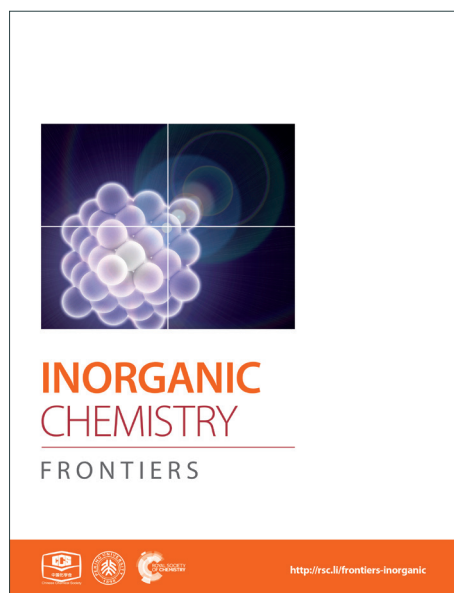
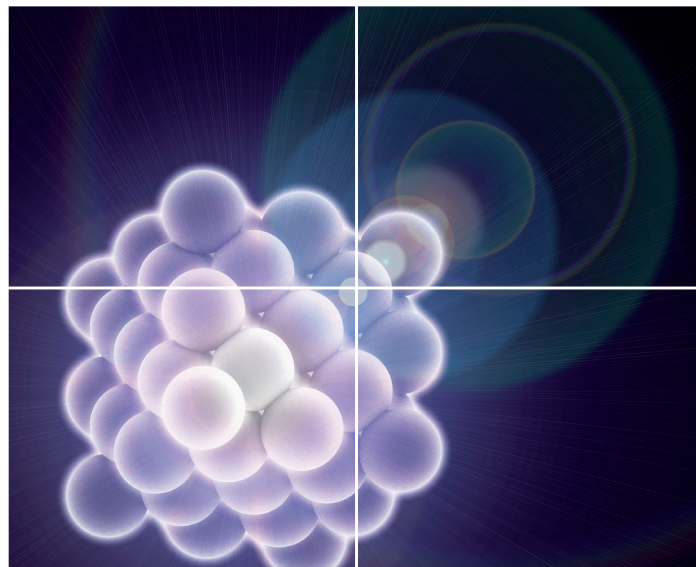


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Size Dependent Effect of New Organometallic Triptycene Tectons on the Dimension of Self-Assembled Macrocycles

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Abstract

Design, synthesis and characterization of two new triptycene containing ditopic Pt(II) organometallic complexes are being reported. These complexes comprise of two peripheral bis(*trans*-trialkylphosphine)platinum units either directly σ -bonded to the central triptycene moiety or connected via bridging ethynyl spacer linkage. The potential utility of these organometallic complexes as ditopic acceptor building block in the construction of neutral metallasupramolecular macrocycles containing the triptycene motif is explored. Triptycene motif containing supramolecules were characterized by multinuclear NMR (including ¹H DOSY), mass spectrometry (MALDI-TOF-MS) and elemental analyses. While the self-assembly of longer acceptor linker with terephthalate results in the formation of a [3+3] self-assembled macrocycle, the use of relatively shorter acceptor linker yields the corresponding [2+2] supramolecular framework. The shape and dimension of these supramolecular structures were also predicted by geometry optimization using PM6 semiempirical molecular orbital methods and results corroborate well with the experimental observations. These two self-assembled macrocycles are unique examples of triptycene based neutral “platinamacrocycles” reported in literature till date. Investigation, as to how the shape and size of the resulting discrete supramolecular framework is affected on changing the length and rigidity of the triptycene based acceptor linkers has been discussed.

Introduction

Design and self-assembly of finite nanoscopic supramolecular coordination complexes (SCCs) via coordination driven self-assembly approach is an important area of research in supramolecular chemistry.¹ In last two decades, a considerable number of 2D metallacycles and 3D metallacages have been reported.² The geometrical shape and size of these supramolecules can be predicted prior to self-assembly based on the ‘bite angle’ of the organic donor and metal containing acceptor tecton.^{2a,b} Several structural motifs [such as ferrocene, carboranes, cavitands, highly aromatic systems (such as anthracene, phenanthrene, perylene, pyrene, etc.), dendrons and others] have been incorporated in these self-assembled supramolecules.³ This has been achieved by design of specific modular subunits containing these structural motifs and subsequently using them as tectons in the self-assembly protocol. Additionally, the shape of the supramolecules has been effectively tailored using building blocks of various dimensions.

Triptycene is the smallest member in the class of compound called iptycenes. Triptycene has a rigid three dimensional framework decorated with three benzene ring in a paddlewheel orientation. Owing to the high level of symmetry associated with its rigid framework, triptycene derivatives have found application in supramolecular chemistry,⁴ material science⁴ and polymer chemistry.⁵ In this context, the use of triptycene motifs as tectons for discrete metallasupramolecular architectures is in very nascent stage.⁶ A detailed literature search has revealed that only a handful of triptycene based organometallic complexes have been reported so far.⁷ Consequently, their use in design of self-assembled metallasupramolecular framework has not been explored. Recently, we have reported (for first time) the use of organometallic triptycene derivatives as building blocks in the design of ionic three dimensional discrete supramolecular cages.^{7b}

