Supporting Information for DT-ART-05-2012-030991

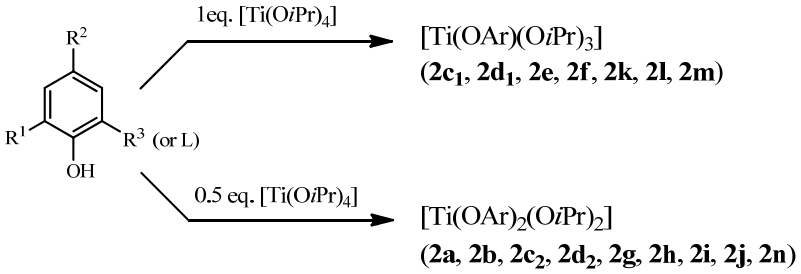
New bis(aryloxy)-Ti(IV) Complexes and Their Use for the Selective Dimerization of Ethylene to 1-Butene

Fabien Grasset,[a] Jean-Benoît Cazaux,[a] Lionel Magna,*[a] Pierre Braunstein[b] and Hélène Oliver-Bourbigou[a]

[a] *IFPEnergies nouvelles Lyon, Rond point de l'échangeur de Solaize, BP3, 69360 Solaize, France. Fax: (+33) 4 37 70 20 66; Tel: (+33) 4 37 70 28 86; E-mail: lionel.magna@ifpen.fr*

[b] *Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 67081 Strasbourg, France*

This document contains additional bonding parameters for the structurally characterized complexes **2d$_1$**, **2f**, **2i**, **2j** and **2n** and information relevant to the catalytic testing.



The letters used in the numbering of the complexes refer to the ligand.

When appropriate, the subscript indicates the number of OAr substituents

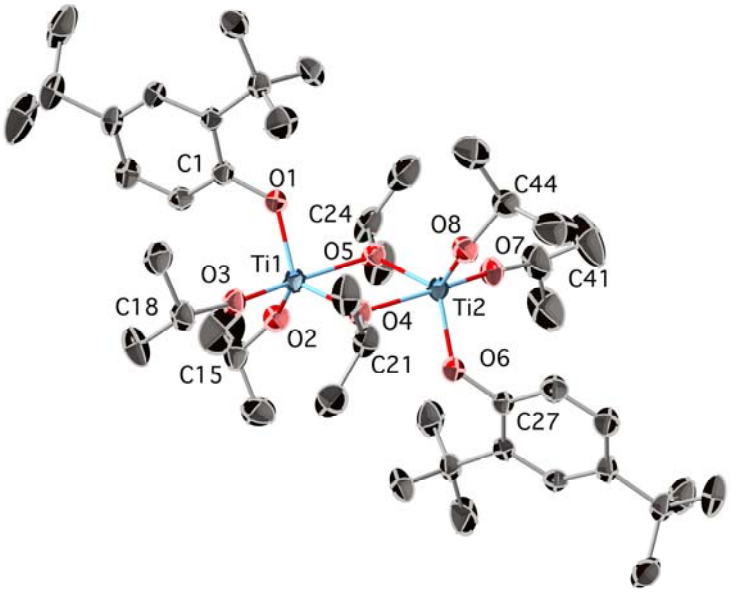


Fig. 1 ORTEP of the solid state structure of **2d$_1$**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. Selected bond distances [Å] and angles [°]: Ti1-O1 1.874(2), Ti1-O2 1.785(2), Ti1-O3 1.7700(15), Ti1-O4 1.9423(15), Ti1-O5 2.117(2), Ti2-O4 2.1164(15), Ti2-O5 1.935(2), Ti2-O6 1.863(2), Ti2-O7 1.770(2), Ti2-O8 1.784(2), O1-C1 1.361(3), O6-C27 1.367(3), O1-Ti1-O2 112.98(8), O1-Ti1-O3 96.87(8), O1-Ti1-O4 123.28(7), O1-Ti1-O5 84.98(7), O2-Ti1-O3 100.14(8), O2 Ti1 O4 117.45(8), O2-Ti1-O5 88.84(7), O3-Ti1-O4 98.24(7), O3-Ti1-O5 169.19(7), O4-Ti1-O5 72.08(6), O4-Ti2-O5 72.24(6), O4-Ti2-O6 83.76(7), O4-Ti2-O7 168.27(8), O4-Ti2-O8 89.64(7), O5-Ti2-O6 123.95(8), O5-Ti2-O7 97.99(8), O5-Ti2-O8 116.25(8), O6-Ti2-O7 96.95(8), O6-Ti2-O8 113.34(9), O7-Ti2-O8 100.73(9), Ti1-O4-Ti2 107.68(7), Ti2-O5-Ti1 107.91(7).

