## Planar Platinum Metallacyclynes Containing One and Two Trialkyne Pockets

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Summary: Efficient syntheses and characterization of a platinum metallacyclyne containing one cyclic enyne pocket (3), the first dinuclear platinum metallacyclyne containing two cyclic enyne pockets (4), and 2,2,6,6-tetraethynyltolan (2) are reported. Syntheses of 3 and 4 employ bidentate phosphines or cis-platinum starting materials and high dilution techniques to effect high yields.

Substituted phenylethynyl compounds<sup>1</sup> and extended rigid-rod structures containing transition-metal  $\sigma$ -bound acetylides and diacetylides<sup>2</sup> are being explored as possible candidates for nonlinear optical (NLO)<sup>2d,3</sup> and liquid-crystalline materials.<sup>2f,4</sup> The d electrons of transition metals in these systems are polarizable and may provide greater NLO activity. Transition-metal  $\sigma$ -bound bis(acetylides) are numerous, including platinum complexes that primarily exist as *trans*-substituted systems. Some cis-substituted platinum systems have been reported;<sup>2a,5,6</sup> however, analogous cyclic structures have not been explored. Ethynyl-substituted tolans such as 2,2'-diethynyltolan (1)<sup>7</sup> and 2,2',6,6'-tetraethynyltolan (2) possess the geometry necessary to give planar metallacycles when their di- and tetraanions are complexed with square-planar transition metals. Delocalization of electrons should be enhanced by the planarity of transition-metal  $\sigma$ -bis(acetylide) cycles, and as delocalization increases NLO properties may be enhanced as well.<sup>3a</sup>

We report herein the syntheses and characterization of two platinum metallacyclynes (i.e., metallacycles

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Scheme 1







<sup>*a*</sup> Reagents and conditions: (*i*) 1.5 equiv of Me<sub>3</sub>SiC=CH, (PhCN)<sub>2</sub>PdCl<sub>2</sub>, PPh<sub>3</sub>, CuI, Et<sub>3</sub>N for 14 h heating to 75 °C; (*ii*) KF, H<sub>2</sub>O, MeOH-THF (5:2) for 10 h; (*iii*) **5**, (PhCN)<sub>2</sub>PdCl<sub>2</sub>, PPh<sub>3</sub>, CuI in Et<sub>3</sub>N-THF (3:1) at 50 °C for 3 days; (*iv*) 6 equiv of Me<sub>3</sub>SiC=CH, (PhCN)<sub>2</sub>PdCl<sub>2</sub>, PPh<sub>3</sub>, CuI in piperidine at 95 °C for 14 h; (*v*) 2 equiv of *cis*-[Et<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub>, CuI in CH<sub>2</sub>Cl<sub>2</sub>-(*i*-Pr)<sub>2</sub>NH (1:4).

containing enyne units) with one and two cyclyne pockets (**3** and **4**) and a tetradentate tetraethynyltolan ligand (**2**) (Schemes 1 and 2). Compound **4** is the first example of a double-pocket cyclyne of either an organic or organometallic type. Two principles were applied in the successful syntheses of **3** and **4**: use of bidentate bis-phosphines or *cis*-platinum starting materials to inhibit isomerization of  $PtCl_2(PR_2R')_2$  to *trans* species and high-dilution conditions to favor formation of smaller oligomers.

[Fdpp]Pt(Tba) (**3**; Scheme 1), where Tba denotes tolan-2,2'-diacetylide, was prepared under high-dilution conditions using 2,2'-diethynyltolan (**1**), bis(benzoni-trile)platinum dichloride (predominantly *cis* with some *trans*),<sup>8</sup> 1,1'-bis(diphenylphosphino)ferrocene (Fdpp, Aldrich), and CuI (2.5%) in diisopropylamine under nitrogen. The reaction mixture was stirred for 6 days, after which an 85% yield of **3** was isolated by column

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## Communications

chromatography on silica gel with 1:3  $CH_2Cl_2$ -hexanes as eluent.<sup>9,10</sup>

Synthesis of 2,2',6,6'-tetraethynyltolan (**2**; Scheme 2) takes advantage of increased activity of the iodo substituent over that of the bromo substituent in 2,6-dibromoiodobenzene (**5**).<sup>11</sup> This selectivity provides an efficient means of constructing **2**, and high yields for each bond formation are observed.<sup>12</sup>