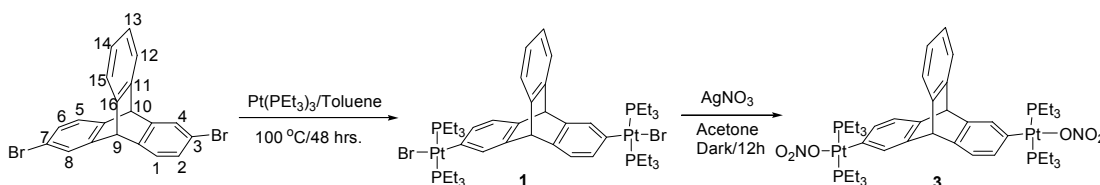
In continuation of our research efforts towards synthesis of new triptycene based donor/acceptor linkers and their use as modified subunits in supramolecular chemistry,^{7a,b} herein we report the synthesis of two new triptycene containing ditopic organoplatinum complexes. Complex **1** was synthesized by double oxidative-addition of Pt(PEt₃)₃ with dibromotriptycene.⁸ Using the σ -acetylide synthetic methodology,⁹ organometallic complex **2** was obtained upon reaction of diethynyltriptycene with *trans*-bis(triethylphosphine)platinum(II). The halogen atoms (bromine/iodine) in these newly synthesized organometallic complexes (**1** and **2**) were subsequently exchanged with more labile nitrate anion by salt metathesis reaction with silver nitrate (**3** and **4** respectively). All new organoplatinum complexes (**1-4**) have been fully characterized by FT-IR and multinuclear NMR spectroscopy, mass spectrometry and elemental analyses techniques. These ditopic triptycene based organometallic linkers are structurally rigid with predefined bite angles and thus they have potential to act as metal-containing acceptor tectons for the construction of discrete metallasupramolecular architectures. To illustrate this point, herein we report the self-assembly of two new platinum(II) based neutral supramolecular macrocycles (**5** and **6**) using triptycene based organometallic linkers **3** and **4** as acceptor unit and ditopic angular carboxylates as bridging ligand. Macrocycles **5** and **6** represent the first example of triptycene based neutral metallasupramolecular architectures. These newly synthesized metallasupramolecular macrocycles were completely characterized by multinuclear NMR spectroscopy including ¹H DOSY, MALDI-TOF mass spectrometry and elemental analyses techniques. Further insight into the shape and size of the neutral macrocycles was obtained via molecular simulation, employing a PM6 semiempirical molecular orbital method. Theoretical calculations suggest that the dimensions of the metallosupramolecules are in nanoscalar range.

Results and Discussion

Synthesis and characterization of triptycene based ditopic organoplatinum acceptor linkers

Halogenated arenes are one of the most popular class of synthons utilized in the design and synthesis of metal-containing acceptor building blocks for subsequent use in coordination driven self-assembly processes.¹⁰ Desired triptycene organoplatinum complex **1** was efficiently

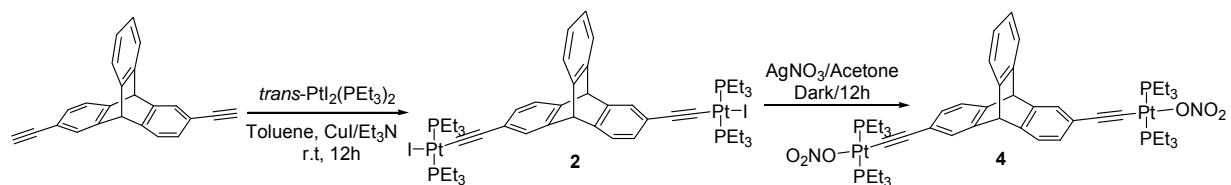
synthesized by double oxidative addition⁸ of Pt(0) to the corresponding 2,6-dibromotriptycene¹¹ in 66% yield as shown in Scheme 1.



Scheme 1. Synthesis of triptycene based organoplatinum complexes **1** and **3**

In past decade, design and synthesis of organoplatinum acceptor complexes containing ethynyl group as spacer (bridging the central core motif and the peripheral metal center) has attracted research attention of supramolecular chemists.¹² Introduction of ethynyl group imparts rigidity to the resulting linker and simultaneously alters its length, shape and directionality (bite angle). Subsequently, supramolecular tectons/building blocks are derived from these molecules with multiple ethynyl spacers, which in turn are utilized for the self-assembly of exciting nanoscale macrocycles and cages.¹²

Reaction of appropriate 2,6-diethynyltriptycene^{5d} with *trans*-PtI₂(PEt₃)₂ in a mixture of toluene (solvent), triethylamine (base) and in the presence of cuprous(I) iodide catalyst, the corresponding di-substituted metal complex **2** was obtained in good yields (Scheme 2).



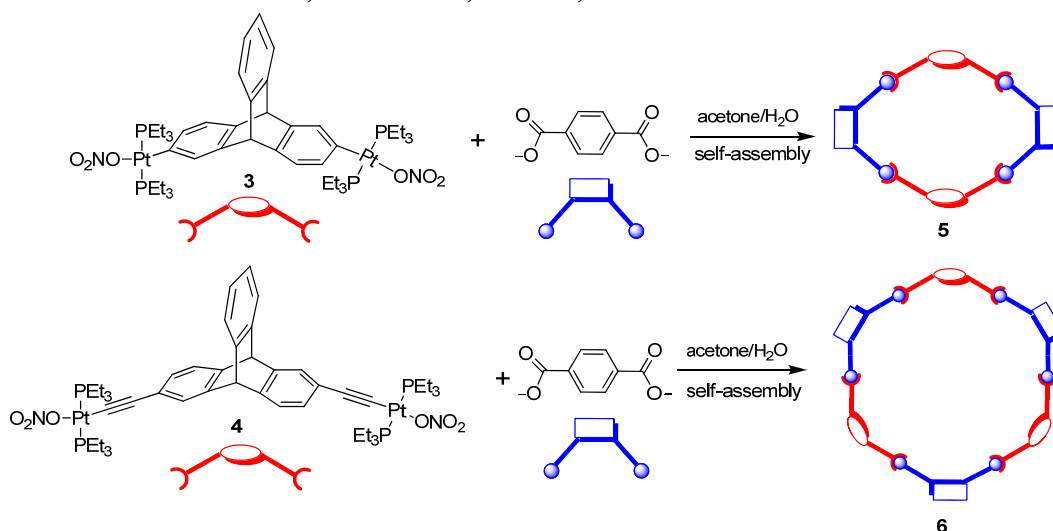
Scheme 2. Synthesis of triptycene based organoplatinum complexes **2** and **4**

