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Synthesis and characterization of pyridine- and thiophene-based platinacyclynes

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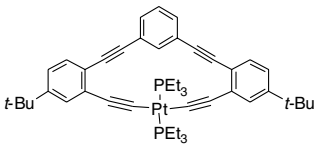
Abstract

Seven heterocyclic macrocycles, including the first platinacycles with pyridine and thiophene rings incorporated into the cyclyne system, are reported. Pt-acetylide cyclynes were assembled via tin transmetallation or amine-mediated oxidative addition with stoichiometric $PtCl_2(PEt_3)_2$ and CuI. The organometallic cyclynes exhibited enhanced electronic properties compared to previously described platinabenzocyclynes.

Keywords: Platinum(II); Acetylide; Metallacycle; Benzocyclyne; Heterocycle

1. Introduction

The last 30 years has seen a noteworthy evolution from simple, acyclic Pt-acetylide complexes [1] to a diverse array of Pt-acetylide assemblies including macrocycles [2], dendrimers [3], oligomeric scaffoldings [4], and polymers [5]. The defined directionality of the square planar platinum atom, the ethynyl group's rigid linearity, and the well-established, straightforward chemistry of platinum and alkyne functionalities have made Pt-acetylide complexes ideal in the construction of these multifaceted systems. Pt-acetylide complexes have shown further utility as an efficient means of introducing stereocenters into metallacycles through ligand exchange [6], facilitating intermolecular cyclization of α,ω-diethynyl monomers through reductive elimination of Pt-bisacetylide intermediates [7], as well as mediating self-assembly for host complexes and chiral platinacyclophanes capable of asymmetric catalysis [8]. Most recently, highly conjugated Pt-acetylide polymers have been thoroughly investigated for use in organic photocells, light-emitting diodes, and models for triplet manifold studies of conjugated polymers [4d,5,9].



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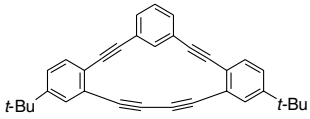

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We recently reported selective metallacyclization of several *cis*- and *trans*-Pt-acetylide macrocycles as well as production of the non-organometallic parent benzocyclynes [10]. A notable deficiency of the benzo[15]cyclyne systems (**1**, **2**) was limited electronic delocalization resultant from cross-conjugation of the central phenyl ring and further compounded by introduction of platinum into the cycle backbone. Based on recent successful production and evaluation of several new heterocyclic macrocycles [2d,2e,7,11], replacement of phenyl moieties in **1** and **2** with heterocycles was subsequently investigated to enhance electronic

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properties through intramolecular charge transfer via π-backbonding and/or donor–acceptor relationships between the metal, heteroatoms, and π-conjugated network. We herein describe the synthesis and characterization of four new platinacycles and three new macrocycles with heterocycles incorporated into the cycle backbone and discuss the electronic delocalization via comparison of UV–Vis spectra.

