Phosphole-Containing Hybrid Calixpyrroles: New Multifunctional Macrocyclic Ligands for Platinum(II) Ions

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Summary: Phosphole-containing hybrid calixpyrroles have been prepared by acid-promoted condensation reactions. σ^3-Calix-[1]phosphole[1]thiophene[2]pyrrole reacts with PtCl$_2$(COD) to afford an unusual type of macrocyclic Pt(II)−monophosphine complex bearing a η^3-cyclooctadienyl ligand, in which the phosphole and pyrrole units bind the Pt−Cl moiety through cooperative, noncovalent bonding interactions.

Calixpyrroles, first prepared by Baeyer in 1886,[1] are of interest in supramolecular and coordination chemistry because of their functions as anion receptors[2] and polyanionic N ligands.[3] A promising way of controlling the binding abilities of this class of compounds is to modify the components of the macrocyclic backbone, which induces changes in the size, shape, and electronic properties of the cavities. In this respect, there is growing interest in the synthesis and host−guest chemistry of hybrid calixpyrroles containing non-pyrrolic arenes such as furan,[4] thiophene,[4c−f] and pyridine.[5] Despite this interest, however, no attempt has been made to incorporate phosphole,[6] which is basically not aromatic and behaves as a neutral P ligand for transition metals.[7] We expected that substitution of a nitrogen

Scheme 1. Synthesis of the σ^4-P,S,N$_2$ and σ^4-P,O,N$_2$ Hybrids
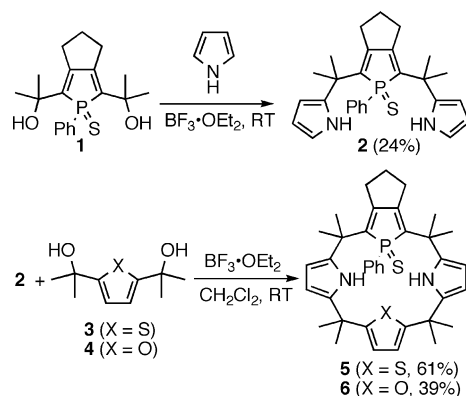
atom of calixpyrrole with a phosphorus atom, namely replacement of a pyrrole unit by phosphole, would provide an unexploited class of multifunctional macrocyclic phosphorus ligands capable of binding transition metals in the structurally well-defined cavity.

Here we report the first examples of phosphole-containing hybrid calixpyrroles. The σ^3-phosphole−pyrrole−thiophene hybrid reacts with PtCl$_2$(COD) to afford an unusual type of macrocyclic Pt(II)−phosphine complex via allylic C−H bond activation of the ligated COD group. In particular, the coordination geometry at the platinum(II) center is defined by cooperative, noncovalent bonding interactions with the phosphole and pyrrole subunits.

Scheme 1 outlines the synthesis of calix[1]phosphole[1]-thiophene[2]pyrroles and calix[1]phosphole[1]furan[2]pyrroles (denoted hereafter as P,S,N$_2$ and P,O,N$_2$ hybrids). Treatment of 2,5-bis(1-hydroxy-1-methylethyl)phosphole *P*-sulfide (**1**)[8] with BF$_3$·OEt$_2$ in pyrrole, followed by silica gel column chromatography, gave a mixture of condensation products, from which compound **2** was isolated in 24% yield. The ^{31}P NMR of **2** showed a single peak at δ 69.3 in CDCl$_3$. The BF$_3$·OEt$_2$-promoted dehydrative condensation of **2** with 2,5-bis(1-hydroxy-1-methylethyl)thiophene (**3**)[4c,9] and 2,5-bis(1-hydroxy-1-meth-ylethyl)furan (**4**)[4c,9] afforded the σ^4-P,S,N$_2$ hybrid **5** and the σ^4-P,O,N$_2$ hybrid **6**, respectively.

