Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 3977–3979 **3977**
DOI: 10.1021/ic100390x

Dithiodiolate Ligands: Group 4 Complexes and Application in Lactide Polymerization

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Received February 26, 2010

Dithiodiolate ligands were synthesized by reacting 1,2-ethanedithiol or 1,2-benzenedithiol with 2,2-bis(trifluoromethyl)oxirane, led selectively to mononuclear octahedral group 4 complexes of the type [{OSSO}M(OR)$_2$], which features C_2 symmetry and fluxional behavior, and were highly active in the ring-opening polymerization of *rac*- and L-lactide.

Poly(lactic acid) (PLA) is often referred to as "bioplastic" or "greenplastic" because it is produced from renewable resources and because of its ability to biodegrade.[1] Having mechanical properties similar to those of polystyrene.[2] it may replace less environmentally friendly plastics in packaging applications, while its biocompatibility enables its application in biomedical products.[3,4] The preferred method for producing PLA is ring-opening polymerization (ROP) of the dilactone of lactic acid—lactide—because it enables control of the molecular weight and tacticity, which affect the plastic's mechanical properties and its tendency to degrade.[5] Polymerization of L-lactide leads to isotactic PLA, whereas polymerization of *rac*-lactide can lead to atactic, heterotactic, stereoblock, or stereocomplex PLA as determined by the catalyst employed.[6] Therefore, in the past decade, considerable efforts were made to design well-defined metal-based catalysts as active polymerization initiators. In comparison to other metals, group 4 metal complexes are less explored for cyclic ester ROP.[7−13] Typical catalysts are composed of chelating phenoxo-type spectator ligands and labile alkoxo groups.[14,15] Of those, zirconium (and hafnium) complexes are typically more active and exhibit superior stereocontrol in comparison to the analogous titanium species.[12,13]

Chelating ligands featuring phenoxo-type anionic ligands have dominated the coordination chemistry of oxophilic main-group and transition metals and have led to numerous successful catalysts[16] while the related nonaromatic alkoxo-based ligands have been explored to a lesser extent.[17] For example, complexes of {OSSO}-type dithiodiphenolate ligands have led to the isospecific polymerization of styrene (when bound to titanium)[18] and to heteroselective polymerization of *rac*-lactide (when bound to scandium),[19] whereas {OSSO}-type dithiodiolate ligands have never been reported, to our knowledge. Herein, we describe the synthesis of the first dithiodiolate ligand precursors, their coordination chemistry around group 4 metals, and the application of these complexes in the ROP of *rac*- and L-lactide.

The ligands were designed to include either an aliphatic or an aromatic two-carbon bridge between the sulfur donors and two trifluoromethyl groups on the α-carbon atoms to sterically and electronically diminish the bridging tendency of

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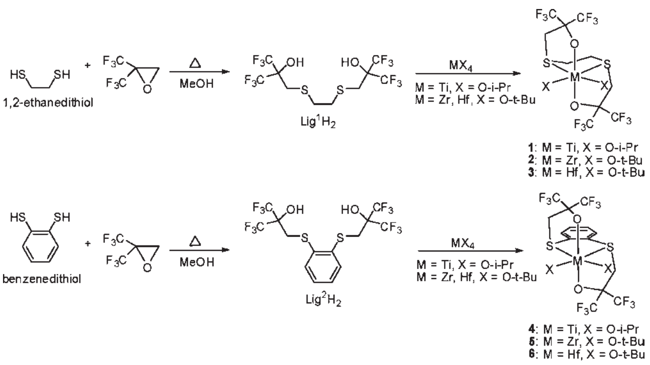
Scheme 1. Dithiodiolate Ligands and Their Group 4 Metal Complexes



the oxygen donors.[20] The two ligand precursors Lig^1H_2 and Lig^2H_2 were conveniently prepared in a one-step synthesis by reacting 2,2-bis(trifluoromethyl)oxirane with 1,2-ethanedithiol and 1,2-benzenedithiol, respectively (see the Supporting Information). Each ligand was then reacted with Ti(O-*i*-Pr)$_4$, Zr(O-*t*-Bu)$_4$, and Hf(O-*t*-Bu)$_4$ to give well-defined mononuclear complexes of the type [{OSSO}M(OR)$_2$] in good yield (see Scheme 1).[21] The complexes were easily isolated as white solids by the removal of volatiles under reduced pressure and pentane washings. All of the complexes (and in particular complex **4**) showed signs of decomposition within a few days. Therefore, spectroscopic characterization and polymerization reactions were performed shortly after their preparation.

