Title: Synthesis, Structures, and Coordinating Properties of Phosphole-Containing Hybrid Calixpyrroles

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Abstract: Symmetric and asymmetric hybrid calixpyrroles containing a $\sigma^4$-phosphole or $\sigma^4$-2,3-dihydrophosphole unit (symmetric and asymmetric $\sigma^4$-P,N$_2$,X-hybrids: X = S, O) were prepared by using acid-promoted condensation reactions of the corresponding $\sigma^4$-phosphatripyrranes with 2,5-bis(1-hydroxy-1-methylethyl)heteroles. The X-ray crystallographic analyses of the symmetric and asymmetric $\sigma^4$-P,N$_2$,X-hybrids show that the cavity sizes of the $\sigma^4$-P,N$_2$,S-hybrids are larger than those of the $\sigma^4$-P,N$_2$,O-hybrids, mainly reflecting the difference in edge-to-edge distances of the thiophene and furan rings. The symmetric $\sigma^4$-P,N$_2$,X-hybrids and the asymmetric $\sigma^4$-P,N$_2$,S-hybrid were successfully converted to the corresponding $\sigma^3$-forms by reductive desulfurization at the phosphorus center. Each of the symmetric $\sigma^3$-P,N$_2$,X-hybrids was obtained as a mixture of two conformers, where the lone pair of the phosphorus atom is located inside (in) and outside (out) the cavity. While, the interconversion between the in and out type conformers of the asymmetric $\sigma^3$-P,N$_2$,S-hybrid was sufficiently slow to isolate each of them. The complexation reactions of the symmetric $\sigma^3$-P,N$_2$,S-hybrid with Au(I), Pt(II), and Pd(II) ions afforded both of the in and out type complexes, where the in type complexes were the thermodynamically favored products. In the complexation reactions of the asymmetric $\sigma^3$-P,N$_2$,S-hybrids, the stereochemistry at the phosphorus center was retained to give in or out type complex exclusively. In the in-in type trans-M(II)–bis(phosphine) complexes (M = Pt, Pd) derived from the symmetric and asymmetric $\sigma^3$-P,N$_2$,S-hybrids, the M–Cl fragment is bound above the cavities of the two macrocycles. The crystal structures and the $^1$H NMR spectra of these M(II) complexes reveal that the P,N$_2$,S-hybrid calixpyrroles bind the M–Cl fragments through the P–M coordination and the cooperative NH–Cl hydrogen-bonding interactions.