The halogen atoms (bromine/iodine) in these newly synthesized organometallic complexes (**1** and **2**) were subsequently exchanged with more labile nitrate anions by salt metathesis reaction with silver nitrate. Nitrate salts (**3** and **4**) were obtained in excellent yields (Scheme 1 and 2). These triptycene-organoplatinum complexes are white coloured solids that are stable in air/moisture with high solubility in common organic solvents. FTIR spectrum of complexes **2** and **4** exhibit intense peak at 2111 cm⁻¹ and 2121 cm⁻¹ respectively due to the ethynyl functional group. The ¹H NMR also suggested formation of the desired organometallic complexes due to the appearance of a singlet peak between 5.06 and 5.31 ppm corresponding to the bridgehead protons of complexes **1-4** (Supporting information). As expected, appearance of peaks in the range $\delta = 0.95$ to 2.20 ppm for complexes **1-4** are attributed to the ethyl group of PEt₃ units bound to Pt(II) centers. Organometallic complexes were also characterized by ³¹P{¹H} NMR spectroscopy (Supporting information). The ³¹P{¹H} NMR spectra of both halogenated complexes **1** and **2** show a sharp singlet at 12.39 and 8.56 ppm respectively with concomitant

^{195}Pt satellites ($\Delta^1J_{\text{PPt}} = 1383$ Hz for **1** and 1166 Hz for **2**). In case of nitrate salts **3** and **4**, the ^{31}P resonance due to phosphine group shows a downfield shift in peak position compared to the corresponding halo analogues with the appearance of singlet at 18.23 ppm ($\Delta^1J_{\text{PPt}} = 1453$ Hz) and 20.19 ppm ($\Delta^1J_{\text{PPt}} = 1244$ Hz) respectively. These chemical shifts observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR are in expected range for a *trans*-PtP₂ systems connected to arene⁸ and ethynyl moiety.⁹ In the ^{31}P NMR of complexes **1** and **2**, the appearance of a single sharp singlet also suggests that phosphine groups are chemically equivalent with a *trans* orientation of phosphine groups at the square planar Pt(II) centre. Formation of complexes **1-4** were further confirmed by mass spectrometry (ESI-MS) analyses and elemental analyses (supporting information).

Self assembly of 2D macrocycles

Triptycene based organoplatinum complexes **3** and **4** are ditopic (having two reactive sites) moieties and hence are potential acceptor tectons that may be reacted with appropriate ditopic donor ligands to yield metallamacrocycle via coordination driven self-assembly paradigm. In order to test this hypothesis, an acetone solution of **3** was reacted with an aqueous solution of disodium terephthalate in 1:1 stoichiometric ratio at ambient temperature (Scheme 3). This resulted in a gradual precipitation of a neutral assembly **5** as a white solid, which upon washing (with water) and recrystallization (from chloroform) yielded white microcrystalline solid (81% isolated yield). The product obtained in this self-assembly reaction is highly soluble in common organic solvents such as DCM, chloroform, ethanol, methanol and THF.



Scheme 3. Synthesis of molecular macrocycles **5** and **6**

The product thus obtained was subjected to NMR spectroscopic analysis to ascertain its composition. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of the product recorded in CDCl_3 , exhibited a sharp singlet (δ 16.14 ppm) with accompanying ^{195}Pt satellites ($^1J_{\text{PPt}} = 1459$ Hz) shifted upfield relative to the precursor acceptor linker **3** by 2 ppm, suggesting the formation of a highly symmetrical self-assembled species in which all phosphorous atoms are chemically equivalent (Figure 1a). The shift in the peak position of ^{31}P NMR signal is a clear indication of new metal-ligand

coordination. ^1H NMR spectrum of the product (Figure 1b) also suggested the incorporation of both terephthalate (sharp singlet at 7.96 ppm assigned to protons on the phenyl ring of terephthalate unit) and triptycene motif (peaks at 5.07 ppm due to the bridgehead proton). Integration of ^1H peaks corresponding to terephthalate and that due to triptycene motif suggests presence of these two tectons in 1:1 stoichiometric ratio. Thus coordination between triptycene containing Pt^{II}_2 unit and terephthalate is confirmed from the multinuclear NMR spectra of the product. Additionally, this organometallic macrocycle advocates (**5**) a single trace in the ^1H DOSY NMR (supporting information), indicating the formation of a single product and thereby ruling out the presence of additional species such as other macrocycles or oligomers in solution. However, NMR spectroscopy technique does not predict the number of each unit (organometallic acceptor/organic donor) present in the self-assembled product. In such a situation, mass spectrometry has been utilized as a powerful tool to interpret the composition of the macrocyclic product. In the present case, MALDI-TOF-MS spectrometric analysis confirmed the actual composition of the macrocycle **5** (supporting information). The MALDI-TOF-MS spectrum of **5** showed two peaks at $m/z = 2560.9$ and $m/z = 2582.9$ corresponding to $[2+2+\text{H}]^+$ and $[2+2+\text{Na}]^+$ species, assuming $[2+2]$ self-assembly between two units each of triptycene containing Pt^{II}_2 unit and terephthalate. These signals were isotopically resolved (Figure 2a) and these are in good agreement with theoretically calculated isotopic distribution patterns, assuming $[2+2]$ self-assembled macrocycle.

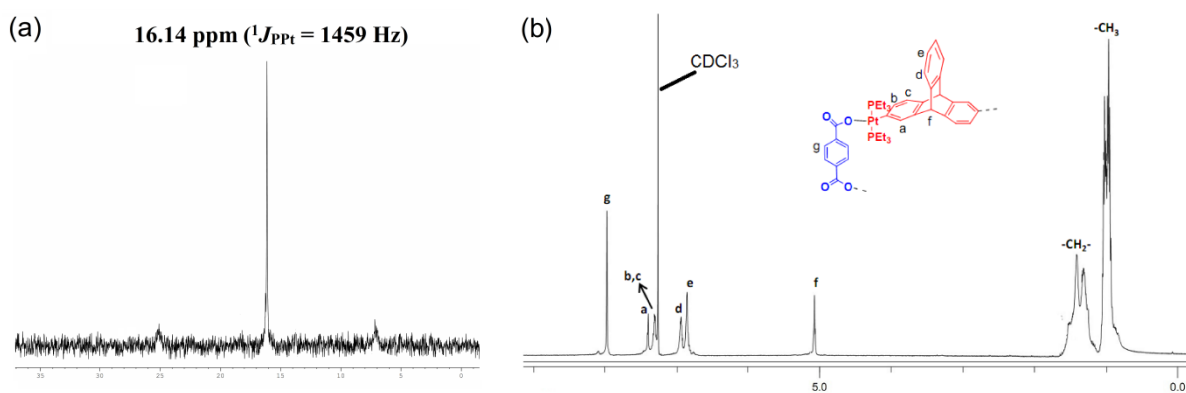


Figure 1. (a) $^{31}\text{P}\{^1\text{H}\}$ NMR and (b) ^1H NMR spectrum of macrocycle **5** in CDCl_3

