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Self-Assembly in Inorganic Chemistry

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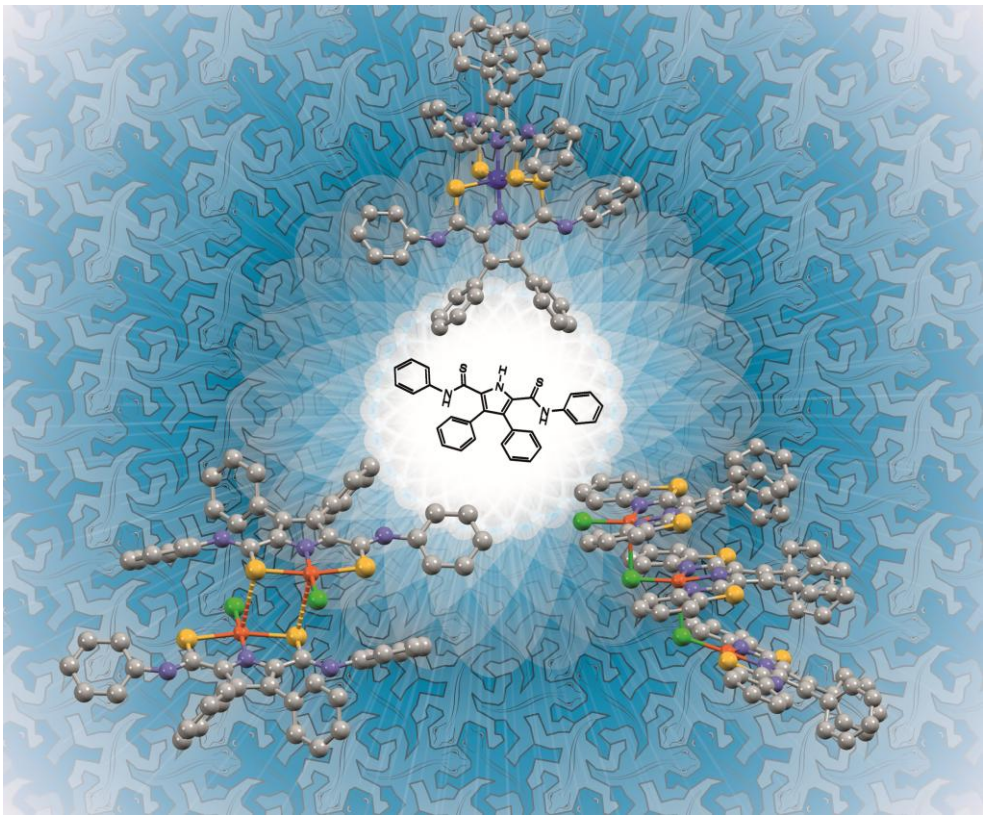

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PAPER

Self-assembled palladium(II) "click" cages: synthesis, structural modification and stability†

Synøve Ø. Scott,[a] Emma L. Gavey,[a] Samuel J. Lind,[a] Keith C. Gordon[a,b] and James D. Crowley*[a]

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Readily synthesised and functionalised di-1,2,3-triazole "click" ligands are shown to self-assemble into coordinatively saturated, quadruply stranded helical $[Pd_2L_4](BF_4)_4$ cages with Pd(II) ions. The cages have been fully characterised by elemental analysis, HR-ESMS, IR, ^{1}H, ^{13}C and DOSY NMR, DFT calculations, and in one case by X-ray crystallography. By exploiting the CuAAC "click" reaction we were able to rapidly generate a small family of di-1,2,3-triazole ligands with different core spacer units and peripheral substituents and examine how these structural modifications affected the formation of the $[Pd_2L_4](BF_4)_4$ cages. The use of both flexible (1,3-propyl) and rigid (1,3-phenyl) core spacer units led to the formation of discrete $[Pd_2L_4](BF_4)_4$ cage complexes. However, when the spacer unit of the di-1,2,3-triazole ligand was a 1,4-substituted-phenyl group steric interactions led to the formation of an oligomeric/polymeric species. By keeping the 1,3-phenyl core spacer constant the effect of altering the "click" ligands' peripheral substituents was also examined. It was shown that ligands with alkyl, phenyl, electron-rich and electron-poor benzyl substituents all quantitatively formed $[Pd_2L_4](BF_4)_4$ cage complexes. The results suggest that a wide range of functionalised palladium(II) "click" cages could be rapidly generated. These novel molecules may potentially find uses in catalysis, molecular recognition and drug delivery.

