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Abstract

The *trans*-palladium bis(σ -acetylide) complex (Et₃P)₂Pd(C₃₀H₁₂) (**2**) was synthesized from hexane **4** in 77% yield via a simple three-step process. The X-ray crystal structure of **2** shows a strained and warped annulenic core upon insertion of the organometallic fragment. UV–vis data of the molecule suggest limited electronic delocalization throughout the metallacycle.

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Keywords: Palladium(II); Platinum(II); Acetylide; Diacetylene; Metallacycle; X-ray structure

1. Introduction

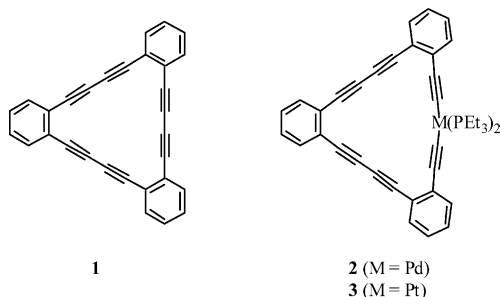
Highly conjugated carbon-rich organic [1] and organometallic compounds [2] and their polymers [3] have become one of the most studied new materials in last decade, eliciting excitement from chemists, physicists, materials scientists, and engineers. Organic chemists have been interested in these compounds not only because of the synthetic challenges in preparing them and the pure structural beauty of the molecules, but also because of their unique electronic structures and the corresponding properties and stabilities. One important reason of interest in these materials are predictions and, in some cases, confirmation of conducting [4] and nonlinear optical (NLO) [5] properties. Dehydrobenzoannulenes (DBA, e.g. **1**) [6], one particular subset of carbon-rich organics, have been recognized as promising precursors for the preparation of materials characterized by these properties, as well as utilized in the development of novel topochemical polymerization reactions [7]. Our interest in the NLO properties of DBAs has led us to pursue two approaches to increase the optical

activity of the annulene skeleton. One successful method has been to judiciously attach donor–acceptor moieties around annulenic systems [8], increasing the polarization and thus the NLO activity of the DBAs [9]. The other route has been to insert transition metals directly into the annulenic circuit [10]. This latter method is an attractive strategy since the d electrons of the transition metal in such a complex induce the polarization in the annulene π circuit.

From a design perspective, the combination of acetylene ligands and *trans*-metal centers is appealing because of the rigid nature of the alkyne ligands and the defined directionality of the metal center. Cyclic σ -acetylide complexes, of which there are a limited number of examples [11,12], most notably *only one* Pd complex [12b], are especially alluring. These can be used to create exceptionally rigid molecules which can be employed as building blocks for the preparation of supramolecular networks [13]. Use of the α,ω -polyyne intermediates, generated for the stepwise assembly of DBAs, prior to intramolecular cyclization should provide a facile route to *trans*- σ -bis(acetylide) macrocycles. We describe herein the synthesis and characterization of 'palladadehydrobenzo[19]annulene' [14] complex **2** (Pd[19]DBA), which incorporates a *trans*-bis(triethylphosphine)palladium fragment, and contrast these results with known 'platinadehydrobenzo[19]annulene' **3** (Pt[19]DBA) [10].

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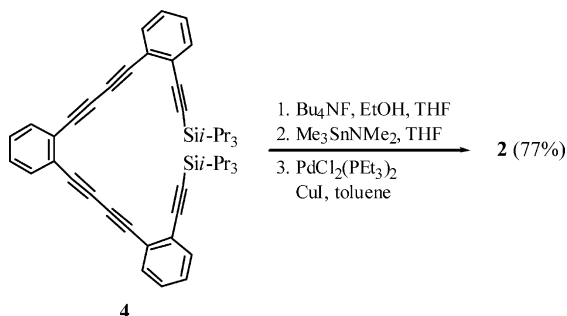
E-mail address: haley@oregon.uoregon.edu (M.M. Haley).



2. Results and discussion

The straightforward preparation of **2** is shown in Scheme 1. Desilylation of α,ω -polyyne **4** [15] with excess Bu_4NF proceeded in near quantitative yield. Without further purification, the resultant brown oil was treated with $\text{Me}_3\text{SnNMe}_2$, thus replacing the terminal alkyne hydrogens with $-\text{SnMe}_3$ [16]. Cyclization was accomplished by stirring the bis(stannane) with $\text{PdCl}_2(\text{PEt}_3)_2$ and CuI overnight in deaerated toluene [11a,17]. Concentration of the intense yellow solution and chromatography of the residue afforded **2** as a bright yellow solid in 77% yield. Whereas the parent [18]DBA **1** [15] was poorly soluble in common organic solvents, inclusion of the *trans*-bis(triethylphosphine)metal fragments in the carbon backbone of **2** (and **3**) greatly improved macrocycle solubility.