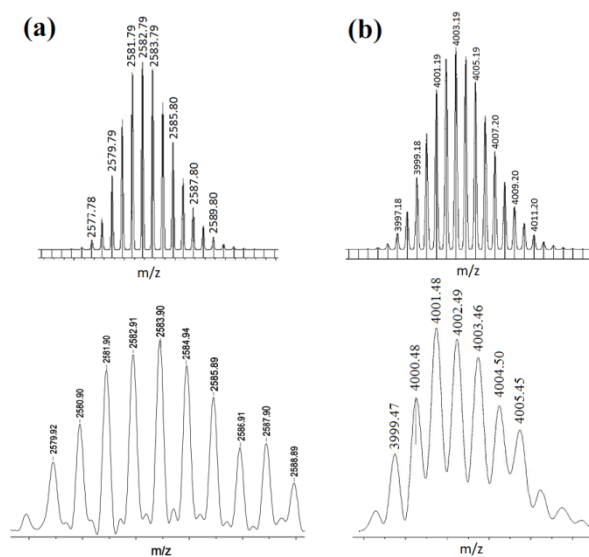


Figure 2. Theoretical (top) and experimental (bottom) MALDI-TOF-MS spectra of (a) macrocycle **5** and (b) macrocycle **6**

Both organometallic complexes **3** and **4** have a central triptycene core and contain two Pt(II) acceptor centers (with the same predefined bite angle). Moreover, in both **3** and **4**, the same phosphine ligands are attached to the Pt(II) center. However, the latter is longer in length than the former, because of the presence of the ethynyl spacer groups in **4** that bridge the triptycene core and the peripheral Pt(II) centers. Reaction of acceptor linker **4** with disodium terephthalate proceeded in similar manner as described in case of **3**, with the yield of a white microcrystalline solid (**6**, isolated yield 78%). ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR (supporting information) of the product suggested incorporation of both subunits (organometallic triptycene based acceptor unit and terephthalate) as well as formation of a highly symmetrical product (sharp ^{31}P singlet at 18.30 ppm with concomitant Pt satellites; $^1J_{\text{PPt}} = 1258$ Hz). Furthermore, a single diffusion coefficient in the ^1H DOSY NMR points towards the formation of a single product and ruled out the possibility of oligomeric species in solution (supporting information). In this case also, the product obtained was subjected to MALDI-TOF-MS analysis to identify its composition. MALDI-TOF-MS analysis of **6** exhibited formation of [3+3] macrocycle due the presence of a peak at $m/z = 4001.4$ corresponding to $[3+3+\text{Na}]^+$ species. This peak ($m/z = 4001.4$) was also isotopically resolved and was found to be in good agreement with its theoretical distribution (Figure 2b). Interestingly, in this case evidence for the formation of [2+2] self-assembled product was not observed in MALDI-TOF-MS spectrometric studies. This is evident from the absence of molecular ion peaks for [2+2] adducts at $m/z = 2653.8$ $[2+2+\text{H}]^+$ and 2675.7 $[2+2+\text{Na}]^+$ in MALDI-TOF-MS analysis. Thus mass spectrometric studies indicated that use of a longer acceptor tecton (**4**) results in the formation of a [3+3] self-assembled metallamacrocycle, while a relatively smaller acceptor tecton (**3**) yields a [2+2] supramolecular framework (Scheme 3). All our attempts to obtain X-ray quality single crystals in case of self-assembled macrocycles **5** and **6** were unsuccessful. However, to explain the observed difference in composition of the self-

assembled products upon use of acceptor linkers of different sizes, thermodynamic parameters of dimeric and trimeric adducts were calculated using PM6 semiempirical molecular orbital method.¹³ On comparing [2+2] and [3+3] metallacycles, it is known that the formation of [3+3] adduct is entropically disfavored, as a smaller number of molecular ensembles would result compared to the number of [2+2] macrocycles that can be generated using same number of building blocks.¹⁴ Therefore, in case of linker **4**, the anomalous formation of [3+3] self-assembled macrocycle **6** over entropically more preferable [2+2] product can be explained by comparing the stabilization energy which is brought by a single monomer of the adduct. The energy (heat of formation) optimization by PM6 semiempirical molecular orbital method reveals that for linker **4**, the stabilization energy for the single monomer of the [3+3] adduct is $E_{[3+3]}/3 = (-1656.64/3) = -552.21$ KJ/mol. On the other hand, in case of [2+2] adduct, the stabilization energy of the single monomer is $E_{[2+2]}/2 = (-981.50/2) = -490.75$ KJ/mol. Therefore in case of [3+3] adduct, the stabilization energy which is brought by a single monomer of the adduct is higher than that of [2+2] adduct by 61.46 KJ/mol. This energy calculation strongly supports the observed formation of [3+3] macrocycle over [2+2] structure in case of linker **4** as indicated by MALDI-TOF-MS analysis. Additionally, the geometry of the macrocycles **5** and **6** were also optimized by PM6 molecular orbital methods. Internal dimensions of the macrocycles **5** and **6** are depicted in figure 3. Optimized geometry of the macrocycles **5** and **6** reveal that in both cases, platinum centers display slightly distorted square planar geometry resulting from the coordination of oxygen atoms of dicarboxylate ligands.

