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COMMUNICATIONS

Tetrakis(2-hydroxyphenyl)ethene and Derivatives. A Structurally Preorganized Tetradentate Ligand System for Polymetallic Coordination Chemistry and Catalysis

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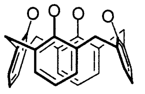
The use of structurally preorganized polydentate ligand systems to direct the assembly of polymetallic coordination complexes is important to both supramolecular chemistry and catalysis.[1] In this context, calix[4]arenes[2] (**I**) have been a widely used polyaryloxide structural motif for organizing coordination complexes[3] and modeling solid oxide supports and zeolite surfaces.[4] The analogy to oxide surfaces, however, is not particularly apt: calixarenes lack the conformational rigidity inherent to surface binding sites, promoting chelating over bridging coordination modes. The connectivity also limits the introduction of sterically isolating substituents adjacent to the binding sites,[5] rendering metal complexes susceptible to uncontrolled intermolecular aggregation.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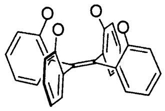
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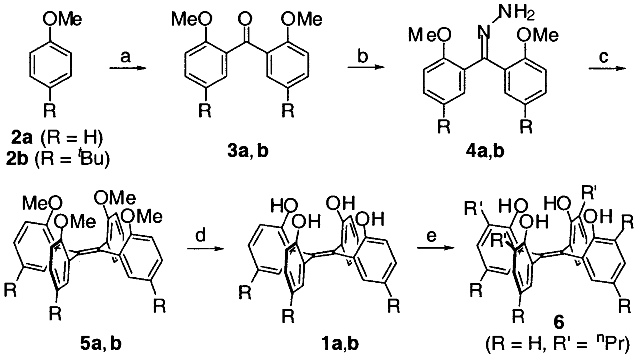
In this Communication, we report the development of an alternative, topologically distinct tetradentate ligand system for coordination chemistry, catalysis, and supramolecular chemistry: tetrakis(2-hydroxyphenyl)ethene (**1a**) and substituted derivatives. The design exploits the relative planarity of the ethylene core to constrain the binding domain from inward collapse but retains a degree of calixarene-like conformational freedom associated with correlated rotation of the aryl groups.[6] For the conformation that places the aryl groups perpendicular to the ethylene plane and the four hydroxy groups in the same hemisphere (e.g., **II**), the ligand presents a roughly square array of oxygen atoms for metal binding (vide infra). The design inherently accommodates the introduction of alkyl substituents adjacent to the metal binding sites.

Although several tetrakis(2-substituted) tetraphenylethylene compounds are known,[7] oxygen-substituted derivatives are virtually unprecedented.[8] Nonetheless, an efficient four-step synthesis of tetrakis(2-hydroxyphenyl)ethene (**1a**) has been developed (Scheme 1).[9] The synthesis exploits the acid-catalyzed coupling of diaryldiazomethanes, a classical olefination procedure.[10,11] Thus, 2,2′-dimethoxybenzophenone (**3a**) was prepared by ortho-metalation of anisole[12] and converted to hydrazone **4a**.[9] Oxidation to the diazomethane derivative was accomplished using nickel peroxide,[13] and the crude product was coupled efficiently using catalytic *p*-toluenesulfonic acid. Exhaustive demethylation of **5a** under standard conditions proceeded nearly quantitatively. The highly soluble tetrakis(5-*tert*-butyl-2-hydroxyphenyl)ethene (**1b**) was prepared analogously, although more elaborate product isolations were required in this more lipophilic series.[9] The syntheses of **1a** and **1b** are readily adaptable to larger scales.

Scheme 1 [a]



[a] Conditions: (a) (i) BuLi, TMEDA, Et_2O, −65 °C, (ii) Me_2NCOCl, (iii) H_2O (**3a**, 77%; **3b**, ca. 60%); (b) $H_2NNH_2·H_2O$, *n*-BuOH, Δ (**4a**, 95%; **4b**, quantitative); (c) (i) NiO_2, CH_3CN, 0 °C, (ii) catalytic TsOH (**5a**, 87%; **5b**, 46% from **3b**); (d) BBr_3, CH_2Cl_2, −65 °C → room temperature (**1a**, 90%; **1b**, 87%); (e) (i) C_3H_5Br, K_2CO_3, acetone, (ii) 200 °C, (iii) 600 psi H_2, Pd/C, MeOH (60% from **1a**).