Compounds **5** and **6** are yellow solids and were fully characterized by standard spectroscopic techniques. In their mass

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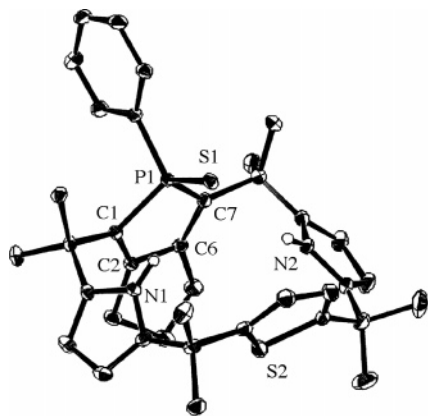
Figure 1. ORTEP diagram of **5** (30% probability ellipsoids). Except for NH, hydrogen atoms have been omitted for clarity. Selected bond lengths and distances (Å): S1—P1, 1.9724(5); C1—C2, 1.344(2); C2—C6, 1.485(2); C6—C7, 1.341(2); S1···N1, 3.37; S1···N2, 3.62.

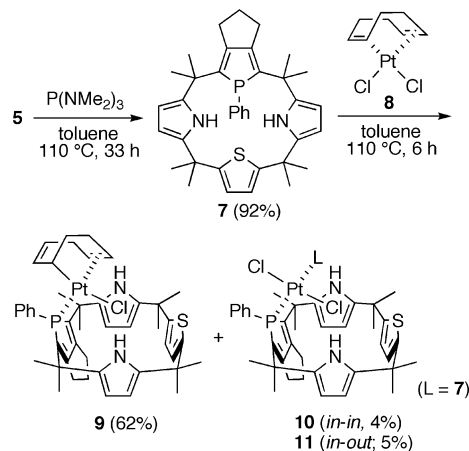|	**5**: X = S	**6**: X = O
a	5.68	5.67
b	5.44	4.94
c	5.00	5.01
c'	5.06	5.03
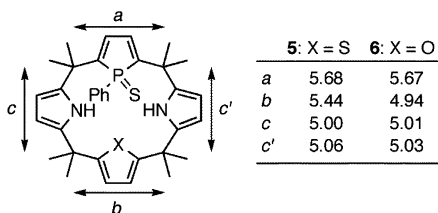
Figure 2. Edge-to-edge distances (Å) of **5** and **6**.

spectra, parent ion peaks were observed at m/z 609 (for **5**) and m/z 595 (for **6**), attributable to the 1:1 adduct between **2** and **3**/**4**. The crystal structures of **5** and **6** were further elucidated by X-ray crystallography (Figure 1 for **5**; Figure S1 (Supporting Information) for **6**).[10,11] The P,S,N$_2$ hybrid **5** has a partial cone conformation, whereas the P,O,N$_2$ hybrid **6** adopts a cone conformation. Both **5** and **6** provide a trapezoid-like cavity, which the P=S moiety is located inside. As shown in Figure 2, the cavity size of **5** is slightly larger than that of **6**, mainly reflecting the difference in edge-to-edge distances between the thiophene and furan subunits. In both compounds, the pyrrole rings are tilted considerably, to direct their N—H group toward the sulfur atom of the P=S group. The observed N···S1 distances of 3.34–3.62 Å imply that a hydrogen-bonding interaction is present between the sulfur atom and the N—H protons in **5** and **6**.[12]

To prepare a σ^3 type of phosphole-containing calixpyrrole, reductive desulfurization of the σ^4-P,S,N$_2$ hybrid **5** was examined (Scheme 2). When it was heated with 2.8 equiv of P(NMe$_2$)$_3$ in refluxing toluene for 33 h, **5** was completely consumed to afford the σ^3-P,S,N$_2$ hybrid **7** in 92% yield. The ^{1}H and ^{31}P NMR spectra indicate that **7** exists as a mixture of two conformers. At 25 °C, two ^{31}P peaks were observed at δ

(10) Crystal data for **5**: C$_{74}$H$_{86}$N$_4$P$_2$S$_4$, M_r = 1221.7, triclinic, a = 12.9517(19) Å, b = 12.9645(19) Å, c = 20.395(3) Å, α = 82.092(4)°, β = 83.090(4)°, γ = 86.680(4)°, V = 3364.4(8) Å^3, space group P$\bar{1}$, Z = 2, μ(Mo Kα) = 2.333 cm^{-1}, 26 815 reflections measured, 14641 unique reflections, 744 parameters, R_w = 0.1329, R = 0.0493 (I > 2.00σ(I)), GOF = 1.076. One of the phenyl groups is disordered at two locations.

