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Quasi-Planar Homopolymetallic and Heteropolymetallic Coordination Arrays. Surface-Like Molecular Clusters of Magnesium and Aluminum

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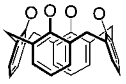
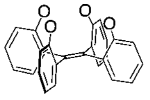
Heterogeneous inorganic coordination catalysts supported on oxo-surfaces (e.g., SiO_2, Al_2O_3) can provide exquisite productivity and selectivity, nowhere more impressively than in the area of olefin polymerization catalysis.[1] Despite intensive investigation, however, the coordination chemistry and active-site structures of heterogeneous catalysts supported on main group metal oxides remain poorly defined, even for commercially important Ziegler−Natta catalysts.[1,2] Consequently, structure/reactivity relationships in such systems are empirically defined and largely speculative, limiting opportunities to understand and exploit such polymetallic arrays in the design of "surface-mimetic" coordination catalysts.

Both simple and "designed" ligand systems have been used to model surface coordination chemistry. Soluble silsesquioxane fragments provide the greatest electronic fidelity to silica itself but typically lead to the formation of monometallic complexes, which effectively model only the remote "corner sites" of silica.[3] Silsesquioxane complexes of Lewis acidic main group metals can provide polymetallic complexes,[3c] but most form dimeric globular clusters in preference to surface-like arrays. Alkoxide and aryloxide ligands, including many polydentate systems, have been extensively investigated, providing a range of homopolymetallic and heteropolymetallic clusters with typical globular structures.[4−6] Preorganized calix[4]arene ligands (**I**),[4c,5] for example, lack the conformational rigidity necessary to enforce high nuclearity bridging motifs, collapsing instead into chelated low nuclearity coordination modes and ligand-encapsulated structures.



I



II

The tetrakis(2-aryloxy)ethylene ligand system **II**[7] offers an inherently more rigid tetradentate binding surface, retaining lateral rotational freedom but severely constraining inward collapse. Here we report that with the addition of sterically isolating *ortho*-substituents,[8] these ligand systems provide the first structurally relevant surface-like models for the self-assembled heteropolymetallic main group coordination arrays presumed to be relevant to the composition of supported Ziegler−Natta precatalysts.

Two sterically differentiated ligands have been investigated, varying considerably the bulk of the critical 3-substituents. To mimic the magnesium-treated surface of standard silica-supported precatalysts, tetrakis(2-hydroxy-3-propylphenyl)ethene **1**[7a] and tetrakis(5-*tert*-butyl-2-hydroxy-3-trimethylsilylphenyl)ethene **2**[7d] were thus converted to the corresponding trimagnesium salts **3a**,**b** and **4a**,**b** by treatment with 4 equiv of methyl magnesium chloride and allyl magnesium bromide, respectively (eq 1).[9] All four products were isolated as analytically pure crystalline solids and revealed simple, conspicuously similar, NMR spectra indicative of a highly symmetrical coordination environment.

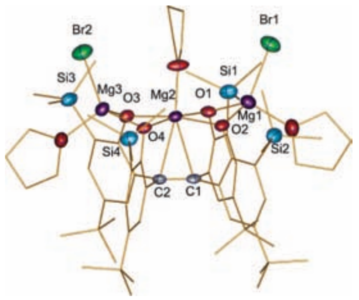
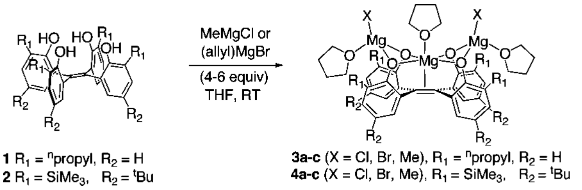


Figure 1. Molecular structure of **4b**. H-atoms omitted for clarity. Selected bond lengths (Å) Mg1−O1 1.995(4), Mg1−O2 1.969(5), Mg2−O1 2.087(4), Mg2−O2 2.087(4), Mg2−O3 2.106(4), Mg2−O4 2.068(4), Mg3−O3 1.958(4), Mg3−O4 1.978(4), Mg2−C1/Mg2−C2 2.559(6), C1−C2 1.346(8).

Bromide salts **3b** and **4b** were characterized by X-ray crystallography,[10] revealing that the strongly Lewis acidic magnesium atoms organize both ligands into quasi-planar surface analogues (Figure 1). Two distinct magnesium coordination environments are observed, with the pseudo-octaheral central magnesium located 0.15 Å above the plane defined by the four oxygens of the ligand. The close proximity of the metal to the ethene bridge suggests the presence of a magnesium−olefin bonding interaction[11] (Mg−C = 2.559−2.581 Å), although the spectroscopic data are not definitive.[9] The terminal magnesium atoms are pseudotetrahedral and significantly further above the plane than the central magnesium.



(1)

Consistent with the presence of alkyl residues on the surface of alkylmagnesium-treated silica,[1] the reactions of halide complexes **3a**/**4a** with additional Grignard reagent convert both materials cleanly to crystalline dialkyl derivatives **3c**/**4c**. Complexes **3c**/**4c** are also obtained directly from the free ligand upon treatment with excess Grignard (eq 1). Solution NMR spectroscopy suggests little structural change occurs upon alkylation; this is confirmed by the solid state structure of complex **3c** (Figure 2).[9] The $Mg-C_{alkyl}$ bond lengths are within expected parameters for structurally characterized alkylmagnesium compounds.[12]

