodo counterpart 5. With this knowledge, we decided to synthesize dendrimers bearing dibromopalladium-biscarbene moieties. We identified two possible approaches to the metallacarbene dendrimers, one of which involved coupling the pre-formed complex onto the periphery of a dendrimer. Note that compounds 4, 6 and 7 have focal groups that could be linked to appropriate functional groups. The second approach consists of coupling the precursor of the metallacarbenes to a dendritic structure to form the complex in the final step. Firstly, we tried to bind a previously formed biscarbene complex to 3,5-dihydroxybenzyl alcohol. However, all attempts to couple 4, 6 or 7 to the core were unsuccessful. For these reasons, the introduction of the metal in the final step was the best choice. We decided to use 3,5-bis[3,3-bis(1H-1,2,4-triazol-1-yl)propoxy]benzyl alcohol (9), which was previously synthesized by our group³⁶ by the reaction of a slight excess of mesylate 8 (obtained by a standard mesylation reaction of 2) with 3,5dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 (Scheme 2). Quaternization of N5 in all 1,2,4triazole rings was performed by reaction with a large excess of



Scheme 2 Synthesis of dinuclear tetracarbene complex 11.

n-butyl tosylate at 100 °C to render the tetrasalt **10** in good yield (Scheme 2). The structure of **10** was confirmed by the presence of the ¹H NMR signals for the *n*-butyl and tosyl protons and by the shift of the triazole H5 signal from 8.41 ppm to 10.62 ppm. The presence of a unique set of 1,2,4-triazole signals indicates that all N5 atoms were quaternized.

Finally, carbene-dendron **11** was synthesized by reaction of the salt **10** with a slight excess of both palladium acetate and potassium bromide with a yield of 67%. The ¹H NMR spectrum shows patterns consistent with palladium-biscarbene moieties. The most important feature observed was the loss of the ¹H NMR signal corresponding to H5 and the appearance of a ¹³C NMR signal at 163.4 ppm, which corresponds to the carbene carbon bound to palladium.

In a similar way to monometallic complexes,¹⁶ we propose that the carbene metallacycle moieties must have boat-like structures with two main conformations in a non-equimolar boat-to-boat equilibrium. The alkyl chains bound to the methyne bridges of the metallacyclic rings will interchange their axial–equatorial arrangements.

We proceeded to turn our attention to the synthesis of larger structures and, to this end, we attempted to couple the metallodendron **11** to several cores. However, all attempts to form ether or ester linkages were unsuccessful, meaning that formation of the metallacarbene in the final step is the preferred strategy once again. Dendritic system 3,5-bis[3,3-bis(1*H*-1,2,4-triazol-1-yl)propoxy]benzyl terephthalate (**12**) was obtained by the Schötten–Baumann reaction of dendron **9** with terephthaloyl chloride (Scheme 3). After work-up, the pure product was isolated in 45% yield. A new signal was observed at 8.14 ppm in the ¹H NMR spectrum that integrates for 4H and this is due to the *core* resonance. The MS (MALDI-TOF) shows two peaks at 1115.3 and 1137.3 due to (M + H)⁺ and (M + Na)⁺, as expected for the target structure.

Quaternization of all N5 atoms of **12** was carried out by reaction with a large excess of *n*-butyl tosylate at 100 °C (Scheme 3). A long reaction time (5 days) was required to obtain the octa-salt **13**. This is a result of the low solubility of the partially quaternized species. The ¹H NMR signals due to the butyl and tosyl groups in **13** are similar to those for the equivalent groups in compound **10** and the triazolium H5 signals are shifted to 10.64 ppm. The latter fact confirms the structure of **13**. In the ¹H NMR spectrum there is only one set of signals for the triazole rings. This indicates that all heterocycles have been alkylated. Finally, the dendritic carbene **14** was obtained by reaction of the salt **13** with palladium acetate and potassium bromide as described for **11**. The MS and NMR data confirm the formation of the carbenes. The MS-MALDI-TOF spectrum shows a peak at 2504.1 D corresponding to $[M - Br]^+$. ¹H NMR signals corresponding to H5 of the triazolium rings are absent and a ¹³C NMR signal is observed at 162.3 ppm due to the carbone carbons bound to palladium. These data are consistent with the formation of a multicarbene complex.