The structure of **1a** was determined in the solid state by X-ray crystallography,[9] revealing a degree of both intramolecular and intermolecular organization. Thus, the four aryl groups are nearly perpendicular to the plane of the olefin and engage in pairwise intramolecular hydrogen-bonding on opposite faces of the molecule (Figure 1). The crystal is further organized into extended one-dimensional ladders, linked by intermolecular hydrogen bonds (see diagram in the Supporting Information). The increased structural rigidity of the ligand thus disfavors the formation of a fully intramolecular array of hydrogen bonds, as observed for calix[4]arenes in the cone conformation.[2] In solution, the aryl rings rotate rapidly, as established by variable-temperature ^1H NMR spectroscopy.

A convergent approach to 3-substituted tetrakis(2-hydroxyphenyl)ethenes is complicated by steric effects: hydrazone formation fails for benzophenones bearing large 3-substituents. The Claisen rearrangement, however, provides an efficient ortho-alkylation protocol (Scheme 1).[14] Nucleophilic allylation and thermolysis yields tetrakis(3-allyl-2-hydroxyphenyl)ethene[9] cleanly; complete hydrogenation of the side chains requires high pressure, providing tetrakis(3-*n*-propyl-2-hydroxyphenyl)ethene **6** in high yield.[9] Despite the 3-substituents, rapid rotation of the aryl rings is maintained.

To confirm the potential of this preorganized ligand system for applications to coordination chemistry, an investigation into both main group and transition metal chemistry has been initiated. Although designed for multiple metal coordination, ligand **1a** also accommodates tetradentate chelation in the case of larger polyvalent metal ions. Thus, dark blue molybdenum(V) complex **7**[9] was prepared from the tetrasodium salt of **1a** and $(C_5Me_5)MoCl_4$.[15] The

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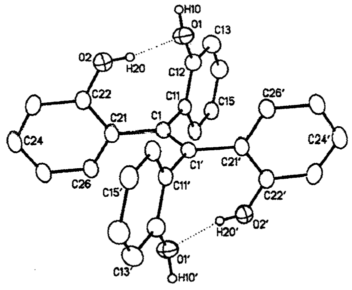

Figure 1. ORTEP diagram of compound **1a**.

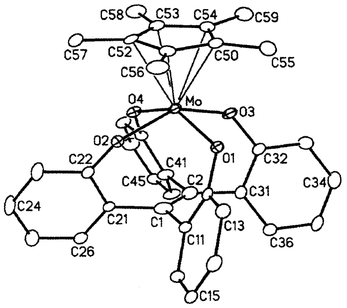

Figure 2. ORTEP diagram of molybdenum complex **7**.

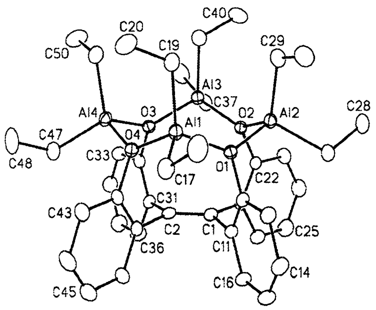

Figure 3. ORTEP diagram of tetrakis(diethylaluminum) complex **8**.

structure, confirmed by X-ray crystallography (Figure 2), is closely analogous to those of other Mo(V) tetraalkoxide complexes.[16,17] The Mo−O bonds are nearly equidistant, and the ligand assumes a slightly distorted propeller conformation, with the aryl rings canted 4−14° from perpendicular with respect to the ethene plane.

A stronger demonstration of the organizational potential of this ligand template is provided by the polymetallic complex obtained upon treatment of **1a** with excess triethylaluminum in pentane. Tetrakis(2-diethylaluminoxyphenyl)ethene (**8**) precipitates from solution and was isolated in 65% yield; complex **8** is the only product observed spectroscopically in solution.[9] The ^{1}H NMR spectrum, invariant from −80 to 100 °C, shows four inequivalent sets of ethyl groups, integrating to eight ethyl groups per ligand. This suggests a robust C_2-symmetric aluminum/oxygen structure in solution; X-ray crystallography[9] confirms this $(AlO)_4$ structure in the solid state (Figure 3).[18]

Neither the calix[4]arenes nor other conformationally less constrained tetradentate aryloxy binding templates provide structurally similar higher order polymetallic complexes.[19,20] The conformationally constrained *tridentate* ligand, tris(3,5-di-*tert*-butyl-2-phenyloxy)methane, however, organizes a lower order but similarly robust tris(aluminum/oxygen) crown complex analogous to complex **8**.[21]

Tetrakis(2-hydroxyphenyl)ethene and derivatives thus provides a versatile, topologically unique, and conformationally constrained tetradentate aryloxy ligand environment. Differentiation of the ligand binding sites, additional variation in peripheral substitution pattern, and applications to polymetallic coordination chemistry and catalysis are in progress.

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Supporting Information Available: Experimental procedures and complete characterization of all new compounds (PDF); details of the crystallography for compounds **1a**, **7**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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