Factor F_{430}-like Catalysis of [NiL] (L = Dianion of 6,8,15,17-Tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) in the Reduction of Alkyl Halides

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The reduction of alkyl halides by $NaBH_4$ is efficiently catalysed by [NiL] (L = dianion of 6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine), a plausible active species being $[Ni^IL]^-$

The dianion (L) of 6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine exhibits framework flexibility, unlike porphyrin, which allows a co-ordinated metal ion to change oxidation states easily.[1] Thus, transition-metal L complexes would be expected to be employed as a model of metalloenzymes. However, this is not the case.

Factor F_{430}, a nickel(II) complex of a highly hydrogenated porphyrin, is an active site of methyl coenzyme M reductase which participates in the reduction of carbon dioxide to methane.[2] The framework flexibility of the hydroporphyrin is considered essential in the reduction of Ni^{II} to Ni^I, which is a key step in catalysis.[2] Model reactions of Factor F_{430} have been scarcely investigated, except the electrochemical reduction of alkyl halides by nickel(I) hydroporphyrins.[3] In this work, we attempted to use the nickel(II) L complex as a model of Factor F_{430} and to apply it in reduction of alkyl halides, expecting that the nickel(I) active species would be easily formed because of the framework flexibility of L.

The reduction of bromocyclohexane by $NaBH_4$ catalysed by [NiL] **1**[4] proceeded smoothly in $MeOCH_2CH_2OCH_2CH_2OMe$–EtOH (Table 1).† The yield of cyclohexane was almost the same as the consumption of bromocyclohexane. Turnover numbers reached 13.3 after 6 h, indicating that the reaction is catalytic. No reaction occurred either in the absence of **1** or in the presence of [CuL][5] **2** and [Ni(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinate)[6] **3** instead of **1**. The reduction proceeded more slowly in $MeOCH_2CH_2OCH_2CH_2OMe$–MeOH (9:1) and tetrahydrofuran (thf)–MeOH (9:1) than in $MeOCH_2CH_2OCH_2CH_2OMe$–EtOH, and only a little in dimethylformamide (dmf)–MeOH (9:1) and $MeOCH_2CH_2OCH_2CH_2OMe$.

The catalytic activity depends on the substrate. Chlorocyclohexane was not reduced by **1** + $NaBH_4$, and reduction of 1-bromoadamantane was also remarkably slow compared to that of bromocyclohexane. However, iodocyclohexane was rapidly reduced. The half-wave potentials of bromocyclohexane and 1-bromoadamantane (−2.29 and −2.38 V *vs.* saturated calomel electrode in dmf)[7] are not so different as to account for their reactivities, suggesting electron transfer is not the crucial reaction step. As is often considered in the uncatalysed reduction of alkyl halides by $NaBH_4$,[8] nucleophilic substitution is a plausible mechanism, consistent with the reactivity orders bromocyclohexane > 1-bromoadamantane and iodo- > bromo- > chloro-cyclohexane.

Table 1 Catalytic reduction of alkyl halides[a]

Catalyst	Solvent[b]	Turnover number
1[c]	Diglyme–EtOH (9:1)	0
1	Diglyme	0.1
1	Diglyme–MeOH (9:1)	6.2
1	Diglyme–EtOH (9:1)	5.6[d]
1	Diglyme–EtOH (9:1)	13.3
1	thf–MeOH (9:1)	2.8
1	dmf–MeOH (9:1)	0.2
2	Diglyme–EtOH (9:1)	0
1[e]	Diglyme–EtOH (9:1)	30.9
1[e]	Diglyme–EtOH (9:1)	173[f]
1[e]	Pyridine–EtOH (9:1)	0.8
3[e]	Pyridime–EtOH (9:1)	0
1[g]	Diglyme–EtOH (9:1)	1.7

[a] Substrate:catalyst = 50:1, 6 h. Substrate is bromocyclohexane unless otherwise stated. [b] Diglyme = $MeOCH_2CH_2OCH_2CH_2OMe$. [c] Substrate = chlorocyclohexane. [d] 2 h. [e] Substrate = iodocyclohexane. [f] Substrate:catalyst = 250:1, 45 h. [g] Substrate = 1-bromoadamantane.

Compound **1** is ESR-silent, consistent with a planar structure and low-spin d^8 electron configuration.[9] The ESR spectrum of a degassed mixture of **1** and $NaBH_4$ (1:100) in $MeOCH_2CH_2OCH_2CH_2OMe$–MeOH (9:1) showed a rhombic signal ($g_{\parallel}$ = 2.26 and $g_{\perp}$ = 2.13), indicating the formation of nickel(I) species. This signal rapidly decreased after the addition of bromocyclohexane, suggesting its catalytic intermediacy. Reduction of nickel porphyrins has been reported to produce ligand anion radicals with ESR signals at about g = 2.0.[3,10] Thus, the framework flexibility of L would allow **1** to be reduced to Ni^I, which is essential for the catalysis. When **1** was reduced by Na/Hg (100 equivalents of Na per **1**) in thf, a relatively strong ESR signal was observed ($g_{\parallel}$ = 2.10 and $g_{\perp}$ = 2.01) due to the formation of $Na^+[Ni^IL]^-$.[11] The difference in the ESR spectra between **1** + $NaBH_4$ and **1** + Na/Hg suggests that either H^- or BH_4^- co-ordinates to Ni^I in the **1** + $NaBH_4$ system, and is a plausible candidate for the active species.[12] In summary, the reduction of alkyl halide by $NaBH_4$ is efficiently catalysed by compound **1**, which is reduced to nickel(I) species like Factor F_{430}.

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† In a typical run, $NaBH_4$ (5.0×10^{-3} mol), compound **1** (5.0×10^{-5} mol), bromocyclohexane (2.5×10^{-3} mol) and $MeOCH_2CH_2OCH_2CH_2OMe$–EtOH (9:1 v/v, 5.0 cm^3) were mixed under N_2 at 30 °C. The product and reactant were analysed by GLC.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research (Nos. 03640524 and 04750698) from the Ministry of Education, Science and Culture, Japan.

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Received 21*st May* 1992; *Communication* 2/02654F