Nickel Complexes as Soluble Catalysts for Reductive Dehalogenation of Aromatic Halides

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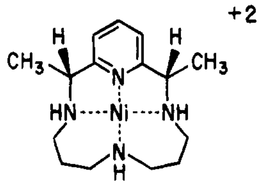
Nickel(II) complexes **1** and **2** are soluble catalysts for reductive dehalogenation of aromatic bromides and polychlorobenzenes by sodium borohydride at 25–45 °C in aqueous ethanol, aqueous acetonitrile, or ethanol–acetonitrile. Deuterium incorporation experiments, and rate retardation by added cumene, point to a radical-chain mechanism. Hydrazine can replace borohydride as a source of reducing power. Reactivity toward this reducing system increases with increasing halogen content of the substrate, a finding that parallels prior observations of dechlorination in natural sediments.

Simple nickel(II) salts react with sodium borohydride in water or ethanol solution to form a black precipitate ("nickel boride") which is a powerful catalyst for hydrogenation[1] and hydrogenolysis[2] under heterogeneous conditions. In solvents of greater coordinating power, such as dimethylformamide, nickel(II) chloride and sodium borohydride reportedly constitute a soluble hydrogenation catalyst.[3]

Nickel(II) complexes of certain tetraazacycles were reported to form soluble complexes with borohydride,[4] but no catalytic activity was ascribed to those substances. We have found that nickel(II) complexes **1**[5] and **2**[6] effectively promote reductive dehalogenation of aromatic halides by borohydride. In this paper we report on the scope and mechanism of this homogeneous reduction process, which is more broadly applicable and more convenient than methods previously described for aromatic dehalogenation. The use of hydrazine in place of borohydride as reductant is also described.



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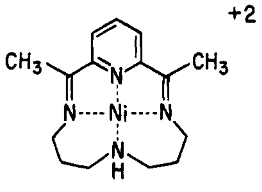

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Results

Treatment of the amber solution of **1** (counterion tetrafluoroborate) in acetonitrile (λ_{max} 463 nm) with an ethanol solution of sodium borohydride caused rapid formation of a blue-violet solution (λ_{max} 559 nm). These observations are similar to those reported by Curtis[4] for Ni(II) complexes of saturated tetraazacycle ligands.

The blue-violet solution of **1**/$NaBH_4$ in ethanol–acetonitrile smoothly converts aromatic bromides to the corresponding hydrocarbon in *ca.* 1 h or less at 25–45 °C (Table 1). In practice, a large excess of borohydride is used, along with a small quantity of **1** (0.1–0.2 mol per mol of substrate). Aqueous ethanol or aqueous acetonitrile can also serve as solvent. In the partially aqueous solution, turbidity sometimes develops as the reaction proceeds, probably due to the low solubility of sodium borate.

Equally good results were obtained with **2**. In this case treatment with borohydride produces initially a green solution which changes during a few minutes to the same blue-violet color observed with **1**. Presumably borohydride converts **2** to **1**, possibly a mixture of stereoisomers.[5] We have not examined the reaction of **2** with borohydride in detail, but it appears that the active species in the reduction of aromatic halides is the same whether **1** or **2** is used.

Under conditions where 1-bromonaphthalene is rapidly reduced, 1-chloronaphthalene reacts slowly. At 60 °C, 15% conversion to naphthalene occurred in 500 min and 40% after 1300 min. Chlorobenzene is similarly slow to react. Polychlorobenzenes, on the other hand, react readily to suffer stepwise replacement of chlorine (Table 2).

Ester and nitrile functions do not interfere. The conversion of both bromo- and chlorobenzonitriles to benzonitrile contrasts with results reported[7] for dehalogenation with triphenylphosphine Ni(O) complexes. It is also important to note that the heterogeneous reducing systems formed by combination of transition metals with either $NaBH_4$ or $LiAlH_4$[8] rapidly reduce benzonitrile to benzylamine. No benzylamine or corresponding halobenzylamine was found in the dehalogenation of chloro- or bromobenzonitrile with **1**/$NaBH_4$.