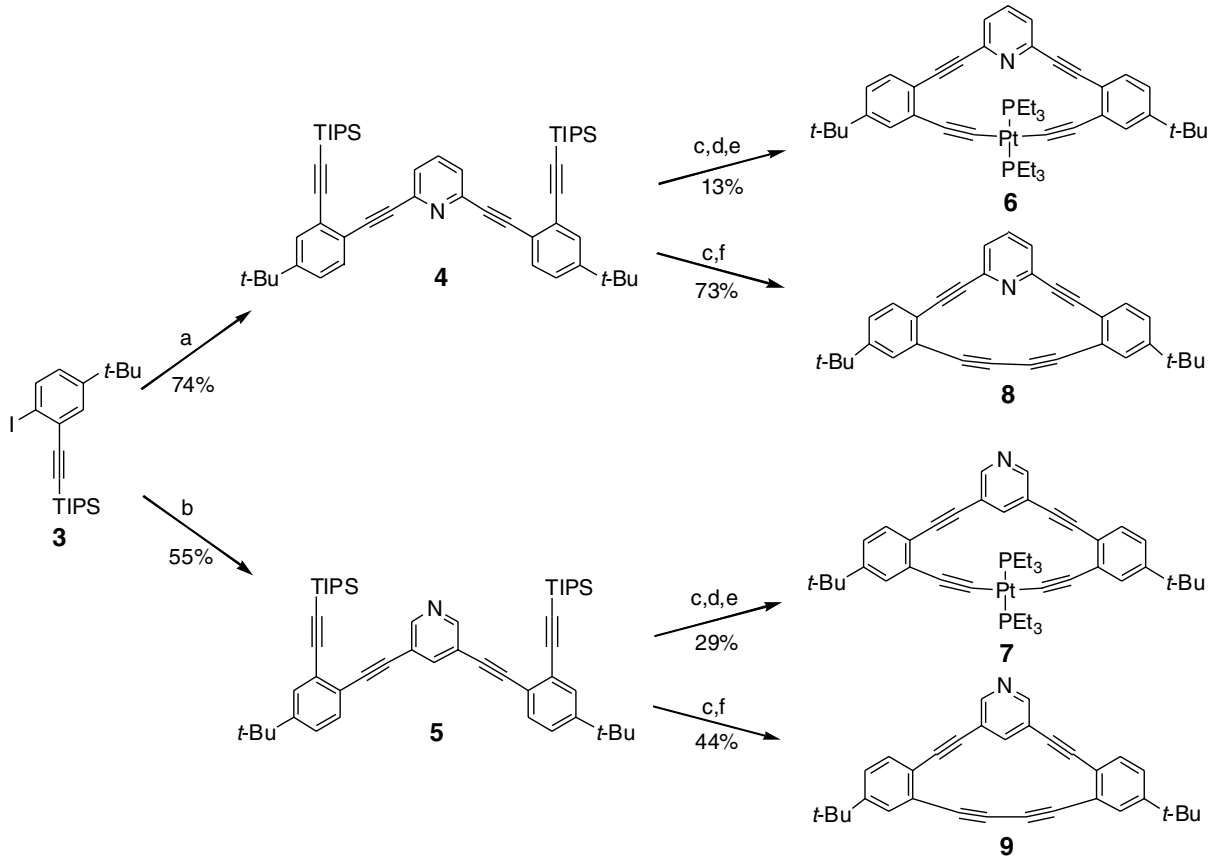
2. Results and discussion

2.1. Synthesis of pyridocyclynes

Production of pyridine analogs of cycles **1** and **2** began with Pd-catalyzed cross-coupling of 2,6- and 3,5-diethynylpyridine [2d,12] with previously reported ethynylarene **3** [13] to afford isomeric α,ω-polyynes **4** and **5** in 74% and 55% yields, respectively (Scheme 1). Platinacycles **6** and **7** were obtained from their corresponding isomeric precursor in low yield, the result of competing oligomerization, by a three-step metallacyclization procedure [10] consisting of desilylation with Bu_4NF [14], treatment with Me_3SnNMe_2 [15], and final transmetallation with *trans*-$PtCl_2(PEt_3)_2$ and CuI [16]. Oxidative alkyne homocoupling of desilylated α,ω-polyynes **4** and **5** with CuCl and pyridine [17] provided cyclynes **8** and **9** in 73% and 44% yields, respectively.

The ^{31}P NMR spectra of platinacycles **6** (δ 11.13, $J = 2381$ Hz) and **7** (δ 10.60, $J = 2316$ Hz) showed characteristic *trans* J_{P-Pt} values [2b,4b,10] with both resonances shifted downfield in contrast to **1** (δ 10.49). The interior proton resonances of cycles **7** (δ 9.09) and **9** (δ 8.90) also showed enhanced electron deficiency in ^1H NMR when compared to benzocyclyne **1** (δ 7.74). The significant downfield shift in ^1H NMR (>1 ppm) can be rationalized by the electron deficiency of the 4-pyridine position [18] further compounding the deshielding effects of ethynyl anisotropy and close proximity of the platinum atom (~3 Å) [19].

Crystals of **6** suitable for single-crystal X-ray diffraction were obtained by diffusion of hexanes into a concentrated THF solution (Fig. 1). Ethynyl distortion was most significant in the acetylene linker σ-bonded to the platinum (C1 11.5°, C2 14.7°) in comparison to the monoynes bridging phenyl rings (C9 5.7°, C10 2.6°) (Table 1). Similar to **1**, insertion of platinum into the cyclyne resulted in a significant distortion of the carbon-rich backbone with the alkylated phenyl rings twisted in relation to each other (Fig. 1b). The platinum atom exhibited ~10° distortion from square planar with the PEt_3 ligands bent away from the cycle core. The



Scheme 1. Synthesis of cycles **6**–**9**. Conditions: (a) 2,6-diethynylpyridine, $Pd(PPh_3)_4$, CuI, *i*-Pr_2NH, THF, 50 °C; (b) 3,5-diethynylpyridine, $Pd(PPh_3)_4$, CuI, *i*-Pr_2NH, THF, 50 °C; (c) Bu_4NF, THF, MeOH; (d) Me_3SnNMe_2, THF; (e) *trans*-$PtCl_2(PEt_3)_2$, CuI, THF; and (f) CuCl, pyridine, MeOH, 50 °C.

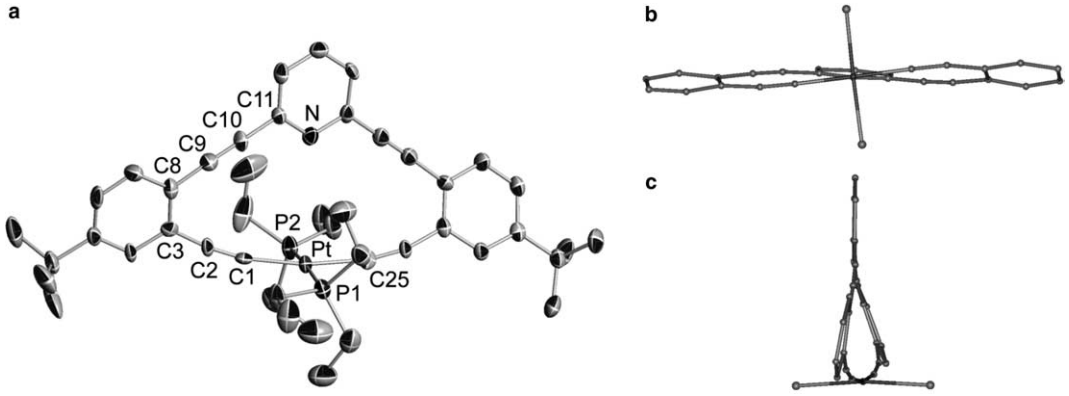


Fig. 1. (a) ORTEP of platinacyclyne **6** with ellipsoids drawn at the 50% probability level. (b) View of **6** along C_2 axis through platinum atom (Et and *t*-Bu groups removed for clarity). (c) View of **6** along C1-Pt–C25 (Et and *t*-Bu groups removed for clarity).

Table 1
Selected bond lengths (Å) and angles (°) for platinacyclynes **1**, **6**, and **12**