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Introduction

Inspired by nature, the use of self-assembly to generate functional metallosupramolecular systems from relatively "simple" building blocks (metal ions and ligands) has received considerable attention in recent years.[1] The sustained interest in this area is driven by the potential applications of these metallosupramolecular architectures. Systems have been exploited for the molecular recognition and encapsulation[2] of a wide variety of molecules including highly reactive species,[3] biomolecules,[4] aromatic systems,[5] anions,[6] drugs,[7] and environmental pollutants.[8] Other metallosupramolecular architectures have shown promise as molecular reaction flasks,[9] catalysts[10] and even stimuli responsive[11] machine-like systems have been developed. While there are now a wide variety of ligand scaffolds available for the generation of metallosupramolecular systems many of them require time consuming and expensive multi-step syntheses or are generated under conditions that do not readily allow the incorporation of "useful" functional groups. As such there is still a need for mild, modular synthetic methods that allow for easy functionalisation of metallosupramolecular systems. One such method is the Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes (the CuAAC "click" reaction) and there has recently been an explosion of interest in the use of the CuAAC reaction to generate functionalised ligand architectures containing 1,2,3-triazole units.[12] This interest is driven by the desire to use 1,2,3-triazoles as readily synthesised and functionalised surrogates for the ubiquitous pyridine ligands. While the 1,2,3-triazole unit can potentially coordinate through both the N2[13] and N3[14] nitrogens a number of studies have shown that simple 1,4-substituted-1,2,3-triazole ligands can interact with metals ions in a monodentate fashion,[15,16] suggesting that these "click" ligands could potentially be used to replace pyridine donor units within supramolecular polydentate ligand architectures.[17]

The palladium–pyridine metal–ligand interaction is frequently exploited in the construction of metallosupramolecular macrocyclic and cage architectures and most commonly dipyridyl ligands are used as the connecting unit in the assembly process.[18] As such, we set out to show that readily synthesised and functionalised di-1,2,3-triazole ligands could be used in place of these more commonly utilised dipyridyl ligands in the self-assembly of palladium containing metallosupramolecular systems. In preliminary work, we have previously demonstrated that the "click" ligands, **1a** and

[a]*Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: jcrowley@chemistry.otago.ac.nz; Fax: +64 3 479 7906; Tel: +64 3 479 7731*

[b]*MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand*

† Electronic supplementary information (ESI) available: Experimental procedures, ^{1}H NMR, DOSY and ESMS spectra, ^{1}H NMR stacked plots, MMFF and DFT calculations and crystallographic data. CCDC reference numbers 819051 and 819052. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10551e

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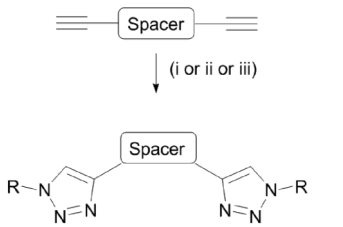
1b, self-assemble into M_2L_2 metallomacrocycles[19] with Ag(I) ions and M_2L_4 helical molecular cages[20] with Pd(II). Herein we extend that work by using the CuAAC reaction to rapidy and safely generate a family of di-1,4-substituted-1,2,3-triazole ligands with different central and peripheral substituents and examine the effect of these structural modifications on the formation of the Pd_2L_4 helical cages.

Results and discussion

Ligand synthesis and characterisation

The synthesis of the di-1,2,3-triazole ligands (**1a–f**, **2a** and **3a**) was safely achieved without the need to isolate the potentially explosive azide intermediates by employing the previously described one-pot procedures outlined in Scheme 1.[21]



1a (Spacer = 1,3-phenyl, R = Bn)
1b (Spacer = 1,3-phenyl, R = PFBn)
1c (Spacer = 1,3-phenyl, R = 4-MeOCOBn)
1d (Spacer = 1,3-phenyl, R = 4-MeOBn)
1e (Spacer = 1,3-phenyl, R = Ph)
1f (Spacer = 1,3-phenyl, R = n-hexyl)
2a (Spacer = 1,3-propyl, R = Bn)
3a (Spacer = 1,4-phenyl, R = Bn)

Scheme 1 (i) RBr or RCl, NaN_3, $CuSO_4{\cdot}5H_2O$, ascorbic acid, Na_2CO_3, DMF/H_2O (4 : 1), RT, 20 h; (ii) (a) $C_6H_{13}Br$, NaN_3, NaI, DMF/H_2O (4 : 1), MW, 250 W, 125 °C, 45 min, (b) $CuSO_4{\cdot}5H_2O$, ascorbic acid, Na_2CO_3, DMF/H_2O (4 : 1), RT, 20 h; (iii) (a) phenyl boronic acid, NaN_3, CuCl, MeOH, reflux, 6 h; (b) $CuSO_4{\cdot}5H_2O$, H_2O, sodium ascorbate, RT, 20 h. Isolated yields after chromatography.

