Inorg. Chem. **2007**, *46*, 8114–8116

Inorganic Chemistry
Communication

Group 4 Complexes of a New [OSSO]-Type Dianionic Ligand. Coordination Chemistry and Preliminary Polymerization Catalysis Studies

Ad Cohen, Adi Yeori, Israel Goldberg, and Moshe Kol*

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences,
Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel

Received July 10, 2007

A straightforward synthesis of a new type of tetradentate dianionic [OSSO]-type ligand is described. This ligand features an ethylenedithiol core bridged via methylene groups to substituted phenols, thus representing an S analogue of the [ONNO]-type Salan ligands. The [OSSO]H_2 ligand precursor reacted with titanium(IV) isopropoxide and with zirconium(IV) *tert*-butoxide to give the corresponding [OSSO]–M$(OR)_2$ complexes, which formed as single C_2-symmetric isomers but were fluxional according to variable-temperature NMR. An X-ray structure of [OSSO]–Zr(O-t-Bu)$_2$ supported the *fac*–*fac* wrapping mode of the ligand. The dibenzyl complex [OSSO]–Zr(bn)$_2$ that was obtained by a reaction between the ligand precursor and tetrabenzylzirconium was found to be an active 1-hexene polymerization catalyst upon activation with $B(C_6F_5)_3$, leading to a stereoirregular polymer despite its C_2 symmetry.

The design of multidentate ligands that can wrap around early transition metals and lead to complexes of well-defined geometry and symmetry and possibly to olefin polymerization catalysts is a major theme in current inorganic chemistry.[1] Tetradentate dianionic ligands that feature a “sequential” array of donors and lead to octahedral group 4 complexes are especially appealing. Depending on the nature of the donors and bridging groups, they may wrap around the metal in a *fac*−*fac* mode, giving C_2-symmetric complexes in which the two labile groups have cis orientation. The [ONNO]-type diamine diphenolate Salan ligands,[2−5] whose Zr and Ti complexes follow this coordination mode and lead to isospecific polymerization of α-olefins,[6] feature a 6−5−6 array of chelate rings. In this work, we describe the synthesis of an [OSSO]-type sulfur analogue of the Salan ligands, i.e., a ligand in which the *N*-Me donors were replaced with S donors, the coordination chemistry of this ligand around Ti and Zr, and a preliminary 1-hexene polymerization catalysis study (Figure 1).

Group 4 complexes of tetradentate [OSSO]-type diphenolate ligands have been recently developed by Okuda and were shown to lead to interesting chemical activities such as the isotactic polymerization of styrene.[7−9] The S donors in those ligands are attached directly to the phenol groups,

---

* To whom correspondence should be addressed. E-mail: moshekol@post.tau.ac.il.

(1) For several recent reviews on new catalysts for α-olefin polymerization, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1493. (c) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30.

(2) (a) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706. (b) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200.

(3) (a) Yeori, A.; Groysman, S.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2005**, *44*, 4466. (b) Yeori, A.; Goldberg, I.; Shuster, M.; Kol, M. *J. Am. Chem. Soc.* **2006**, *128*, 13062.

(4) For the related Salophan ligand, see: Groysman, S.; Sergeeva, E.; Goldberg, I.; Kol, M. *Eur. J. Inorg. Chem.* **2005**, 2480. For the related Salalen ligand, see: Yeori, A.; Gendler, S.; Groysman, S.; Goldberg, I.; Kol, M. *Inorg. Chem. Commun.* **2004**, 280.

(5) See also: Busico, V.; Cipullo, R.; Pellecchia, R.; Ronca, S.; Roviello, G.; Talarico, G. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15321 and references cited therein.