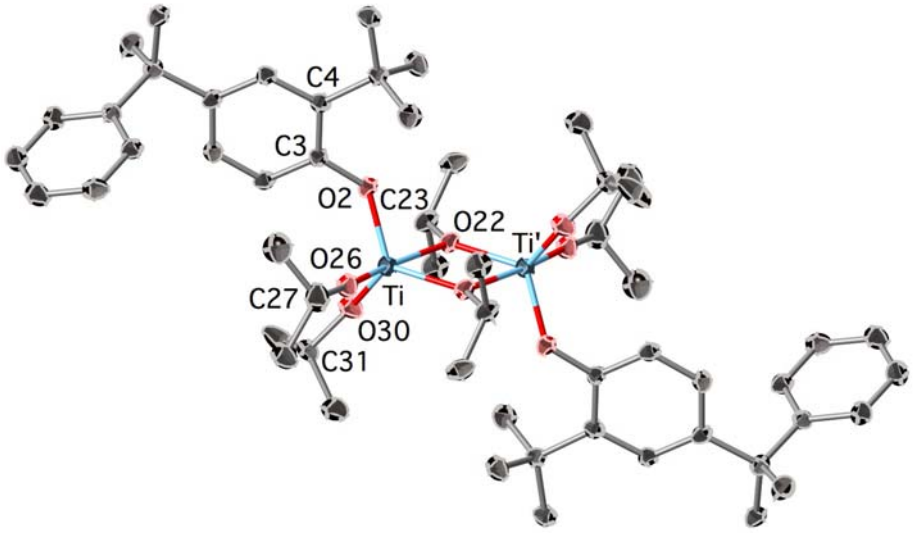


Fig. 3 ORTEP of the solid state structure of **2f**. H atoms are omitted for clarity. Ellipsoids include 50% of the electron density. Selected bond distances [Å] and angles [°]: Ti-O2 1.8537(15), Ti-O22 2.1112(15), Ti-O22' 1.9385(15), Ti-O26 1.777(2), Ti-O30 1.787(2), O2-C3 1.352(2), O22-C23 1.447(2), O30-C31 1.416(3); O22-Ti-O2 84.98(6), O22-Ti-O22' 72.55(7), O2-Ti1-O22' 120.70(7), O22-Ti-O26 170.10(7), O2-Ti-O26 97.79(7), O22'-Ti-O26 98.00(7), O22-Ti- O30 87.49(7), O2-Ti-O30 112.51(7), O22-Ti-O30 120.15(7), O26-Ti-O30 100.11(8), Ti-O2-C3 133.8(1), Ti-O22-C23 117.5(1), Ti-O22-C23 134.4(1).

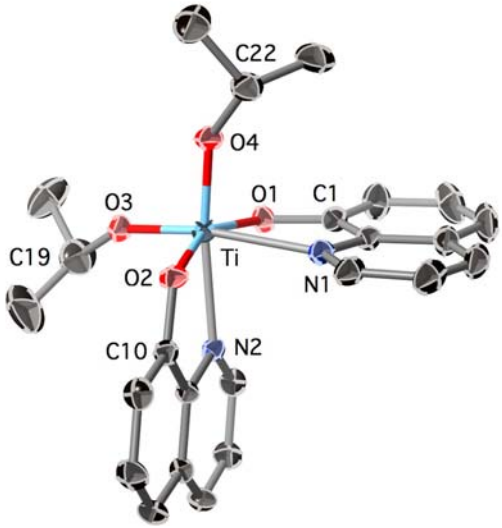


Fig. 3 ORTEP of the solid state structure of **2j**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. Selected bond distances [Å] and angles [°]: Ti-O1 1.962(1), Ti-O2 1.959(1), Ti-O3 1.797(1), Ti-O4 1.795(1), Ti-N1 2.2514(15), Ti-N2 2.2359(14); O1-Ti-O2 155.21(5), O1-Ti-O3 94.37(6), O1-Ti-O4 100.88(6), O2 Ti-O3 101.62(6), O2-Ti-O4 94.03(6), O3-Ti-O4 102.56(6), O1-Ti-N1 75.93(5), O1-Ti-N2 85.11(5), O2-Ti-N1 84.56(5), O2-Ti-N2 76.31(5), O3-Ti-N2 89.51(6), O4-Ti-N2 165.97(6), O3-Ti-N1 165.77(6), O4-Ti-N1 89.65(6), N1-Ti-N2 79.43(5), C1-O1-Ti 120.7(1), C10-O2-Ti 120.5(1), C19-O3-Ti 149.31(15), C22-O4-Ti 147.0(1).

