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Phosphorus-Containing Hybrid Calixphyrins: Promising Mixed-Donor Ligands for Visible and Efficient Palladium Catalysts

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There has been a great deal of interest in the coordination chemistry of phosphorus-containing macrocyclic ligands,[1] because (1) the metal center is supported and stabilized by multidentate platforms, and (2) various coordination environments are available by changing the components of the macrocycles. However, the potential utility of this class of ligands in transition metal catalysis has not been explored much, partly because of a lack of information on the relationship between their structural properties and their catalytic activities. Calixphyrins are a class of compounds containing multidentate platforms derived from porphyrins and calixpyrroles.[2] Owing to the involvement of both sp^2- and sp^3-*meso*-carbons, calixphyrins possess reasonable rigidity and flexibility that are beneficial for designing efficient catalysts. We expected that replacement of the pyrrole nitrogen atom of calixphyrin with a phosphorus atom, namely replacing the pyrrole unit by phosphole, would provide a new class of macrocyclic P,N-mixed-donor ligands capable of generating a coordinatively unsaturated metal center by flipping motion under appropriate conditions.[3] Here we report the first examples of P,S-containing hybrid calixphyrins of the 5,10-porphodimethene type. The palladium−P,N$_2$,S−calixphyrin complex, displaying a characteristic reddish purple color, has been found to catalyze the Heck reaction with high efficiency at elevated temperatures.

The synthesis of phosphole-containing hybrid calixphyrins is summarized in Scheme 1. Treatment of a CH_2Cl_2 solution containing σ^4-2,5-bis[(pyrrol-2-yl)methyl]phosphole **1**[4] and 2,5-bis[hydroxy(phenyl)methyl]thiophene **2**[5] with $BF_3{\cdot}OEt_2$ at room temperature gave a mixture of condensation products, which was then reacted with 2.2 equiv of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to afford σ^4-phosphorus-containing P,N$_2$,S-hybrid calixphyrins **3** and **4** in 24% and 5% yield, respectively. When treated with excess $P(NMe_2)_3$, the σ^4-hybrid **3** was converted to the σ^3-P,N$_2$,S-hybrid **5** in 66% yield with a small amount of the side-product **6**.

The calixphyrins **3**−**6** were fully characterized by standard spectroscopic techniques. The ^{31}P chemical shifts of **3** and **5** are close to those of **4** and **6**, suggesting that the pyrrole−thiophene−pyrrole (**N**−**S**−**N**) ring reduction does not significantly affect the electronic character of the phosphorus atom. The crystal structure of **5** was further elucidated by X-ray diffraction analysis (Figure 1).[6] The σ^3-P,N$_2$,S-hybrid **5** is composed of a flat **N**−**S**−**N** plane and the phosphole ring that stands almost perpendicular to the **N**−**S**−**N** plane. Probably because of steric reasons, the *P*-phenyl group is located outside the macrocycle. The observed structural features are quite different from those of the 5,10-porphodimethene type of calix[4]phyrin, which exhibits a nonplanar, twisted conformation.[2c]

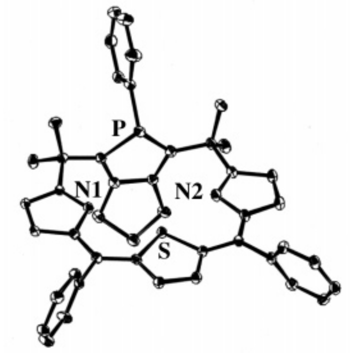
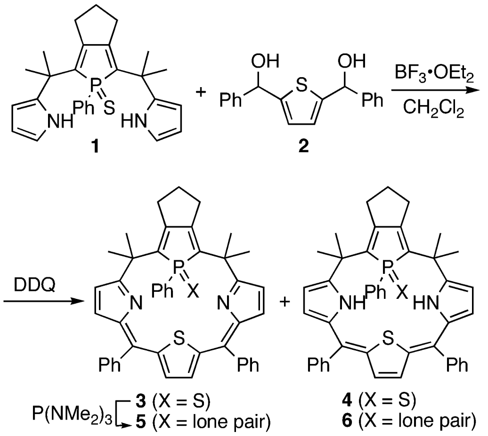
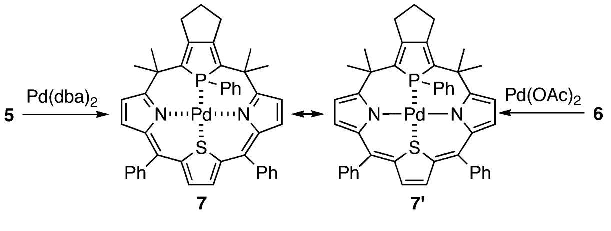


Figure 1. ORTEP diagram of **5** (30% probability ellipsoids). Hydrogen atoms and the solvent molecules are omitted for clarity.

Scheme 1. Synthesis of Hybrid Calixphyrins.



Scheme 2. Synthesis of Hybrid Calixphyrin−Pd Complex.



The σ^3-P,N$_2$,S-hybrid **5** is a new type of macrocyclic P,N,S-mixed-donor ligand for transition metal complexes. To prepare a palladium complex, **5** was treated with $Pd(dba)_2$ in CH_2Cl_2 at room temperature (Scheme 2). After 3 h, the palladium complex **7** was obtained as an air and thermally stable, purple solid in 92% yield. The metathesis of **6** with $Pd(OAc)_2$ afforded the same complex, **7**, in quantitative yield. These results revealed that the σ^3-P,N$_2$,S-hybrid calixphyrins would behave as redox-active macrocyclic ligands.