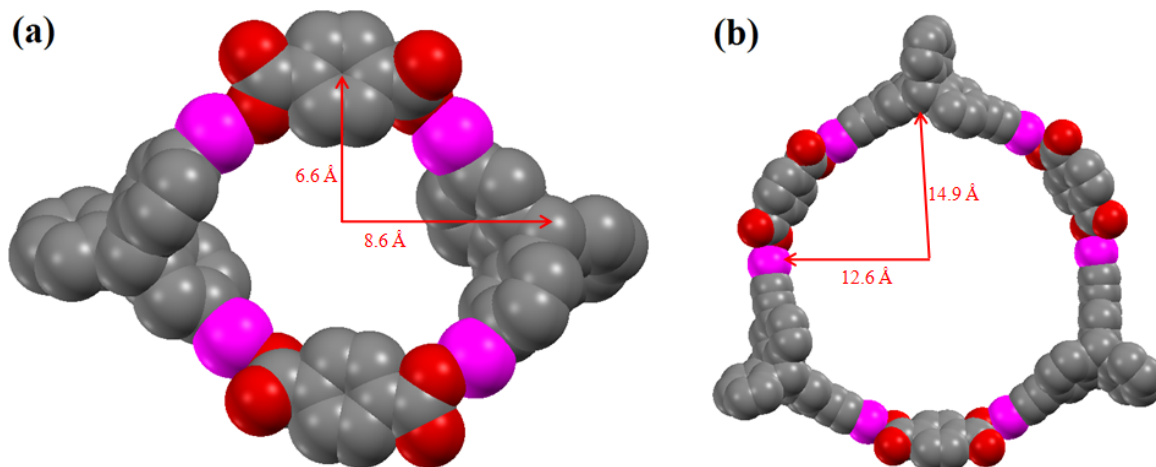


Figure 3. Simulated spacefill molecular model of (a) macrocycle **5** and (b) macrocycle **6** optimized by PM6 semiempirical molecular orbital methods. Phosphine ligands and H atoms are omitted for clarity (grey: C, red: O, pink: Pt)

Conclusion

In summary, we report the synthesis of two new triptycene containing organoplatinum complexes containing two Pt(II) centers in reasonably good yields. In these complexes, the triptycene core is either σ -bonded to the peripheral bis(*trans*-trialkylphosphine)platinum units

directly or via a bridging ethynyl spacer unit. These triptycene containing ditopic Pt^{II}₂ organometallic complexes and their corresponding nitrate salts were characterized with FT-IR, multinuclear NMR spectroscopy, mass spectrometry and elemental analyses. The presence of triptycene or ethynyltriptycene backbone imparts rigidity to these organometallic complexes. Moreover, the separation of the Pt(II) centers has been spatially tuned by the inclusion or exclusion of ethynyl groups. Further, the potential of these organometallic tectons as supramolecular acceptor synthons in coordination driven self-assembly protocol has been tested/explored. In this regard, two neutral nanoscalar metallamacrocycles (**5** and **6**) have been constructed using these triptycene based organoplatinum complexes in conjugation with a dicarboxylate anion (terephthalate). Multinuclear NMR spectroscopy, including ¹H DOSY, of these supramolecules (**5** and **6**) ruled out formation of multiple oligomeric species and suggested formation of single highly symmetrical discrete moieties. The chemical composition of these macrocycles are determined by mass spectrometric (MALDI-TOF-MS) analysis, which indicated the formation of a [3+3] self-assembled metallamacrocycle (**6**) in cases of longer acceptor linker **4**, while the use of relatively short linker **3** yields the [2+2] supramolecular framework **5**. The formation of entropically disfavoured [3+3] self-assembled adduct in case of linker **4** was further supported by results obtained from computational calculations. The comparison of stabilization energies, optimized by PM6 semiempirical molecular orbital method, suggests preferential formation of [3+3] adduct over corresponding [2+2] adduct in case of linker **4** as experimentally observed by MALDI-TOF-MS analysis. The shape and dimension of these nanoscalar frameworks were also predicted from molecular simulations using PM6 semiempirical molecular orbital methods. To the best of our knowledge, self-assembled macrocycles **5** and **6** are unique examples of triptycene based neutral “platinamacrocyles” till date. To summarize, facile and efficient synthetic protocol for the construction of neutral metallasupramolecular framework containing triptycene motif has been described. Additionally, the effect of change in the dimension of the triptycene based acceptor building block on the shape and size of the resulting supramolecular framework is studied. Triptycene based organometallic acceptors, as described in this manuscript, has immense potential in the design of new self-assembled Supramolecular Coordination Complexes (SCCs) and Metal–Organic Frameworks (MOFs). The platinamacrocyles reported in literature are known to be very stable and have several applications in terms of host-guest chemistry. Due to the presence of large void space in the cavity, the newly synthesized platinamacrocyles reported herein may also have interesting host-guest properties. Studies are currently undergoing in our laboratory in this direction.

Experimental Section:

General Details:

All chemicals and anhydrous solvents used in this work were purchased from commercial sources and used without further purification. 2,6-dibromotriptycene,¹¹ 2,6-diethynyltriptycene^{5d} and tris(triethylphosphine)platinum(0)¹⁵ were prepared by following the reported literature procedures. FTIR spectra were recorded in a PerkinElmer Spectrum 400 FT-IR

spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on Bruker 400 or 500 MHz spectrometers. Elemental analyses were carried out using a Thermo Scientific Flash 2000 Organic Elemental Analyzer. MALDI-TOF-MS spectra of the compounds were recorded using a Bruker UltrafleXtreme™ MALDI-TOF/TOF mass spectrometer. DOSY NMR measurements were performed on a Bruker AV 500 NMR spectrometer using a 5mm gradient probe at 298K. DOSY experiments were done with a standard Bruker pulse sequence (ledbpgp2s) with longitudinal eddy current delay.

Synthesis of 2,6-bis(*trans*-Pt(PEt₃)₂Br)Triptycene (1): To a 25 ml Schlenk flask containing one equiv. 2,6-dibromotriptycene (38 mg, 0.09 mmol) and four equiv. Pt(PEt₃)₃ (200 mg, 0.364 mmol), 10 ml dry toluene was added in a glove box. The reaction mixture was stirred for 48 h at 100 °C under nitrogen. Resulting light yellow coloured solution was evaporated to dryness under vacuum in a rotary evaporator. Yellow coloured residue thus obtained was purified by column chromatography over silica gel eluting with DCM/hexane (2.5:1, upto 9:1, v/v) affording pure organometallic complex **1** as white solid.