Deuterium Incorporation. When 1,2,4,5-tetrachlorobenzene was treated with **1** and $NaBH_4$ in D_2O–acetonitrile, the resulting 1,2,4-trichlorobenzene (**3**) exhibited an NMR spectrum consisting of well-separated multiplets (H_a δ 7.47; H_b 7.38; H_c 7.19) of equal intensity (integration ratios, respectively 1.00:1.02:1.00). When $NaBD_4$ (98% D) was used in H_2O–acetonitrile under the

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[1] Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *85*, 1003. Brown H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1963**, *85*, 1005. Ganem, B.; Osby, J. O. *Chem. Rev.*, **1986**, *86*, 763.

[2] Truce, W. E.; Roberts, F. E. *J. Org. Chem.* **1963**, *28*, 961. Truce, W. E.; Perry, F. M. *J. Org. Chem.* **1965**, *30*, 1316.

[3] Strohmeier, W.; Steigerwald, H. *Z. Naturforschung B* **1977**, *32b*, 111.

[4] Curtis, N. F. *J. Chem. Soc.* **1965**, 924.

[5] Karn, J. L.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1149. Ochiai, E.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1798.

[6] Curry, J. D.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 592.

[7] Lin, S.-T.; Roth, J. A. *J. Org. Chem.* **1979**, *44*, 309.

[8] Osby, J. O.; Heinzman, S. W.; Ganem, B. *J. Am. Chem. Soc.* **1986**, *108*, 67.

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same conditions, the relative intensities were 1.00:0.998: 0.043, indicative of >95% deuterium incorporation.

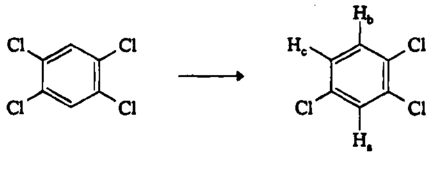

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Table 3 presents the results obtained with 1-bromonaphthalene. No deuterium was introduced from $NaBH_4/D_2O$, while 84% deuterium incorporation occurred with $NaBD_4/D_2O$.

Table 1. Dehalogenation by $NaBH_4$ and Nickel Complex 1 or 2

substrate	catalyst/ solvent[a]	temp, °C	reactn time (min)	product (%)
1-bromonaphthalene	**2**/A	40	60	naphthalene (99,[b] 96[c]) 1,1′-binaphthyl (0.6[b])
2,6-dibromobiphenyl	**2**/B	25	60	biphenyl (100[b])
1,3-dibromobenzene	**1**/C	40	40	benzene (see Figure 3)
1,4-dibromobenzene	**1**/C	40	40	benzene (see Figure 3)
ethyl 3-bromobenzoate	**1**/D	40	15	ethyl benzoate (90[b])
3-bromobenzonitrile	**1**/C	40	50	benzonitrile (90[b])
4-bromobenzonitrile	**1**/C	40	50	benzonitrile (101[b])
4-chlorobenzonitrile	**1**/D	45	1400	benzonitrile[d]

[a] A, 2:1 ethanol−acetonitrile; B, 4:1 ethanol−acetonitrile; C, 2:5 ethanol−acetonitrile; D, 4:1 ethanol−water. [b] Yield by GLC. [c] Isolated yield. [d] Benzonitrile was the only product observed; neither benzylamine nor 4-chlorobenzylamine could be detected.

Table 2. Dechlorination by $NaBH_4$ and Nickel Complex 1 or 2

substrate	catalyst/ solvent[a]/ temp, °C	reactn time (h)	products		
			$C_6H_3Cl_3$	$C_6H_4Cl_2$	C_6H_5Cl
1,2,3,4-$C_6H_2Cl_4$	**1**/E/40	1.3	73% 1,2,4	3.2% 1,2	trace
			10% 1,2,3	4.5% 1,3	
				7.6% 1,4	
1,2,4,5-$C_6H_2Cl_4$	**1**/F/40	1.3	68% 1,2,4	12%	trace
1,2,3-$C_6H_3Cl_3$	**1**/D/32	0.3	23%	37% 1,2	
				40% 1,3	
		0.7		42% 1,2	8%
				50% 1,3	
1,2,4-$C_6H_3Cl_3$	**1**/B/45	0.5	53%	2.1% 1,2	
				9.4% 1,3	
				32% 1,4	
		1.8		2.7% 1,2	7%
				19% 1,3	
				72% 1,4	
1,2-$C_6H_4Cl_2$	**2**/B/45	5		27%	73%
1,3-$C_6H_4Cl_2$	**2**/B/45	5		75%	25%
1,4-$C_6H_4Cl_2$	**2**/B/45	5		95%	5%

[a] See footnote a to Table 1; E, 6:1 ethanol−acetonitrile; F, 10:1 acetonitrile−water.