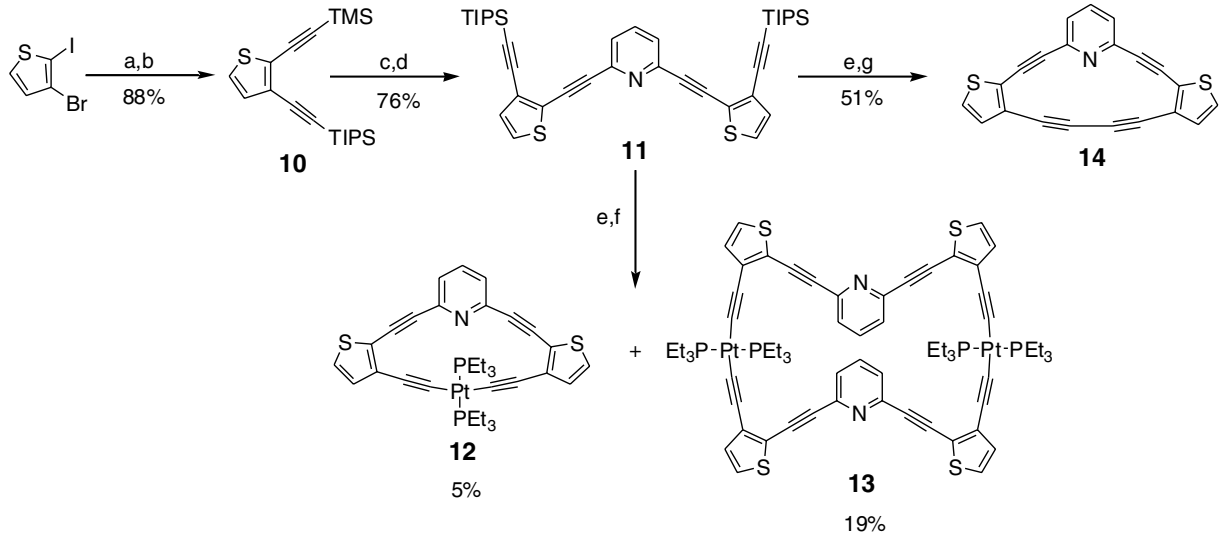
Complex	**1**[a]	**6**	**12**
Bond lengths (Å)			
Pt–P(1)	2.291(5)	2.291(2)	2.287(6)
Pt–C(1)	2.001(15)	1.975(8)	1.993(3)
C(1)–C(2)	1.188(19)	1.237(11)	1.204(3)
C(9)–C(10)	1.136(18)	1.178(12)	1.204(3)
C(11)–N	N/A	1.352(11)	1.346(3)
C(8)–S(1)	N/A	N/A	1.730(2)
Bond angles (°)			
P(1)–Pt–P(2)	172.4(3)	173.0(9)	172.8(2)
C(1)–Pt–C(X)	170.7(8)[b]	170.5(3)[c]	170.1(9)[d]
Pt–C(1)–C(2)	169.8(14)	168.5(8)	168.0(2)
C(1)–C(2)–C(3)	168.8(16)	165.3(9)	167.8(2)
C(8)–C(9)–C(10)	173.0(2)	174.3(10)	173.9(3)
C(9)–C(10)–C(11)	178.1(18)	177.4(10)	178.6(3)

[a] Ref. [10].
[b] X = C1′.
[c] X = C25, molecule is not centrosymmetric.
[d] X = C21, molecule is not centrosymmetric.

Pt–N distance (4.05 Å) and steric congestion of the central cavity precludes Pt–N coordination or inclusion chemistry.

2.2. Synthesis of thienocyclynes

Differentially silylated diethynylthiophene **10** was obtained by sequential Pd-catalyzed ethynylation of 3-bromo-2-iodothiophene [11d] in 88% overall yield (Scheme 2). Treatment of **10** with mild base selectively removed the more labile TMS groups. Without further purification, the free acetylene intermediate was cross-coupled to 2,6-dibromopyridine to provide tetrayne **11** in good yield. Application of amine-mediated oxidative metallacyclization conditions [1d,20] to desilylated tetrayne **11** afforded platinacycle **12** as well as bis-Pt-acetylide dimer **13**, both unique as the first reported platinacycles with thiophene and pyridine rings incorporated into the cycle backbone. A higher yield of dimer is rationalized by the elevated temperature and associated thermal energy increase of the



Scheme 2. Synthesis of cycles **12**–**14**. Conditions: (a) TMSA, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF; (b) TIPSA, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, THF, 90 °C; (c) K_2CO_3, MeOH, Et_2O; (d) 2,6-dibromopyridine, $Pd(PPh_3)_4$, CuI, *i*-Pr_2NH, THF, 50 °C; (e) Bu_4NF, THF, MeOH; (f) *trans*-$PtCl_2(PEt_3)_2$, Et_2NH, CuI, 50 °C; and (g) CuCl, pyridine, MeOH, 50 °C.

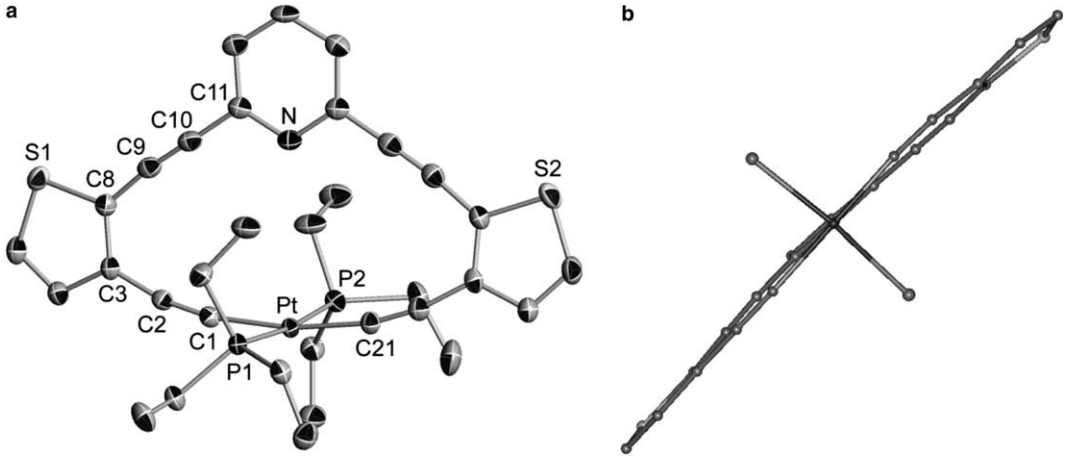


Fig. 2. (a) ORTEP of platinacyclyne **12** with ellipsoids drawn at the 50% probability level. (b) View of cycle **12** along C_2 axis through platinum atom (Et and *t*-Bu groups removed for clarity).

alternate metallacyclization procedure, which favored competing intermolecular coupling over monocyclization. Glaser homocoupling of deprotected **11** provided cyclyne **14** in 51% yield.

