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

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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.

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