Table 3. Deuterium Incorporation into Naphthalene by Reduction of 1-Bromonaphthalene

entry	catalyst	reductant[a]	solvents[b]	naphthalene % monodeuterated
a	**2**	$NaBH_4$	$D_2O + CH_3CN$	0
b	**2**	$NaBD_4$	$D_2O + CH_3CN$	84
c	**2**	$NaBH_4$	$C_2H_5OD + CH_3CN$	0
d	**2**	$NaBD_4$	$C_2H_5OH + CH_3CN$	28
e	**1**	$NaBD_4$	$C_2H_5OH + CH_3CN$	26
f	**1**	$NaBH_4$	$C_2D_5OD + CH_3CN$	24
g	**1**	$NaBH_4$	$C_2H_5OH + CD_3CN$	<2
h	**1**	$NaBD_4$	$C_2D_5OD + CD_3CN$	88

[a] $NaBD_4$ is 98 atom % D. [b] C_2D_5OD and D_2O are 99.9 atom % D.

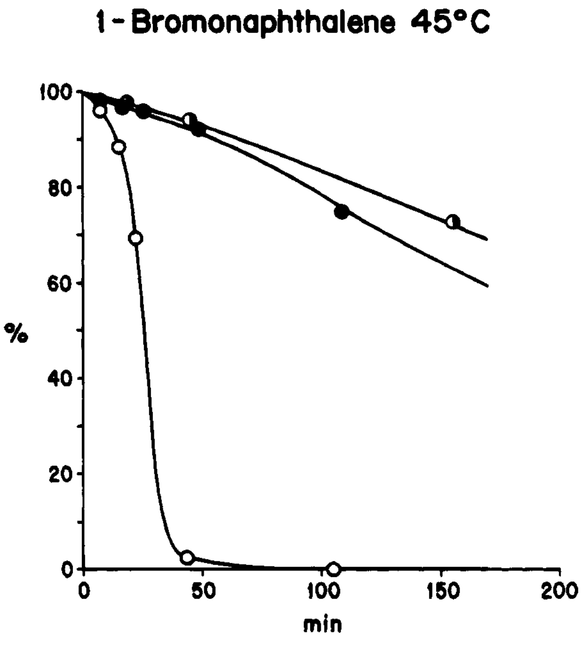

Figure 1. Effect of added cumene on debromination of 1-bromonaphthalene by 0.012 M **1** and 0.3 M $NaBH_4$ in 1:2 ethanol−acetonitrile at 45 °C: (○) no added cumene; (●) 0.7 M cumene; (◑) 1.4 M cumene.

Deuterium incorporation experiments in ethanol−acetonitrile solvent revealed still more about the reaction mechanism (Table 3, entries c−h). It is clear that hydrogen is introduced into the product from *both* borohydride *and* from CH bonds of ethanol. (It could not be demonstrated with certainty whether acetonitrile was a minor hydrogen donor.) A kinetic isotope effect is evident (entries e, f, and h). Comparison of the maximum D-incorporation into 1,2,4-trichlorobenzene (>95%) and naphthalene (84−88%) suggests that the effect is greater in the latter case. However, some introduction of hydrogen from the ligand in **1** or **2** remains a possibility, and no reliable estimate of the kinetic isotope effect can be made from our data.

Effect of Cumene. The results of deuterium incorporation experiments pointed to the likelihood of a radical mechanism. To test that possibility cumene was chosen as a superior hydrogen donor that is unaffected by the reducing agent (in the absence of organic halide). Figure 1 shows the effect of cumene on the rate of debromination of 1-bromonaphthalene by **1**/$NaBH_4$ in the ethanol−acetonitrile solvent system. In the presence of 1.4 M cumene, the conversion was only 32% after 240 min (approximately 7 half-lives in the absence of cumene) and analysis revealed that *bicumyl* had been formed to the extent of *ca.* 0.1 bicumyl per naphthalene. No bicumyl was formed when either bromonaphthalene or the catalyst (**1**) was omitted from the system.