(6) For related “sequential” [ONNO] tetradentate ligands and complexes giving isotactic polymerization, see: (a) Lamberti, M.; Consolmagno, M.; Mazzeo, M.; Pellecchia, C. *Macromol. Rapid. Commun.* **2005**, *26*, 1866. (b) Strianese, M.; Lamberti, M.; Mazzeo, M.; Tedesco, C.; Pellecchia, C. *J. Mol. Catal. A: Chem.* **2006**, *258*, 284. (c) Kirillov, E.; Lavanant, L.; Thomas, C.; Roisnel, T.; Chi, Y.; Carpentier, J.-F. *Chem.*−*Eur. J.* **2007**, *13*, 923.

(7) For several reports on group 4 complexes of 5−5−5 [OSSO] ligands, see: (a) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964. (b) Capacchione, C.; De Carlo, F.; Zannoni, C.; Okuda, J.; Proto, A. *Macromolecules* **2004**, *37*, 8918. (c) Capacchione, C.; Manivannan, R.; Barone, M.; Beckerle, K.; Centore, R.; Oliva, L.; Proto, A.; Tuzi, A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2005**, *24*, 2971. (d) Beckerle, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, *25*, 3019.

(8) For several recent reports on non-group 4 complexes of 5−5−5 and related [OSSO] ligands, see: (a) Ma, H.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770. (b) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818.

(9) For several reports on olefin polymerization catalysis employing [OSO] phenolate ligands, see: (a) van der Linden, A.; Schaverien, C. J.; Meijbboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (b) Sernetz, F. G.; Mülhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562. (c) Natrajan, L. S.; Wilson, C.; Okuda, J.; Arnold, P. L. *Eur. J. Inorg. Chem.* **2004**, 3724. (d) Braune, W.; Ma, H.; Spaniol, T. P.; Okuda, J. *Organometallics* **2005**, *24*, 1953. (e) Wisniewska, D.; Janas, Z.; Sobota, P.; Jerzykiewicz, L. B. *Organometallics* **2006**, *25*, 6166.

10.1021/ic701370t CCC: $37.00

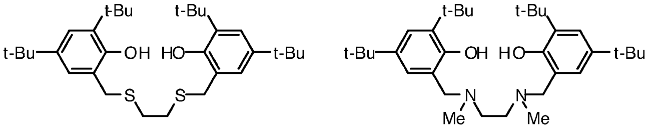
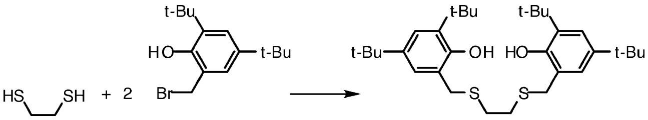


Figure 1. [OSSO] ligand precursor and its [ONNO] Salan analogue.

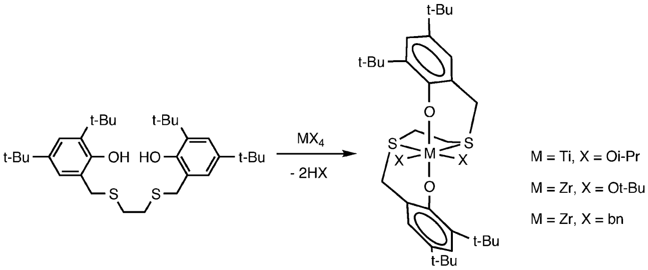
Scheme 1. Synthesis of the Ligand Precursor $[OSSO]H_2$



yielding a more compact 5−5−5 array of chelate rings. The Salan ligands are conveniently synthesized by the Mannich condensation, which is not applicable to the [OSSO]-type analogues.[10] We therefore turned to an alternative synthesis relying on the effective nucleophilic character of the S donor. Reacting ethylenedithiol with 2 equiv of 2-(bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol, which is synthesized from the corresponding phenol on a multigram scale,[11] gave the parent ligand precursor, $[OSSO]H_2$, in typical yields of 80%. The poor nucleophilic character of the phenol O enables its application in its nonprotected form in this reaction (Scheme 1).[12]