Crystals of metallacycle **2** suitable for single-crystal X-ray diffraction were obtained at 5 °C by slow diffusion of hexanes into a concentrated ethyl acetate solution. Although **2** is isostructural with **3** [10], the two molecules crystallize in different crystal systems and space groups. The overall features of the solid state structures are very similar (Table 1) [18]. The structure of **2** is shown in Fig. 1. The $\text{C}_{30}\text{H}_{12}$ ligand is doubly σ -bonded to a square-planar Pd(II) center which has retained *trans* geometry. As consequence of incorporation of a metal center within the annulene backbone, the strain manifests itself as distortions of the triple bond angles from linearity, primarily on the side containing



Scheme 1.

Table 1
Selected bond lengths (Å) and bond angles (°) for Pd[19]DBA (**2**) and Pt[19]DBA (**3**)

	2	3 ^a
<i>Bond lengths</i>		
M–P(1) ^b	2.291(2)	2.281(3)
M–C(1) ^b	2.004(7)	1.995(9)
C(1)–C(2)	1.202(8)	1.211(10)
C(2)–C(3)	1.432(9)	1.425(11)
C(3)–C(8)	1.398(9)	1.406(11)
C(8)–C(9)	1.437(9)	1.427(12)
C(9)–C(10)	1.200(9)	1.209(12)
C(10)–C(11)	1.359(10)	1.375(12)
C(11)–C(12)	1.194(9)	1.189(12)
C(12)–C(13)	1.421(10)	1.422(12)
C(13)–C(13 ⁱ)	1.419(12)	1.392(11)
<i>Bond angles</i>		
C(1)–M–C(1 ⁱ) ^b	169.2(4)	169.5(3)
M–C(1)–C(2) ^b	167.2(7)	171.6(8)
C(1)–C(2)–C(3)	175.2(8)	175.4(10)
C(2)–C(3)–C(8)	122.1(6)	120.4(8)
C(3)–C(8)–C(9)	120.0(6)	120.5(8)
C(8)–C(9)–C(10)	174.5(8)	176.8(10)
C(9)–C(10)–C(11)	178.6(8)	177.8(10)
C(10)–C(11)–C(12)	177.6(8)	177.1(10)
C(11)–C(12)–C(13)	174.8(7)	175.1(10)
C(12)–C(13)–C(13 ⁱ)	121.6(4)	122.5(8)
P(1)–M–C(1) ^b	86.4(2)	88.0(2)
P(1)–M–C(1 ⁱ) ^b	93.8(2)	92.0(2)
P(1)–M–P(1 ⁱ) ^b	178.5(2)	176.2(1)

Ref. [18].

^a Average of chemically equivalent but crystallographically inequivalent bond lengths and angles.

^b M represents the Pt and Pd metal centers.

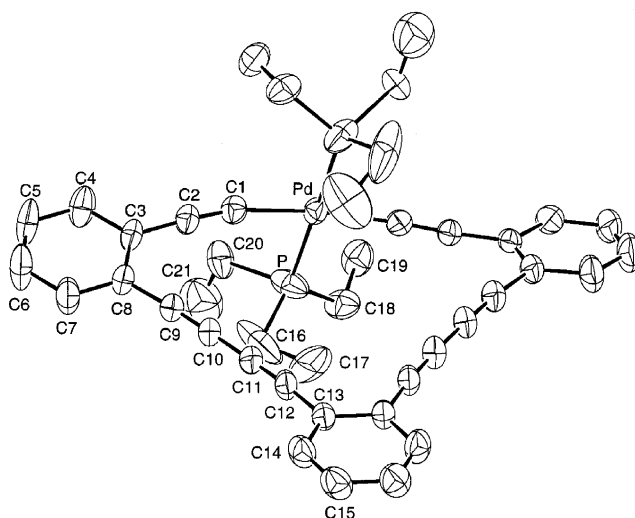


Fig. 1. Thermal ellipsoid plot of Pd[19]DBA (**2**) drawn at the 30% probability level.

the metal (**2**: 4.8–12.8°; **3**: 4.6–9.4°). The C(1)–M–C(1ⁱ) bond angle is also quite deformed from linearity (**2**: 10.8°; **3**: 10.5°). Smaller degrees of distortion (1.4–5.5°) are also evident on the all-carbon diyne sides. Despite

the added strain, the metal–phosphine [Pd–P = 2.291(2) and Pt–P = 2.281(3) Å] and metal– σ -alkyne [Pd–C = 2.004(7) and Pt–C = 1.995(9) Å] bond lengths are consistent with those observed in other pallada- [12b] and platina- σ -acetylides [11,12].