Figure 2 illustrates the effect of cumene on the dechlorination of 1,2,3-trichlorobenzene. In this case the rate retardation is less dramatic, the half-life being approximately doubled. The ratio of *ortho*/*meta*-dichlorobenzenes formed (1.16) was unaffected by addition of cumene. (This ratio is somewhat solvent-dependent; note in Table 2 that the *meta* isomer predominates slightly in ethanol−water.)

The effect of cumene on the dechlorination of 1,2,4,5-tetrachlorobenzene was similar. At 40 °C in the presence of 0.7 M cumene, the half-life was increased by 80% and

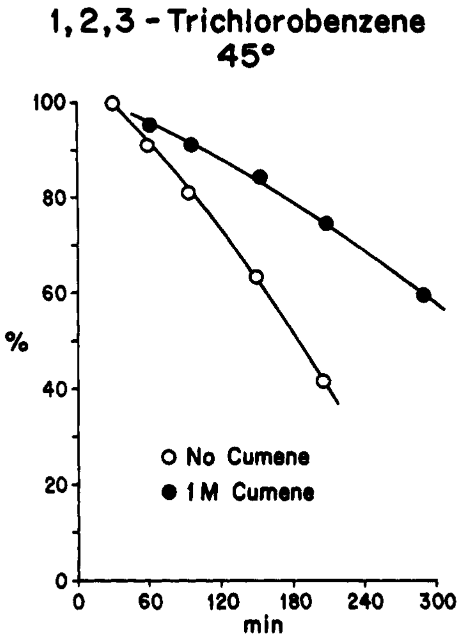

Figure 2. Effect of added 1 M cumene on dechlorination of 1,2,3-trichlorobenzene by 0.01 M **1** and 0.3 M $NaBH_4$ in 3:5 ethanol–acetonitrile at 45 °C.

bicumyl was found to the extent of 0.03 mol per mol conversion of tetrachlorobenzene.

Reaction Mechanism. The deuterium incorporation pattern, the rate retardation by cumene, and the formation of bicumyl indicate a radical-chain mechanism. Similarities may be noted between the present reaction and the dehalogenations effected by organotin hydrides.[9–12] However, the elaborate redox chemistry of nickel complexes[13,14] suggests caution in drawing mechanistic analogies with the latter reaction.

It is now established that alkyl halides are converted to free radicals by Ni(I) complexes,[15–18] which have been generated from the corresponding Ni(II) complexes electrochemically[16–18] or by reduction with sodium amalgam.[15,16] There is no direct evidence for a Ni(I) species[13] in the **1**/$NaBH_4$ system, but a closely related Ni(I) complex has been prepared[19] by borohydride reduction, and we propose that the key step in aromatic dehalogenation is that shown in eq 1 (where L is the ligand of **1**).

$$\mathrm{LNi(I)} + \mathrm{RX} \rightarrow \mathrm{LNi(II)} + \mathrm{R}^{\bullet} + \mathrm{X}^{-} \tag{1}$$

Previous investigators[15–18] have offered differing views of the mechanism of this process (eq 1) based on studies involving aliphatic halides. Our data on aromatic halides are best explained by an electron-transfer mechanism as indicated in eqs 2 and 3 (see Discussion).

$$\mathrm{LNi(I)} + \mathrm{RX} \rightarrow \mathrm{LNi(II)} + \mathrm{RX}^{-\bullet} \tag{2}$$

$$\mathrm{RX}^{-\bullet} \rightarrow \mathrm{R}^{\bullet} + \mathrm{X}^{-} \tag{3}$$

High yields obtained in the dehalogenation reaction indicate that aryl radicals efficiently abstract hydrogen under these conditions. Abstraction of a hydrogen atom from borohydride (eq 4) has precedent[11,20] and is consistent with the observed deuterium incorporation results in aqueous acetonitrile. An alternative *indirect* pathway for hydrogen donation by borohydride may involve an intermediate Ni(II) hydride species (eqs 5 and 6). Evidence for formation of Ni(II) hydride species by borohydride treatment of other Ni(II) complexes has been presented.[21] Electron transfer from $BH_3^{-\bullet}$ or from LNi(I) to aryl halide (eq 1) completes the chain process.