Simply mixing either 1,6-heptadiyne, 1,4-diethynylbenzene or 1,3-diethynylbenzene with the appropriate benzylic bromide or chloride, NaN_3, $CuSO_4{\cdot}5H_2O$, Na_2CO_3 and ascorbic acid in DMF/H_2O (4 : 1) at room temperature followed by stirring for 20 h (Scheme 1) provided, after work up, the desired ligands (**1a–d**, **2a**, **3a**) in excellent yields (79–94%). The n-hexyl substituted ligand, **1f**, was obtained in 86% yield by reacting 1,3-diethynylbenzene with 1-azidohexane under the same conditions as above. The 1-azidohexane was safely formed *in situ* from 1-bromohexane and NaN_3 using microwave irradiation (125 °C, 250 W, 45 min) and reacted immediately. The phenyl substituted ligand, **1e**, was synthesised in 45% yield from 1,3-diethynylbenzene, phenyl boronic acid and NaN_3 using a modified version of the one-pot CuAAC method developed by Gao.[22]

The di-1,2,3-triazole ligands (**1a–f**, **2a** and **3a**) have been fully characterised by elemental analysis, electrospray mass spectrometry (ESMS), IR, ^1H and ^{13}C NMR (ESI†) and in one case (**1d**) by X-ray crystallography (Fig. 1, Table 1, ESI†). The X-ray crystal structure of **1d** unambiguously confirmed the bond connectivity

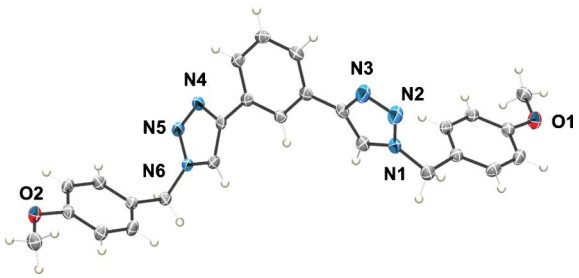


Fig. 1 A labeled ORTEP diagram showing the molecular structure of the di-1,2,3-triazole ligand **1d**. The thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°) for **1d**; N1 N2 1.343(3), N2 N3 1.311(3), N4 N5 1.318(3), N5 N6 1.343(3), N1 N2 N3 107.3(2), N4 N5 N6 106.9(2).

Table 1 Crystallographic data for **1d** and **4c**

Compound	**1d**	**4c**
	CCDC 819052	CCDC 819051
Formula	$C_{26}H_{24}N_6O_2$	$C_{112}H_{96}B_4F_{16}N_{24}O_{16}{\cdot}Pd_2$
Formula weight	452.51	2594.17
Crystal system, Space group	Monoclinic, *Pc*	Monoclinic, *C*2/*c*
a/Å	20.910(6)	27.9204(17)
b/Å	5.727(4)	22.5838(14)
c/Å	9.4091(12)	24.610(3)
α (°)	90	90
β (°)	101.318(33)	122.689(3)
γ (°)	90	90
V/Å^3	1104.8(9)	13060.2(20)
Z	2	4
Cryst. size, color, habit	0.68 × 0.43 × 0.15 mm, colourless, needle	0.32 × 0.16 × 0.14 mm, colourless, block
ρ_{calc}/mg mm^{-3}	1.360	1.494
μ/mm^{-1}	0.090	0.376
Reflections collected	31245	43487
Independent reflections (R_{int})	4074 (0.0481)	7217 (0.0687)
Data/restraints/parameters	4074/2/309	7217/12/826
Goodness-of-fit on F^2	1.116	1.044
Final R_1 and wR_2 indexes [$I > 2\sigma(I)$]	0.0315, 0.0757	0.0515, 0.1495
Final R_1 and wR_2 indexes [all data]	0.0368, 0.0864	0.0632, 0.1566
Largest difference in peak and hole/e Å^{-3}	0.129 and –0.163	0.850 and –1.147

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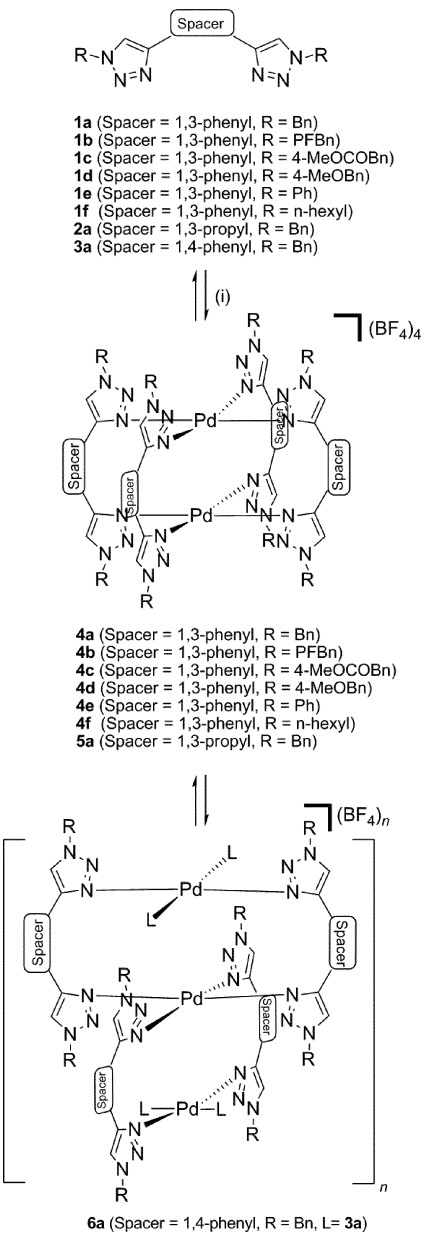
and illustrates, as expected, that 1,4-substituted triazole units are formed.

