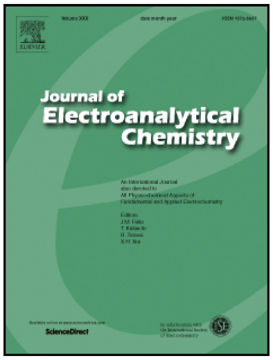

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Catalytic reduction of 1-bromodecane and 1-iododecane by electrogenerated, structurally modified nickel(I) salen

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Abstract

Cyclic voltammetry and controlled-potential (bulk) electrolysis have been used to characterize the behavior of a structurally modified nickel(I) salen species, that can be electrogenerated at carbon cathodes in dimethylformamide (DMF) containing 0.10 M tetra-*n*-butylammonium tetrafluoroborate (TBABF$_4$) to catalyze the reductions of 1-bromodecane (**1**) and 1-iododecane (**2**). This nickel(I) complex possesses a methyl protecting group on each imino (C=N) bond, as well as a *N*-methyl-*N*-phenylaminomethyl moiety on each aryl group. In its active form, the nickel(I) species can reduce **1** or **2** at a more positive potential than is needed to reduce either substrate directly at a carbon cathode. Bulk electrolysis of the parent nickel(II) complex in the presence of **1** and **2** results in a mixture of *n*-eicosane, *n*-decane, 1-decene, and *N*,*N*-dimethylundecanamide, that were identified and quantitated with the aid of gas chromatography–mass spectrometry (GC–MS) and gas chromatography (GC). A mechanistic scheme is proposed to account for the formation of the various products. Robustness of the new nickel(I) catalyst was also investigated and was compared to that encountered with unmodified nickel(I) salen.

Keywords: Electrochemical reduction; Glassy carbon cathodes; Nickel(I) salen; Alkyl monohalides; Carbon–halogen bond cleavage

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