Bridging two platinum centers with 2,2',6,6'-tetraethynyltolan (**2**) was accomplished by reacting it with *cis*-bis(triethylphosphine)platinum dichloride and CuI (5.0%) in a mixture of 1:4 CH<sub>2</sub>Cl<sub>2</sub>:(*i*-Pr)<sub>2</sub>NH under nitrogen. This highly dilute solution was stirred at room temperature for 2 weeks. Removal of solvent, workup, and chromatographic separation on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as the eluent gave a 65.6% yield of ([Et<sub>3</sub>P]<sub>2</sub>Pt)<sub>2</sub>(Tta) (**4**; Tta denotes tolan-2,2',6,6'-tetraacetylide).<sup>13</sup>

X-ray crystal structures of these compounds (Figures 1 and 2) confirm their high symmetry, with **3** and **4** crystallizing in space groups C2/c and  $I\bar{4}$ , respec-

(10) Anal. Calcd for  $C_{52}H_{36}FeP_2Pt$  (2  $CH_2Cl_2$  in crystal structure lost on standing): C, 64.1; H, 3.7; P, 6.4. Found: C, 65.77; H, 4.05; P, 5.75. FDMS: *m/e* 486.5 (M<sup>2+</sup>), 973 (M<sup>+</sup>, <sup>195</sup>Pt, <sup>56</sup>Fe). <sup>1</sup>H NMR (300 MHz):  $\delta$  (vs CDCl<sub>3</sub>) 4.22 (d, 4H), 4.32 (s, 4H), 6.60 (d, 2H), 7.03 (m, 4H), 7.35 (t, 8H), 7.43 (t, 4H), 7.51 (dd, 2H), 7.88 (m, 8H);  $\delta$  (vs CD<sub>2</sub>-Cl<sub>2</sub>) 4.23 (m, 4H), 4.33 (m, 4H), 6.60 (m, 2H), 7.06 (m, 4H), 7.3–7.5 (overlapping m, 14H), 7.85 (m, 8H);  $\delta$  (vs C $G_{6D_6}$ ) 3.75 (t, 4H), 4.06 (q, 4H), 6.87 (td, 2H), 6.96 (td, 2H), 7.0–7.1 (overlapping m, 14H), 7.66 (dd, 2H), 7.99 (m, 8H), ~10% protic solvent residual coupled to <sup>195</sup>Pt( $J_{Pt-H} = 157$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz):  $\delta$  (vs. CD<sub>2</sub>Cl<sub>2</sub>) 73.27 (t,  $J_{P-C} = 3.56$  Hz), 75.66 (AXX', <sup>1</sup> $J_{P-C} = 63.69$  Hz, <sup>3</sup> $J_{P-C} = 2.01$  Hz [2 routes]), 76.10 (t,  $J_{P-C} = 5.23$  Hz), 92.94 (s), 96.03 (nonet, bound CH<sub>2</sub> routes]), 71.10 (AXX', <sup>3</sup> $J_{trans}P-C = 152.77$  Hz, <sup>3</sup> $J_{cls}P-C = 0.00$  Hz,  $J_{P-P} = 15$  Hz), 112.555 (s), 127.19 (s), 127.35 (s), 128.28 (t,  $J_{P-C} = -1.49$  Hz,  $J_{P-C} = -1.98$  Hz,  $J_{P-P} = 15$  Hz), 135.25 (t,  $J_{P-C} = 59.60$  Hz, <sup>3</sup> $J_{P-C} = 1.40$  Hz [2 routes]), 75.72 (t,  $J_{P-C} = 5.16$  Hz), 93.00 (s), 108.89 (AXX', <sup>3</sup> $J_{trans}P-C = 36.54$  Hz, <sup>3</sup> $J_{cls}P-C = -1.98$  Hz,  $J_{P-P} = 15$  Hz), 120.94 ( $J_{P+C} = 2.199$  Hz,  $J_{P-P} = 15$  Hz), 130.46 (br), 130.74, 130.96, 133.28 (AXX', <sup>3</sup> $J_{P-C} = 5.93$  Hz). <sup>31</sup>P(<sup>1</sup>H) NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (vs 85% H<sub>3</sub>PO<sub>4</sub>), 14.77 ( $J_{P-P} = 2406.9$  Hz).