The exposed magnesium "surface" of this system provides a convenient template for transmetalation of magnesium for aluminum, giving heteropolymetallic Mg/Al complexes[6] while retaining the general surface-like structure. Selective sequential substitution of the terminal magnesium centers is accomplished with remarkable control, cleanly providing trimetallic Mg_2Al and Al_2Mg complexes **5**/**6** and **7**/**8** on treatment with 1 and 4 equiv of diethylaluminum chloride, respectively (Scheme 1).[9] All four heterotrimetallic complexes **5**−**8**

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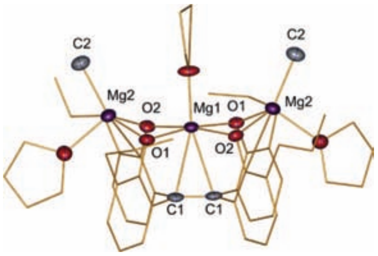


Figure 2. Molecular structure of **3c**. All H-atoms are omitted for clarity. Selected bond lengths (Å) Mg1−O1 2.0491(17), Mg1−O2 2.0719(16), Mg2−O1 2.0111(19), Mg2−O2 1.989(2), Mg2−C2 2.112(3), Mg1−C1 2.583(3).

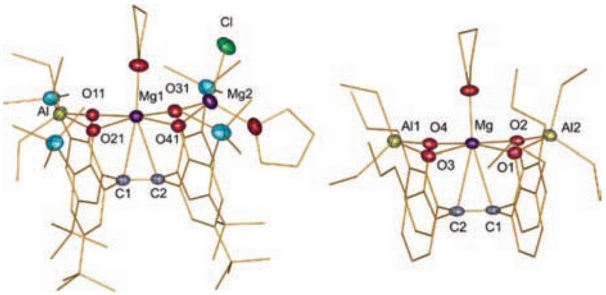
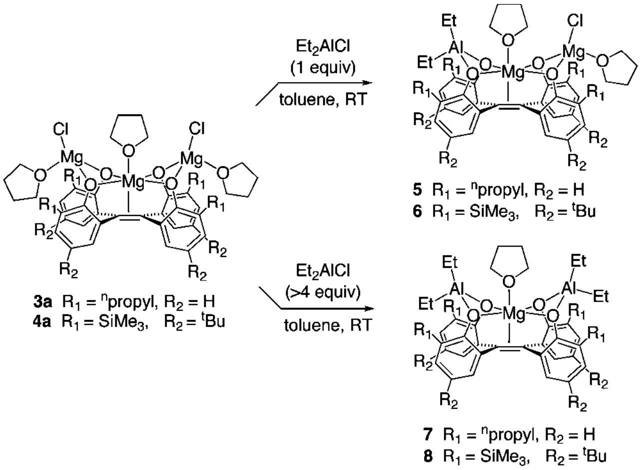


Figure 3. Molecular structures of **6** (left) and **7** (right). H-atoms are omitted for clarity. Selected bond lengths for **6**: Al−O11 1.846(2), Al−O21 1.841(2), Mg1−O11 2.110(2), Mg1−O21 2.137(2), Mg1−O31 1.986(2), Mg1−O41 1.989(2), Mg2−O31 1.986(2), Mg2−O41 1.989(2), Mg1−C1 2.571, Mg1−C2 2.623. **7**: Al1−O3 1.852(2), Al1−O4 1.860(2), Al2−O1 1.856(2), Al2−O2 1.847(2), Mg−O1 2.066(2), Mg−O2 2.076(2), Mg−O3 2.070(2), Mg−O4 2.061(2), Mg−C1 2.636(3), Mg−C2 2.638(3).

Scheme 1



were characterized by X-ray crystallography; one complex in each series is illustrated (Figure 3).[13] An excess of Et$_2$AlCl is required to drive the second substitution to completion, presumably a result of the deactivation of Et$_2$AlCl by coordination with liberated THF and/or MgCl$_2$.[14] The difference in kinetic reactivity between the central magnesium, a chelated bis(aryloxide), and the two mono(aryloxide) "wings" is both reasonable and predictable. The reduction in lability of the second terminal magnesium center after exchange of the first is more subtle but must arise from communication of the difference in coordination environment across the central magnesium center.

Tetrakis(2-hydroxyphenyl)ethene frameworks are thus suitable templates for the controlled assembly of surface-like polymetallic coordination complexes relevant to silica-supported catalysts. Controlled formation of magnesium and magnesium/aluminum derivatives provides a natural basis for the rational evaluation of structure/reactivity relationships (e.g., magnesium content) in Ziegler−Natta polymerization catalysis using a unique series of compositionally well-defined precatalyst complexes. The isolation of persistent ternary Mg/Ti/Al arrays, compositionally representative of active Ziegler−Natta catalysts, is ultimately targeted.

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Supporting Information Available: Experimental procedures and complete characterization data for all new compounds; details of the X-ray crystallography for complexes **3b**, **3c**, **4b**, **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Detailed experimental procedures and complete characterization data are provided as Supporting Information.

(10) X-ray diffraction data obtained for chloride complex **3a** were sufficient to establish connectivity but did not refine acceptably. The corresponding bromide **3b** is spectroscopically nearly identical and crystallographically well-behaved.

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(13) Isolation and purification of highly lipophilic complex **8** are complicated by very high solubility in hydrocarbon media; a series of 3-substituted tetrakis(2-hydroxyphenyl)ethene ligands lacking the extraneous 5-*tert*-buyl substitutents is currently in development.

(14) This result contrasts the crown-like polyaluminum complexes isolated from reactions of **1** and **2** with excess trialkylaluminum reagents. The aluminum coordination chemistry of 3-substituted tetrakis(2-hydroxyphenyl)ethene ligand systems will be reported in a separate account: Fujita, M.; Lightbody, O. C.; Stryker, J. M., forthcoming manuscript.

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