Fig. 2 displays the result of single-crystal X-ray diffraction of **12**. Compared to **6**, ethynyl distortion was more evenly distributed in the two acetylene units σ-bonded to the platinum (C1 12°, C2 12.2°) but analogous around the monoynes (C9 6.1°, C10 1.4°) bridging the heterocycles (Table 1). The platinum complex exhibited comparable geometry distortion to **6**; however, the overall structure lacked the extent of symmetrical ring twisting displayed by **1** and **6**, likely the result of replacement of phenyl rings with thiophene moieties.

2.3. Spectroscopic and physical characterization

The materials properties of the new cyclynes were explored to elucidate enhanced optical and thermal properties beyond those of parent cycles **1** and **2**. The key issues we sought to address were the result of heterocycle incorporation on electronic absorption spectra, fluorescence emission, and thermal decomposition. Fig. 3 displays the electronic absorption spectra for the new cycles and comparison to their respective non-heterocyclic parent. All three new organometallic cycles (**6**, **7**, and **12**) displayed comparable bathochromic shifts in λ_{cutoff} to >400 nm, a minimum of 65 nm beyond platinabenzocyclyne **1**. Heterobenzocyclynes **8** and **9** did not show a significant change in λ_{max} or λ_{cutoff} beyond benzo[15]cyclyne **2**, but cycle **14** exhibited a 30 nm bathochromic shift in λ_{max}. Although metallacycles **6**, **7**, and **12** did not show significant enhancement in λ_{max} or λ_{cutoff} beyond parent cyclynes **8**, **9**, and **14**, the organometallic cycles surprisingly did not exhibit a large hypsochromic shift observed with metallacyclization of cyclyne **1**. The low energy, bathochromic shift of the metallacycles combined with semi-empirical HOMO/LUMO calculations [21] supports an enhanced charge-transfer model between the platinum and heterocyclic conjugated ligand. Additionally, the similarity in bathochromic shift for pyridine isomers indicated that acetylide ligand substitution on the central pyridine ligand was not a significant electronic factor, an assertion supported by similar calculated π-electron densities of *ortho* and *meta* sp^2 C atoms of the pyridine ring [19].

The non-organometallic cyclynes (**8**, **9**, and **14**) are fluorescent chromophores that exhibit either blue or green emission upon exposure to UV light (365 nm). Pyridine-based cycles **8** and **9** displayed a single emission

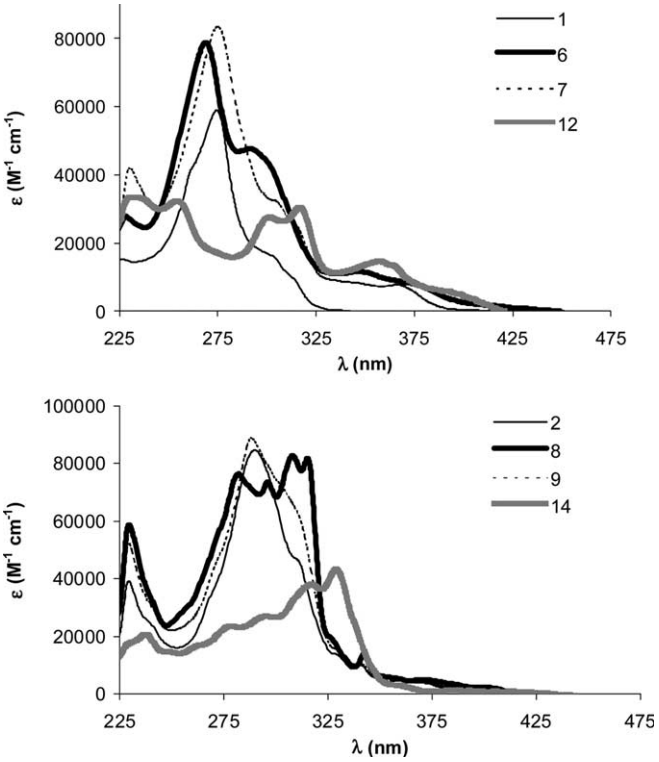


Fig. 3. Electronic absorption spectra of cycles **1**, **2**, **6**–**9**, **12**, and **14**.

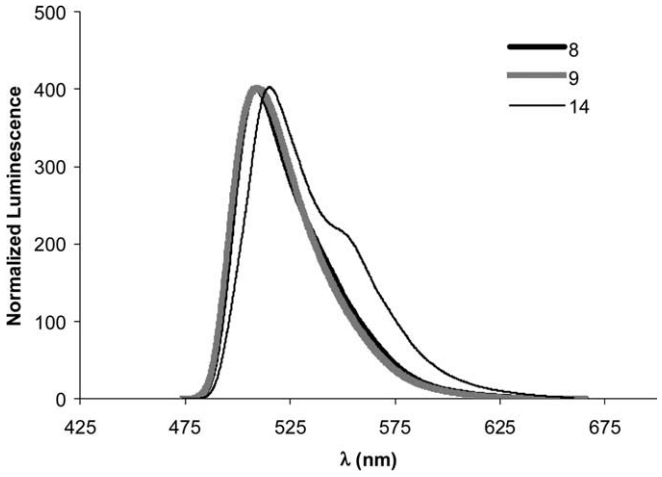


Fig. 4. Normalized fluorescence emission of **8**, **9**, and **14** ($\lambda_{ex} = 459$ nm).

($\lambda_{max} = 509$ nm) identical to benzocyclyne **2** (Fig. 4) but with a marked qualitative increase in fluorescence. Compound **14** exhibited a bathochromic shift of 7 nm in emission λ_{max} (516 nm) as well as the addition of a broad shoulder at 550 nm. Similar to cycle **1**, the new organometallic cyclynes displayed no significant fluorescent emission.