One of the more striking features in the crystal structures of both **2** and **3** is the distinct nonplanarity of the hydrocarbon ligand. The amount of deplanarization in both compounds is difficult to quantitate as the planes of the benzene rings are not only bent with respect to each other but also twisted. Atoms C(13), C(13ⁱ), and Pd are close to the mean plane of macrocycle **2**, while the deviation of the remaining atoms in the C₃₀H₁₂ ligand varies from 0.291 Å above for C(7) to 0.240 Å below the mean plane for C(4). The deviation in **3** is somewhat greater, ranging from 0.470 to –0.283 Å. The best description for these distortions is that the annulenic core has warped like an overheated phonograph record. Vollhardt et al. have observed deplanarization in their π -electron-rich, phenylene-based hydrocarbons and calculated such distortions to be energetically insignificant in their flexible molecules [19]; similar logic should apply to the floppy hydrocarbon ligand in **2** and **3**. Unlike the distortions observed by Bunz and co-workers [20], our ‘warping’ cannot be attributed solely to the organometallic fragment.

Unlike its platinum analogue **3** [10], the crystal structure of **2** revealed no significant tilting of the ligands (16° vs. 0°, respectively) about the C–M–C bond (i.e. perpendicularity of the phosphine ligands to the plane of the macrocycle). It is likely that the tilt in **3** is due to crystal packing factors, which seems reasonable since the isostructural metallacycles pack in different space groups. Such tilting has been observed in *trans*-bis(acetylides) [12b] and not in others [12c,d], though in the former factors such as sterics were invoked; similar constraints are not operational in our macrocycles.

In order to understand the extent of electron delocalization in our molecules, the UV–vis absorption spectra of **2** and **3** were obtained. Compared to DBA **1**, the end absorption of compound **2** (λ_{max} = 391 nm) has shifted bathochromically by ca. 25 nm; compound **3** is similarly shifted (λ_{max} = 393 nm). Analogous to other extended *trans*-bis(σ -acetylide) complexes [2e,11a], these two absorptions are attributable to metal-to-ligand charge transfer (MLCT) bands. While tempting to attribute the shifts to delocalization throughout the metallacycles caused by extended electronic conjugation through the metal centers [10], Diederich and co-workers have shown that, despite efficient MLCT, electronic conjugation along the entire backbone of Pt-bridged acetylenic nanostructures (and thus NLO response) is quite limited [2e,11a]; delocalization in our metallacycles should also be similarly restricted. This conclusion is also supported by the ¹H-NMR data. Whereas cyclization to form **1**

resulted in a downfield shift of the arene protons (ca. 0.2 ppm) due to the presence of a ring current in the macrocycle [7d,15], an analogous change was not observed upon formation of **2** or **3**.

3. Conclusions

In conclusion, the Pd-containing dehydrobenzo[19]annulene has been synthesized in very good yield. The X-ray crystal structure of complex **2** shows varying degrees of strain in the annulenic core upon insertion of the metal fragment, with a majority of the strain contained on the side of metal incorporation. The UV–vis spectral study of complexes **2** and **3** shows only limited electronic communication through the metal centers. Work is currently directed toward the preparation of metal-containing bis-macrocycles and macrocycles with multiple metal centers; these studies will be the subject of future reports.

4. Experimental

4.1. General data

¹H and ¹³C-NMR spectra were recorded using a Varian Inova 300 NMR 300 (¹H: 299.94 MHz, ¹³C: 75.43 MHz, ³¹P: 121.42 MHz) spectrometer and were obtained in CDCl₃. Chemical shifts (δ) are expressed in ppm downfield from SiMe₄ using the residual protonated solvent as internal standard (CDCl₃—¹H: 7.26, ¹³C: 77.0). ³¹P-NMR shifts are expressed in parts per million downfield to 85% H₃PO₄–H₂O as external standard. Coupling constants are expressed in Hertz. Toluene was distilled from CaH₂ under an atmosphere of N₂ prior to use. THF was distilled from Na and benzophenone under an atmosphere of N₂ prior to use. All other chemicals were of reagent quality and used as obtained from the manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230–400 mesh). Baker pre-coated silica gel plates were used for analytical (200 × 50 × 0.25 mm) thin layer chromatography. Reactions were carried out in an inert atmosphere (dry N₂ or Ar) when necessary.

