

Functionalized Macrocyclic Ligands: Big Building Blocks for Metal Coordination

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Received September 6, 2002

Summary: Two large, conjugated, macrocyclic ligands, **5a** and **5b**, have been efficiently prepared from easily accessible precursors. Both macrocycles incorporate a 3,5-diethynylpyridine subunit, making them suitable for further elaboration, as demonstrated via their coordination to give Pt complexes **6a** and **6b**.

The predictable and directional bonding of organic ligands allows for the engineering of supramolecular coordination complexes with extraordinary structures and functional properties.¹ Using both rigid and flexible molecular spacers, well-ordered architectures such as molecular squares,² cages,³ and tubular structures⁴ have been constructed, utilizing a range of transition metals as the vertexes. Nearly all of these examples, however, exploit linear, aromatic ligands such as pyridine or bipyridine and their derivatives.

We have been intrigued with the synthesis of conjugated macrocycles that function in a manner analogous to that of linear, pyridine-derived ligands. Specifically, our efforts have focused on the incorporation of pyridyl groups into the framework of cross-conjugated macrocycles such that the orientation of the pyridine nitrogen outward from the core allows for the preparation of a variety of hybrid metal–organic structures and organized materials.⁵ Indeed, macrocycles with shape-persistent cores⁶ display unique physical properties and association behavior that have, through the incorpora-

tion of appropriate functionality, led to their adaptation for use as sensors⁷ and in host–guest chemistry.⁸ Particularly interesting are the recent reports of functionalized macrocycles that form well-ordered layers on metal surfaces directed by secondary bonding interactions.^{6a,9}

Herein, we report the synthesis of two new macrocyclic ligands, **5a** and **5b**. Macrocyclic ligand **5a** is prepared using a series of Pd-catalyzed cross-coupling and Cu-catalyzed oxidative homocoupling reactions. A common precursor, oligomeric **4**, is readily elaborated into the larger ligand, platinacycle **5b**, through incorporating a transition-metal– σ -acetylide linkage.¹⁰ The presence of Pt within the macrocyclic core is expected to facilitate further elaboration via displacement of the phosphine ligands.¹¹ Complex **6a** and the interesting bimetallic species **6b** have been prepared and demonstrate the coordinative ability of these large, macrocyclic ligands. Crucial to the employment of any supramolecular building block is a fundamental knowledge of its structural attributes, and therefore a thorough discussion of the solid-state characteristics of these molecules is presented.

The synthesis of the diphenylvinylidene-functionalized macrocycle **5a** is outlined in Scheme 1. Oligomer **3** was prepared by the Pd-catalyzed cross-coupling of 3,5-diethynylpyridine with 2 equiv of vinyl triflate **2**, as previously reported.^{5b} Protodesilylation of oligomer **3**, followed by a second iteration of the cross-coupling step with **2**, led to the formation of extended oligomer **4**.¹²

After desilylation with TBAF, divergent elaboration of deprotected **4** provides macrocycles **5a** and **5b**. Treatment of the deprotected polyyne with CuI and TMEDA in CH₂Cl₂ in the presence of air leads to the

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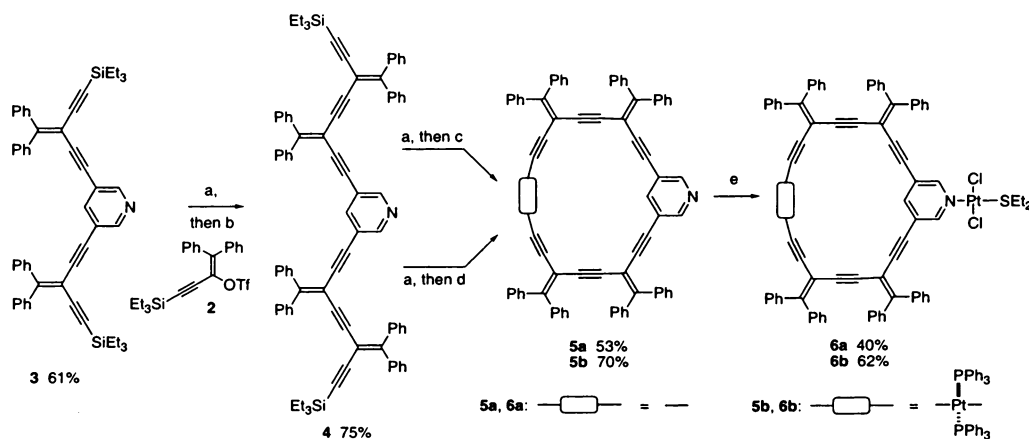
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(12) Full details of the synthesis and characterization of compounds **4–6** are provided as Supporting Information.

