Pergamon

Tetrahedron Vol. 51, No. 15, pp. 4471-4482, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01134-6

Titanium Catalyzed Reduction of Aromatic Halides by Sodium Borohydride

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Abstract: The reduction of aryl halides by sodium borohydride is catalyzed by titanium complexes; di(cyclopentadienyl)titanium dichloride (titanocene dichloride) is highly effective. The reaction scope and mechanism are solvent dependent. In dimethylformamide (DMF), an adduct of DMF and sodium borohydride is formed which reduces simple aryl halides by a non-radical, likely nucleophilic route. Dimethylamino- substituted products are formed, as are simple dechlorinated species. In dimethylacetamide or in ethers, a radical-based reaction involving activated titanocene borohydride takes place, and only dechlorinated products result.

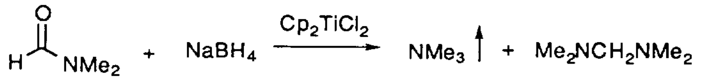
INTRODUCTION

Given the widespread occurrence of chloroorganics as environmental pollutants,[1] it was our interest to develop methodology which could be used to reductively dechlorinate such species under mild conditions. At the outset of our studies, various transition metal complexes had been explored as catalysts to activate sodium borohydride for such reduction, but no generally appealing methodology had yet emerged. For example, nickel salts had been exploited for this purpose,[2] but product contamination with nickel was possible, and many nickel compounds are classified as hazardous.[3] It had also been reported[4] that di(cyclopentadienyl)titanium dichloride (titanocene dichloride) could catalyze the reduction of certain aryl halides by sodium borohydride, but only aryl iodides were reduced efficiently; aryl chlorides were not. Furthermore, this process took place in dimethylformamide (DMF), and DMF has considerable toxicity. These observations not withstanding, the notion of developing titanium complex-catalyzed reduction of aryl halides by sodium borohydride was intriguing: Hydrolyzed byproducts of reduction - borates and TiO_2 - are relatively benign. We have now developed a titanium complex catalyst system which is in fact effective for reduction of aryl chlorides. Interestingly, it involves a mechanism and active reagents which are entirely different from those which exist in DMF: In DMF, reduction occurs by a nucleophilic pathway effected by a complex borohydride reducing agent; in other solvents, reduction occurs by a radical pathway involving reduced titanium complex catalysts.

RESULTS AND DISCUSSION

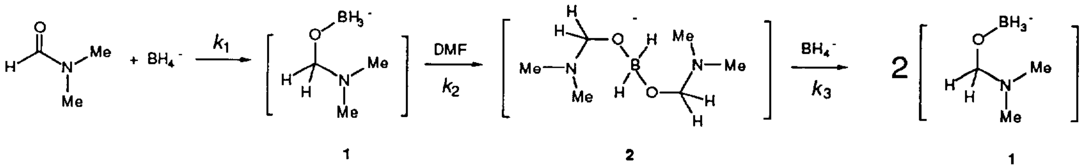
Reduction of Polychlorinated Aryl Chlorides by Sodium Borohydride, Catalyzed by Titanium Complexes in DMF.

