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Communications

Synthesis and Crystallographic Characterization of a Platinadehydrobenzo[19]annulene

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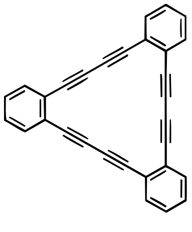
Summary: The efficient synthesis and characterization of the trans-platinum complex $(Et_3P)_2Pt(C_{30}H_{12})$ *(**2**, PtDBA) is described. The X-ray crystal structure shows that a strained and warped annulenic core results upon insertion of the organometallic fragment. UV−vis data suggest electronic delocalization is present in the macrocycle.*



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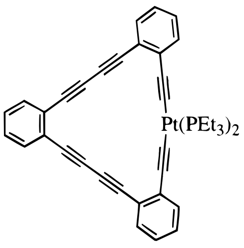

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In recent years, dehydrobenzoannulenes (DBA, *e.g.*, **1**) have been recognized as useful precursors in the development of novel topochemical polymerization reactions.[1] The renewed interest in DBAs and their corresponding polymers has been attributed to possible conducting[2] and nonlinear optical (NLO)[3] properties in these materials. Greater NLO activities in DBAs might be achieved when polarizability of the conjugated system is increased by either (1) donor−acceptor substitution at the annulenic core[4] or (2) insertion of a transition metal within the annulenic circuit.[5] The latter option is especially intriguing since the d electrons of the transition metal in such a complex induce the polarization in the DBA circuit. We recently reported a new synthesis of DBAs via stepwise assembly of the macrocycles.[6] Use of the α,ω-polyyne intermediates prior to intramolecular cyclization should provide a viable route to transition-metal *trans*-σ-bis(acetylide) macrocycles. Although σ-bound acetylides and diacetylides have been

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(1) (a) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294. (b) Guo, L.; Bradshau, J. D.; Tessier, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 243. (c) Baldwin, K. P.; Simons, R. S.; Rose, J.; Zimmerman, P.; Hercules, D. M.; Tessier, C. A.; Youngs, W. J. *Ibid.* **1994**, 1257. (d) Baldwin, K. P.; Matzger, A. J.; Scheiman, D. A.; Tessier, C. A.; Vollhardt, K. P. C.; Youngs, W. J. *Synlett* **1995**, 1215.

(2) (a) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 3326. (b) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Organometallics* **1989**, *8*, 2089. (c) *Organic Superconductivity*; Kresin, V. Z., Little, W. A., Eds.; Plenum Press: New York, 1990.

(3) (a) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (b) Abe, A.; Kimura, N.; Tabata, S. *Macromolecules* **1991**, *24*, 6238. (c) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341. (d) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (e) Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, *5*, 804. (f) Meyers, L. K.; Langhoff, C.; Thompson, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 7560.

(4) (a) Tykwinski, R. R.; Schreiber, M.; Gramlich, W.; Seiler, P.; Diederich, F. *Adv. Mater.* **1996**, *8*, 226. (b) Bosshard, C.; Spreiter, R.; Günter, P.; Tykwinski, R. R.; Schreiber, M.; Diederich, F. *Ibid.* **1996**, *8*, 231. (c) Tykwinski, R. R.; Schreiber, M.; Carlon, R. P.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1996**, *79*, 2249. (d) Pak, J. J.; Haley, M. M. Manuscript in preparation.

(5) (a) Faust, R.; Diederich, F.; Gamlich, V.; Seiler, P. *Chem. Eur. J.* **1995**, *1* (2), 111. (b) Bradshaw, J. D.; Guo, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1996**, *15*, 2582. (c) Zhang, D.; McConvile, D. B.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1997**, *16*, 824.

(6) (a) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956. (b) Haley, M. M.; Brand, S. C.; Pak, J. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 836.