Reacting the ligand precursor $[OSSO]H_2$ with titanium(IV) isopropoxide in ether at room temperature led cleanly to a yellow solid complex in ca. 97% yield after workup. NMR characterization supported its assignment as an $[OSSO]Ti(O\text{-}i\text{-}Pr)_2$-type complex; no trace of a homoleptic $[OSSO]_2Ti$ complex was detected even when a large excess of $[OSSO]H_2$ was employed. The $[OSSO]Ti(O\text{-}i\text{-}Pr)_2$ complex appears to be C_{2v}-symmetric at room temperature according to the sharp singlets of the methylene groups in the ^1H NMR spectrum (rather than AB systems for diastereotopic protons in a C_2-symmetric environment). Such symmetry could result either from a *mer*−*mer* C_{2v}-symmetric octahedral complex or from fast-exchanging *fac*−*fac* C_2-symmetric octahedral enantiomers. Alternatively, a tetrahedral complex in which the S donors are not bound is also consistent with this symmetry. Variable-temperature ^1H NMR experiments of $[OSSO]Ti(O\text{-}i\text{-}Pr)_2$ in toluene-d_8 in the range of −60 to +20 °C provided clear evidence for a fluxional behavior of the complex (see the Supporting Information). In the lower temperature range, the $S-CH_2-Ar$ methylene protons assume the familiar AB pattern consistent with C_2 symmetry and a *fac*−*fac* wrapping mode. The free energy of activation for the fluxional process was calculated from the line shape of the $S-CH_2-Ar$ protons to be $\Delta G^{\ddagger} = 48 \pm 1$ kJ mol^{-1}.[13] Such fluxional behavior was not observed for the group 4 Salan complexes. However, a fluxional behavior was reported for several $[OSSO]TiX_2$ complexes of the more compact 5−5−5 [OSSO] ligands. Notably, only those [OSSO] ligands featuring nonbulky phenolate substituents gave rise to fluxional complexes, whereas the bulkier ones led to configurationally stable complexes. Thus, even though the 6−5−6 $[OSSO]Ti(O\text{-}i\text{-}Pr)_2$ complex described herein carries bulky *o-tert*-butyl groups, it is substantially more flexible than the most flexible 5−5−5 $[OSSO]Ti(O\text{-}i\text{-}Pr)_2$ complex (containing *o*-H groups; $\Delta G^{\ddagger} = 56.5 \pm 1$ kJ mol^{-1}).[7c] The source of the high flexibility in the 6−5−6 $[OSSO]Ti(O\text{-}i\text{-}Pr)_2$ complexes and its possible dependence on phenolate substituent bulk are currently under study.

Scheme 2. Synthesis of the Ti and Zr Metal Complexes



A clean reaction was also observed between the ligand precursor $[OSSO]H_2$ and $Zr(O\text{-}t\text{-}Bu)_4$ in diethyl ether, giving $[OSSO]Zr(O\text{-}t\text{-}Bu)_2$ in practically quantitative yield as a single isomer (Scheme 2). The Zr complex appeared to be C_2-symmetric at room temperature, as is evident from the AB pattern of the $S-CH_2-Ar$ protons. Variable-temperature NMR experiments in toluene-d_8 in the range of +40 to +95 °C pointed again to a fluxional behavior (see the Supporting Information). However, a much higher barrier for enantiomer interconversion ($\Delta G^{\ddagger} = 71 \pm 1$ kJ mol^{-1}) was found. The higher barrier for interconversion observed for Zr relative to Ti is unusual because steric effects are expected to play a less significant role around the larger metal center.[14,15] This behavior may be rationalized if considerable weakening or complete detachment of S−M bonds has to take place and if the soft-S/soft-Zr interaction is relatively strong.