Scheme 1^a

^a Reaction conditions: (a) TBAF, THF; (b) **2** (2 equiv), Pd(PPh₃)₄, CuI, Et₂NH, THF, 60 °C; (c) CuI, TMEDA, CH₂Cl₂, O₂, 25 °C; (d) *trans*-PtCl₂(PPh₃)₂, CuI, Et₂NH, 40 °C; (e) *trans*-PtCl₂(SEt₂)₂, CH₂Cl₂, 25 °C.

formation of macrocyclic ligand **5a**. Treatment of the deprotected intermediate with *trans*-PtCl₂(PPh₃)₂ at high dilution in Et₂NH, in the presence of a catalytic amount of CuI,¹⁴ leads to the formation of platinumacycle **5b**. Ligands **5a** and **5b** are both quite robust, surviving indefinitely under ambient conditions. Thermally, **5a** decomposes at 104 °C, whereas platinumacycle **5b** is substantially more stable, melting at 248 °C.

Single crystals of **5a** and **5b**, suitable for X-ray crystallographic analysis, were grown from CH₂Cl₂/acetone solutions at 4 °C.¹⁵ The ORTEP diagram of **5a** (Figure 1, top) reveals the dimensions of this macrocyclic ligand, which spans 5.3 Å (C(3A) to C(20)) by 9.0 Å (C(13) to C(27)). The pentagon-shaped macrocycle has adopted a psuedo-envelope conformation in the solid state, one in which the vinylidene carbon C(13) rests 1.52 Å outside of a plane defined by the remaining four vertexes of the pentagon that includes C(17), C(23), C(27), and the centroid of the pyridine ring (Py_{cent}). As a result of this puckering, the dihedral angle between the C(17)–C(23)–C(27)–Py_{cent} and C(17)–C(13)–Py_{cent} planes is 31°. The macrocycle is relatively free from strain, as reflected in the mean alkyne bond angle of

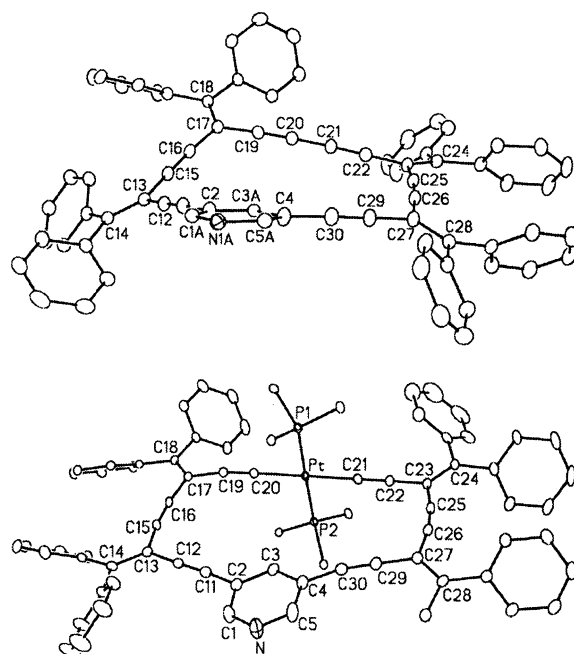


Figure 1. (top) ORTEP drawing of **5a** (20% probability level), showing the psuedo-envelope conformation. (bottom) ORTEP drawing of **5b** (20% probability level). Only the ipso carbons of the triphenylphosphine ligands are shown, for clarity. Selected bond lengths (Å): Pt–P(1) = 2.3059(17), Pt–P(2) = 2.2958(17), Pt–C(20) = 1.994(6), Pt–C(21) = 1.993(6), C(19)–C(20) = 1.215(8), C(21)–C(22) = 1.203(8). The cocrystallized solvent is not shown in either case.

