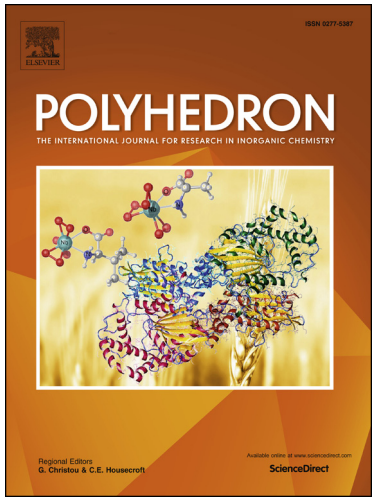

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PII: S0277-5387(17)30802-1
DOI: https://doi.org/10.1016/j.poly.2017.12.019
Reference: POLY 12976

To appear in: *Polyhedron*

Received Date: 29 September 2017
Accepted Date: 13 December 2017

Please cite this article as: Y. Kiliç, I. Kani, Selective Catalytic Oxidation of Alkenes Employing Homobinuclear Manganese(II) Catalysts with TBHP, *Polyhedron* (2017), doi: https://doi.org/10.1016/j.poly.2017.12.019

Selective Catalytic Oxidation of Alkenes Employing Homobinuclear Manganese(II) Catalysts with TBHP

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Abstract

The two novel homobinuclear compounds $[Mn_2{}^{(II,II)}(\mu_{1,1}\text{-}4\text{-}CH_3\text{-}C_6H_4COO)_2(phen)_4](ClO_4)_2$ (**1**) and $[Mn_2{}^{(II,II)}(\mu_{1,3}\text{-}4\text{-}CH_3\text{-}C_6H_4COO)_2(bipy)_4](ClO_4)_2$ (**2**), where bipy = 2,2-bipyridine and phen = 1,10-phenanthroline, have been synthesized and characterized by elemental analyses and spectral methods (UV-vis, FTIR, and X-ray). A single-crystal X-ray diffraction structure analysis of the compounds revealed that the manganese atom is octahedrally coordinated. In compound **1**, the binuclear(II) structure is monodentate, bridged with one oxygen atom of carboxylate ligand in $\mu_{1,1}$ mode, and each Mn(II) center is coordinated with two phen ligands. In compound **2**, the binuclear(II) structure is *syn-anti* bidentate, bridged with two oxygen atoms of carboxylate ligand in $\mu_{1,3}$ mode, and each Mn(II) center is coordinated with two bipy ligands. The Mn–Mn separation is 3.441 (1) Å and 4.450 (1) Å for **1** and **2**, respectively. The catalytic potentials of these compounds have been tested for the oxidation reaction of various olefins (i.e., styrene, cyclohexene, ethyl benzene, 1-hexene, 1-octene). The oxidation reactions were carried out in the presence of catalytic amounts of **1** and **2** with a peroxide oxygen donor (TBHP=*tert*-Butyl hydroperoxide) in acetonitrile at 70°C. On comparing the catalytic activities of **1** and **2**, both catalysts showed good activity (~100% conv. in 24 h.) in the oxidation of studied alkenes, and excellent conversion was obtained for cyclohexene (~100% conv. in 3 h.; TON = 265 and TON = 257, respectively, for **1** and **2**).

Keywords: catalysis, manganese, oxidation, alkene