Our aim was to highlight any influence that the dendritic nature of the system may have on the catalytic activity of these complexes. In order to compare the reactivity of the dendritic structures 11 and 14 with the non-dendritic complex 4, we turned our attention to the Heck reaction shown in Table 3. The quantities of catalyst were 0.5 mol% of 11 and 0.063 and 0.006 mol% of 14. The results are shown in Table 4. One important finding is that the dendritic complexes show a higher activity than the non-dendritic ones (cf. entries 3 and 4, Table 3, with 1 and 2, Table 4). A detailed analysis of the experimental data shows that 4 has half the amount of palladium as 11, but the former required 8 h for completion of the reaction whereas only 1 h was required with the latter. This indicates that 11 is a better catalyst than 4. On the other hand, in 0.063 mol% of 14 there is half the amount of palladium as in 0.5 mol% of 4 and the conversions are similar but in 8 h for 4 and 1.5 h for 14. Another interesting observation is that 0.063 mol% of 14 has a quarter of the amount of palladium as in 0.5 mol% of 11, however the times to complete the reactions were not very different, with the former requiring 1.5 h to complete the reaction and the latter 1 h. These observations indicate a cooperative effect of the palladium atoms in the dendritic system. These results agree with those previously reported by Astruc³⁷ and de Jesús et al.³⁸

All reactions were quenched on the addition of metallic mercury (300 eq.). This observation is consistent with the possible formation of Pd(0) nanoparticles.^{35a}

The C–C coupling reactions of *n*-butyl acrylate and less reactive halides were investigated with 4-chlorobenzaldehyde and bromobenzene using **14** as catalyst. In these cases, higher quantities of catalyst (0.12% mol) and longer reaction times (40-47 h) were necessary to obtain moderate yields ($\sim 30\%$).

Table 4Heck reaction between 4-bromobenzaldehyde and n-butyl acry-late using compounds 11 and 14 as catalysts

Entry ^a	Cat.	% Cat.	<i>t</i> (h)	Conversion (%) ^b
1	11	0.5	1	99
2	14	0.063	1.5	96
3	14	0.006	20	18

^{*a*} Reaction conditions are the same as used in Table 3. ^{*b*} Conversions of the reactions were estimated by ¹H NMR.



Scheme 3 Synthesis of the dendritic octacarbene structure 14.

Conclusion

The following conclusions can be drawn from the work described here. 3-Substituted-propane-1,1-diylbis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)palladium(II) dibromide can be incorporated into dendritic structures to give first generation dendritic metallacarbenes. These complexes display a modest catalytic activity in the Heck reaction. Mononuclear palladabiscarbene **4** (bearing bromides) shows higher activity than the iodidecontaining counterpart **5**. The catalytic activity increases as the quantity of palladium increases. Tetranuclear dendritic compound **14** is more active than the dinuclear derivative **11** and the latter is more active than the non-dendritic mononuclear compound **4**. This trend is consistent with a cooperative effect of the palladium atoms in the dendritic system.

Experimental section

Solvents were purified by distillation from appropriate drying agents before use. All reagents were used as received and without further purification. When necessary, work was carried out using standard Schlenk techniques under an atmosphere of dry argon. Melting points were determined in capillary tubes on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser. Electron Impact (EI) (working at 70 V and 200 °C), Fast Atom Bombardment (FAB) mass spectrometry (using *m*-NBA as matrix) and MALDI-TOF experiments were performed on a VG Autospec

instrument at the Servicio Interdepartamental de Investigación, Universidad Autónoma de Madrid. NMR spectra were recorded in CDCl₃ or DMSO-d₆ on a Varian Inova-500 instrument with TMS or the solvent carbon signal as standards, operating at 500 MHz for ¹H and 125 MHz for ¹³C. Chemical shifts are expressed in parts per million. The signals were assigned with the aid of NOESY-1D. Xray diffraction experiments were run using a Bruker SMART-CDD diffractometer at the Universidad de la Coruña. Monocrystals were grown from solutions in dichloromethane/diethyl ether (see Table 5 for crystallography data). UV-vis absorbance spectra were obtained using a Hewlett-Packard HP8453 spectrometer and quartz cuvettes with a path length of 1 cm. Solutions of biscarbenes 4 and 5 in THF (spectrophotometric grade, Sigma–Aldrich, Inc.) were prepared at a concentration of 3 mM. THF was used to obtain background spectra. The syntheses of products 2-9 have been described previously.^{16,36} Anhydrous dimethylformamide was obtained from Fisher (Fair Lawn, NJ) and transferred into a helium atmosphere drybox (Vacuum Atmospheres Corp., Hawthorne, CA). Electrochemical grade tetra-n-butylammonium phosphate was obtained from Fluka and transferred into the drybox. The electrochemical cell for cyclic voltammetry (CV) consisted of a 1.5 mm Pt disc inlaid in glass as the working electrode, a coiled Pt wire as the counter electrode, and a Ag wire as a quasireference electrode. Prior to each experiment, the working electrode was polished with 0.3 µm alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in water, and then sonicated in ethanol for 1 min and rinsed with acetone before transferring into the glovebox. Cyclic voltammograms were recorded using a CH Instruments model