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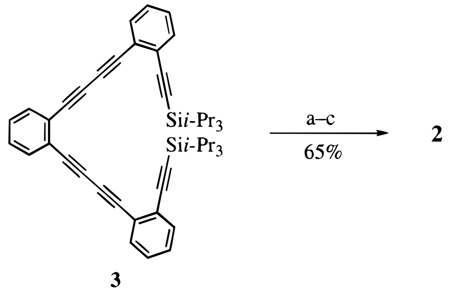
Scheme 1[a]



[a] Reagents: (a) Bu_4NF, EtOH, THF; (b) Me_3SnNMe_2, THF; (c) *trans*-$PtCl_2(PEt_3)_2$, CuI, toluene.

explored on many occasions,[3b,7] only a few cyclic structures have been reported.[5] We describe herein the synthesis and characterization of the first "*trans*-platinadehydrobenzo[19]annulene" (**2**, PtDBA).[8]

The synthesis of PtDBA was based on established procedures (Scheme 1). Thus, bis(silyl)-protected α,ω-polyyne **3**[6b] (0.103 g, 0.15 mmol) was desilylated by treatment with excess Bu_4NF in 9:1 THF/ethanol (20 mL). Without further purification, the resultant brown oil was mixed with Me_3SnNMe_2 (0.063 g, 0.30 mmol) in THF (20 mL) at room temperature.[9] The solvent was removed in vacuo leaving the bis(stannane) as a dark brown oil in nearly quantitative yield. The crude tin derivative was redissolved in deaerated toluene (30 mL), subsequently treated with *trans*-$PtCl_2(PEt_3)_2$ (0.053 g, 0.105 mmol) and CuI (0.010 g, 0.05 mmol),[5a,7e] and stirred at room temperature for 12 h. Evaporation of the volatiles and chromatography over silica gel (1:1 hexanes/CH_2Cl_2) afforded a bright yellow solid (0.078 g) in 65% yield.[10] Whereas the parent dehydrobenzo[18]annulene (**1**)[6b] proved to be poorly soluble in common organic solvents, inclusion of the *trans*-bis(triethylphosphine)platinum fragment in the carbon backbone dramatically improved product solubility. Crystals of **2** suitable for single-crystal X-ray diffraction were formed by slow diffusion of hexanes into a concentrated ethyl acetate solution at 5 °C.

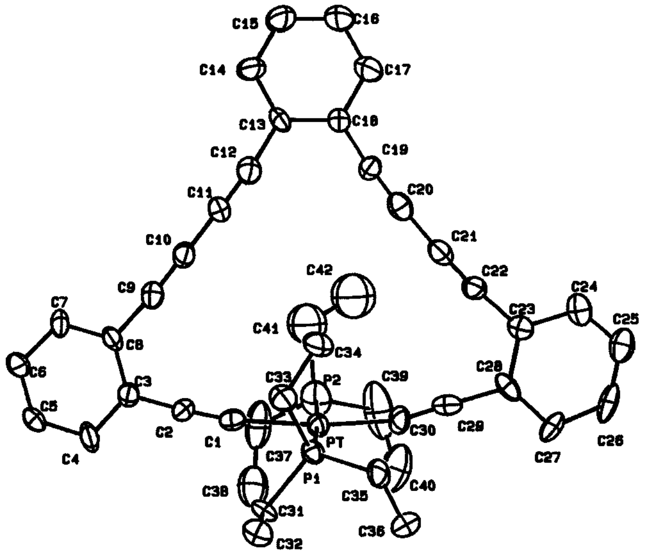


Figure 1. Thermal ellipsoid plot of PtDBA (**2**) drawn at the 30% probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt−P(1), 2.283(3); Pt−P(2), 2.277(4); Pt−C(1), 2.00(1); Pt−C(30), 1.996(10); C(1)−C(2), 1.198(12); C(2)−C(3), 1.456(13); C(28)−C(29), 1.429(13); C(29)−C(30), 1.213(13); P(1)−Pt−P(2), 176.3(1); C(1)−Pt−C(30), 170.4(4); Pt−C(1)−C(2), 169.7(9); Pt−C(30)−C(29), 172(1); C(1)−C(2)−C(3), 175(1); C(28)−C(29)−C(30), 175(1).