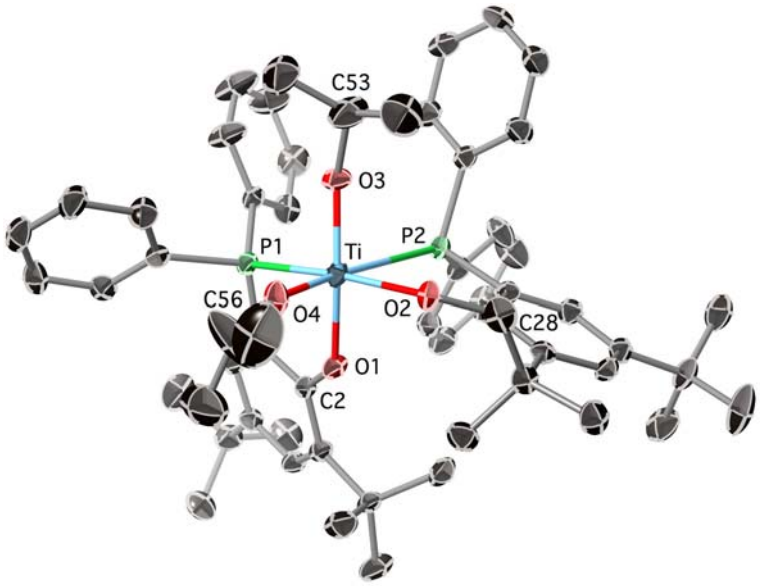


Fig. 4 ORTEP of the solid state structure of **2n**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. Selected bond distances [Å] and angles [°]: Ti-O1 1.983(3), Ti-O2 1.874(3), Ti-O3 1.800(3), Ti-O4 1.777(3), Ti-P1 2.5967(15), Ti-P2 2.8764(15), O1-C2 1.339(5), O2-C28 1.342(5), O3-C53 1.401(6), O4-C56 1.386(8); O4-Ti-O3 100.50(17), O4-Ti-O2 103.50(15), O3-Ti-O2 100.37(15), O4-Ti-O1 96.30(16), O3-Ti-O1 157.02(16), O2-Ti-O1 90.75(14), O4-Ti-P1 97.68(12), O3-Ti-P1 88.49(12), O2-Ti-P1 155.02(11), O1-Ti-P1 73.74(10), O4-Ti-P2 174.26(12), O3-Ti-P2 82.74(12), O2-Ti-P2 71.13(10), O1-Ti-P2 81.94(11), P1-Ti-P2 87.10(5), C2-O1-Ti 133.7(3), C28-O2-Ti 138.0(3), C53-O3-Ti 154.0(4), C56-O4-Ti 162.0(5).

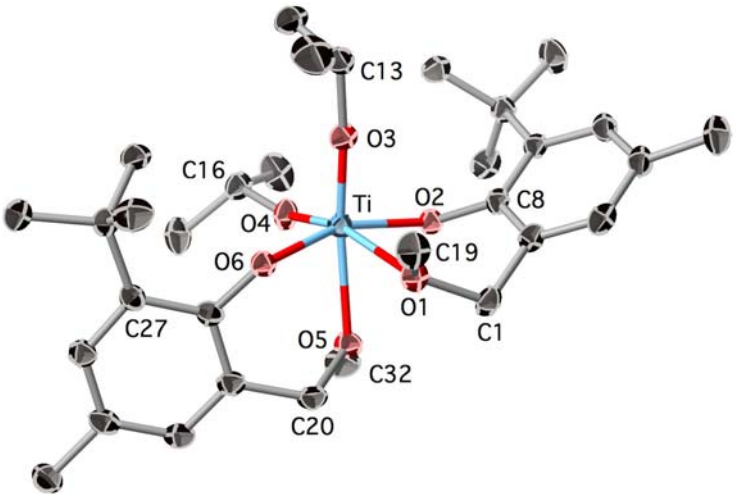


Fig. 5 ORTEP of the solid state structure of **2i**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. There are two independent, slightly different molecules in the unit cell. Data for one of them are given below. Selected bond distances [Å] and angles [°]: Ti2-O1 2.2321(15), Ti2-O2 1.9366(14), Ti2-O3 1.7627(14), Ti2-O4 1.7748(15), Ti2-O5 2.2689(14), Ti2-O6 1.9403(13); O1-Ti2-O2 80.84(6), O1-Ti2-O3 93.00(7), O1-Ti2-O4 162.29(6), O1-Ti2-O5 74.79(6), O1-Ti2-O6 81.40(6), O2-Ti2-O3 98.23(6), O2-Ti2-O4 95.72(6), O2-Ti2-O5 82.14(5), O2-Ti2-O6 158.23(6), O3-Ti2-O5 167.61(7), O3-Ti2-O6 95.16(6), O4-Ti2-O5 87.55(6), O4-Ti2-O6 97.38(7), O5-Ti2-O6 81.14(5), C1-O1-Ti2 118.3(1), C19-O1-Ti2 120.2(1), C8-O2-Ti2 129.7(1), C13-O3-Ti2 171.4(2), C16-O4-Ti2 161.25(14), C32-O5-Ti2 119.47(13), C20-O5-Ti2 116.1(1), C27-O6-Ti2 129.9(1).

Ethylene oligomerization reactor

Example of reaction profil :