Symmetric tetradentate ligands may wrap in three geometries around octahedral metal centers designated as *mer*–*mer* (trans), *fac*–*fac* (cis-α), or *fac*–*mer* (cis-*β*).[22] Because the sulfur donors become stereogenic upon binding to the metal, the possible symmetries of the isomers of these {OSSO} complexes are C_2, C_s, or C_1. Single peaks of the methylene groups in the ^{1}H NMR spectra of all complexes at room temperature were consistent with C_{2v}-symmetric species. This indicates a dynamic process of low barrier that interconverts isomers of lower symmetry. These isomers could be observed by variable-temperature NMR. For example, the titanium complex **1** dissolved in toluene-d_8 showed coalescence of a broad signal of the $-SCH_2C(CF_3)_2-$ group and a single peak of the $-SCH_2CH_2S-$ group at −45 °C, which split to two sets of two doublets at −65 °C. This corresponds to a C_2-symmetric complex having a low barrier to enantiomer interconversion of 11.7 kcal mol^{-1}. Slightly higher barriers for interconversion were found for zirconium (**2**) and hafnium (**3**) complexes of Lig^1 of 13.4 and 13.8 kcal mol^{-1}, respectively (see the Supporting Information). The complexes of Lig^2 (**4**–**6**) were even more fluxional, with the titanium and zirconium complexes showing only broadening of the peaks upon cooling to −65 °C (estimated $\Delta G^{\ddagger} < 10.0$ kcal mol^{-1}). It is notable that similar low barriers for interconversion are observed for the two ligands around the three metals. In comparison, the barrier for interconversion showed a strong dependence on the metal for the dithiodiphenolate ligands (featuring a 6–5–6 chelate array): 11.5 kcal mol^{-1} for [{OSSO}Ti(O-*i*-Pr)$_2$] and 17.0 kcal mol^{-1} for the complex of the softer metal [{OSSO}Zr(O-*t*-Bu)$_2$].[23] For the dithiodiphenolate complexes [{OSSO}Ti(O-*i*-Pr)$_2$] (featuring a 5–5–5 chelate array), a barrier for interconversion that depended on the ligand bulk was found, with the lowest being 13.4 kcal mol^{-1}.[24,25]

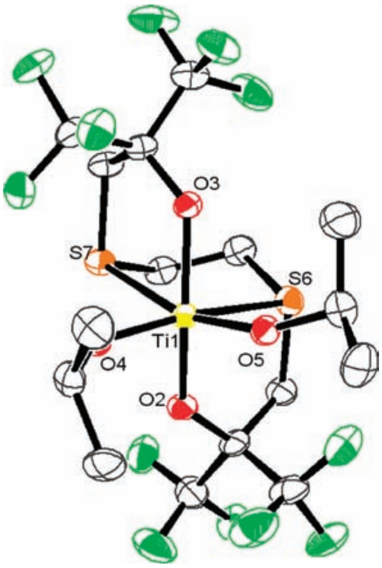


Figure 1. ORTEP representation of complex **1** with 50% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg) for Lig^{1}Ti(O-*i*-Pr)$_2$: Ti1–O2, 1.938(3); Ti1–O3, 1.921(3); Ti1–O4, 1.792(3); Ti1–O5, 1.751(3); Ti1–S6, 2.762(1); Ti1–S7, 2.740(1); O2–Ti1–O3, 150.0(1); S6–Ti–S7, 78.6(4); O4–Ti–O5 106.0(1).