2406.9 H2). (11) (a) Du, C-J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*(16), 3162–3165. (b) 2,6-Dibromoiodobenzene (**5**): <sup>1</sup>H NMR (300 MHz) δ (vs CDCl<sub>3</sub>) 7.54 (d, 2H), 7.05 (t, 1H). (c) 2,6-Dibromoethynylbenzene (**6**): <sup>1</sup>H NMR (300 MHz) δ (vs CDCl<sub>3</sub>) 7.53 (d, 2H), 7.02 (t, 1H), 3.67 (s, 1H); <sup>13</sup>C{H} NMR (75 MHz) δ (vs CDCl<sub>3</sub>) 81.07, 86.87, 126.27, 126.96, 130.44, 131.54. (d) 2,2',6,6'-Tetrabromotolan (7): <sup>1</sup>H NMR (300 MHz) δ (vs CDCl<sub>3</sub>) 95.49, 126.90, 127.12, 130.50, 131.75. Anal. Calcd: C, 34.05; H, 1.22; Br, 64.72. Found: C, 33.36; H, 1.19; Br, 63.79. (d) 2,2',6,6'-Tetrakis((trimethylsilyl)ethynyl)tolan (**8**): <sup>1</sup>H NMR (300 MHz) δ (vs CDCl<sub>3</sub>) 7.40 (dd, A of ABB', 2H), 7.16 (BB' of ABB', 1H), 0.13 (s, 18H); <sup>13</sup>C{H} NMR (75 MHz) δ (vs CDCl<sub>3</sub>) 0.05, 94.94, 99.55, 103.44, 126.26, 127.46, 129.69, 131.69. Anal. Calcd: C, 72.53; H, 7.52. Found: C, 72.38; H, 7.61. (d) 2,2',6,6'-Tetrathynyltolan (4): <sup>1</sup>H NMR (300 MHz) δ (vs CDCl<sub>3</sub>) 7.49 (d, 2H), 7.22 (t, 1H), 3.29 (s, 1H).

(12) Conditions iv and v give 83% and 90% yields per bond formed, respectively.

(13) Anal. Calcd for  $C_{46}H_{66}P_4Pt_2$ : C, 48.76; H, 5.87; P, 10.93. Found: C, 48.92; H, 5.76; P, 10.67. FDMS: M<sup>+</sup> 1132 (<sup>195</sup>Pt<sub>2</sub>). <sup>1</sup>H NMR (300 MHz):  $\delta$  (vs CDCl<sub>3</sub>) 1.16 (m, 36H), 2.12 (m, 24H), 7.07 (t, 2H), 7.26 (d, overlaps solvent);  $\delta$  (vs CD<sub>2</sub>Cl<sub>2</sub>) 1.19 (m, 36H), 2.15 (m, 24H), 7.17 (dd, 2H), 7.29, 7.32, and 7.35 (B' portion of ABB', 4H). <sup>13</sup>C (<sup>1</sup>H) NMR (75 MHz):  $\delta$  (vs CD<sub>2</sub>Cl<sub>2</sub>) 8.64 (<sup>3</sup>J<sub>Pt-C</sub> = 21.18 Hz), 17.82 (m), 96.55 (s), 106.50 (AXX' + <sup>1</sup>/<sub>3</sub> AMXX', <sup>2</sup>J<sub>Pt-C</sub> = 294.87 Hz, <sup>3</sup>J<sub>trans-P-C</sub> = 34.08 Hz, <sup>3</sup>J<sub>cls-P-C</sub> = -1.59 Hz, J<sub>P-P'</sub> = 18 Hz), 111.97 (AXX' + <sup>1</sup>/<sub>3</sub> AMXX', J<sub>Pt-C</sub> = 530.96 Hz, <sup>2</sup>J<sub>trans-P-C</sub> = 141.07 Hz, <sup>2</sup>J<sub>cls-P-C</sub> = 23.71 Hz, calcd J<sub>P-P'</sub> = 18 Hz), 126.28 (s), 128.00 (<sup>4</sup>J<sub>Pt-C</sub> = 9.42 Hz), <sup>31</sup>P[<sup>4</sup>H] NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (vs 85% H<sub>3</sub>PO<sub>4</sub>) 4.424 (J<sub>Pt-P</sub> = 2275.7 Hz).



**Figure 1.** Thermal ellipsoid drawing of [Fdpp]Pt(Tba) (**3**) drawn at the 50% probability level. H atoms and 2 CH<sub>2</sub>-Cl<sub>2</sub> molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt-P1 = 2.319(1), Pt-C1 = 1.994(3), C1-C2 = 1.197(4), C5-C5a = 1.200(6), Fe-C10 = 2.001(3), Fe-C11 = 2.021(3), Fe-C12 = 2.053(3), Fe-C13 = 2.044(3), Fe-C14 = 2.032(3), P1-C10 = 1.796(3), P1-C15 = 1.833(3), P1-C21 = 1.819(3); P1-Pt-P1a = 101.46(4), C1-Pt-C1a = 82.9(2), Pt-P1-C10 = 119.98(9), Pt-C1-C2 = 170.6(2), C1-C2-C3 = 175.9(3), C4-C5-C5a = 178.0(2).