175.3°. Furthermore, the vinylidene bond angles C(12)–C(13)–C(15) = 111.1(4)°, C(16)–C(17)–C(19) = 113.3(3)°, C(22)–C(23)–C(25) = 113.1(3)°, and C(26)–C(27)–C(29) = 113.0(3)° are only slightly less than those of the acyclic oligomer **4**.¹⁶

Crystallographic analysis of **5b** shows that the macrocyclic core is slightly wider than that of **5a**, spanning 4.9 by 10.2 Å (Figure 1, bottom). The conjugated skeleton is nearly planar with a maximum deviation from planarity of 0.07 Å, and the P(1)–Pt and Pt–P(2) bonds are almost exactly perpendicular to the plane of the macrocycle. Unexpectedly, the Pt–acetylide linkage

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(15) Crystallographic data are as follows. Compound **5a**: C₇₃H₄₃N·0.5CH₂Cl₂ (formula weight 976.55) crystallized in the triclinic space group *P*1 (No. 2) with *a* = 10.4978(8) Å, *b* = 17.2773(14) Å, *c* = 17.4207(14) Å, α = 116.6701(14)°, β = 95.7338(16)°, γ = 91.9950(18)°, *V* = 2798.1(4) Å³, *Z* = 2, ρ_{calcd} = 1.159 g cm⁻³, μ(Mo Kα) = 0.112 mm⁻¹, *T* = -80 °C, *R*₁(*F*) = 0.0866 (5429 reflections with *F*_o² ≥ 2σ(*F*_o²)), and *wR*₂(*F*²) = 0.2980 for all 11 265 unique data. Compound **5b**: C₁₀₉H₇₃NPt·0.5CH₂Cl₂·acetone (formula weight 1754.25) crystallized in the triclinic space group *P*1 (No. 2) with *a* = 14.6025(13) Å, *b* = 17.2169(15) Å, *c* = 20.0200(17) Å, α = 107.5427(17)°, β = 109.1503(16)°, γ = 94.3186(16)°, *V* = 4448.0(7) Å³, *Z* = 2, ρ_{calcd} = 1.310 g cm⁻³, μ(Mo Kα) = 1.695 mm⁻¹, *T* = -80 °C, *R*₁(*F*) = 0.0571 (13 339 reflections with *F*_o² ≥ 2σ(*F*_o²)), and *wR*₂(*F*²) = 0.1520 for all 18 125 unique data. Compound **6a**: C₇₇H₅₃Cl₂NPtS^{1/3}·CHCl₃ (formula weight 1330.03) crystallized in the monoclinic space group *P*2₁/*n* (an alternate setting of *P*2₁/*c* (No. 14)) with *a* = 19.9238(15) Å, *b* = 17.3126(13) Å, *c* = 20.0804(15) Å, β = 106.9222(13)°, *V* = 6626.5(9) Å³, *Z* = 4, ρ_{calcd} = 1.333 g cm⁻³, μ(Mo Kα) = 2.312 mm⁻¹, *T* = -80 °C, *R*₁(*F*) = 0.0802 (9989 reflections with *F*_o² ≥ 2σ(*F*_o²)), and *wR*₂(*F*²) = 0.2327 for all 13 527 unique data. Compound **6b**: C₁₁₃H₈₃Cl₂NPt₂S·3CH₂Cl₂ (formula weight 2264.66) crystallized in the triclinic space group *P*1 (No. 2) with *a* = 15.0241(11) Å, *b* = 18.4070(13) Å, *c* = 20.9726(15) Å, α = 64.8410(10)°, β = 88.1120(10)°, γ = 72.132(2)°, *V* = 4964.4(6) Å³, *Z* = 2, ρ_{calcd} = 1.515 g cm⁻³, μ(Mo Kα) = 3.134 mm⁻¹, *T* = -80 °C, *R*₁(*F*) = 0.0382 (15 112 reflections with *F*_o² ≥ 2σ(*F*_o²)), and *wR*₂(*F*²) = 0.0950 for all 19877 unique data.