Single crystals of **1** were grown from cold pentane, and its X-ray structure was solved. The structure features a mononuclear complex of octahedral geometry around the titanium center; i.e., the sulfur donors are bound to the metal, completing an array of 5–5–5-membered chelating rings.[26] Lig^1 binds in a *fac*–*fac* mode around the titanium metal center (Figure 1), which is consistent with the species observed in the ^{1}H NMR spectra at low temperature. Following this wrapping mode, the diolate oxygen atoms are located mutually trans, and the monodentate ligands are mutually cis and are trans to the sulfur donors. The chelating ligand bond lengths of S–Ti (2.74–2.76 Å)[24] and O–Ti (1.92–1.94 Å)[24] are typical, indicating unstrained binding. A narrow O3–Ti–O2 angle of 150.0° (relative to 163.8° for the related {ONNO} ligand)[25] results from the "pulling-backwards" of the ligand by the long S–Ti bonds, thus leaving a relatively open space for the labile groups.

Preliminary activity studies of these complexes included polymerization of 300 equiv of *rac*-lactide in the melt and in a toluene solution at 75 °C (see the Supporting Information).

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[25] Titanium complexes of {ONNO} ligands featuring the same diolate arms appeared rigid at room temperature. See:Lavanant, L.; Chou, T.-Y.; Chi, Y.; Lehmann, C. W.; Toupet, L.; Carpentier, J.-F. *Organometallics* **2004**, *23*, 5450.

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All complexes were able to catalyze the ROP of *rac*-lactide; however, the activity and stereoselectivity varied depending on the metal, whereas the nature of the bridge between the two sulfur donors (i.e., Lig^1 vs Lig^2) was considerably less significant. The two titanium complexes **1** and **4** showed the lowest activities and led to practically atactic PLA for polymerizations carried out in a neat monomer at 144 °C. Still, consumption of ca. 150 equiv of *rac*-lactide in the melt within 17 min (by **4**) corresponds to one of the highest activities reported to date for titanium complexes.[10,12,13] Higher activities and a clear inclination toward heterotacticity were found for the zirconium and hafnium complexes **2**, **3**, **5**, and **6** of the two ligands. For polymerizations in the melt, the hafnium complexes were somewhat more active than the zirconium complexes. In particular, an almost quantitative consumption of 300 equiv of *rac*-lactide within 1 min (and 3000 equiv within 5 min) by complex **6** corresponds to the highest activity of any group 4 metal catalyst reported to date, to our knowledge.[12,13,15] The PLA obtained featured a degree of heterotacticity (P_r) of approximately 70%. Running the polymerizations in toluene solutions at lower temperatures resulted in higher degrees of heterotacticities, with the highest being 89% achieved by complex **5** at 75 °C. Molecular weight distributions in the range of PDI = 1.17−1.78 and lower than expected molecular weights indicate that transesterification processes are taking place.

As expected, catalysts that exhibit a mild tendency for heterotactic enchainment in the melt showed a relatively high activity toward L-lactide as well.[27] For example, all complexes of Lig^2 fully consumed 300 equiv of L-lactide within 15−25 min (see the Supporting Information).

In conclusion, the first dithiodiolate ligands were synthesized via a straightforward one-step reaction. The ligands led to C_2-symmetric complexes around octahedral centers of group 4 metals that exhibited a high degree of fluxionality. These complexes were highly active in the ROP of lactide, showing a tendency for heterotactically enriched PLA in the polymerization of *rac*-lactide. The study of the coordination chemistry of these ligands around other metals and further possible catalytic applications are underway.

Acknowledgment. We thank the Israel Science Foundation and the United States−Israel Binational Science Foundation for financial support.

Supporting Information Available: Experimental details for synthesis of the ligands and complexes and crystallographic data of complex **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Although polymerization demonstrates a relatively high activity toward L-lactide, it is significantly slower than that of *rac*-lactide because of a mild kinetic preference for consecutive polymerization of D- and L-lactide to give heterotactically enriched poly(lactide).