The reaction between sodium borohydride and DMF. It is well known that mixing $NaBH_4$ and DMF at elevated temperature is dangerous,[5] especially at high concentration. Following an induction period, rapid evolution of a flammable gas can result, which has been identified as trimethylamine.[5e] It has been suggested[5e] that adventitious acid present in DMF can initiate the condensation of DMF and $NaBH_4$ to give an adduct that is a powerful reducing agent which subsequently gives trimethylamine by reduction of the DMF. When we mixed $NaBH_4$ with DMF (at 95 °C), we did note trimethylamine,[6] but concomitant evolution of bis(dimethylamino)methane also occurred, and product formation was slow, even after two hours. It seemed possible that a Lewis acidic titanium complex could take the place of the putative, adventitious acid, so that the reducing power of this adduct could be systematically exploited. Indeed, when Cp_2TiCl_2 (0.6 mmol) was added to a fresh sample of $NaBH_4$ (30.0 mmol) in DMF, a 30 min induction period was noted (95 °C), followed by rapid effervescence of trimethylamine. The duration of the induction period depended on the concentration of added titanium complex:[6] at 0.3 mmol Cp_2TiCl_2, the induction period was 50 min; at 0.16 mmol Cp_2TiCl_2, it was 60 min. In each case, about 15 mmol of Me_3N and an approximately equal amount of bis(dimethylamino)methane were evolved; the rate of formation of the amines following the induction period was qualitatively independent of Ti complex concentration. Thus, the role of the Ti species seems only to shorten the induction period for formation of the active reducing reagent; a Ti reagent, *per se*, is not the active reagent for the DMF reduction.


(1)

$$\mathrm{HC(O)NMe_2} + \mathrm{NaBH_4} \xrightarrow{\mathrm{Cp_2TiCl_2}} \mathrm{NMe_3}\uparrow + \mathrm{Me_2NCH_2NMe_2} \qquad (1)$$

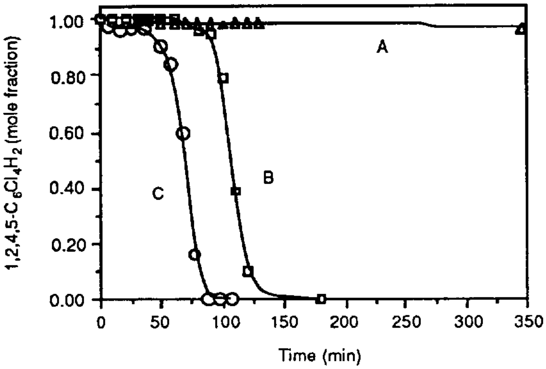
The nature of the reducing agent. Reaction between $NaBH_4$ and DMF apparently generates an adduct formulated[6] as Na^+ $BH_3(OCH_2NMe_2)^-$, **1**: when $NaBH_4$ (1.1 mmol) and Cp_2TiCl_2 (0.04 mmol) in DMF-d_7 (1 ml) were heated at 95 °C for *ca.* 1 h and then cooled to 25 °C, ^{11}B NMR analysis of the reaction mixture showed, in addition to the quintet for BH_4^- at δ -39.11 (*versus* $Et_2O{\bullet}BF_3$), a new quartet, at δ -7.95 ($^1J_{B\text{-}H}$ = 97 Hz), comparable in chemical shift to $BH_3(OCH_3)^-$ (δ -7.0; $^1J_{B\text{-}H}$ = 88 Hz).[7] We proposed[6] that reaction between **1** and DMF gives **2**, and rapid ligand metathesis between **2** and BH_4^- generates 2 equivalents of **1**. Therefore the concentration of **1** increases dramatically after its initial formation, and **2** can yield either reduced (trimethylamine) or dimethylaminated product (bis[dimethylamino]methane).

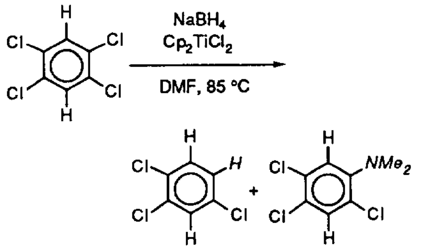


Scheme 1. Proposed autocatalytic production of **1**, in which **1** or **2** can serve as either a H^- or a NMe_2^- donor, and in which k_2 and $k_3 > k_1$.