Yield: 84 mg, 71%, mp 237-238 °C; ^1H NMR (CDCl₃, 400 MHz): δ 1.13-1.22 (m, 36H, -CH₃), 1.48-1.57 (m, 24H, -CH₂-), 5.06 (s, 2H, -CH), 6.82-6.93 (m, 6H, Ar-H), 7.26-7.29 (m, 2H, Ar-H), 7.32-7.33 (m, 2H, Ar-H). ^{31}P NMR (CDCl₃, 162 MHz): δ 12.39 ($\Delta^1 J_{\text{P-Pt}} = 1383$ Hz). IR (KBr): 2961, 2925, 2876, 2852, 1585, 1450, 1413, 1378, 1255, 1240, 1168, 1035, 848, 764, 742 cm⁻¹. Anal. Calcd. For C₄₄H₇₂Br₂P₄Pt₂: C, 41.45; H, 5.69. Found: C, 41.57; H, 5.81. ESI-MS: m/z calcd for [M-Br]⁺: 1193.3, found 1194.29.

Synthesis of 2,6-bis(*trans*-Pt(PEt₃)₂I)ethynyltriptycene (2): One equiv. 2,6-diethynyltriptycene (27.7 mg, 0.092 mmol) and four equiv. *trans*-diiodobis(triethylphosphine)platinum (252 mg, 0.368 mmol) were charged in a 25 ml Schlenk flask in the glove box. Subsequently, 12 ml dry toluene and 4 ml freshly distilled triethylamine were added under nitrogen. The solution was stirred for 10 min at room temperature before addition of 0.2 equiv CuI in one portion. After overnight stirring at room temperature, triethylammoniumiodide precipitated out from solution, which was separated by filtration. Toluene was evaporated in rotary evaporator and resulting yellow residue was purified by column chromatography on silica gel eluting with 3% ethyl acetate in hexane first and then increasing to 6% ethyl acetate in hexane to isolate the complex **2** as white solid.

Yield: 83 mg, 64%, mp 240-242 °C; ^1H NMR (CDCl₃, 400 MHz): δ 1.09-1.73 (m, 36H, -CH₃), 2.14-2.20 (m, 24H, -CH₂-), 5.29 (s, 2H, -CH), 6.90 (dd, $J = 7.6$, $J = 1.2$, 2H, Ar-H), 6.96-6.99 (m, 2H, Ar-H), 7.20-7.22 (d, $J = 7.6$, 2H, Ar-H), 7.25 (s, 2H, Ar-H), 7.34-7.36 (m, 2H, Ar-H). ^{31}P NMR (CDCl₃, 162 MHz): δ 8.56 ($\Delta^1 J_{\text{P-Pt}} = 1166$ Hz). IR (KBr): 3061, 2961, 2930, 2874, 2111, 1610, 1465, 1409, 1376, 1251, 1031, 767, 742 cm⁻¹. Anal. Calcd. For C₄₈H₇₂I₂P₄Pt₂: C, 40.69; H, 5.12. Found: C, 40.82; H, 5.26. ESI-MS: m/z calcd for [M-I]⁺: 1289.28, found 1289.00.

Synthesis of complex 3 and 4: To a stirred solution of complex **1** or **2** (0.03 mmol) in chloroform, AgNO₃ (10.2 mg, 0.06 mmol) was added in one portion. The reaction mixture was stirred overnight in dark at room temperature. The resulting yellow precipitate of silver halide was filtered through a bed of celite and the filtrate was evaporated to dryness to obtain the corresponding nitro complex **3** or **4** as white solid.

Complex 3. Yield: 35 mg, 94%, mp 234-236 °C; ¹H NMR (CDCl₃, 400 MHz): δ 0.95-1.09 (m, 36H, -CH₃), 1.24-1.46 (m, 24H, -CH₂-), 5.10 (s, 2H, -CH), 6.78 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.86 (d, *J* = 7.2, 2H, Ar-H), 6.95-6.98 (m, 2H, Ar-H), 7.30-7.32 (m, 4H, Ar-H). ³¹P NMR (CDCl₃, 162 MHz): δ 18.23 ($\Delta^1 J_{\text{PPt}} = 1453$ Hz). IR (KBr): 2962, 2925, 2875, 2853, 1585, 1465, 1444, 1376, 1276, 1237, 1034, 997, 765, 738 cm⁻¹. Anal. Calcd. For C₄₄H₇₂N₂O₆P₄Pt₂: C, 44.79; H, 5.64; N, 2.18. Found: C, 44.92; H, 5.74; N, 2.25. ESI-MS: *m/z* Calcd. for [M-NO₃]⁺: 1176.37, Found: 1176.13.

Complex 4. Yield: 36 mg, 93%, mp 204-206 °C; ¹H NMR (CDCl₃, 500 MHz): δ 1.15-1.21 (m, 36H, -CH₃), 1.87-1.93 (m, 24H, -CH₂-), 5.31 (s, 2H, -CH), 6.87 (d, *J* = 7.2 Hz, 2H, Ar-H), 6.99-7.00 (m, 2H, Ar-H), 7.21-7.23 (m, 4H, Ar-H), 7.35-7.37 (m, 2H, Ar-H). ³¹P NMR (CDCl₃, 202 MHz): δ 20.19 ($\Delta^1 J_{\text{PPt}} = 1244$ Hz). IR (KBr): 2966, 2932, 2877, 2121, 1476, 1467, 1384, 1277, 1036, 989, 768, 743 cm⁻¹. Anal. Calcd. For C₄₈H₇₂N₂O₆P₄Pt₂: C, 41.29; H, 5.64; N, 2.33. Found: C, 41.37; H, 5.71; N, 2.4. ESI-MS: *m/z* Calcd. for [M-NO₃]⁺: 1224.37, Found: 1224.40.

Synthesis of 2D macrocycles 5 and 6: To a 2 mL acetone solution containing 0.015 mmol of dinitrate (**3** or **4**), 0.5 mL aqueous solution of disodium terephthalate (0.015 mmol) was added dropwise with continuous stirring (5 min), whereupon a white product precipitated. This was centrifuged, washed several times with water and subsequently dried in vacuum. The product was collected, and recrystallized from chloroform and washed with ether to obtain the macrocycle **5** or **6** as white microcrystalline solid.