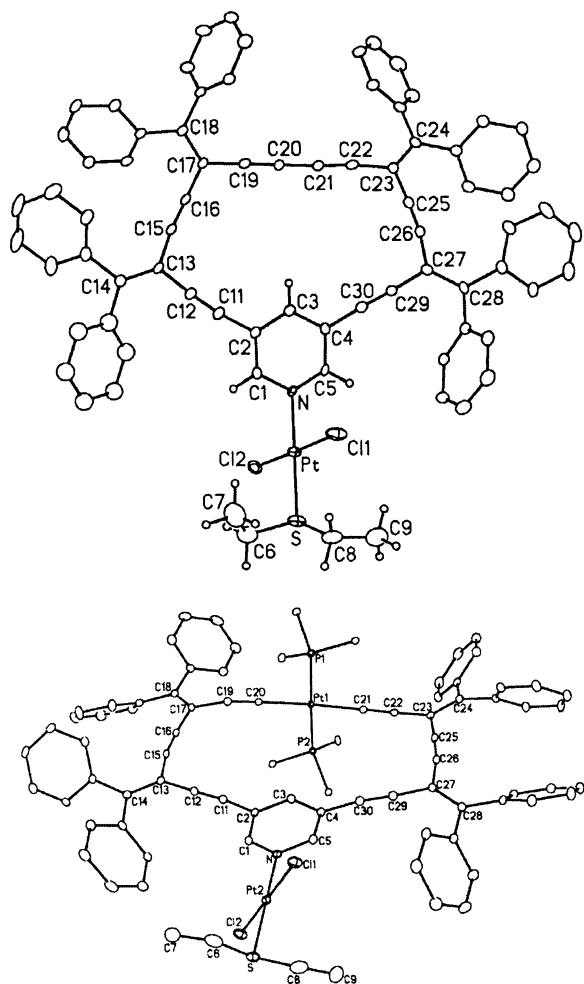


Figure 2. (top) ORTEP drawing of **6a** (20% probability level). Selected bond lengths (Å) and angles (deg): Pt–N = 2.062(7), Pt–S = 2.271(3), Pt–Cl(1) = 2.285(3), Pt–Cl(2) = 2.304(3); C(12)–C(13)–C(15) = 112.2(8), C(16)–C(17)–C(19) = 114.2(7), C(22)–C(23)–C(25) = 112.4(8), C(26)–C(27)–C(29) = 113.0(8), N–Pt–S = 177.4(2), Cl(1)–Pt–Cl(2) = 178.41(10). (bottom) ORTEP drawing of **6b** (20% probability level). Only the ipso carbons of the triphenylphosphine ligands are shown, for clarity. Selected bond lengths (Å) and angles (deg): Pt(2)–N = 2.051(4), Pt(2)–S = 2.2665(14), Pt(2)–Cl(1) = 2.3029(14), Pt(2)–Cl(2) = 2.2909(14), Pt(1)–P(1) = 2.3076(12), Pt(1)–P(2) = 2.3037(12), Pt(1)–C(20) = 2.004(4), Pt(1)–C(21) = 1.998(4), C(19)–C(20) = 1.201(6), C(21)–C(22) = 1.209(6); C(12)–C(13)–C(15) = 112.8(4), C(16)–C(17)–C(19) = 111.1(4), C(22)–C(23)–C(25) = 113.6(4), C(26)–C(27)–C(29) = 112.6(4), P(1)–Pt(1)–P(2) = 177.28(4), C(20)–Pt(1)–C(21) = 176.36(19), N–Pt(2)–S = 176.04(12), Cl(1)–Pt(2)–Cl(2) = 178.87(5). The cocrystallized solvent is not shown in either case.