Reduction of Aryl Chlorides. Simple aryl chlorides are reported[4] to be unreactive with the $NaBH_4$-DMF mixture; we found that polychlorinated aryl halides could be reduced. For example, 1,2,4,5-tetrachlorobenzene was converted to a mixture of 1,2,4-trichlorobenzene and N,N-dimethyl-2,4,5-trichloroaniline (1:1.2) using $NaBH_4$ (10 equiv.) and Cp_2TiCl_2 (0.1 equiv.) in DMF after 2 hours at 85 °C (Equation 2). Similarly, 1,3,5-trichlorobenzene gave N,N-dimethyl-3,5-dichloroaniline and a trace of 1,3-dichlorobenzene. As had been found for amine generation, no reduced product was detected at least for 4 h in the absence of Cp_2TiCl_2 (Figure 1A).

When 10 m*M* Cp_2TiCl_2 was added to a similar mixture of $NaBH_4$ and DMF, the reduction of 1,2,4,5-tetrachlorobenzene occurred very slowly ($k_{obs} = 3.7 \times 10^{-5}$ sec^{-1}) for 60 min, followed by rapid reduction ($k_{obs} = 1.4 \times 10^{-3}$) (Figure 1C). By decreasing the Cp_2TiCl_2 concentration to 3 m*M*, the rate of reduction was not increased, but the induction period was lengthened to 120 min (Figure 1B). (All reactions were conducted under pseudo-first order conditions using 0.1*M*, aryl halide and 1.0*M*, $NaBH_4$). When $NaBH_4$ and Cp_2TiCl_2 were heated in DMF at 95 °C for 60 min and then 1,2,4,5-tetrachlorobenzene was added, the rate of reduction of the halide was nearly the same as when the aryl halide was present initially. Therefore, the aryl halide does not participate in the $NaBH_4$-Cp_2TiCl_2-DMF reaction induction period.

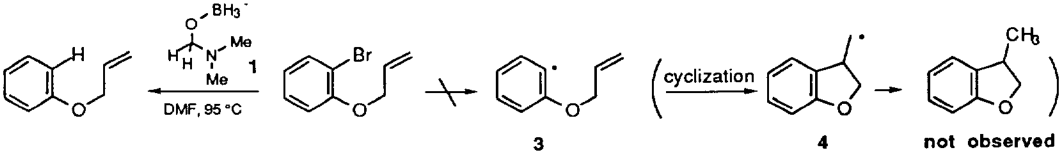




(2)

Figure 1. Reduction of 1,2,4,5-tetrachlorobenzene.

The mechanism of reduction in DMF. To probe the mechanism of aryl halide reduction, 2-bromophenyl allyl ether was treated with a freshly prepared solution of **1** at 95 °C; the only isolable product was phenyl allyl ether (10%). Since 2-allyloxyphenyl radical **3** rapidly cyclizes to **4** ($k_{cycl} = 6.3 \times 10^9$ sec^{-1} at 25 °C),[8] reduction involving a radical intermediate appears to be excluded (Scheme 2). Further tests also argued against a radical process. For example, nitrobenzene, acrylonitrile or dioxygen, each a radical inhibitor,[9] had no effect on reduction rates or induction periods, and when $NaBH_4$, DMF and Cp_2TiCl_2 were heated at 95 °C for 1 h with a mixture of 1,3,5-trichlorobenzene and TEMPO (10 equiv), only dimethy-3,5-dichloroaniline and no TEMPO-trapped products[10] were obtained.

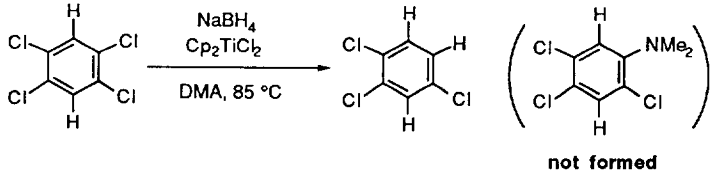


Scheme 2. Reduction of 2-bromophenyl allyl ether by **1**.