4.2. Synthesis of Pd[19]DBA (**2**)

A solution of α,ω -polyyne **4** (102 mg, 0.15 mmol) in THF and EtOH (9:1, 20 ml) was treated with Bu₄NF (3.0 ml, 1 M THF solution). After stirring at room temperature (r.t.) for 1 h, the mixture was diluted with Et₂O (25 ml), washed with water (3 × 25 ml) and brine (2 × 25 ml), and then dried (MgSO₄). Without further purification, the resultant brown oil was mixed with Me₃SnNMe₂ (63 mg, 0.30 mmol) in THF (20 ml) at r.t.

After stirring for 2 h, 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 deareated toluene (30 ml), subsequently treated with $\text{PdCl}_2(\text{P}(\text{Et}_3)_2)$ (52 mg, 0.125 mmol) and CuI (10 mg, 0.05 mmol) and stirred at r.t. for 12 h. Evaporation of the volatiles and chromatography over silica gel (1:1 hexanes: CH_2Cl_2) afforded **2** (69 mg, 77%) as a bright yellow solid. M.p.: 121 °C (dec.). ^1H -NMR (CDCl_3) δ 7.62 (AA'BB'm, 2H), 7.54 (d, $J = 7.8$ Hz, 2H), 7.38–7.29 (m, 4H), 7.25 (t, $J = 7.8$ Hz, 2H), 7.12 (t, $J = 7.8$ Hz, 2H), 2.17–2.02 (m, 12H), 1.30–1.15 (m, 18H). ^{13}C -NMR (CDCl_3): δ 134.55, 132.82, 131.62, 129.52, 128.80, 128.40, 124.42, 124.33, 123.27, 121.69 (t, $J_{\text{P-C}} = 16.6$ Hz), 109.40 (t, $J_{\text{P-C}} = 3.6$ Hz), 84.00, 80.02, 79.00, 76.20, 17.02 (t, $J_{\text{P-C}} = 14.1$ Hz), 8.76. ^{31}P -NMR (CDCl_3): δ 18.79 (s). IR (KCl): $\nu = 2103\text{ cm}^{-1}$. UV-vis (CH_2Cl_2) λ_{max} 391 nm. Anal. Calc. for $\text{C}_{42}\text{H}_{42}\text{P}_2\text{Pd}$: C, 70.54; H, 5.92. Found: C, 70.37; H, 5.72%.

5. Crystallography

Single crystals of **2** were mounted on fibers and protected with a thin coat of epoxy resin. Crystal data and other experimental details are summarized in Table 2. The diffraction measurements were made at 23 °C with a Nonius CAD-4 serial diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). No reflections wholly in the range $\chi = 80\text{--}100^\circ$ at all values of ψ were strong enough to yield reliable scans. The non-hydrogen atoms were located by SIR-92 [21] *E*-maps. Hydrogen atoms

Table 2
Summary of crystal structure data for metallacycle **2**

Molecular formula	$\text{C}_{42}\text{H}_{42}\text{P}_2\text{Pd}$
Molecular weight	715.14
Crystal size (mm^3)	$0.06 \times 0.14 \times 0.40$
Crystal system	Monoclinic
Space group	<i>I</i> 2/a
<i>a</i> (Å)	15.3337(11)
<i>b</i> (Å)	14.306(2)
<i>c</i> (Å)	16.778(3)
β (°)	93.61(1)
<i>V</i> (Å ³)	3673(1)
<i>Z</i>	4
D_{calc} (g cm^{-3})	1.293
μ ($\text{Mo-K}\alpha$) (cm^{-1})	6.20
<i>F</i> (0 0 0)	1480
$2\theta_{\text{max}}$ (°)	50
Independent reflections	3224
Observed reflections [$I \geq \sigma(I)$]	1914
Used in refinement	3223
Refined parameters	204
$R(F)/wR$ [$I \geq \sigma(I)$]	0.072/0.068
$R(F^2)/wR(F^2)$ (all data)	0.115/0.137
Goodness-of-fit on F^2	1.56
Residual extrema in final difference map (e \AA^{-3})	1.38 to −2.56

were included at calculated, updated positions with $\text{B(H)} = 1.2\text{ B(C)}$. The final difference syntheses confirmed the absence of solvent. The TEXSAN program suite [22] was used in all calculations.

6. Supplementary material

Crystallographic data (comprising of hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analyses have been deposited with the Cambridge Crystallographic Centre (Deposition No. 209566 (**2**) and 209681 (**3**) [18]). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

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