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

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Abstract: The reactions of $[\text{ReCl}_2\{\eta(2)\text{-N}_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2](1)$ with 2-aminopyrimidine ($\text{H}(2)\text{Npyrm}$), 2,2'-bipyridine (bpy) and tetraethylthiuram disulfide (tds), in MeOH upon reflux, lead to the new $\eta(1)$ -(benzyldiazenido)-rhenium(III) complexes $[\text{ReCl}\{\eta(1)\text{-N}_2\text{C}(\text{O})\text{Ph}\}(\text{HNpyrm})(\text{PPh}_3)_2](2)$ and $[\text{ReCl}_2\{\eta(1)\text{-N}_2\text{C}(\text{O})\text{Ph}\}(\text{bpy})(\text{PPh}_3)](3)$, and the known oxo(diethyldithiocarbamato)dirhenium(v) complex $[\text{Re}_2\text{O}_2(\mu\text{-O})\{\text{Et}_2\text{NC}(\text{S})\text{S}\}_4](4)$, respectively. The $\text{Et}_2\text{NC}(\text{S})\text{S}$ ligands in 4 result from S-S bond rupture of tds molecules. The obtained compounds have been characterized by IR, ^1H -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 CH_2Cl_2 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.

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