Summary. The reduction of aryl halides by sodium borohydride in DMF in the presence of titanium complexes occurs by an autocatalytic process in which the titanium complex promotes the addition of $NaBH_4$ to DMF to generate **1**. Complex **1** reduces or dimethylaminates DMF or aryl chlorides, and aryl chloride reduction occurs by a non-radical, likely nucleophilic pathway. Titanium complexes, themselves, are not the active reducing agents, and overall reaction times are affected by varying concentrations of added titanium species simply by adjustment of induction periods for the formation of **1**. This reduction procedure suffers practical limitations: Rapid formation of trimethylamine and tetramethyldiaminomethane is not only dangerous, but also consumes $NaBH_4$ in byproduct formation. These drawbacks, plus the fact of DMF toxicity,[11] prompted us to further explore aryl halide reduction by $NaBH_4$ catalyzed by titanium complexes.

Reduction of Polychlorinated Aryl Chlorides by Sodium Borohydride, Catalyzed by Titanium Complexes in Amide Solvents Other than DMF.

In the expectation that steric bulk would cause suppression of borohydride attack on solvent, dimethylacetamide (DMA), N-methylpyrrolidinone (NMP), and tetramethylurea were examined[12] as reaction media for aryl halide reduction, and significant differences were noted *versus* the DMF system. For example, 1,2,4,5-tetrachlorobenzene was reduced smoothly without an induction period in DMA by $NaBH_4$ in the presence of Cp_2TiCl_2 (Equation 3), but reduction occurred quite slowly (k_{obs}= 2.3 x 10^{-5} sec^{-1}; Table I). Also, pseudo-first-order rate constants for reduction in DMA were dependent on the concentration of titanium complex added, and only trichlorobenzene was produced; no products of solvent fragment attack on the arene were observed.



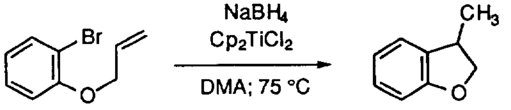
(3)

Cp_2TiCl_2 (M)	Solvent	k_{obs} (sec^{-1})^a	k_{obs} (solv)/k_{obs} (DMF)
0.01	DMF^b	1.41 x 10^{-3}	1.0
0.01	DMA	2.27 x 10^{-5}	0.016
0.01	NMP	2.40 x 10^{-5}	0.017
0.01	NMP	4.02 x 10^{-5}	0.029^c
0.02	tetramethylurea	6.87 x 10^{-5}	0.048

^{a}0.1 *M* $C_6H_2Cl_4$; 1.0 *M* $NaBH_4$; 95 °C; ^{b}Rate measured after induction period; ^{c}LiCl (1.2 *M*) added

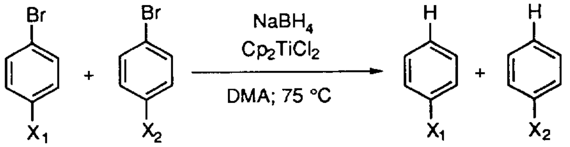
Table I. Reduction rates for 1,2,4,5-tetrachlorobenzene in various solvents.

The mechanism of reduction in DMA. In marked contrast to results obtained in DMF, when 2-bromophenyl allyl ether was treated with Cp_2TiCl_2-$NaBH_4$ in DMA, 3-methyldihydrobenzofuran was produced as the sole product. This suggests that aryl radical **3** was generated, which was trapped at a rate slower than that of cyclization.[8]



(4)

A series of substituted bromobenzenes was studied under competition conditions, and relative reactivities were found to be strongly substituent dependent. If reduction of the aryl halide occurred by nucleophilic attack, a simple correlation between $\log(k_X/k_H)$ and σ_p would exist;[13] no good correlation was found.[12] Especially noteworthy are relative rates for reduction of CH_3- and CH_3O-substituted analogs; these would be predicted to be quite different according to their σ_p values. In contrast, an excellent correlation between relative reduction rates and aryl halide reduction potentials was observed,[12] suggesting that reduction proceeded by an outer sphere electron transfer pathway: the less negative the reduction potential, the faster chemical reduction.