Crystals of $[OSSO]Zr(O\text{-}t\text{-}Bu)_2$ suitable for X-ray analysis were grown from a diethyl ether/pentane solution at −35 °C, and the structure was solved (Figure 2).[16] The structure is consistent with the solution spectroscopic data revealing the *fac*−*fac* wrapping mode of the [OSSO] ligand around the Zr, giving an overall (noncrystallographic) C_2 symmetry and a cis relationship between the two monodentate alkoxo groups [O5−Zr−O7 = 105.79(8)°]. The S−Zr bond lengths of ca. 2.84 Å are typical for R_2S-Zr bonds.[9c,17]

---

(10) Tshuva, E. Y.; Gendeziuk, N.; Kol, M. *Tetrahedron Lett.* **2001**, *42*, 6405.

(11) Appiah, W. O.; DeGreef, A. D.; Razidlo, G. L.; Spessard, S. J.; Pink, M.; Young, V. G., Jr.; Hofmeister, G. E. *Inorg. Chem.* **2002**, *41*, 3656.

(12) For the use of this nonprotected phenol in amine(phenolate) ligand synthesis, see: Marinescu, S. C.; Agapie, T.; Day, M. D.; Bercaw, J. E. *Organometallics* **2007**, *26*, 1178. For the use of the protected phenol in amine(phenolate) ligand synthesis, see: Axe, P.; Bull, S. D.; Davison, M. G.; Gilfillan, C. J.; Jones, M. D.; Robinson, D. E. J. E.; Turner, L. E.; Mitchell, W. L. *Org. Lett.* **2007**, *9*, 223.

(13) Günther, H. *NMR Spectroscopy*; John Wiley and Sons: New York, 1980; p 241.

(14) For a higher barrier for interconversion in Ti vs Zr complexes of aminetris(phenolate) tripodal complexes, see: Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783.

(15) The Zr complex $[OSSO]Zr(O\text{-}i\text{-}Pr)_2$ also appeared to be C_2-symmetric at room temperature according to the AB pattern of the $S-CH_2-Ar$ protons.

(16) Crystal data for $[OSSO]Zr(O\text{-}t\text{-}Bu)_2$: $C_{40}H_{66}O_4S_2 \cdot 0.5C_5H_{12}$, $M = 801.84$, monoclinic, $P2_1/n$, $a = 13.0210(2)$ Å, $b = 17.7530(2)$ Å, $c = 19.5070(4)$ Å, $\beta = 93.0590(5)°$, $V = 4502.8(1)$ Å^3, $Z = 4$, $D_c = 1.183$ g cm^{-1}, $T = 110$ K, 10 709 unique reflns, R1 = 0.0495 and wR2 = 0.1447 for 7745 reflns with $I > 2\sigma(I)$.

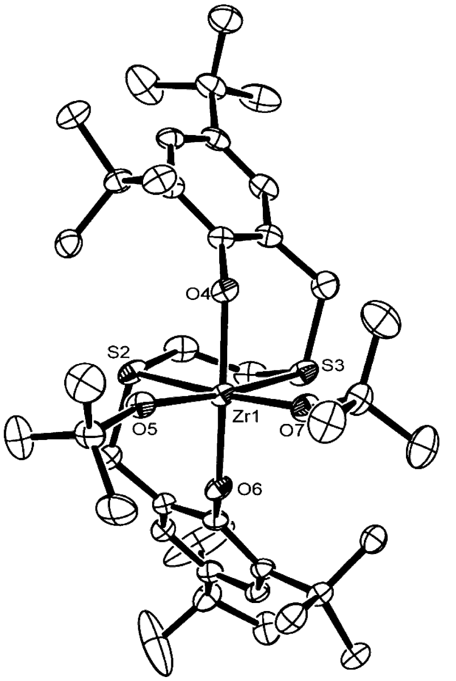


Figure 2. ORTEP representation of [OSSO]Zr(O-t-Bu)$_2$ with 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Zr−O7 1.927(2), Zr−O5 1.931(2), Zr−O4 2.027(2), Zr−O6 2.032(2), Zr−S3 2.8279(7), Zr−S2 2.8485(7), S2−Zr−S3 73.80(2), O4−Zr−O6 151.48(7), O5−Zr−O7 105.75(8), C40−O5−Zr1 161.6(2), C44−O7−Zr 161.6(2).