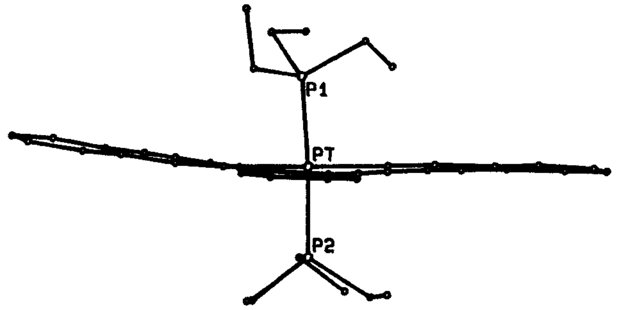


Figure 2. Side view of a single molecule of **2** along the mean plane of the macrocycle.

The thermal ellipsoid plot of **2** is shown in Figure 1.[11] The crystal structure clearly shows retention of the *trans* geometry and the additional strain placed on the molecule by metal incorporation—the sp bond angles on the side containing the platinum fragment are distorted up to 10° from linearity. Smaller degrees of distortion (3−6°) from linearity are also observed on the all-carbon sides. The most striking abnormalities of the crystal structure of **2** are that the annulenic core is not planar (Figure 2) and that the triethylphosphine ligands are not perpendicular to the plane of the macrocycle (Figure 3). There are no close intermolecular contacts; thus, crystal packing forces are believed to be minimal. Semiempirical calculations accurately replicate the geometrical distortions.[12] The amount of deplanarization in **2** is difficult to quantitate as the planes of the benzene rings are not only bent with respect to each other but

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[7] For some recent examples, see: (a) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203. (b) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (c) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276. (d) Lichtenberger, D. L.; Renshaw, S. K.; Wong, A.; Tagge, C. D. *Organometallics* **1993**, *12*, 3522. (e) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1992**, *424*, 87. (f) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165.

[8] Chemical Abstracts Service names compound **2** as [1,2-phenylenebis[(1,3-butadiyne-1,4-diyl-2,1-phenylene-2,1-ethynediyl)]bis(triethylphosphine)platinum. In lieu of this complicated name, we feel that describing **2** as an annulene derivative is more straightforward. Using this classification, molecule **2** would thus be a 5-platina-3,4,6,7,10,11,12,13,16,17,18,19-dodecadehydro-1:2,8:9,14:15-tribenzo[19]annulene bis(triethylphosphine) complex, a name easily shortened to "platinadehydrobenzo[19]annulene".

[9] (a) Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944. (b) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295.

[10] Anal. Calcd for **2** ($C_{42}H_{42}P_2Pt$): C, 62.76; H, 5.27. Found: C, 62.42; H, 5.30. Mp: 167 °C (dec). IR (KCl, CH_2Cl_2): $\nu = 1416$, 2298 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (dd, $J = 3.6$, 6.0 Hz, 2H), 7.53 (bd, $J = 7.8$ Hz, 2H), 7.37−7.29 (m, 4H), 7.25 (bt, $J = 7.8$ Hz, 2H), 7.10 (bt, $J = 7.8$ Hz, 2H), 2.20−1.99 (m, 18H), 1.31−1.16 (m, 18H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 135.21, 133.27, 132.92, 129.89, 129.38, 129.14, 124.77, 124.04, 119.29 (t, $J_{P-C} = 14.5$ Hz), 108.60, 84.58, 80.45, 79.51, 76.58, 16.88 (m), 8.87 (m). ^{31}P NMR (121 MHz, $CDCl_3$): δ 11.19 ($J_{Pt-P} = 2344$ Hz).

[11] X-ray structure analysis of **2**: $a = 14.446(2)$ Å, $b = 17.184(3)$ Å, $c = 29.856(3)$ Å, $V = 7411(3)$ Å^3, 295 K, orthorhombic, space group *Pbca*, $Z = 8$, $\rho_{calc} = 1.441$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $\mu = 3.94$ mm^{-1}, $2\theta_{max} = 50°$, 7189 independent reflections, 3772 observed ($I \geq 1.5\sigma(I)$), structure refinement (C atoms anisotropic, H atoms riding) with TEXSAN v. 5.0, 388 parameters, $R = 0.050$, $R_w = 0.045$.