Formation of palladium(II) "click" cage complexes

With a small family of di-1,2,3-triazole ligands available, we initially examined the effect of the central spacer unit on Pd cage formation (Scheme 2). The di-benzyl substituted ligands **1a** (1,3-phenyl spacer), **2a** (1,3-propyl spacer) and **3a** (1,4-phenyl spacer) with central spacer units of different geometries and flexibilities were reacted with $[Pd(CH_3CN)_4](BF_4)_2$ in CD_3CN or d_6-DMSO solution at RT for 1 h, then the resulting reaction mixtures were examined using *in situ* ^{1}H NMR and ESMS. As outlined in our preliminary communication,[20] simply stirring the 1,3-phenyl linked ditriazole ligand, **1a** (2 equiv.) with $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.) in acetonitrile led to quantitative formation of the cage complex **4a**.



Scheme 2 (i) $[Pd(CH_3CN)_4](BF_4)_2$, CD_3CN or d_6-DMSO, 1 h, RT; or $[Pd(CH_3CN)_4](BF_4)_2$, CD_3CN, 16 h, 70 °C.

The ^{1}H NMR spectrum (CD_3CN, 298 K) of the cage complex, **4a** shows one set of sharp signals (Fig. 2b and ESI†). All the proton resonances (except H_a) in the ^{1}H NMR spectra of **4a** are shifted upfield relative to the "free" ligand **1a**, characteristic of face-to-face π–π stacking interactions (Fig. 2a and 2b). Conversely, the proton resonance of H_a is shifted downfield compared to the corresponding resonance in the "free" ligand due to the electron withdrawing effect of the palladium(II) ions, indicative of the formation of a cage architecture in which H_a is in close proximity to the metal ions. The ESMS spectrum of **4a** shows a series of isotopically resolved peaks consistent with the formulation $[Pd_2(\mathbf{1a})_4\text{-}n(BF_4)]^{n+}$ (n = 1–4) and is almost devoid of fragmentation, illustrating the remarkable stability of the cage architecture. X-ray crystallography confirmed unambiguously that **4a** is a coordinatively saturated, quadruply stranded helical cage.[20]

The *in situ* ^{1}H NMR spectrum of the palladium complex, **5a**, formed by reacting the flexible 1,3-propyl linked ditriazole ligand, **2a** (2 equiv.) with $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.) in CD_3CN indicates the clean quantitative formation of a single species. The triazole proton on the ligand undergoes a large downfield shift indicative of complexation to Pd(II) ions (ESI†). However, the proton resonances due to the benzyl substituents of the ligands are shifted upfield suggesting that some kind of face-to-face π–π stacking interaction is present. The ESMS spectrum of palladium complex, **5a**, exhibits peaks at m/z = 1906 $[Pd_2(\mathbf{2a})_4(BF_4)_3]^+$, 909 $[Pd_2(\mathbf{2a})_4(BF_4)_2]^{2+}$, and 411 $[Pd_2(\mathbf{2a})_4]^{4+}$ which all correspond to ions of the intact molecular cage structure. Additionally, there are a number of large fragment ions, m/z = 841 $[Pd(\mathbf{2a})_2(H_2O)(H)]^+$, 359 $[\mathbf{2a}+H]^+$ suggesting that the flexible cage, **5a** is less stable than **4a** under the conditions of the ESMS experiment.

In stark contrast to **4a** and **5a**, the *in situ* ^{1}H NMR and ESMS spectra of the palladium complex, **6a**, formed by reacting the ligand, **3a** (2 equiv.) with $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.) in d_6-DMSO shows no evidence of cage formation. The ^{1}H NMR spectrum (d_6-DMSO, 298 K) of **6a** shows one set of broad signals (ESI†), which are only slightly shifted from the corresponding values of the free ligand. The ESMS spectrum of **6a** is dominated by three peaks at m/z = 714 $[Pd_2(\mathbf{3a}\text{-}H)_3(H_2O)(Na)(BF_4)_2]^{2+}$, 497 $[Pd(\mathbf{3a}\text{-}H)]^+$, and 393 $[\mathbf{3a}+H]^+$ none of which are due to the intact molecular cage structure, in fact no ions corresponding to the molecular cage can be detected. In combination these results indicate that the palladium(II) complex **6a** is an oligomeric or polymeric species rather than a discrete molecular cage.