and the increased planarity slightly add to the strain present in the conjugated framework of the ligand. The mean alkyne bond angle is 173.8° with a minimum angle of $169.4(8)^\circ$ (C(4)–C(30)–C(29)). The vinylidene bond angles C(16)–C(17)–C(19) = $112.1(5)^\circ$, C(12)–C(13)–C(15) = $112.7(6)^\circ$, C(26)–C(27)–C(29) = $114.1(6)^\circ$, and C(22)–C(23)–C(25) = $111.4(6)^\circ$ are on average the same as found in **5a**. The P(1)–Pt–P(2) and C(20)–Pt–C(21) bond angles at $177.77(6)^\circ$ and $179.6(3)^\circ$, re-

spectively, are consistent with those observed in unstrained Pt acetylides.^{10e} Thus, the strain that is imparted as a result of increasing planarity is accommodated primarily by a distortion of the acetylenic π -system, rather than in the metal–acetylide linkage.

To examine the coordinative ability of these large, macrocyclic ligands and the associated changes in structure, complexes **6a** and **6b** were prepared (Scheme 1). Addition of *trans*-PtCl₂(SEt₂)₂ to a CH₂Cl₂ solution of **5a** or **5b** and stirring at room temperature for 1–2 days gave **6a** and **6b** as robust, orange crystalline solids. Interestingly, the thermal stability of **6a** is substantially greater than that of the uncoordinated ligand **5a**, with **6a** decomposing only at 238°C .

X-ray crystallographic analysis was performed on single crystals of **6a** and **6b** grown by slow evaporation of a CHCl₃ and CH₂Cl₂/acetone solution, respectively. The ORTEP diagram of **6a** (Figure 2, top) shows that the coordinated macrocycle adopts a more planar conformation in comparison to the unbound ligand **5a**; C(23) is only 0.56 Å from the plane defined by the other four vertices of the pentagon C(17)–C(13)–Py_{cent}–C(27), and the dihedral angle between the C(17)–C(13)–Py_{cent}–C(27) and C(17)–C(23)–C(27) planes is 10.9° . Surprisingly, the increased planarity does not coincide with an increase in strain. The four vinylidene bond angles of **6a** are comparable to those of the uncoordinated ligand, **5a**. The alkyne bond angles are similarly unaffected, with an average bond angle of 175.4° . The geometry about Pt is square planar, with an angle between the N–C(1)–C(2)–C(3)–C(4)–C(5) and N–Pt–Cl(1)–Cl(2)–S planes of 47.4° .

In contrast, the ORTEP diagram of complex **6b** (Figure 2, bottom) reveals that the macrocyclic portion of this complex is planar and almost completely unchanged upon coordination to the Pt center. All alkyne and vinylidene bond angles are consistent with those observed in the unbound ligand **5b**. All Pt–carbon, Pt–phosphorus, and Pt–nitrogen bond lengths and related bond angles are similarly unaffected.

We have described a synthetic route to highly functionalized macrocyclic ligands and demonstrated their ability to bind to transition metals via the preparation of **6a** and **6b**. Solid-state structural characterization of this series of compounds outlines skeletal changes as a function of metal coordination. Future efforts will focus on elaboration of these macrocyclic systems to afford higher order transition-metal complexes.

Acknowledgment. We are grateful for financial support provided by the University of Alberta and the Natural Sciences and Engineering Research Council of Canada (NSERC). K.C. thanks NSERC for a graduate scholarship.

Supporting Information Available: Text and figures giving synthetic and spectral details for **4**, **5a,b**, and **6a,b** and tables and figures giving X-ray crystallographic details for **5a,b** and **6a,b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020738K