(11) Crystal data for **6**: C$_{37}$H$_{43}$N$_2$OPS, M_r = 594.79, orthorhombic, a = 11.2995(14) Å, b = 16.673(2) Å, c = 18.066(2) Å, V = 3403.7(7) Å^3, space group P2$_1$2$_1$2$_1$, Z = 4, μ(Mo Kα) = 1.722 cm^{-1}, 276 625 reflections measured, 7803 unique reflections, 380 parameters, R_w = 0.1042, R = 0.0404 (I > 2.00σ(I)), GOF = 1.038.

(12) The N···S distances for the N—H···S hydrogen bonds in silver–antimony sulfides were reported to be 3.20–3.65 Å: Vaqueiro, P.; Chippindale, A. M.; Cowley, A. R.; Powell, A. V. *Inorg. Chem.* **2003**, *42*, 7846–7851.

Scheme 2. Synthesis of the σ^3-P,S,N$_2$ Hybrid and Pt(II) Complexes

31.4 and 32.1 ([D$_8$]toluene), suggesting that interconversion between the conformers occurs slowly on the NMR time scale at this temperature. At 70 °C, however, these two peaks coalesced.

With the σ^3-P,S,N$_2$ hybrid **7** in hand, we set out to prepare a macrocyclic platinum(II)–phosphine complex. Thus, heating a mixture of **7** and an equimolar amount of PtCl$_2$(COD) (**8**) in toluene for 6 h, followed by silica gel column chromatography and GPC separation, gave the Pt(II)–mono(phosphine) complex **9** in 62% yield as a pale yellow crystalline solid (Scheme 2). In addition to **9**, small amounts of the *trans*-Pt(II)–bis(phosphine) complexes **10** and **11** were isolated as byproducts.[13] In the ^{31}P NMR spectra, characteristic peaks with two ^{31}P—^{195}Pt satellites were observed at δ 51.1 (for **9**), δ 46.7 (for **10**), and δ 45.5, 46.5 (for **11**). The coupling constants (J_{P-Pt}) observed for the bis(phosphine) complexes **10** and **11** are 2400–2560 Hz, implying that the two phosphine ligands are coordinated in a trans geometry.[14] In the ^{1}H NMR of **9**, four olefinic resonances of the COD-derived ligand appeared separately in the range of δ 5.50–6.56.

The structure of **9** was successfully elucidated by X-ray crystallography (Figure 3).[15] The platinum center adopts a square-planar geometry with the phosphorus and chlorine atoms in a cis orientation. The σ^3-P,S,N$_2$ macrocycle unit provides a trapezoid cavity with a cone conformation, in which the phosphole ring leans toward the outside, for binding the Pt(II) ion. It should be noted here that two pyrrole rings are tilted to direct the NH protons toward the chlorine atom bound to platinum. The observed Cl···N distances of 3.34 and 3.40 Å are close to the reported values (3.264(7)–3.331(7) Å) for a chloride ion complex of *meso*-octamethylcalix[4]pyrrole.[2a] Thus, there is a cooperative hydrogen-bonding interaction between the Pt—Cl moiety and the two NH protons, which contributes to defining the coordination geometry at the platinum center in **9**. The COD-like group coordinates as an anionic, 1,2-η^2-6-σ-cycloocta-1,4-dienyl ligand, where the C38—C39 double bond

(13) On the basis of the NMR spectra, they were assigned as the in-in and in-out types of complexes, where in and out denote that the Pt—Cl bond is located inside and outside the cavity, respectively.

(14) The trans stereochemistry and the in-in conformation of **10** were confirmed by X-ray crystallography, though the full refinement has been hampered by the presence of an unidentified peak.