**Figure 2.** Thermal ellipsoid drawing of one of the two conformers of  $[Et_3P]_2Pt(Tta)$  (4) drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1-P1 = 2.306(6), Pt1-P2 = 2.308(6), Pt2-P3 = 2.312(7), Pt2-P4 = 2.292(7), Pt1-C1 = 1.93(2), Pt1-C14 = 1.99(2), Pt2-C7 = 1.97(2), Pt2-C8 = 2.00(2), C1-C2 = 1.23(3), C13-C14 = 1.20(3), C6-C7 = 1.24(3), C8-C9 = 1.21(3), C15-C16 = 1.18(2); P1-Pt1-P2 = 98.8(2), P3-Pt2-P4 = 98.0(3), C1-Pt1-C14 = 81.1(9), C7-Pt2-C8 = 83.1(9), Pt1-C1-C2 = 175(2), Pt1-C14-C13 = 177(2), C1-C2-C3 = 171(2), C12-C13-C14 = 173(2), Pt2-C7-C6 = 175(2), Pt2-C8-C9 = 173(2), C5-C6-C7 = 173(2), C8-C9-C10 = 175(2), C4-C15-C16 = 177(2), C11-C16-C15 = 179(2).

tively.<sup>14–17</sup> Acetylene and acetylide C–C distances in **3** and **4** are all within 1.18-1.24 Å, and acetylene

<sup>(9)</sup> Second-order AXX' <sup>13</sup>C NMR spectral lines were modeled with the spin simulation portion of the computer program VNMR (version 5) based on LAOCOON, and LAME algorithms: VNMR version 5, Varian Associates, 1995.

<sup>(14)</sup> X-ray data for **3**: monoclinic, *C*2/*c* (No. 15), *a* = 15.919(3) Å, *b* = 19.063(4) Å, *c* = 16.800(3) Å,  $\beta$  = 116.88(3)°, *Z* = 4. Data were collected at 130 K in the range 1.81–27.50° in  $\theta$  and were corrected for absorption using  $\psi$ -scan data. Atomic positions were determined principally by direct methods.<sup>14</sup> Refinement<sup>15</sup> for data with *I* > 2 $\sigma$ (*I*) (4701 reflections) gave R1 = 0.0248 and wR2 = 0.0525; for all data (5211 reflections) R1 = 0.0318 and wR2 = 0.0548.

C-C-C angles are nearly linear. Greater deviation from linearity is observed for the Pt-C-C angle than for the C-C-C angle of the acetylide in **3**, while in **4** the angles deviate from linearity within respective esd's of one another. The positive <sup>31</sup>P NMR chemical shifts and the magnitudes of the  ${}^{195}Pt-{}^{31}P$  coupling constants for **3** ( $J_{Pt-P} = 2406.9 \text{ Hz}$ ) and **4** ( $J_{Pt-P} = 2275.7 \text{ Hz}$ ) are consistent with a cis configuration for the phosphines and for the acetylides about platinum.<sup>2c,18</sup> The 81.1-83.1° C-Pt-C angles dictated in these compounds by the ethynyl-substituted tolans are among the smallest observed.<sup>19</sup> Planarity of 4 provides for efficient electron delocalization with the platinum and central carbon framework deviating slightly from planarity.<sup>20</sup> The angle between the plane of Pt2, P3 and P4 and that of Pt1, Pt2, and carbons C1-C22 in 4 is 18.77(0.39)°. The latter plane deviates by only 3.32(0.37)° from that of Pt1, P1, and P2. In contrast the torsion of the plane of Pt and two P atoms from that of the Pt and cyclyne frame in 3 is 17.97(0.06)°. <sup>195</sup>Pt-<sup>13</sup>C spin coupling extends through up to four bonds of the enyne frameworks of 3 and 4. And in 4, C4 and C11 exhibit the inner three peaks of a 1:8:18:8:1 splitting pattern indicative of coupling to both Pt atoms. It is also interesting that multiple pathways exist in **3** for  ${}^{31}P-{}^{13}C$  coupling of the cyclopentadienyl carbons: through the carbon  $\pi$  system, Fe center, or Pt center. Spin coupling transmitted

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(19) The smallest comparable angle in the literature<sup>5b</sup> is  $84.5(6)^{\circ}$  for a Pt(II) compound with two C=CC(OH)Me<sub>2</sub> groups tethered together by a hydrogen-bonding water molecule.