$$\mathrm{R}^{\bullet} + \mathrm{BH_4}^{-} \rightarrow \mathrm{RH} + \mathrm{BH_3}^{-\bullet} \tag{4}$$

$$\mathrm{LNi(II)} + \mathrm{BH_4}^{-} \rightarrow \mathrm{LNi(II)H} + [\mathrm{BH_3}] \tag{5}$$

$$\mathrm{R}^{\bullet} + \mathrm{LNi(II)H} \rightarrow \mathrm{RH} + \mathrm{LNi(I)} \tag{6}$$

It is clear from deuterium incorporation experiments that hydrogen abstraction from ethanol (or an ethoxyborane[22]) occurs in that solvent (eq 7). The resulting hydroxyethyl radical evidently continues the kinetic chain by transfer of an electron to substrate, but details of that process are unclear. Abstraction of hydrogen from cumene (eq 7) yields the unreactive cumyl radical which dimerizes to bicumyl.

$$\mathrm{R}^{\bullet} + \mathrm{CH_3CH_2OH} \rightarrow \mathrm{RH} + \mathrm{CH_3\dot{C}HOH} \tag{7}$$

$$\mathrm{R}^{\bullet} + \mathrm{C_6H_5CH(CH_3)_2} \rightarrow \mathrm{RH} + \mathrm{C_6H_5\dot{C}(CH_3)_2} \tag{8}$$

A mechanism in which R• abstracts hydride from borohydride (the S_{RN} mechanism, eq 9, where Y may be hydrogen or alkoxide) was rendered very unlikely in the present case. The work of Bunnett[23] strongly suggests that a radical-anion such as **4** would dissociate to a phenyl radical and bromide ion (eq 10) more rapidly than it would transfer an electron to dibromobenzene. The result would be direct conversion of dibromobenzene to benzene without the intermediacy of bromobenzene.

$$\mathrm{R}^{\bullet} + \mathrm{H\text{-}BY_3} \rightarrow \mathrm{RH}^{-\bullet} + \mathrm{BY_3} \tag{9}$$

$$\mathrm{C_6H_4Br_2} \rightarrow (\mathrm{C_6H_4Br_2})^{-\bullet} \rightarrow (\mathrm{C_6H_4Br})^{\bullet} \rightarrow \underset{\mathbf{4}}{(\mathrm{C_6H_5Br})^{-\bullet}} \rightarrow \mathrm{C_6H_5}^{\bullet} \rightarrow \mathrm{C_6H_6} \tag{10}$$

Our data for *m*- and *p*-dibromobenzene (Table 1) describe a two-step reaction (Figure 3) in which bro-

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[9] Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

[10] Groves, J. T.; Kittisopikul, S. *Tetrahedron Lett.* **1977**, 4291.

[11] Groves, J. T.; Ma, K. W. *J. Am. Chem. Soc.* **1974**, *96*, 6527.

[12] Corey, E. J. Suggs, J. W. *J. Org. Chem.* **1975**, *40*, 2554.

[13] Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

[14] Lewis, J.; Schoreder, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1085.

[15] Helvenston, M. C.; Castro, C. E. *J. Am. Chem. Soc.* **1992**, *114*, 8490.

[16] Stolzenberg, A. M.; Stershic, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 5397.

[17] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713.

[18] Gosden, C.; Healy, K. P.; Petcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, 972.

[19] Arai, T.; Kondo, H.; Sakaki, S. *J. Chem. Soc., Dalton Trans.* **1992**, 2753.

[20] Barltrop, J. A.; Bradbury, D. *J. Am. Chem. Soc.* **1973**, *95*, 5085.

[21] Holah, D. G.; Hughes, A. N.; Hui, B. C. *Can. J. Chem.* **1977**, *55*, 4048. Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C.-T. *Can. J. Chem.* **1978**, *56*, 2552.

[22] Tabaei, S.-M. H.; Pittman, C. U., Jr.; Mead, K. T. (*J. Org. Chem.*, **1992**, *57*, 6669) have shown that alkoxyborohydrides in THF slowly dechlorinate aryl chlorides at 68 °C and that the reaction is accelerated by nickel chloride. The nickel-containing reaction mixtures were reported to be heterogeneous, so it is not clear whether the reactions described are mechanistically related to those reported in the present paper.