Table 5Crystallography data for compounds 4 and 7

Compound	4	7	
Empirical formula	$C_{15}H_{26}Br_2N_6OPd$	$C_{16}H_{28}Br_2N_6O_3PdS$	
Formula weight	572.64	650.72	
<i>T</i> (K)	298(2)	298(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Rhombohedral	Monoclinic	
Space group	RĪ	$P2_1/n$	
a(Å)	20.1373(7)	10.4862(6)	
$b(\dot{A})$	20.1373(7)	15.5606(9)	
$c(\dot{A})$	20.1373(7)	14.7375(8)	
α (°)	117.27	90°	
$\beta(\circ)$	117.27	100.5700(10)°	
γ (°)	117.27	90°	
Volume (Å ³)	3442.3(2)	2363.9(2)	
Z	6	4	
Density (calculated) (mg m^{-3})	1.657	1.828	
Absorption Coefficient (mm ⁻¹)	4.304	4.282	
F(000)	1692	1288	
Crystal size (mm)	$0.55 \times 0.18 \times 0.17$	$0.50 \times 0.48 \times 0.30$	
Index ranges	$-26 \le h \le 26$	$-12 \le h \le 13$	
-	$-26 \le k \le 25$	$-19 \le k \le 11$	
	$-18 \le l \le 26$	$-18 \le l \le 15$	
R(int)	0.0358	0.0233	
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	
Data/restraints/parameters	5576/0/264	4836/0/272	
Goodness-of-fit on F^2	1.043	1.054	
Final R_1 values $[I > 2\sigma(I)]$	0.0365	0.0337	
Final w R_2 values $[I > 2\sigma(I)]$	0.0973	0.0885	
Largest diff. peak and hole $(e \cdot Å^{-3})$	1.128 and -1.083	0.625 and -0.943	

660 Electrochemical Workstation (Austin, TX) and are collected in the Supporting Information.[†]

Computational methods

All calculations reported in this paper were performed within the Density Functional Theory,²⁰ using the hybrid three-parameter functional customarily denoted as B3LYP.²¹ The standard 6-31G*²² basis set, as implemented in the GAUSSIAN 03²⁴ suite of programmes, was used to describe hydrogen, carbon, nitrogen and oxygen atoms. Palladium atoms were described by the Hay–Wadt effective core potential.²³ This computational treatment is denoted as B3LYP/6-31G*&LANL2DZ. The reported differences in energy include zero-point vibration energy corrections, denoted as Δ ZPVE. Harmonic analysis showed that all conformers had only one imaginary frequency. Geometric features of all compounds are collected in the Supporting Information.[†]

Synthesis of the tetra-salt 10

A mixture of **9** (0.200 g, 0.406 mmol) and *n*-butyl tosylate (15 mL) was heated and stirred at 100 °C in a 25 mL round-bottomed flask for 72 h. The crude material was washed with ethyl acetate and the product was obtained as a colourless solid after crystallization from ethanol/diethyl ether. Yield: 85%; mp: 158–162 °C; $\delta_{\rm H}(d_6$ -DMSO) 0.86 (12H, t, *J* 7.3 Hz, NCH₂CH₂CH₂CH₂CH₃), 1.27 (8H, sxt, *J* 7.3 Hz, NCH₂CH₂CH₂CH₂CH₃), 1.27 (8H, NCH₂CH₂CH₂CH₂CH₃), 2.28 (12H, s, *p*-CH₃C₆H₄SO₃), 3.14 (4H, q, *J* 6.8 Hz, CHCH₂CH₂CH₂O), 4.10 (2H, t, *J* 5.4 Hz, ArCH₂OH), 4.26 (4H, t, *J* 7.3 Hz, CHCH₂CH₂CH₂O), 5.23 (1H, t, *J* 5.4 Hz, OH), 6.26

(1H, s, C_{para}), 6.39 (2H, s, C_{ortho}), 7.11, 7.47 (16H, AA'BB' system, *J* 8 Hz, *p*-CH₃C₆H₄SO₃), 7.75 (2H, t, *J* 6.8 Hz, CHCH₂CH₂O), 9.45 (4H, s, 3-H_{triazole}), 10.62 (4H, s, 5-H_{triazole}); $\delta_{C}(d_{6}$ -DMSO) 13.2, 18.8, 20.8, 30.5, 47.8, 62.5, 69.4, 71.4, 99.3, 99.9, 105.0, 106.0, 125.4, 128.1, 137.8, 144.6, 145.3, 145.4, 158.7; *m/z* (ESI) 1233 [M – TsO]⁺.

