Author(s): Kirillov, AM (Kirillov, Alexander M.); Alegria, ECBA (Alegria, Elisabete C. B. A.); da Silva, MFCG (Guedes da Silva, M. Fatima C.); Martins, LMDRS (Martins, Luisa M. D. R. S.); Sousa, C (Sousa, Catarina); Pombeiro, AJL (Pombeiro, Armando J. L.)

Title: Synthesis, characterization and redox behaviour of benzoyldiazenido- and oxorhenium complexes bearing N,N- and S,S-type ligands

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Abstract: The reactions of [ReCl2{eta(2)-N2C(O)Ph}(PPh3)(2)](1) with 2-aminopyrimidine (H(2)Npyrm), 2,2'-bipyridine (bpy) and tetraethylthiuram disulfide (tds), in MeOH upon reflux, lead to the new eta(1)-(benzoyldiazenido)-rhenium(III) complexes [ReCl{eta(1)-N2C(O)Ph}(HNpyrm)(PPh3)(2)](2)and [ReCl2{eta(1)-N2C(O)Ph}(bpy)(PPh3)] (3), and the known oxo(diethyldithiocarbamato)dirhenium(v)complex [Re2O2(mu O){Et2NC(S)S}(4)](4), respectively. The Et2NC(S)S ligands in 4 result from S-S bond rupture of tds molecules. The obtained compounds have been characterized by IR, H-1, P-31{H-1} and C-13{H-1} NMR spectroscopies, FAB(+)-MS, elemental and single-crystal X-ray diffraction (for 2 and 4)analyses. Complex 2 represents the first structurally characterized Re compound derived from 2-aminopyrimidine. Besides, the redox behaviour of 2-4 in CH2Cl2 solution has been studied by cyclic voltammetry, and the Lever electrochemical ligand parameter (E-L)has been estimated, for the first time, for HNpyrm. The electrochemical results are discussed in terms of electronic properties of the Re centres and the ligands. (C) 2009 Elsevier B. V. All rights reserved.

Addresses: [Kirillov, Alexander M.; Alegria, Elisabete C. B. A.; Guedes da Silva, M. Fatima C.; Martins, Luisa M. D. R. S.; Pombeiro, Armando J. L.] TU Lisbon, Inst Super Tecn, Ctr Quim Estrutural, P-1049001 Lisbon, Portugal; [Alegria, Elisabete C. B. A.; Martins, Luisa M. D. R. S.; Sousa, Catarina] ISEL, Dept Engn Quim, P-1950062 Lisbon, Portugal; [Guedes da Silva, M. Fatima C.] ULHT Lisbon, P-1749024 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: pombeiro@ist.utl.pt

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