The stability of the isomeric "cages", **4a** and **6a**, was further examined computationally using DFT (ESI†). Consistent with the experimental findings, the energy minimised structure of **4a** was found to be a quadruply stranded helical cage, whereas the "cage" **6a** formed a lantern shaped species whose calculated enthalpy of formation (ΔH_{form}) was ~300 kJ mol^{-1} higher than the isomeric **4a** helical cage. Space-filling molecular models (ESI†) of **6a** indicate that the reason for this large energy difference is the presence of a severe steric interaction between the 1,4-phenyl spacer units of the **2a** ligands within the cage structure. This steric clash would be relieved by oligomerization.

We next examined whether altering the di-1,2,3-triazole ligands peripheral substituents had an effect on cage formation. As

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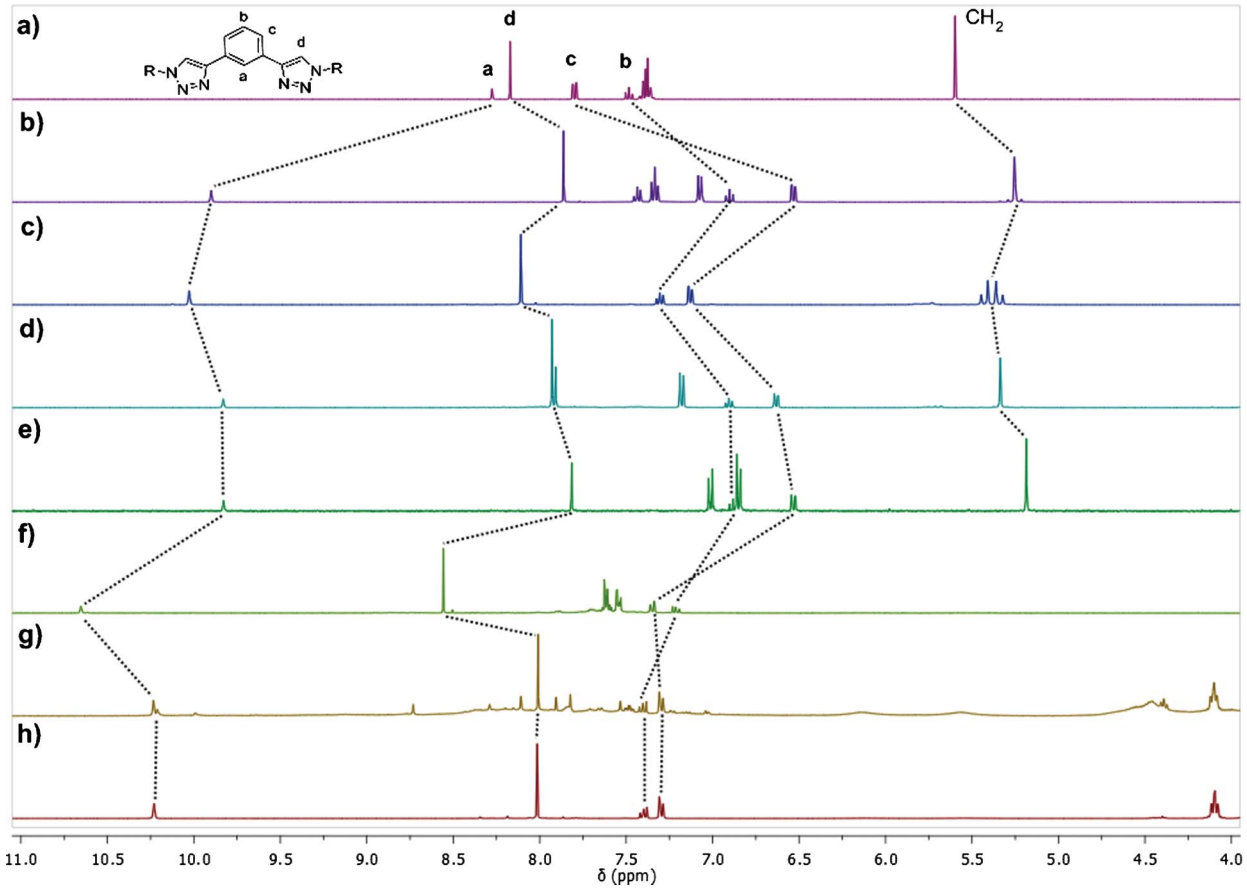