Synthesis of the palladium-tetracarbene 11

Compound 10 (0.150 g, 0.105 mmol), DMSO (2 mL), KBr (58 mg, 0.480 mmol) and Pd(OAc)₂ (56 mg, 0.250 mmol) were added, in this order, to THF (100 mL) in a 500 mL two-necked roundbottomed flask. The resulting brown suspension was stirred for 5 min. The THF was removed under reduced pressure and the DMSO was removed in a bulb-to-bulb oven at 60 °C, 2×10^{-1} mmHg. The residue was washed with carbon tetrachloride (3 \times 50 mL) and the product was extracted with THF (3×80 mL). The THF was evaporated and the product was purified by column chromatography (silica gel, CH₂Cl₂/acetone 16:1 to 8:1) to give an orange solid. Yield 67%; mp: 164 °C; $\delta_{\rm H}(d_6$ -DMSO) 0.92 (12H, t, J 7.3 Hz, NCH₂CH₂CH₂CH₃), 1.32 (8H, sxt, J 7.4 Hz, NCH₂CH₂CH₂CH₃), 1.87 (8H, m, J 7.2 Hz, NCH₂CH₂CH₂CH₃), 3.47 (4H, m, J 6.5 Hz, CHCH2CH2O), 4.05 (4H, t, J 7.1 Hz, CHCH₂CH₂O), 4.28 (4H, dt, J 13.2 and 6.8 Hz, one H for each NCH₂CH₂CH₂CH₃), 4.39 (2H, s, ArCH₂OH), 5.07 (4H, dt, J 13.2 and 6.8 Hz, one H for each NCH₂CH₂CH₂CH₃), 6.40 (1H, t, J 2.1 Hz, C_{para}), 6.53 (2H, d, J 1.7 Hz, C_{ortho}), 6.85 (2H, t, J 7.2 Hz, CHCH₂CH₂O), 8.29 (4H, s, 3-H_{triazole}); $\delta_{\rm C}(d_6$ -DMSO) 13.6, 19.6, 32.9, 39.2, 49.6, 62.7, 70.6, 72.5, 101.0, 107.2, 141.6, 143.6, 159.3, 163.4; *m/z* (FAB⁺) 1225.1 [M – H₂O]⁺.

3,5-Bis[3,3-bis(1*H*-1,2,4-triazol-1-yl)propoxy]benzyl terephthalate (12)

A mixture of compound 9 (0.740 g, 1.50 mmol) and anhydrous freshly distilled triethylamine (200 µL, 1.430 mmol) was dissolved in anhydrous THF (20 mL) under Ar in a 100 mL Schlenk tube. A solution of terephthaloyl chloride (0.120 g, 0.590 mmol) in anhydrous THF (10 mL) was added dropwise and the reaction mixture was heated under reflux under an inert atmosphere for 16 h. After this period of time, the solvent was evaporated. The residue was dissolved in dichloromethane (60 mL) and washed with water (3 \times 20 mL). The organic layer was dried over anhydrous Na₂SO₄. The product was finally washed with cold methanol. The pure compound was obtained as colourless crystals. Further purification was achieved by column chromatography (silica gel, ethyl acetate/methanol 3:1). Yield: 45%; mp: 197-200 °C; $\delta_{\rm H}$ (CDCl₃) 3.09 (8H, br s, CHCH₂CH₂O), 3.88 (8H, br s, CHCH₂CH₂O), 5.27 (4H, s, ArCH₂O), 6.26 (2H, s, C_{para}), 6.53 (4H, s, Cortho), 6.97 (4H, t, J 7.1 Hz, CHCH2CH2O), 7.99 (8H, s, 3-H_{triazole}), 8.14 (4H, s, core), 8.40 (8H, s, 5-H_{triazole}); δ_C(d₆-DMSO) 33.3, 62.5, 66.6, 68.6, 101.2, 107.3, 129.8, 133.9, 138.6, 143.1, 152.7, 159.3, 165.4; m/z (MALDI-TOF) 1137.3 [M + Na]⁺, 1115.3 [M + H]+.