[23] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3612. Bunnett, J. F.; Traber, P. P. *J. Org. Chem.* **1978**, *43*, 1867. Bunnett, J. F.; Shafer, S. J. *J. Org. Chem.* **1978**, *43*, 1873, 1877.

mobenzene formed in the first step is reduced to benzene in a somewhat slower second step, with no indication of the behavior observed by Bunnett.[23] We conclude that hydride transfer to R$^\bullet$ is not an important pathway in dehalogenation with **1**/NaBH$_4$.

Hydrazine as Reductant. A mechanism in which borohydride serves to generate active nickel species, rather than reacting directly with substrate, is supported by the finding that hydrazine can replace borohydride as a source of reducing power. Treatment of 1-bromonaphthalene with **1** and hydrazine hydrate in aqueous ethanol led to rapid formation of naphthalene at 60 °C. Because hydrazine decomposes at an appreciable rate under these conditions, it was necessary to add it portionwise to sustain a rapid rate of debromination. Conversion was 66% in 4.25 h, 98% in 24 h. Under the same conditions 1,2,4-trichlorobenzene was reduced (30% conversion in 4 h) to a mixture of dichlorobenzenes in the ratio *o*:*m*:*p* = 1.0:4.3:14, in satisfactory agreement with the selectivity observed when NaBH$_4$ was the electron source (Table 2).

The dehalogenating system **1**/N$_2$H$_4$ needs further study. For some substrates it might prove superior to **1**/NaBH$_4$, particularly since solubility and workup problems are avoided. A limitation may be the nucleophilic reactivity of hydrazine toward the more activated aryl halides.[24]

Discussion

There is abundant evidence[25] that dechlorination of polychlorobiphenyls (PCBs) occurs in natural sediments containing methanogenic bacteria. It has also been shown[26] that factor F-430, a nickel–corphin complex of bacterial origin, promotes *in vitro* dechlorination of CCl$_4$ and polychloroethylenes in the presence of suitable reductants. In general, increased chlorine content of the substrate is associated[25,26] with increased rate of dechlorination in these systems, in striking agreement with results reported here and with the findings of Helvenston and Castro.[15]

Considerable selectivity is observed in reduction of substrates with nonequivalent chlorines (Table 2). According to the mechanism proposed here, that selectivity occurs in the dissociation of the radical anion (eq 3). It is reassuring to note that 1,2,4-trichlorobenzene is reduced by **1**/NaBH$_4$ to a dichlorobenzene mixture that has the composition (4.8% ortho, 21.6% meta, and 74% para) which is in reasonable agreement with the composition (6.5% ortho, 18.2% meta, 75% para) reported[27] for dechlorination of the same substrate using the radical-anion lithium 4,4′-di-*tert*-butylbiphenyl as electron source. This agreement supports our conclusion that aromatic substrates react with these reduced nickel complexes by electron transfer, rather than by atom transfer or oxidative addition processes.[28]

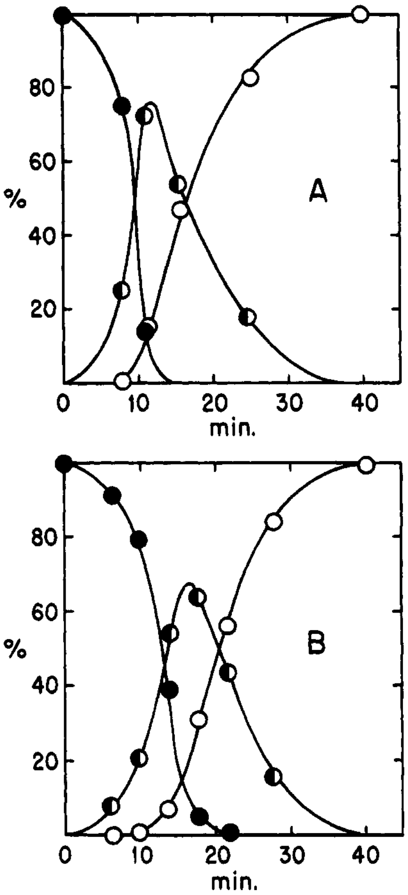

Figure 3. Debromination of (A) 1,3-dibromobenzene and (B) 1,4-dibromobenzene by **1** and NaBH$_4$ in 2:5 ethanol–acetonitrile at 40 °C: (●) dibromobenzene; (◐) bromobenzene; (○) benzene.