Fig. 2 Partial *in situ* ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of a) the ligand **1a**, b) the dipalladium(II) cage complex **4a**, c) the dipalladium(II) cage complex **4b**, d) the dipalladium(II) cage complex **4c**, e) the dipalladium(II) cage complex **4d**, f) the dipalladium(II) cage complex **4e**, g) the reaction mixture of **1f** and $[Pd(CH_3CN)_4](BF_4)_2$ after 1 h at RT and h) the dipalladium(II) cage complex **4f** obtained after heating (g) for 16 h at 70 °C.

the preceding experiments indicated that the 1,3-phenyl spacer unit provided the most stable Pd-cages, this core unit was kept constant and the peripheral substituents were altered to give the small family of ligands **1b–1f**, which were then treated with $[Pd(CH_3CN)_4](BF_4)_2$ in an attempt to assemble the cages **4b–4f** (Scheme 2). ^{1}H NMR and positive ion ESMS experiments were used to probe the structures of the resulting complexes. As for the parent cage, **4a**, simply mixing the 1,3-phenyl linked ditriazole ligands, **1b–e** (2 equiv.) with $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.) in CD_3CN led to quantitative formation of the cage complexes **4b–e** in less than 1 h at RT, as evidenced by the *in situ* ^{1}H NMR spectra (Fig. 2c–f). The ^{1}H NMR spectra (CD_3CN, 298 K) of the cage complexes, **4b–e** show one set of sharp signals (Fig. 2c–f and ESI†), with the characteristic downfield shift of the H_a proton resonance indicative of cage formation. Most of the other proton resonances in the ^{1}H NMR spectra of **4b–e** are shifted upfield relative to the "free" ligand due the face-to-face π–π stacking interactions, providing strong evidence that each of the different dipalladium(II) complexes adopts a helical cage structure in solution and this is further supported by DFT calculations *vide infra*.

In contrast to what was observed for **1a–e**, mixing the ligand **1f** (2 equiv.) with $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.), under identical conditions to those discussed before, did not lead to quantitative formation of the cage complex **4f**. After 1 h at RT the *in situ* ^{1}H NMR spectrum of the reaction mixture indicated that a number of species were present (Fig. 2g and the ESI†). This was a somewhat surprising result as space-filling molecular models (SPARTAN 08, MMFF) indicate that there are no obvious steric impediments to the formation of any of the cages **4a**, **4e** or **4f** (Fig. 3a–c). Van Koten and co-workers[16] have previously shown that the binding strength of 1,4-substituted-1,2,3-triazole "click" ligands can be readily tuned by altering the peripheral substituents and that alkyl substituted 1,2,3-triazoles form the most stable metal–ligand complexes. We postulated that the higher metal–ligand binding strength of the n-hexyl substituted ligand **1f** led to slower metal–ligand exchange kinetics, therefore heating the reaction mixture should increase the rate of the ligand exchange processes and allow the formation of the thermodynamic cage product. Indeed simply heating the reaction mixture at 70 °C for 16 h led to the quantitative formation of a single species whose ^{1}H NMR spectrum was very similar to the other palladium(II) cages, indicating the formation of the n-hexyl substituted cage **4f** (Fig. 2h). The energies of formation (ΔH_{form}) for the alkyl (**4f**), benzyl (**4a**) and phenyl (**4e**) substituted cages were also calculated computationally using DFT (ESI†). Consistent with the experimental findings and chemical intuition the alkyl substituted cage (**4f**) was found to be 97 kJ mol^{-1} more stable than the benzyl substituted cage (**4a**) which was in turn 19 kJ mol^{-1} more stable than the phenyl cage (**4e**) (ESI†).

The ESMS spectra of the complexes **4b–f** are similar to that observed for the parent compound, **4a**. They each show a series