(20) The largest deviation from the least-squares plane of Pt1, Pt2, and carbons C1-C22 inclusive is 0.171 Å (0.021) for C8.

through the Fe center as well as through the carbon  $\pi$  system is observed in free Fdpp.<sup>21</sup>

"Tweezer" transition-metal bis( $\sigma$ -acetylides) have been reported to complex transition metals having a variety of oxidation states.<sup>6</sup> **3** and **4** have the necessary proximity of the acetylides and an additional uncoordinated alkyne for further metal complexation, as has been demonstrated in analogous silicon heterocyclynes.<sup>22</sup> The additional avenue of metal complexation of these compounds may further enhance the physical properties of extended systems. The structures of  $\mathbf{3}$ ,  $\mathbf{4}$ , and  $[Et_3P]_2Pt(Tba)^{23}$  provide the foundation for constructing extended two-dimensional systems of planar metallacycles bridged by planar multidentate phosphines such as tetrakis(diphenylphosphino)tetrathiafulvalene.<sup>24</sup> Incorporation of chiral phosphines is under investigation as a means of altering NLO properties of these structures.

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**Supporting Information Available:** For **3** and **4**, singlecrystal X-ray experimental tables of data collection and structure solution details, bond distances and angles, atomic coordinates, thermal parameters, and least-squares-plane deviations (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(21) Fdpp <sup>13</sup>C{H} NMR: (a) Pouchert, C. J.; Behnke, J. *The Aldrich Library of* <sup>13</sup>C and <sup>1</sup>H FT NMR Spectra, 1st ed.; Aldrich Chemical: Milwaukee, WI, 1993; Vol. 3, 772B. (b) (75 MHz)  $\delta$  (vs CDCl<sub>3</sub>) 72.50 (dd, <sup>3</sup>J<sub>P-C</sub> = 3.68 Hz, <sup>3</sup>J<sub>P-C</sub> = 1.84 Hz), 73.77 (d, <sup>2</sup>J<sub>P-C</sub> = 14.72 Hz), 76.72 (d, overlaps solvent, <sup>1</sup>J<sub>P-C</sub> = ca. 7.36 Hz), 128.13, 128.22, 128.52, 133.34, 133.60, 138.94 (d, <sup>1</sup>J<sub>P-C</sub> = 10.12 Hz);  $\delta$  (vs CD<sub>2</sub>Cl<sub>2</sub>) 72.72 (AXX', <sup>3</sup>J<sub>P-C</sub> 3.84 Hz, <sup>3</sup>J<sub>P-C</sub> 1.59 Hz, J<sub>P-P'</sub> = 0.575 Hz), 74.11 (d, <sup>1</sup>J<sub>P-C</sub> = 14.91 Hz), 77.04 (d, <sup>1</sup>J<sub>P-C</sub> = 8.11 Hz), 128.44 (<sup>3</sup>J<sub>P-C</sub> = 6.81 Hz), 128.79, 133.71 (d, <sup>2</sup>J<sub>P-C</sub> = 19.46 Hz), 139.45 (d, <sup>1</sup>J<sub>P-C</sub> = 10.37 Hz). (22) Guo, L.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J.

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<sup>(15)</sup> SHELXTL PLUS version 4.03, Siemens Analytical Instruments, Inc., Madison, WI, 1990.

<sup>(16) (</sup>a) Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993. (b) R1 is based on F, and R2 is based upon  $F^2$ .

<sup>(17)</sup> X-ray data for **4**: tetragonal,  $\overline{I4}$  (No. 82), a = 29.832(3) Å, c = 10.892(3) Å, Z = 8. Data were collected at 138 K in the range 1.93–25.00° in  $\theta$  and were corrected for absorption using  $\psi$ -scan data. Positions of Pt atoms were determined by direct methods.<sup>14</sup> The remaining atomic positions were determined by successive difference Fourier maps.<sup>15</sup> The model used was that of a racemic twin, the two hands differing in the direction of a 2-fold chiral axis passing through the two Pt atoms. Pt and P atoms were treated as anisotropic vibrators. For data with  $I > 2\sigma(I)$  (4217 reflections) R1 = 0.0614 and wR2 = 0.1135; for all data (5391 reflections) R1 = 0.0896 and wR2 = 0.1259. A solution in the centrosymmetric space group  $I_4_1/a$  is not reported due to a large number of systematic absence violations (84 primarily weak reflections of the type (hk0) h,k = odd, and (00), I = 2n but  $I \neq 4n$ ) and an unsatisfactory refinement. A second data set on another crystal yielded similar results.