Whether the dehalogenation reaction described in this paper, with the key role played by radical-anions, is a suitable model for dehalogenation occurring with biological agents[25,26] is not yet clear. A decision on that point must await studies of the selectivity observed in the different systems toward common polychloro substrates.

Experimental Section

Materials. (2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)nickel (II) bis(tetrafluoroborate) (**2**) was prepared as described previously.[14] It was hydrogenated (H$_2$/Pt) to the tetrahydro derivative (**1**) using the procedure described for the perchlorate salt.[6] Aromatic halides were from Aldrich Chemical Co., except for 2,6-dibromobiphenyl, which was supplied by Dr. H. L. Finkbeiner. Deuterated solvents and NaBD$_4$ were from Aldrich.

Procedures. Dehalogenation with 2 and NaBH$_4$. To a solution of 100 mg (2.6 mmol) of sodium borohydride in 6 mL of ethanol (N$_2$ atmosphere) was added a solution of 35 mg (0.07 mmol) of nickel complex **2** in 3 mL of acetonitrile. After 10 min, the initial green color had faded to a pale violet. Then 294 mg (1.42 mmol) of 1-bromonaphthalene was added (neat), and the solution was kept at 40–45 °C for 1 h, at which point the gentle effervescence had ceased. Water (30 mL) was added and the product was extracted into ether, washed with water, and dried (Na$_2$SO$_4$). Removal of solvent left crystalline naphthalene, 174 mg (96%), which contained 0.6% 1,1′-binaphthyl as determined by GLC.

Dehalogenation with 1 and NaBH$_4$. To a solution of 60 mg (1.6 mmol) of sodium borohydride in 2 mL of ethanol (N$_2$

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[24] Bunnett, J. F. *Chem. Soc. Q. Rev.* **1958**, *12*, 1.

[25] Brown, J. F., Jr.; Bedard, D. L.; Brennan, M. J.; Carnahan, J. C.; Feng, H.; Wagner, R. E. *Science* **1987**, *236*, 709. Brown, J. F., Jr.; Wagner, R. E.; Feng, H.; Bedard, D. L.; Brennan, M. J.; Carnahan, J. C.; May, R. J. *Environ. Toxicol. Chem.* **1987**, *6*, 579. Brown, J. F., Jr.; Wagner, R. E. *Environ. Toxicol. Chem.* **1990**, *9*, 1215. Quensen, J. F., III; Tiedje, J. M.; Boyd, S. A. *Science* **1988**, *242*, 752. For reviews, see: Abramowicz, D. A. *CRC Critical Reviews in Biotechnology*; Steward, G. G., Russell, I., Eds.; CRC Press Inc.: Vol. 10, pp 241–251. Bedard, D. L. *Biotechnology and Biodegradation*; Kamely, D., Chakrabarty, A., Owenn, G. S., Eds.; Adv. App. Biotechnol. Series, Vol. 4, Portfolio Publishing Co., The Woodlands, TX, pp 369–388.

[26] Gantzer, C. J.; Wackett, L. P. *Environ. Sci. Technol.* **1991**, *25*, 715. Krone, U. E.; Thauer, R. K.; Hogenkamp, H. P. *Biochemistry* **1989**, *28*, 4908.

[27] Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1991**, *56*, 3646.

[28] Morrell, D. G.; Kochi, J. *J. Am. Chem. Soc.* **1975**, *97*, 7262.

atmosphere) was added a solution of 90 mg (0.49 mmol) of 4-bromobenzonitrile in 3 mL of acetonitrile. Addition of 25 mg (0.05 mmol) nickel complex **1** dissolved in 2 mL of acetonitrile produced a blue-violet solution which was kept at 40 °C for 50 min. A mild effervescence was noted. Water (20 mL) was added and the product was extracted into 5.0 mL of ether containing naphthalene as internal standard. GLC analysis revealed only benzonitrile (101% based on internal standard) with no detectable benzylamine or 4-bromobenzylamine.