With the exception of **14**, the new cyclynes all exhibited thermal stability up to or beyond 200 °C with distinct exothermic decomposition patterns. The organometallic cycles displayed broad, multi-stage decomposition in contrast to sharp, ordered transitions for the cycles lacking platinum. Cycle **8**, with the N atom lone pair contained inside the cycle core displayed the highest thermal stability (260 °C), almost 10 °C beyond that of phenyl-based **2**.

3. Conclusions

In summary, we have successfully produced several new heterocyclic macrocycles by means of Glaser homocoupling conditions or metallacyclization via tin transmetallation or amine-mediated oxidative addition. Replacement of phenyl moieties in the benzo[15]cyclyne backbone with heterocycles resulted in superior, bathochromic electronic absorption ($\geqslant 65$ nm) in the organometallic cyclynes. This significant shift to lower energy, the result of altering the composition and electronics of the organic ligand, provides a readily available approach for tailoring absorption as well as thermal parameters of small molecule organometallic systems for materials applications. Future work in this area will focus on construction of tris-ligated platinacyclynes.

4. Experimental

4.1. General data

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Varian Inova 300 (^{1}H 299.95 MHz, ^{13}C 75.43 MHz, ^{31}P 121.42 MHz) or Inova 500 (^{1}H 500.10 MHz, ^{13}C 125.75 MHz, ^{31}P 202.44 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual non-deuterated solvent as internal standard ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.0 ppm). UV–Vis spectra were recorded using a Hewlett–Packard 8453 spectrophotometer and extinction coefficients are expressed in $M^{-1}\,cm^{-1}$. Mass spectra were recorded using an Agilent 1100 Series LC/MSD. Emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratories. Melting points were determined on a Meltemp II apparatus or using a TA Instruments DSC 2920 Modulated DSC. THF was purified using an Innovative Technologies solvent system. Et_2NH was distilled prior to use. All other chemicals were of reagent grade and used as obtained from manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230–400 mesh). Rotary chromatography was performed on a Harrison Research Chromatotron model 7924T with EM-Science $60PF_{254}$ silica gel. Precoated silica gel plates (Sorbent Technology, UV_{254}, 200 μm, 5 × 20 cm) were used for analytical thin-layer chromatography.

4.2. General metallacyclization procedure

A solution of α,ω-polyyne (1 equiv), Bu_4NF (3–5 equiv), and 2–3 drops MeOH in THF (10 mL per 0.1 mmol polyyne) was stirred at rt and monitored by TLC until completion (15–30 min). The solution was diluted with Et_2O and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Without further purification, the residue was dissolved in THF (20 mL per 0.1 mmol polyyne) and Me_3SnNMe_2 (1 equiv per terminal ethynyl functionality) was added. The solution was stirred at rt for 2 h and then concentrated in vacuo. Without further purification, the resultant oil was combined with $PtCl_2(PEt_3)_2$ (1 equiv) and CuI (10 mol%) and placed under Ar. Deoxygenated THF (25 mL per 0.1 mmol polyyne) was delivered via cannula and the suspension was stirred under N_2 for 12 h at rt. The reaction mixture was concentrated by rotary evaporation and the desired product was purified by column chromatography on silica gel or by Chromatotron.

4.3. General alkyne homocoupling procedure

A solution of silyl-protected α,ω-polyyne (1 equiv), Bu_4NF (3–5 equiv), and 2–3 drops MeOH in THF (10 mL per 0.1 mmol polyyne) was stirred at rt and monitored by TLC until completion (15–30 min). The solution was diluted with Et_2O and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Without further purification, the residue was dissolved in THF (5 mL per 0.1 mmol polyyne) and added dropwise over a period of 12 h to a stirred suspension of CuCl (25–50 equiv) in pyridine (200 mL) and MeOH (50 mL) at 50 °C. The suspension was stirred an additional

5–10 h and then concentrated in vacuo. The resultant crude material was filtered through a 2.5 cm silica plug and then purified by column chromatography or by Chromatotron.

4.4. Synthesis of α,ω-polyyne (*4*)

A syringe pump was used to deliver a deoxygenated solution of 2,6-diethynylpyridine [12] (80 mg, 0.63 mmol) in THF (10 mL) over 12 h to a stirred, deoxygenated suspension of diethynylarene **3** [13] (637 mg, 1.4 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and CuI (11 mg, 0.06 mmol) in THF (50 mL) and *i*-Pr_2NH (50 mL) at 50 °C. The reaction was stirred an additional 24 h under N_2, then the solvent was removed by rotary evaporation. Chromatography of the residue on silica gel (1:1 hexanes:CH_2Cl_2) afforded **4** (350 mg, 74%) as a yellow, spongy solid. Mp: 67–69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (t, $J = 7.8$ Hz, 1H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 2.1$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.32 (dd, $J = 8.1$, 2.1 Hz, 2H), 1.32 (s, 18H), 1.13 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.88, 143.86, 135.71, 132.35, 129.49, 126.12, 125.75, 125.51, 121.94, 105.59, 94.36, 91.12, 88.41, 34.68, 30.92, 18.68, 11.28. UV–Vis (CH_2Cl_2): λ_{max} (ε) 240 (66 000), 259 (76 000), 297 (28 000), 321 (29 000), 333 (31 000) nm. MS (CI pos) *m*/*z* (%): 754 ($M^+ + 2$, 29), 753 (MH^+, 67), 752 (M^+, 100); $C_{51}H_{69}NSi_2$ (752.27). Anal. Calc. for $C_{51}H_{69}NSi_2$: C, 81.43, H, 9.25, N, 1.86. Found: C, 81.21, H, 9.47, N, 1.86%.