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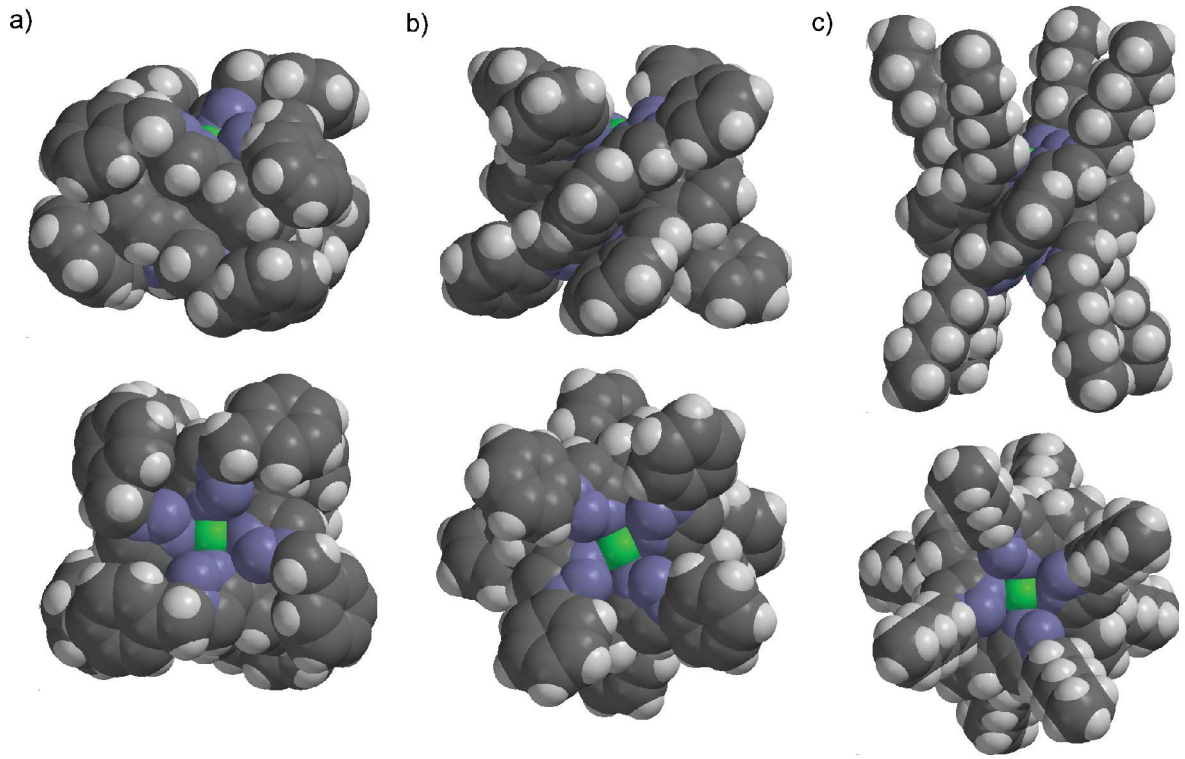

Fig. 3 Space-filling molecular models (SPARTAN 08, MMFF) of a) the benzyl substituted palladium(II) cage complex **4a**, b) the phenyl substituted palladium(II) cage complex **4e**, and c) the hexyl substituted palladium(II) cage complex **4f**. (Spartan '08 for Windows, Wavefunction, Irvine, CA).

Table 2 Diffusion coefficients obtained from ^{1}H DOSY spectra (CD_3CN, 298 K)

Ligand	Diffusion Coefficient (10^{-10} m^2 s^{-1})	Palladium Complex	Diffusion Coefficient (10^{-10} m^2 s^{-1})
1a	6.95	**4a**	3.51
1b	6.51	**4b**	3.25
1c	5.92	**4c**	3.26
1d	6.42	**4d**	3.36
1e	7.15	**4e**	3.76
1f	7.66	**4f**	3.38
2a	7.14	**5a**	4.03

of isotopically resolved peaks consistent with the formulation $[Pd_2(\mathbf{L})_4\text{-}n(BF_4)]^{n+}$ (n = 1–4) and are essentially devoid of fragmentation, further illustrating the remarkable stability of these helical cages (ESI†).

Diffusion-ordered NMR spectroscopy (DOSY)[23] provided additional support for the selective formation of the cages in CD_3CN solution. ^{1}H DOSY spectra (CD_3CN, 298 K) were obtained for the ligands **1a–f** and **2a** and the palladium cages **4a–f** and **5a** (Table 2, ESI†) and each of the proton signals in the individual spectra show the same diffusion coefficients (D) indicating that there is only one species present in solution. The ligands (**1a–1f** and **2a**) showed similar diffusion coefficients ranging from 6.42–7.66 × 10^{-10} m^2 s^{-1} consistent with their similar molecular size. The diffusion coefficients of the palladium cages (**4a–f** and **5a**) ranged from 3.25–4.03 × 10^{-10} m^2 s^{-1} indicating that all of the cages are similar in size. The D_{cage}/D_{ligand} ratio is approximately 0.50 : 1 suggesting that palladium(II) complexes are much larger than the free ligands, providing strong evidence for the selective formation of the larger molecular cage species in CD_3CN solution.[24]