Macrocycle 5. Yield 13.7 mg, 81%; ¹H NMR (CDCl₃, 500 MHz): δ 0.95-1.04 (m, 72H, -CH₃), 1.30-1.53 (m, 48H, -CH₂-), 5.07 (s, 4H, -CH), 6.86 (s, 4H, Ar-H), 6.94-6.95 (m, 8H, Ar-H), 7.30-7.31 (m, 4H, Ar-H), 7.39 (s, 4H, Ar-H), 7.96 (s, 8H, Ar-H). ³¹P NMR (CDCl₃, 162 MHz): δ 16.14 ($\Delta^1 J_{\text{PPt}} = 1459$ Hz). Anal. Calcd. For C₁₀₄H₁₅₂O₈P₈Pt₄: C, 48.82; H, 5.99. Found: C, 48.65; H, 6.13. IR (KBr): 2963, 2929, 2877, 1611, 1454, 1413, 1378, 1330, 1253, 1034, 821, 766, 743 cm⁻¹. MALDI-TOF-MS: *m/z* Calcd. for [M+H]⁺: 2560.81, Found: 2560.9 and Calcd. for [M+Na]⁺: 2582.79, Found: 2582.9.

Macrocycle 6. Yield 13.76 mg, 78%; ¹H NMR (CDCl₃, 500 MHz): δ 1.14-1.19 (m, 108H, -CH₃), 1.87-1.90 (m, 72H, -CH₂-), 5.28 (s, 6H, -CH), 6.85 (d, *J* = 7.5 Hz, 6H, Ar-H), 6.96-6.97 (m, 6H, Ar-H), 7.20-7.21 (m, 12H, Ar-H), 7.33-7.35 (m, 6H, Ar-H), 7.95 (s, 12H, Ar-H). ³¹P NMR (CDCl₃, 162 MHz): δ 18.30 ($\Delta^1 J_{\text{PPt}} = 1258$ Hz). Anal. Calcd. For C₁₆₈H₂₂₈O₁₂P₁₂Pt₆: C, 48.82; H, 5.99. Found: C, 48.65; H, 6.13.

50.68; H, 5.77. Found: C, 50.45; H, 5.91. IR (KBr): 2963, 2926, 2877, 2851, 2114, 1625, 1465, 1377, 1328, 1034, 822, 766, 742 cm^{-1} . MALDI-TOF-MS: m/z Calcd. for $[\text{M}+\text{Na}]^+$: 4001.19, Found: 4001.4.

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Authors' contribution: N.D and S.C conceived the research idea. S.C. synthesized all new triptycene based organometallic complexes and the neutral metallacycles reported in this manuscript. S.B. assisted in the synthesis of some of the literature reported triptycene precursors. J.M. and H.T. optimized the energy minimized geometry of the metallacycles **5** and **6** using PM6 semiempirical molecular modeling method. All authors have contributed to compiling the manuscript and have approved the final manuscript.

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Supporting Information Available: ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for complexes **1-4**, macrocycles **5** and **6**. ESI-MS spectra of complexes **1-4**. MALDI-TOF-MS spectra and ^1H DOSY NMR spectra of macrocycles **5** and **6**. This information is available free of charge via the Internet at <http://pubs.rsc.org/>.

References:

1. (a) J. W. Steed, D. R. Turner and K. J. Wallace, *Core Concepts in Supramolecular Chemistry and Nano chemistry*, Wiley: West Sussex, U.K., 2007; (b) J.-M. Lehn, *Proc. Natl. Acad. Sci.*, 2002, **99**, 4763; (c) J. W. Steed, and J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Ltd: United Kingdom, 2009; (d) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469; (e) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796; (f) K. N. Raymond, *Nature*, 2009, **460**, 585.
2. (a) T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, **113**, 734; (b) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810; (c) M. D. Pluth, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2009, **42**, 1650; (d) M. Yoshizawa and M. Fujita, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 609; (e) M. Yoshizawa, J. K.