4.5. Synthesis of α,ω-polyyne (*5*)

A syringe pump was used to deliver a deoxygenated solution of 3,5-diethynylpyridine [2d] (85 mg, 0.67 mmol) in THF (10 mL) over 12 h to a stirred, deoxygenated suspension of diethynylarene **3** [13] (700 mg, 1.6 mmol), $Pd(PPh_3)_4$ (45 mg, 0.039 mmol), and CuI (15 mg, 0.078 mmol) in THF (50 mL) and *i*-Pr_2NH (50 mL) at 50 °C. The reaction was stirred an additional 24 h under N_2, then the solvent was removed by rotary evaporation. Chromatography of the residue on silica gel with CH_2Cl_2 afforded **5** (276 mg, 55%) as a yellow, spongy solid. Mp: 65–67 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (d, $J = 2.1$ Hz, 2H), 7.92 (t, $J = 2.1$ Hz, 1H), 7.52 (d, $J = 2.1$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.34 (dd, $J = 8.4$, 2.1 Hz, 2H), 1.33 (s, 18H), 1.23 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.96, 150.64, 140.93, 131.94, 129.59, 125.63, 125.56, 122.06, 120.18, 105.47, 94.67, 92.19, 87.95, 34.74, 30.98, 18.68, 11.28. UV–Vis (CH_2Cl_2): λ_{max} (ε) 241 (77 000), 249 (76 000), 261 (88 000), 305 (42 000), 330 (36 000) nm. MS (CI pos) *m*/*z* (%): 755 ($M^+ + 3$, 21), 754 ($M^+ + 2$, 64), 753 (MH^+, 100), 752 (M^+, 100); $C_{51}H_{69}NSi_2$ (752.27).

4.6. Synthesis of trans-platinaheterobenzocyclyne (*6*)

Following desilylation, polyyne **4** (100 mg, 0.13 mmol) was reacted with Me_3SnNMe_2 (54 mg, 0.26 mmol) and then *trans*-$PtCl_2(PEt_3)_2$ (65 mg, 0.13 mmol) and CuI (5 mg, 0.03 mmol) according to general metallacyclization procedure. The crude product was purified by Chromatotron (1 mm plate, 1:2 hexanes:CH_2Cl_2) to yield **6** (15 mg, 13%) as a colorless powder. Recrystallization by vapor diffusion with THF/hexanes afforded light yellow crystals. Mp: 228 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 1.8$ Hz, 2H), 7.29 (d, $J = 7.6$ Hz, 2H), 7.12 (dd, $J = 8.0$, 1.8 Hz, 2H), 2.20–2.05 (m, 12H), 1.31 (s, 18H), 1.17–1.06 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.70, 144.61, 135.24, 132.69, 131.25, 125.95, 124.62, 122.21, 121.44, 107.94, 104.09, 91.31, 90.09, 34.83, 31.16, 16.20 (pseduo-t, $J = 18.7$ Hz), 8.03. ^{31}P NMR (121 MHz, $CDCl_3$): δ 11.13 (pseudo-t, $J = 2381$ Hz). UV–Vis (CH_2Cl_2): λ_{max} (ε) 269 (84 000), 291 (58 000), 346 (18 000) nm. MS (CI pos) *m*/*z* (%): 869 (MH^+, 100), 868 (M^+, 61); $C_{45}H_{57}NP_2Pt$ (868.97). Anal. Calc. for $C_{45}H_{57}NP_2Pt$: C, 62.20, H, 6.61, N, 1.61. Found: C, 62.13, H, 6.93, N, 1.37%.

4.7. Synthesis of trans-platinaheterobenzocyclyne (*7*)

Following desilylation, polyyne **5** (100 mg, 0.13 mmol) was reacted with Me_3SnNMe_2 (54 mg, 0.26 mmol) and then *trans*-$PtCl_2(PEt_3)_2$ (65 mg, 0.13 mmol) and CuI (5 mg, 0.03 mmol) according to general metallacyclization procedure. The crude product was purified by Chromatotron (1 mm plate, 12:1 hexanes:ethyl acetate) to yield **7** (32 mg, 29%) as a pale yellow solid. Mp: 209 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (t, $J = 1.8$ Hz, 1H), 8.57 (d, $J = 1.8$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 2.1$ Hz, 2H), 7.15 (dd, $J = 8.1$, 2.1 Hz, 2H), 2.12–2.06 (m, 12H), 1.32 (s, 18H), 1.16–1.06 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.65, 149.08, 144.24, 132.18, 120.35, 125.71, 122.20, 121.82, 121.23, 116.02 (pseudo-t, $J = 14.7$ Hz), 109.13, 95.49, 87.85, 34.84, 31.16, 16.37 (pseudo-t, $J = 17.4$ Hz), 7.95. ^{31}P NMR (121 MHz, $CDCl_3$): δ 10.60 (pseudo-t, $J = 2316$ Hz). UV–Vis (CH_2Cl_2): λ_{max} (ε) 274 (85 000), 303 (35 000), 315 (28 000), 344 (10 000), 365 (11 000) nm. MS (CI pos) *m*/*z* (%): 871 ($M^+ + 3$, 33), 870 ($M^+ + 2$, 82), 869 (MH^+, 100), 868 (M^+, 72); $C_{45}H_{57}NP_2Pt$ (868.97).

4.8. Synthesis of heterobenzocyclyne (*8*)

Polyyne **4** (100 mg, 0.13 mmol) was deprotected and reacted with CuCl (653 mg, 6.5 mmol), pyridine, and MeOH as described in general alkyne homocoupling procedure. Purification on a Chromatotron plate (1 mm, 2:1 hexanes:CH_2Cl_2) provided **8** (41 mg, 73%) as a pale yellow solid. Mp: 260 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (t, $J = 8.1$ Hz, 1H), 7.53–7.52 (m, 2H), 7.33–7.35 (m, 4H), 7.20 (d, $J = 7.6$ Hz, 2H), 1.31 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.38, 144.63, 136.89, 129.88, 129.47, 127.42, 126.36, 123.58, 122.57, 94.95, 90.30, 81.63, 78.88, 34.86, 30.91. UV–Vis (CH_2Cl_2): λ_{max} (ε) 230

(59 000), 282 (76 000), 296 (74 000), 308 (82 000), 315 (82 000), 342 (12 000) nm. Fluorescence emission ([**8**] $\leqslant 5.7\times10^{-5}$ M in CH_2Cl_2; 459 nm excitation): λ_{max} 509 nm. MS (CI pos) *m/z* (%): 439 ($M^+ + 2$, 46), 438 (MH^+, 100); $C_{33}H_{27}N$ (437.57). Anal. Calc. for $C_{33}H_{27}N$: C, 90.58, H, 6.32, N, 3.20. Found: C, 90.17, H, 5.82, N, 3.12%.