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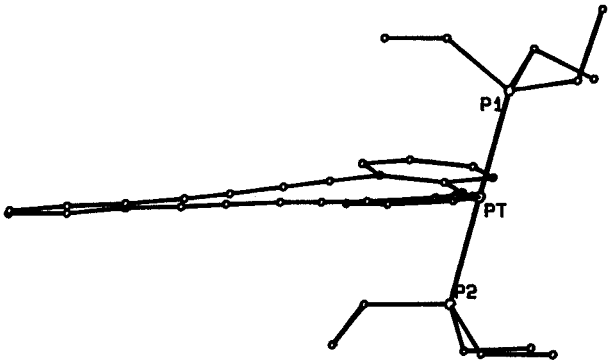

Figure 3. Side view of a single molecule of **2** along the line C(1)−C(30).

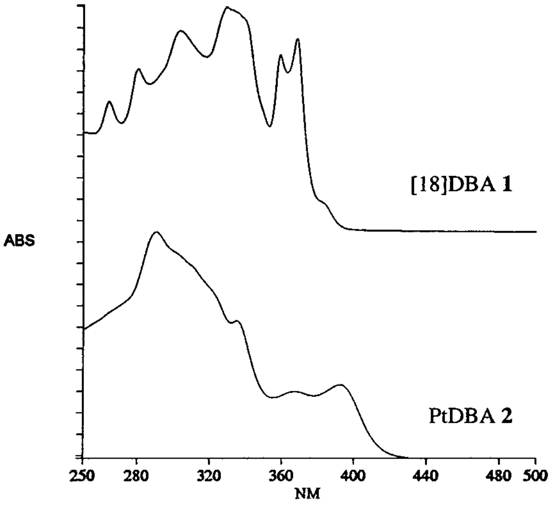

Figure 4. UV−vis spectra of **1** and **2** in CH_2Cl_2.

also twisted. Atoms C(11), C(20), and Pt are close to the mean plane of the macrocycle, while the deviation of the remaining atoms in the $C_{30}H_{12}$ ligand varies from 0.484 Å above for C(6) to 0.283 Å below the mean plane for C(16). The best description for this distortion is that the annulenic core is warped like a phonograph record. Vollhardt *et al.* have recently observed deplanarization for their π-electron-rich, phenylene-based hydrocarbons.[13]

The triethylphosphine ligands of **2** are tilted by *ca.* 16° off the normal to the macrocycle mean plane. In solution at room temperature the ^{31}P NMR spectrum showed **2** to have a dynamic structure as the phosphines are equivalent (δ = 11.19 ppm). Reducing the probe temperature had little or no effect on the ^{31}P NMR data. The cause of the phosphine tilt could be attributable to either electronic effects or crystal packing factors. In either case, the tilt is energetically insignificant as calculations predict the barrier to phosphine "oscillation" to be extremely low, about 0.1 kcal.[12]

A rough estimate for the extent of electron delocalization in platinacycle **2** can be obtained by comparison of the UV−vis absorption spectrum with that of **1** (Figure 4). The highest end absorption in **2** (λ_{max} = 393 nm) is shifted bathochromically compared with the analogous absorption in **1** (λ_{max} = 369 nm). These data are contrary to what was found with a highly conjugated, acyclic system, where insertion of the bis(triethylphosphine)platinum fragment resulted in a hypsochromic shift.[5a] Our work strongly suggests that electronic delocalization in the platinum complex is indeed functional throughout the entire macrocycle. We are currently investigating the fluorescence behavior of **2** as well as the potential nonlinear optical properties.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant CHE-9704171) and the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supporting Information Available: For **2**, text giving structure refinement details and tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and mean planes (22 pages). Ordering information is given on any current masthead page.

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[12] PM3 (tm) calculations were performed on a SGI workstation using Spartan molecular modeling software (Version 4.1.1). The calculations were done on the corresponding Pd complex of **2** as the program does not possess parameters for Pt. Nevertheless, due to the similarities between the two metals, all of the geometrical distortions (bent acetylenes, nonplanar annulene, tilt of phosphines) were duplicated with a very good degree of accuracy. A vast majority of the calculated bond lengths differed by less than 0.02 Å from the crystallographically observed values, and bond angles, by less than 1−2°.

[13] Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478.