The palladium "click" cages, **4a–f**, **5a** were isolated as microcrystalline solids by slow vapour diffusion of diethyl ether into the acetonitrile reaction mixtures and their purity confirmed by elemental analysis. In the case of **4c** this isolation procedure provided crystals of a quality suitable for X-ray crystallographic analysis allowing the molecular structure of **4c** to be determined. Similar to the parent palladium(II) cage, **4a**,[20] the X-ray crystal structure of **4c** illustrates that four **1c** ligands and two Pd(II) ions form a coordinatively saturated, quadruply stranded helical cage with the formula $[Pd_2(\mathbf{1c})_4](BF_4)_4$ (Fig. 4). **4c** crystallises in the monoclinic space group $C2/c$ and the asymmetric unit contains a helical cage and 16 disordered CH_3CN solvates. As with the parent cage the Pd(II) ions of **4c** are found to coordinate to the N3 nitrogens of the triazole ligands (Pd–N bond lengths range from 2.005–2.016 Å)[25] in a distorted square-planar coordination environment (N–Pd–N bond angles vary from 89.4 to 178.9°, Fig. 4). The 1,2,3-triazole donor units are rotated approximately 45° out of the square plane and this twisting generates the overall helical structure with a helical pitch of 90°. The helical cage is additionally stabilised by a number of face-to-face π–π stacking interactions (the centroid-centroid distance 3.745 Å) between the central 1,3-disubstituted phenyl spacer units and 1,2,3-triazole groups on adjacent ligands. Additionally, there are edge-to-face π–π interactions between benzyl groups on adjacent ligands (the carbon-centroid distance 3.722 Å) which potentially further stabilise the cage structure. The helical twisting flattens the cage

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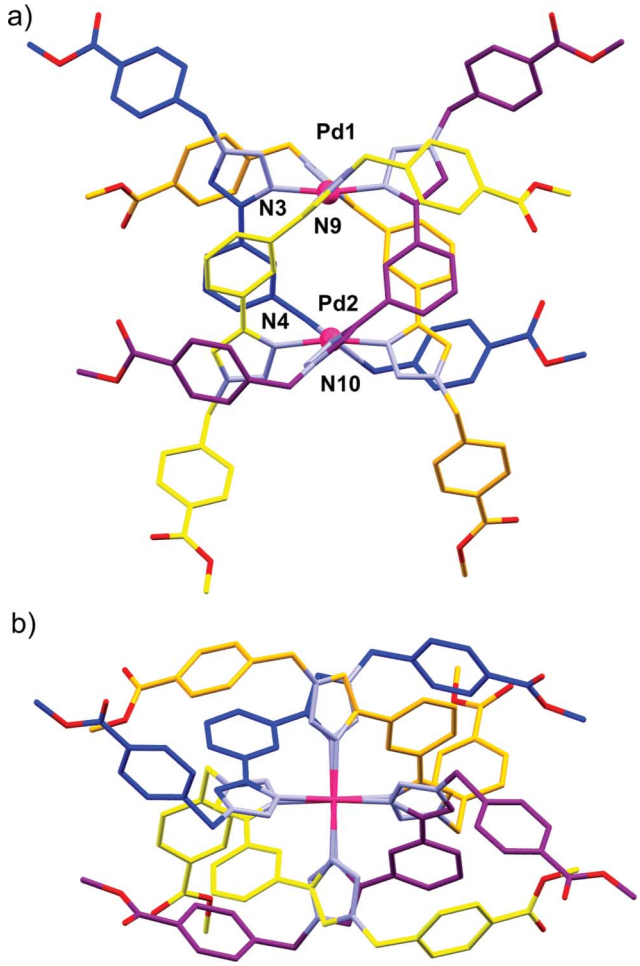

Fig. 4 a) A labeled tube representation (side view) of the molecular structure of the cage **4c**; b) a top view of the molecular structure of **4c**. For clarity, each of the four **1c** ligands are represented in a different colour. The hydrogen atoms, solvent molecules and BF_4^- anions are omitted for clarity. Selected bond lengths (Å) and angles (°) for **4c**; Pd1 N3 2.005(3), Pd1 N9 2.008(6), Pd2 N4 2.016(6), Pd2 N10 2.010(3), Pd1 Pd2 4.9219(7), N3 Pd1 N9 90.1(2), N4 Pd1 N10 89.4(2), N3 Pd1 N3′ 178.9(2), N9 Pd1 N9′ 169.9(2), N4 Pd1 N4′ 169.3(2), N10 Pd1 N10′ 177.5(2) Symmetry Code; $-x$, y, $1/2-z$.

structure and results in a small cage cavity with the dimension 3.5 × 3.8 × 4.9 Å, which while slightly larger than the parent, **4a** cage, appears to be too small to incorporate guest molecules.

We have shown that di-1,4-substituted-1,2,3-triazole "click" ligands can be used as pyridine surrogates to self-assemble coordinatively saturated, quadruply stranded helicate cages with Pd(II) ions. These $[Pd_2(L)_4](BF_4)_4$ cages are stable in solution and the solid state as evidenced by ^{1}H NMR, DOSY, ESMS and X-ray crystallographic experiments. The mild, modular "click" method used to form the di-1,4-disubstituted-1,2,3-triazole ligands should allow the ready synthesis of complex functionalised ligand architectures which could be exploited for the generation of novel metallosupramolecular cages with unique properties.

Acknowledgements

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