(15) Crystal data for **9**: C$_{47}$H$_{56}$Cl$_7$N$_2$PPtS, M_r = 1155.27, monoclinic, a = 11.460(8) Å, b = 18.498(13) Å, c = 22.927(15) Å, β = 91.150(4)°, V = 4859(6) Å^3, space group P2$_1$/n, Z = 4, μ(Mo Kα) = 3.372 cm^{-1}, 38 279 reflections measured, 10 937 unique reflections, 533 parameters, R_w = 0.1449, R = 0.0578 (I > 2.00σ(I)), GOF = 0.960.
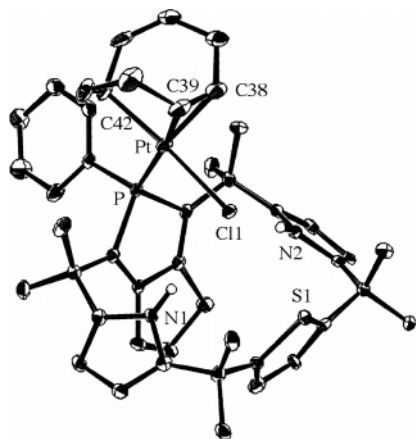
Figure 3. ORTEP diagram of **9**·2CHCl₃ (30% probability ellipsoids). Two chloroform molecules and hydrogens (except for NH) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−Cl1, 2.4228(16); Pt−P, 2.2709(16); Pt−C38, 2.222(9); Pt−C39, 2.211(7); Pt−C42, 2.079(7); C38−C39, 1.353(14); Cl1−Pt−C42, 170.2(2); P−Pt−C42, 96.7(2).

is bound through π coordination (η^2 mode) and the C42 atom is covalently bound to the Pt center (σ mode). The direct conversion of the neutral COD ligand to the anionic, nonsubstituted cycloocta-1,4-dienyl ligand is rare for group 10 chemistry,[16] representing the unique binding ability of the σ^3-P,S,N₂ hybrid **7**.

Plausible reaction pathways for the formation of **9−11** are illustrated in Scheme 3: the σ^3-P,S,N₂ hybrid **7** reacts with **8** to generate complex **12** or **13** as a transient species, from which an allylic proton of the COD ligand is abstracted to produce **9** (path *a*) or the coordinated COD is substituted by the second phosphine **7** to produce **10** and **11** (path *b*).[17] Large steric hindrance around the phosphorus center in **7** probably makes path *b* less favorable than path *a*, resulting in the higher yield of **9** relative to **10** and **11**. From a mechanistic point of view, it is of interest that the allylic C−H bond is activated under neutral conditions with the assistance of the macrocyclic ligand **7**: when triphenylphosphine (PPh₃) was used instead of **7**, only

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(17) No intermediate was observed during the NMR monitoring of this reaction in [D₈]toluene.

Scheme 3. Plausible Reaction Pathways for the Formation of 9−11
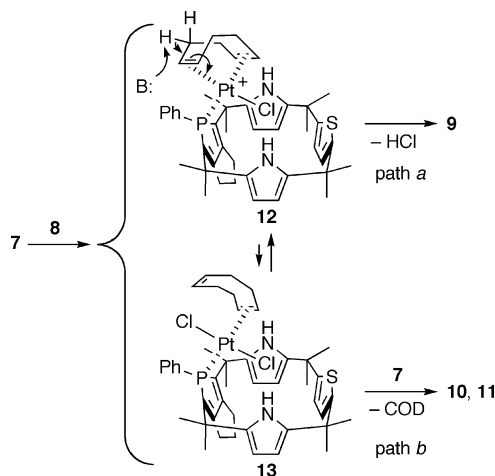
half the amount of **8** was consumed, to yield *cis*-PtCl₂(PPh₃)₂[18] as the sole Pt(II) product under the same reaction conditions.

In summary, we have successfully prepared phosphole-containing hybrid calixpyrroles for the first time and fully characterized their structures. The σ^3-P,S,N₂ hybrid has been found to selectively activate the allylic C−H bond of PtCl₂(COD) under neutral conditions. The observed reactivity and the structure of the resulting Pt(II) complex demonstrate the potential utility of phosphole-containing hybrid calixpyrroles as a new class of multifunctional macrocyclic ligands.

Supporting Information Available: Text giving experimental details, a figure giving an ORTEP diagram of **6**, and CIF files giving crystallographic data for **5**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060300A

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