The crystal structure of **7** was elucidated by X-ray diffraction analysis (Figure 2).[7] The palladium center is coordinated by the

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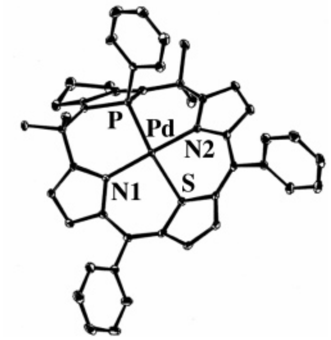
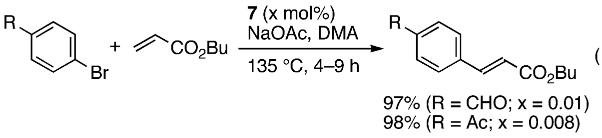


Figure 2. ORTEP diagram of **7** (30% probability ellipsoids). Hydrogen atoms and the solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−P, 2.2135(8); Pd−N1, 2.079(2); Pd−N2, 2.066(2); Pd−S, 2.2667(8); P−Pd−N1, 95.21(7); P−Pd−N2, 85.75(7); S−Pd−N1, 92.93(6); S−Pd−N2, 85.77(7).

four heteroatoms to adopt a distorted square planar geometry. The **N−S−N** unit in **7** is not on the same plane, and the edge-to-edge distances between two meso carbons differ from those in **5** (Figure S1). The phosphole ring leans toward the inside for binding the palladium, and the sulfur atom is deviated from the thiophene ring with a dihedral angle of 20°. The Pd−N bond lengths of 2.066(2)-2.079(2) Å are longer than typical values (2.012 ± 0.018 Å) observed for Pd-coordinated porphyrin-type macrocycles.[8]

The observed carbon−carbon bond lengths of the **N−S−N** unit in **7** are indicative of a noticeable contribution by the canonical structure **7′**, in which the formal oxidation state of Pd is considered to be +2 (Figure S2). This was confirmed by density functional theory calculations on model compounds (for details, see Supporting Information). If the palladium in **7** is deviated from the **N−S−N** plane by flipping motion, however, a coordinatively unsaturated, highly reactive palladium center would be generated. This hypothesis was verified by the variable-temperature NMR measurements of **7**. When heated at 125−135 °C in DMSO-d_6 and DMA-d_9, the thiophene- and pyrrole-derived ^{1}H peaks and the phosphole-^{31}P peak were considerably broadened as compared to those observed at 25 °C (Figure S3). This result indicates that the macrocyclic framework in **7** becomes much more flexible at elevated temperatures, which allows coordinative interaction between the solvents and the face-up palladium center.

Encouraged by the above observations, we examined the catalytic activity of **7** for the Heck reactions of bromoarenes with *n*-butyl acrylate in DMA (eq 1).



As expected, the reactions proceeded at 135 °C to afford the Heck products with turnover numbers of 9700−12300.[9] Although the literature contains more active Heck catalysts,[10] the present results demonstrate that the P-containing hybrid calixphyrins constitute a useful addition to the existing efficient phosphine ligands. It is interesting to note that the catalytic activity of **7** is visually detectable through its characteristic reddish purple color in solution. Such a property is of practical importance in monitoring the activity of the catalyst without isolating it.[11]

In summary, we prepared P,S-containing hybrid calixphyrins for the first time. The σ^3-P,N$_2$,S-hybrids were successfully converted to a visible, macrocyclic palladium complex, which was found to catalyze the Heck reaction with high efficiency. It should be noted here that the coordination number and the oxidation state at the metal center are controllable by changing the size and components of the macrocyclic platform. We anticipate that these characteristics of P-containing hybrid calixphyrins will be of great benefit for designing new classes of transition metal catalysts.

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Supporting Information Available: Experimental details, CIF files for **5** and **7**, and DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) $C_{92}H_{82}Cl_4N_4P_2S_2$, $P2_1/n$, $a = 26.188(5)$ Å, $b = 10.1923(17)$ Å, $c = 31.765(6)$ Å, $\beta = 112.7790(5)°$, $V = 7817(2)$ Å^3, $Z = 4$, $D_c = 1.284$ g cm^{-3}, 17276 obsd, 947 variables, $R_w = 0.1523$, $R = 0.0903$ ($I > 2.00\sigma(I)$), GOF = 1.035.

(7) $C_{46}H_{41}Cl_2N_2PPdS$, $C2/c$, $a = 22.055(5)$ Å, $b = 12.648(3)$ Å, $c = 27.807(7)$ Å, $\beta = 98.3576(11)°$, $V = 7674(3)$ Å^3, $Z = 8$, $D_c = 1.492$ g cm^{-3}, 8751 obsd, 479 variables, $R_w = 0.1276$, $R = 0.0496$ ($I > 2.00\sigma(I)$), GOF = 1.116.

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(9) The Mathey's Pd−tetraphosphole macrocycle catalyzes the Heck reaction of bromobenzene with *n*-butyl acrylate with a TON of 89 after 48 h under the same conditions. See ref 3e.

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(11) Complex **7**: UV/vis (CH_2Cl_2) λ_{max} 524 nm ($\epsilon = 14000$).

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