4.9. Synthesis of heterobenzocyclyne (*9*)

Polyyne **5** (100 mg, 0.13 mmol) was deprotected and reacted with CuCl (653 mg, 6.5 mmol), pyridine, and MeOH as described in general alkyne homocoupling procedure. Purification on a Chromatotron plate (1 mm, 1:7 hexanes:EtOAc) provided **9** (25 mg, 44%) as a pale yellow solid. Mp: 248 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (t, $J = 2.1$ Hz, 1H), 8.50 (d, $J = 1.8$ Hz, 2H), 7.59 (d, $J = 1.5$ Hz, 2H), 7.43–7.35 (m, 4H), 1.33 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.19, 151.66, 146.61, 129.85, 129.46, 126.71, 126.14, 123.41, 121.02, 96.50, 91.91, 82.69, 77.79, 34.89, 30.94. UV–Vis (CH_2Cl_2): λ_{max} (ε) 229 (58 000), 288 (100 000), 312 (74 000), 341 (9000), 389 (3000) nm. Fluorescence emission ([**9**] $\leqslant 5.7\times10^{-5}$ M in CH_2Cl_2; 459 nm excitation): λ_{max} 509 nm. MS (CI pos) *m/z* (%): 439 ($M^+ + 2$, 38), 438 (MH^+, 100); $C_{33}H_{27}N$ (437.57). Anal. Calc. for $C_{33}H_{27}N0.5C_4H_8O_2$: C, 87.28, H, 6.49, N, 2.91. Found: C, 87.71, H, 7.00, N, 2.78%.

4.10. Synthesis of diethynylthiophene (*10*)

TMSA (3.6 mL, 53 mmol) was added to a stirred suspension of 3-bromo-2-iodothiophene [11d] (5.0 g, 17 mmol), $PdCl_2(PPh_3)_2$ (396 mg, 0.6 mmol), and CuI (190 mg, 1 mmol) in THF (100 mL) and *i*-Pr_2NH (100 mL) under an Ar environment. After 1 h, the solvent was removed and the crude product was run through a 2.5 cm silica plug (5:1 hexanes:CH_2Cl_2). Without further purification, the yellow oil was combined with $PdCl_2(PPh_3)_2$ (366 mg, 0.5 mmol) and CuI (175 mg, 0.9 mmol), THF (100 mL), and *i*-Pr_2NH (100 mL) in a sealed tube. The suspension was placed under Ar, TIPSA (10 mL, 47 mmol) was added via syringe, and the mixture was heated for 4 d at 90 °C. The solvent was removed in vacuo and the crude product purified by chromatography on silica (hexanes) to yield **10** (5.4 g, 88%) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (d, $J = 5.2$ Hz, 1H), 6.97 (d, $J = 5.2$ Hz, 1H), 1.14 (s, 21H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.86, 127.46, 126.76, 125.75, 100.45, 96.25, 95.00, 86.22, 18.72, 11.14, −0.24. MS (CI pos) *m/z* (%): 360 (M^+, 19), 355 (100); $C_{20}H_{32}SSi_2$ (360.70).

4.11. Synthesis of α,ω-polyyne (*11*)

A suspension consisting of diethynylthiophene **10** (750 mg, 2.1 mmol), K_2CO_3 (5 equiv), MeOH (10 mL), and Et_2O (15 mL) was stirred at rt for 1 h. The solution was diluted with Et_2O and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Without further purification, a syringe pump was used to deliver a deoxygenated solution of the deprotected intermediate in THF (10 mL) over 12 h to a stirred, deoxygenated suspension of 2,6-dibromopyridine (163 mg, 0.69 mmol), $Pd(PPh_3)_4$ (242 mg, 0.21 mmol), and CuI (80 mg, 0.42 mmol) in THF (50 mL) and *i*-Pr_2NH (50 mL) at 50 °C. The reaction was stirred an additional 24 h under N_2, then the solvent was removed by rotary evaporation. Chromatography of the residue on silica gel with CH_2Cl_2 afforded **11** (343 mg, 76%) as an orange, spongy solid. Mp: 99–100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (t, $J = 7.5$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 5.4$ Hz, 2H), 7.04 (d, $J = 5.4$ Hz, 2H), 1.14 (s, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.47, 136.11, 129.99, 128.27, 127.23, 126.03, 125.56, 100.37, 95.79, 95.63, 82.20, 18.65, 11.21. MS (CI pos) *m/z* (%): 655 ($M^+ + 4$, 41), 653 ($M^+ + 2$, 79), 651 (M^+, 100); $C_{39}H_{49}NS_2Si_2$ (651.28). Anal. Calc. for $C_{39}H_{49}NS_2Si_2$: C, 71.83, H, 7.57, N, 2.15. Found: C, 71.68, H, 7.41, N, 2.06%.