The two S donors and the two *tert*-butoxo O atoms form an almost perfect plane (root-mean-square deviation from the plane of 0.009 Å) in which the Zr center is embedded. The overall structure is similar to that of the Salan−Zr complex [ONNO]Zr(O-t-Bu)$_2$.[14] The similar binding of the *tert*-butoxo groups in both complexes, as is evident from similar O−Zr bond lengths (1.93 Å) and C−O−Zr bond angles (161−167°), supports a similar donation from the S or N donors in the two complexes. In addition, the similar angle between the two *tert*-butoxo groups of 107.8° found for the [ONNO] complex indicates a similar "openness" of the active sites. However, because of the long S−Zr bonds, the [OSSO] ligand appears to be more "recessed" in comparison to the [ONNO] ligand; i.e., it is pulled away from the labile groups. This is evident in a narrower O−Zr−O angle between the phenolate O atoms (151.5 vs 163.0°). The phenolate rings are pulled toward the equatorial S−S−Zr plane, thus bringing the *o*-*tert*-butyl groups close to the metal. However, because they protrude less into the labile groups' quadrants, their directing of an incoming olefin might be inferior.

To assess the potential of this ligand environment in α-olefin polymerization catalysis, we prepared the dibenzylzirconium complex by reacting the ligand precursor [OSSO]H$_2$ with tetrabenzylzirconium. [OSSO]Z(bn)$_2$ was obtained as a yellow solid in high yield. Its ^{1}H NMR spectrum supported a C_2-symmetric complex showing no fluxional behavior at room temperature. Upon activation with tris(pentafluorophenyl)borane in neat 1-hexene at room temperature, an active catalyst had formed. The polymerization was carried almost to completion (93%), and the activity of the catalyst was calculated to be 80 g mmol^{-1} h^{-1}. The ^{13}C NMR spectrum of the poly(1-hexene) revealed a regioregular and stereoirregular (atactic) structure. Gel permeation chromatography analysis revealed a relatively low molecular weight of 7400 g mol^{-1} (PDI = 1.6). This catalyst was found to be active at −20 °C, but the poly(1-hexene) obtained was still atactic. In comparison, the corresponding [ONNO]−Zr catalyst was about 5 times less active but afforded isospecific and living polymerization at room temperature.[2a] The atacticity at low temperature may indicate that a reduced directing power of the phenolate substituents rather than a fluxional catalyst behavior is responsible for the lack of stereocontrol by this [OSSO]-type complex.

In conclusion, the first member of a new family of tetradentate dianionic [OSSO] ligands was synthesized by a straightforward reaction with a bromomethyl-substituted phenol. While the *fac*−*fac* wrapping of this OSSO ligand around Ti and Zr established its structural correlation with the [ONNO] Salan ligands, it was found to be much more flexible than the latter. The long S−M bonds relative to N−M bonds make this ligand more "recessed", which may explain the formation of stereoirregular poly(1-hexene) from the [OSSO]Zr(bn)$_2$ complex. We are currently exploring the synthesis of more "protruding" ligands of this family in an attempt to induce isospecificity.

Acknowledgment. We thank Prof. Gretchen Hofmeister (Carleton College, Northfield, MN) for helpful discussions and Dvora Reshef and Dr. Limor Frish (Tel Aviv University) for technical assistance. We thank the Israel Science Foundation and the U.S.−Israeli Binational Science Foundation for financial support.

Supporting Information Available: Details of the syntheses and characterization of the ligand and the complexes, polymerization procedures, and polymer characterization (PDF) and crystallographic data in CIF format for [OSSO]Zr(O-t-Bu)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701370T

---

(17) Hart, R.; Levason, W.; Patel, B.; Reid, G. *J. Chem Soc., Dalton Trans*. **2002**, 3153.