The data in Table 1 were obtained from reactions carried out by the procedures described above, any modifications being noted.

Dehalogenation with 1 and N_2H_4. A solution of 30 mg (0.06 mmol) **1** in 1 mL of water was added to 0.4 mL of hydrazine hydrate (85% N_2H_4) in 2 mL of water (N_2 atmosphere). Addition of 70 mg (0.34 mmol) of 1-bromonaphthalene dissolved in 5 mL of ethanol gave a homogeneous solution which was held at 60 °C. Samples (*ca.* 0.5 mL) were removed and added to 2 mL of 5% aqueous phosphoric acid and 1 mL of ether, and the ether solution was analyzed by GLC. Conversion to naphthalene was 37% after 100 min. A second 0.4-mL portion of hydrazine hydrate was then added; after 205 min, conversion was 58%. Addition of a third 0.4-mL portion led, after 24 h, to 98% conversion. In a separate experiment 100 mg (0.48 mmol) of 1-bromonaphthalene was converted to 52 mg (85%) of crystalline naphthalene, isolated as colorless crystals, during 24 h at 60 °C. When the catalyst (**1**) was omitted, naphthalene was not formed.

1,2,4-Trichlorobenzene (25 mg, 0.14 mmol) was dissolved in 3 mL of ethanol and 40 mg (0.08 mmol) of complex **1**, dissolved in 3 mL of water, was added. Hydrazine hydrate (0.15 mL) was added in one portion (N_2 atmosphere). After 4 h at 63 °C, a sample was quenched as described above, and GLC analysis indicated 68% starting material, 23% *p*-dichlorobenzene, 6.8% *meta*, and 1.6% *ortho*.

1,2,3-Trichlorobenzene under similar conditions gave 93% conversion during 24 h at 62 °C, to yield 51% *meta*- and 41% *ortho*-dichlorobenzenes, plus 1.5% chlorobenzene.

Effect of Cumene. Parallel reaction mixtures were prepared, one with the indicated quantity of cumene and the other without. An identical quantity of a stock solution of **1** in acetonitrile was added to each reaction vessel (N_2 atmosphere) and the reaction was allowed to proceed at 45 °C while samples were removed, quenched in water/ether, and analyzed by GLC. Results are shown in Figures 2 and 3. *Bicumyl* was identified by GC/MS (*m/e* 119, 91, 79, 77, 51, 41) comparison with an authentic sample prepared as described previously.[29]

Deuterium Incorporation. (a) 1,2,4,5-Tetrachlorobenzene (75 mg, 0.35 mmol) was dissolved in 9 mL of acetonitrile at 40 °C and $NaBD_4$ (100 mg, 2.5 mmol) dissolved in 1 mL of water was added. The nickel complex **1** (30 mg, 0.06 mmol) dissolved in 1 mL, acetonitrile was added under nitrogen. After 80 min at 40 °C, GLC analysis indicated 68% 1,2,4-trichlorobenzene, 19% starting material, and 12% dichlorobenzenes. Passage of the product mixture through a silica gel column with hexane as solvent and eluent served to remove the dichlorobenzenes in the early eluate. The trichlorobenzene product, containing some unreacted tetrachlorobenzene, was examined by proton NMR. The singlet derived from tetrachlorobenzene (δ 7.57) was well removed from the three signals of 1,2,4-trichlorobenzene (**3**) (H_a δ 7.47, H_b 7.38, H_c 7.19). Integration ratios of the three signals were 1.00:0.998:0.043.

When a similar procedure was followed using $NaBH_4$ and D_2O, the integration ratios were 1.00:1.02:1.00.

(b) 1-Bromonaphthalene was treated with $NaBH_4$ (or $NaBD_4$) in acetonitrile–H_2O (or D_2O) in the presence of nickel complex **2**. The reaction was allowed to proceed until conversion was complete. Naphthalene was isolated and examined by proton NMR. Deuterium incorporation was calculated from the integration ratio of α and β hydrogens. Results are given in Table 3. Experiments with the ethanol–acetonitrile solvent system were carried out as described previously and the deuterium incorporation results, determined in the same way, are also given in Table 3.

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[29] Bors, D. A.; Kaufman, M. J.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6975. The author is grateful to Mr. Sreekumar Ramakrishnan for carrying out this preparation.