4.12. Synthesis of platinaheterocyclyne (*12*) and dimer (*13*)

A solution of α,ω-polyyne **11** (1 equiv), Bu_4NF (3–5 equiv), and 2–3 drops MeOH in THF (10 mL) was stirred at rt and monitored via TLC until complete (15–30 min). The solution was diluted with Et_2O and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Without further purification, the residue was combined with $PtCl_2(PEt_3)_2$ (51 mg, 0.1 mmol) and CuI (5 mg, 0.03 mmol) and placed under an Ar environment. Deoxygenated Et_2NH (200 mL) was delivered via cannula and the suspension was stirred under N_2 for 12 h at 50 °C. The reaction mixture was concentrated by rotary evaporation and the crude product was chromatographed via Chromatotron (1 mm plate). Sequential use of mobile phases (1:2 hexanes:CH_2Cl_2, 100% EtOAc) selectively removed monocycle **12** (5 mg, 5%) followed by dimer **13** (19 mg, 19%), both as pale yellow solids. Recrystallization of cycle **12** by vapor diffusion (hexanes:THF) yielded colorless crystals. Compound **12**: Mp: 201 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (t, $J = 7.8$ Hz, 1H), 7.19 (d, $J = 7.8$ Hz, 2H), 7.14 (d, $J = 5.1$ Hz, 2H), 6.86 (d, $J = 5.1$ Hz, 2H), 2.21–2.07 (m, 12H), 1.16–1.08 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): 144.30, 136.19, 135.49, 127.85, 126.08, 123.32, 121.21, 120.00, 103.28, 96.21, 84.37, 16.26 (pseudo-t, $J = 17.2$ Hz), 8.09. ^{31}P NMR (121 MHz, $CDCl_3$): δ 12.10 (pseduo-t, $J = 2362$ Hz). UV–Vis (CH_2Cl_2): λ_{max} (ε) 232 (33 300), 254 (32 200), 301 (27 500), 317 (30 400), 357 (14 800) nm. MS (CI pos) *m/z* (%): 769 (MH^+, 82), 768 (M^+, 100), 709 (60); $C_{33}H_{37}NP_2PtS_2$ (768.81). Anal. Calc. for $C_{33}H_{37}NP_2PtS_2$: C, 51.55, H, 4.85, N, 1.82. Found: C, 51.68, H, 4.38, N, 1.65%. Compound **13**: Mp: 241 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (t, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 7.8$ Hz, 4H), 7.11 (d, $J = 5.1$ Hz, 4H), 6.82 (d,

$J = 5.1$ Hz, 4H), 2.21–2.04 (m, 24H), 1.17–1.06 (m, 36H). ^{13}C NMR: insufficient solubility to obtain spectrum. ^{31}P NMR (121 MHz, $CDCl_3$): δ 11.70 (pseduo-t, $J = 2329$ Hz). UV–Vis (CH_2Cl_2): λ_{max} (ε) 233 (41 000), 300 (33 000), 318 (34 500), 366 (31 700) nm. MS (CI pos) m/z (%): 1537 (MH^+, 31), 1536 (M^+, 23), 603 (100); $C_{66}H_{74}N_2P_4Pt_2S_4$ (1536.30). Anal. Calc. for $C_{66}H_{74}NP_4Pt_2S_4$: C, 51.55, H, 4.85, N, 1.82. Found: C, 51.31, H, 4.97, N, 1.62%.

4.13. Synthesis of heterocyclyne (*14*)

Polyyne **11** (87 mg, 0.13 mmol) was deprotected and reacted with CuCl (350 mg, 3.6 mmol), pyridine, and MeOH as described in general alkyne homocoupling procedure. Purification on a Chromatotron plate (1 mm, 1:5 hexanes:EtOAc) and recrystallization by diffusion (hexanes:EtOAc) provided **14** (22 mg, 51%) as a bright yellow solid. Mp: 190 °C (dec). ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (t, $J = 7.8$ Hz, 1H), 7.20 (d, $J = 5.1$ Hz, 2H), 7.07 (d, $J = 7.8$ Hz, 2H), 6.98 (d, $J = 5.1$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.90, 137.16, 131.05, 128.83, 128.73, 126.92, 121.83, 100.95, 84.94, 80.56, 78.62. UV–Vis (CH_2Cl_2): λ_{max} (ε) 237 (21 000), 279 (23 000), 296 (26 000), 317 (37 500), 329 (44 500) nm. Fluorescence emission ($[\mathbf{14}] \leqslant 7.4 \times 10^{-5}$ M in CH_2Cl_2; 459 nm excitation): λ_{max} 515 nm. MS (CI pos) m/z (%): 339 ($M^+ + 2$, 13), 338 (MH^+, 24), 337 (M^+, 100); $C_{21}H_7NS_2$ (337.00). Anal. Calc. for $C_{21}H_7NS_20.5C_4H_8O_2$: C, 72.42, H, 2.91, N, 3.67. Found: C, 72.14, H, 3.07, N, 3.70%.

5. Crystallography

Intensity data for **6** and **12** were collected at 153 K on a Bruker SMART-APEX diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å). Lorentz and polarization corrections were applied and diffracted data were also corrected for absorption using the SADABS program. Structures were solved by direct methods and Fourier techniques. Structure solution and refinement were based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of the C–H groups were fixed in calculated positions (see Table 2).

Table 2
Summary of crystal structure data for platinacyclynes **6** and **12**

Complex	**6**	**12**
Molecular formula	$C_{45}H_{57}NP_2Pt$	$C_{33}H_{37}NP_2PtS_2$
Molecular weight	868.97	768.81
Crystal size (mm^3)	$0.1 \times 0.08 \times 0.05$	$0.2 \times 0.2 \times 0.1$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbca$
Unit cell dimensions		
a (Å)	12.360(2)	17.084(6)
b (Å)	24.888(4)	17.017(6)
c (Å)	14.913(3)	22.046(8)
α (°)	90	90
β (°)	90.438(3)	90
γ (°)	90	90
V (Å^3)	4587.3(14)	6409.2(4)
Z	4	8
D_{calc} (g/cm^3)	1.363	1.593
F(0 0 0)	1928	3056
$2\theta_{max}$ (°)	52.22	52.78
Independent reflections	9046	6560
Used in refinement	6941	5940
Refined parameters	508	358
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0509$, $wR_2 = 0.1154$	$R_1 = 0.0178$, $wR_2 = 0.0437$
R indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.1279$	$R_1 = 0.0211$, $wR_2 = 0.0451$
Goodness-of-fit on F^2	1.003	1.024
Largest difference in peak and hole (e Å^{-3})	2.389, −1.685	1.058, −0.368

6. Supplementary material

Crystallographic data for the structural analysis (CIF) has been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. 280240 (**6**) and 280241 (**12**)). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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