- Klosterman and M. Fujita, *Angew. Chem., Int. Ed.*, 2009, **48**, 3418; (f) C. G. Oliveri, P. A. Ulmann, M. J. Wiester and C. A. Mirkin, *Acc. Chem. Res.*, 2008, **41**, 1618; (g) D. Samanta and P. S. Mukherjee, *Chem. Comm.*, 2014, **50**, 1595; (h) N. J. Young and B. P. Hay, *Chem. Commun.*, 2013, **49**, 1354; (i) P. Thanasekaran, C.-C. Lee and K.-L. Lu, *Acc. Chem. Res.*, 2012, **45**, 1403; (j) B. Therrien, *Chem. Eur. J.*, 2013, **19**, 8378; (k) T. R. Cook, V. Vajpayee, M. H. Lee, P. J. Stang and K.-W. Chi, *Acc. Chem. Res.*, 2013, **46**, 2464; (l) J. K. Clegga, F. Li and L. F. Lindoy, *Coord. Chem. Rev.*, 2013, **257**, 2536; (m) M. L. Saha, S. Neogi and M. Schmittel, *Dalton Trans.*, 2014, **43**, 3815.
- (a) B. H. Northrop, H.-B. Yang, P. J. Stang, *Chem. Commun.*, **2008**, 5896 and references therein; (b) M. Fujita, S.-Y. Yu, T. Kusukawa, H. Funaki, K. Ogura and K. Yamaguchi, *Angew. Chem., Int. Ed.*, 1998, **37**, 2082; (c) L. Xu, L.-J. Chen and H.-B. Yang, *Chem. Commun.*, 2014, **50**, 5156 and references therein; (d) N. Das, A. M. Arif, P. J. Stang, M. Sieger, B. Sarkar, W. Kaim and J. Fiedler, *Inorg. Chem.*, 2005, **44**, 57984; (e) N. Das, P. J. Stang, A. M. Arif and C. F. Campana, *J. Org. Chem.*, 2005, **70**, 10440.
 - (a) C.-F. Chen, *Chem. Commun.*, 2011, **47**, 1674 and references therein; (b) Y. Jiang and C.-F. Chen, *Eur. J. Org. Chem.*, 2011, 6377 and references therein; (c) C.-F. Chen, Y.-X. Ma, *Iptycene Chemistry: from Synthesis to Applications*, Springer-Verlag: Berlin, 2013; (d) J. H. Chong and M. J. MacLachlan, *Chem. Soc. Rev.*, 2009, **38**, 3301 and references therein; (e) A. K. Crane, B. O. Patrick and M. J. MacLachlan, *Dalton Trans.*, 2013, **42**, 8026; (f) A. K. Crane, E. Y. L. Wong and M. J. MacLachlan, *Cryst. Eng. Comm.*, 2013, **15**, 9811; (g) M. Mastalerz, *Synlett*, 2013, **24**, 781 and references therein; (h) L. Zhao, Z. Li, and T. Wirth, *Chem. Lett.*, 2010, **39**, 658; (i) S. Chakraborty, S. Mondal and N. Das, *Inorg. Chim. Acta*, 2014, **413**, 214; (j) Y. Han, Z. Meng, Y.-X. Ma and C.-F. Chen, *Acc. Chem. Res.*, 2014, **47**, 2026 and references therein.
 - (a) T. M. Swager, *Acc. Chem. Res.*, 2008, **41**, 1181; (b) B. VanVeller, D. Robinson, and T. M. Swager, *Angew. Chem. Int. Ed.*, 2012, **51**, 1182; (c) B. VanVeller, D. J. Schipper, and T. M. Swager, *J. Am. Chem. Soc.*, 2012, **134**, 7282; (d) S. Mondal, S. Chakraborty, S. Bhowmick and N. Das, *Macromolecules*, 2013, **46**, 6824; (e) C. Zhang, Y. Liu, B. Li, B. Tan, C.-F. Chen, H.-B. Xu, X.-L. Yang, *ACS Macro Lett.*, 2012, **1**, 190; (f) C. Zhang, Z. Wang, J.-J. Wang, L. Tan, J.-M. Liu, B. Tan, X.-L. Yang, H.-B. Xu, *Polymer*, 2013, **54**, 6942; (g) C. Zhang, J.-J. Wang, Y. Liu, H. Ma, X.-L. Yang, H.-B. Xu, *Chem. Eur. J.*, 2013, **19**, 5004. (h) S. Mondal and N. Das, *RSC Adv.*, 2014, **4**, 61383.
 - (a) C. Azerraf and D. Gelman, *Organometallics*, 2009, **28**, 6578; (b) C. Azerraf and D. Gelman, *Chem. Eur. J.*, 2008, **14**, 10364; (c) A. Ishii, N. Nakata, R. Uchiumi and K. Murakami, *Angew. Chem., Int. Ed.*, 2008, **47**, 2661; (d) A. Ishii, H. Kamon, K. Murakami and N. Nakata, *Eur. J. Org. Chem.*, 2010, 1653; (e) N. Nakata, R. Uchiumi, T. Yoshino, T. Ikeda, H. Kamon and A. Ishii, *Organometallics*, 2009, **28**, 1981; (f) Y. Yamaguchi, N. Nakata and A. Ishii, *Eur. J. Inorg. Chem.*, 2013, **30**, 5233; (g) S. Toyota, H. Okuhara and

- M. Ōki, *Organometallics*, 1997, **16**, 4012; (h) H.-B. Yang, K. Ghosh, N. Das and P. J. Stang, *Org. Lett.*, 2006, **8**, 3991.
7. (a) S. Chakraborty, S. Mondal, Q. Li and N. Das, *Tetrahedron Lett.*, 2013, **54**, 1681; (b) S. Chakraborty, S. Mondal, S. Bhowmick, J. Ma, H. Tan, S. Neogi and N. Das, *Dalton Trans.* **2014**, 43, 13270; (c) A. Dubey, A. Mishra, J. W. Min, M. H. Lee, H. Kim, P. J. Stang and K.-W. Chi, *Inorg. Chim. Acta*, 2014, **423**, 326.
8. J. Manna, C. J. Kuehl, J. A. Whiteford and P. J. Stang, *Organometallics*, 1997, **16**, 1897.
9. S. Leininger and P. J. Stang, *Organometallics*, 1998, **17**, 3981.
10. (a) S. Leininger, M. Schmitz and P. J. Stang, *Org. Lett.*, 1999, **1**, 1921; (b) C. J. Kuehl, C. L. Mayne, A. M. Arif and P. J. Stang, *Org. Lett.*, 2000, **2**, 3727; (c) Y. K. Kryschenko, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 5193; (d) H.-B. Yang, A. M. Hawkrige, S. D. Huang, N. Das, S. D. Bunge, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2007, **129**, 2120.
11. Z. Chen and T. M. Swager, *Macromolecules*, 2008, **41**, 6880.
12. (a) H.-B. Yang, K. Ghosh, N. Das and P. J. Stang, *Org. Lett.* 2006, **8**, 3991; (b) M.-C. K. Wong and V. W.-W. Yam, *Acc. Chem. Res.*, 2011, **44**, 424; (c) C.-H. Tao and V. W.-W. Yam, *J. Photochem. Photobiol., C*, 2009, **10**, 130; (d) S. Li, J. Huang, F. Zhou, T. R. Cook, X. Yan, Y. Ye, B. Zhu, B. Zheng and P. J. Stang, *J. Am. Chem. Soc.*, 2014, **136**, 5908; (e) S. Shanmugaraju, H. Jadhav, Y. P. Patil and P. S. Mukherjee, *Inorg. Chem.*, 2012, **51**, 13072; (f) S. Shanmugaraju, A. K. Bar, K.-W. Chi and P. S. Mukherjee, *Organometallics*, 2010, **29**, 2971; (g) J. Zhang, X.-D. Xu, L.-J. Chen, Q. Luo, N.-W. Wu, D.-X. Wang, X.-L. Zha and H.-B. Yang, *Organometallics*, 2011, **30**, 4032; (h) W. Wang and H.-B. Yang, *Chem. Commun.*, 2014, **50**, 5171 and references therein; (i) D. Samanta and P. S. Mukherjee, *Dalton Trans.*, 2013, **42**, 16784.
13. J. J. P. Stewart, *J. Mol. Model.*, 2007, **13**, 1173.
14. N. Das, A. Ghosh, A. M. Arif and P. J. Stang, *Inorg. Chem.*, 2005, **44**, 7130.
15. T. Yoshida, T. Matsuda, S. Otsuka, G. W. Parshall, and W. G. Peet, *Inorg. Synth.*, 1990, **28**, 122.