

Author(s): Silva, TFS (Silva, Telma F. S.); Luzyanin, KV (Luzyanin, Konstantin V.); Kirillova, MV (Kirillova, Marina V.); da Silva, MFG (Guedes da Silva, M. Fatima); Martins, LMDRS (Martins, Luisa M. D. R. S.); Pombeiro, AJL (Pombeiro, Armando J. L.)

Title: Novel Scorpionate and Pyrazole Dioxovanadium Complexes, Catalysts for Carboxylation and Peroxidative Oxidation of Alkanes

Source: Advanced Synthesis & Catalysis, 352 (1): 171-187 JAN 2010

Language: English

Document Type: Review

Author Keywords: Alkanes; Carboxylation; C-H Bond Activation; Oxovanadium Complexes; Peroxidative Oxidation; Scorpionate Ligands

KeyWords Plus: Vanade-Dependent Haloperoxidases; Copper Trethanolamine Complexes; Ono Donor Ligands; Acetic-Acid; Coordination Chemistry; Vanadium Complexes; Hydrogen-Peroxide; Highly Efficient; Spectroscopic Characterization; Mild Conditions

Abstract: The dioxovanadium(V) complexes [VO₂(3,5-Me(2)Hpz)(3)][BF₄] (1) (pz = pyrazolyl), [VO₂{SO₃C(pz)(3)}] (2), [VO₂{HB(3,5-Me(2)pz)(3)}] (3) and [VO₂{HC(pz)(3)}][BF₄] (4), bearing pyrazole or scorpionate ligands, were obtained by reaction of triethyl vanadate [VO(OEt)(3)] with hydrotris(3,5-dimethyl-1-pyrazolyl)methane [HC(3,5-Me(2)pz)(3)] or 3,5-dimethylpyrazole (3,5-Me(2)Hpz; 1), lithium tris(1-pyrazolyl)methanesulfonate {Li[SO₃C(pz)(3)]}, 2, potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate {K[HB(3,5-Me(2)pz)(3)]}, 3 and hydrotris(1-pyrazolyl)methane [HC(pz)(3)], 4, respectively. Treatment of [VO(OEt)(3)] with potassium hydrotris(1-pyrazolyl)borate {K[HB(pz)(3)]} led to the mixed eta(3)-tris(pyrazolyl)borate and eta(2)-bis(pyrazolyl)borate oxovanadium(IV) complex [VO{HB(pz)(3)}{H₂B(pz)(2)}], 5. The compounds were characterized by elemental analyses, IR, NMR and EPR spectroscopy, FAB and ESI mass spectrometry, cyclic voltammetry and, for 5, also by single crystal X-ray diffraction analysis. All complexes exhibit catalytic activity in the single-pot carboxylation [in trifluoroacetic acid/potassium peroxodisulfate (CF₃COOH/K₂S₂O₈)] of gaseous alkanes (methane and ethane) to carboxylic acids (yields up to 40%. TONs up to 157) and in the peroxidative oxidation [in water/acetonitrile (H₂O/NCMe)] of liquid alkanes (cyclohexane and cyclopentane) to the corresponding alcohols and ketones (yields up to 24%, TONs up to 117), under mild conditions.

Addresses: [Silva, Telma F. S.; Luzyanin, Konstantin V.; Kirillova, Marina V.; Guedes da Silva, M. Fatima; Martins, Luisa M. D. R. S.; Pombeiro, Armando J. L.] TU Lisbon, Inst Super Tecn, Ctr Quim Estrutural, P-1049001 Lisbon, Portugal; [Guedes da Silva, M. Fatima] ULHT Lisbon, P-1749024 Lisbon, Portugal; [Martins, Luisa M. D. R. S.] ISEL, Dept Engrn Quim, P-1959007 Lisbon, Portugal

Reprint Address: Pombeiro, AJL, TU Lisbon, Inst Super Tecn, Ctr Quim Estrutural, Complexo 1, Av Rovisco Pais, P-1049001 Lisbon, Portugal.

E-mail Address: poimbeiro@ist.utl.pt

Publisher: Wiley-V C H Verlag GMBH

Publisher Address: PO BOX 10 11 61, D-69451 Weinheim, GERMANY

ISSN: 1615-4150

DOI: 10.1002/adsc.200900660

ISO Source Abbrev.: Adv. Synth. Catal.

ISI Document Delivery No.: 553BL