Synthesis of the octa-salt 13

A mixture of **12** (0.225 g, 0.195 mmol) and *n*-butyl tosylate (15 mL) was heated and stirred at 100 °C in a 25 mL round-bottomed flask for 5 d. The crude material was washed with hot ethyl acetate and the product was obtained as a colourless solid. Yield: 58%; mp: 168–173 °C (decomposition); $\delta_{\rm H}(d_6$ -DMSO) 0.84 (24H, br s, NCH₂CH₂CH₂CH₂CH₃), 1.24 (16H, br s, NCH₂CH₂CH₂CH₂CH₃), 1.75 (16H, br s, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂O), 4.14 (8H, br s, CHCH₂CH₂O), 4.24 (16H, br s, NCH₂CH₂CH₂CH₂CH₂CH₃), 5.26 (4H, s, ArCH₂O), 6.45 (2H, s, C_{para}), 6.57 (4H, s, C_{ortho}), 7.10 and 7.47 (32H, AA'BB' system, *J* 6.5 Hz, *p*-CH₃C₆H₄SO₃), 7.78 (4H, br s, CHCH₂CH₂O), 8.1 (4H, s, core), 9.45 (8H, s, 3-H_{triazole}), 10.64 (8H, s, 5-H_{triazole}). $\delta_{\rm C}(d_6$ -DMSO) 13.2, 18.7, 20.7, 30.5, 47.7, 62.6, 66.5, 71.3, 100.7, 107.3, 125.4, 128.1, 129.7, 133.5, 137.9, 144.7, 145.3, 145.4, 159.0, 164.8.

Synthesis of the palladium-octacarbene 14

Compound **13** (0.120 g, 0.104 mmol), DMSO (2 mL), KBr (47 mg, 0.394 mmol) and Pd(OAc)₂ (40 mg, 0.179 mmol) were added, in that order, to THF (100 mL) in a 500 mL two-necked round-bottomed flask. The resulting brown suspension was stirred for 5 min. The THF was evaporated under vacuum (20 mmHg) and the DMSO was distilled in a bulb-to-bulb oven at 60 °C, 2×10^{-1} mmHg. The residue was washed with water (2×10 mL) to give the product as an orange solid. Yield: 77%; mp: 227–229 °C (decomposition); $\delta_{\rm H}(d_6$ -DMSO) 0.87 (24H, t, *J* 7.2 Hz, NCH₂CH₂CH₂CH₂), 1.22 (16H, sxt, *J* 7.5 Hz, NCH₂CH₂CH₂CH₃), 1.84 (16H, m, NCH₂CH₂CH₂CH₃), 3.49 (8H, quin, *J* 5.5 Hz, CHCH₂CH₂CH₂O), 4.18 (16H, br s, CHCH₂CH₂CH₃), 5.30 (4H, s, ArCH₂O), 6.49 (2H, s, C_{para}), 6.62 (4H, s, C_{ortho}), 6.98 (4H, t, *J* 7.3 Hz, CHCH₂CH₂CH₂O), 8.18 (4H, s, core), 8.90 (8H, s, 3-H_{triazole}); $\delta_{\rm C}(d_6$ -DMSO) 14.1, 19.6,

32.8, 39.4, 49.0, 63.4, 67.1, 76.7, 101.1, 107.3, 130.5, 134.3, 138.7, 145.5, 160.0, 162.3, 165.5. *m*/*z* (MALDI-TOF) 2540.1 [M – Br]⁺.

General method for the Heck reactions

A dimethylacetamide (5 mL) suspension of the corresponding aryl halide (2 mmol), sodium acetate (2.2 mmol), the appropriate NHC-Pd catalyst (0.5%, 0.063% or 0.006% mol depending on the case) and, where appropriate, tetra-n-butylammonium bromide (2 mmol) was degassed, and then *n*-butyl acrylate (2.8 mmol) was added. The resulting suspension was stirred and heated to 125 °C. For analysis of the reaction, aliquots of 0.4 mL were taken and dissolved in 3.5 mL of dichloromethane. Then 5 mL of 5% HCl was added and the mixture stirred for 15 min. The organic laver was then separated and successively washed with water (15 mL), dried (Na₂SO₄), and evaporated under vacuum. Conversions of the reactions were estimated by ¹H NMR spectroscopy. To isolate the product, the reaction mixture was worked-up in a similar way to the aliquots but using 35 mL of CH₂Cl₂, 50 mL of 5% HCl and 150 mL of water. The pure product was obtained by bulb-to-bulb distillation at 188 °C and 2 mmHg.

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