(5)

Substituent X	k_X/k_H	$\log(k_X/k_H)$	σ_p[13]	$E_{1/2}$(V)[14]
NMe_2	0.23	-0.64	-0.63	-1.97
OMe	0.57	-0.24	-0.28	-1.84
Me	0.58	-0.24	-0.14	-1.84
H	1.00	0	0	-1.81
F	3.28	0.52	0.15	
Cl	5.80	0.76	0.24	-1.61
CF_3	10.3	1.01	0.53	-1.53

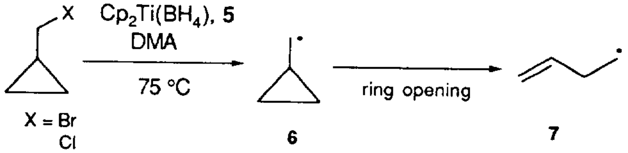
Table II. Relative rates for reduction of *p*-substituted bromobenzenes.

Studies of both electrochemical reduction of aryl halides[14] and oxidative addition[15] of aryl halides to low-valent metal complexes *via* electron transfer show rapid halide loss from an initially formed aryl halide radical anion which gives the aryl radical, consistent with reduction results for 2-bromophenyl allyl ether. The aryl radical generated could abstract hydrogen from either free[16] or Ti-coordinated borohydride or solvent. When 4-bromochlorobenzene was treated with $NaBD_4$ and Cp_2TiCl_2 in DMA at 52 °C, both chlorobenzene (25%) and chlorobenzene-d_1 (75%) were obtained in 76% overall yield.

Summary. Rates of reduction of aryl halides in DMA or other amide solvents were slower than in DMF, but, since solvent attack was suppressed, the efficiency of $NaBH_4$ usage improved dramatically. However, catalyst turnover was low and more than one equivalent of $NaBH_4$ was used for C-X bond reduction.

Reduction of Aryl Halides by $NaBH_4$ Catalyzed by Titanium Species in Ethereal Solvents.

The active catalyst for reduction of aryl halides in ethers. Titanocene borohydride, $Cp_2Ti(BH_4)$, **5**, is readily prepared from Cp_2TiCl_2 and $NaBH_4$ in various solvents,[17] and therefore we considered **5** to be possibly the active species for reduction of aryl halides in non-DMF amide solvents. Titanocene borohydride did indeed smoothly reduce bromo- or chloromethylcyclopropane to a mixture of methylcyclopropane and 1-butene (in approx. ratios 2:1 and 1:1, respectively); the formation of ring opening products suggests and intermediate cyclopropylmethyl radical (**6**) which rapidly ring opens[18] to **7** ($k = 2.1 \times 10^8$ sec^{-1} ; see Scheme 5). But, the reactivity of **5** toward aryl halides was quite low. For example, no reduction of 4-bromochlorobenzene was observed in 3h at 54 °C in DME or 2-methoxyethyl ether, while complete reduction of this substrate occurred in DMA in 30 min. Interestingly, although Cp_2TiCl_2 and $NaBH_4$ were active for reduction of 4-bromochlorobenzene in DMA at 50 °C, no reduction occurred when preformed **5** was heated with 4-bromochlorobenzene under similar conditions. However, when $NaBH_4$ was added to this reaction mixture, catalyzed reduction occurred immediately. Furthermore, when a mixture of $NaBH_4$, aryl halide, Cp_2TiCl_2 and 2-methoxyethyl ether was heated at 55 °C for four hours no reduction was observed, but addition of DMA initiated reduction. Clearly, although **5** alone is inactive for aryl halide reduction, it can be activated to this end.



Scheme 3. Reduction of bromo- and chloromethylcyclopropane by **5** occurs by a radical pathway.

We proposed[19] that small amounts of N,N-dimethylethylamine might be generated by reduction of DMA, and this amine might somehow activate **5**. To test this hypothesis, $NaBH_4$, Cp_2TiCl_2, and 4-bromochlorobenzene were heated in diglyme at 55 °C for 7h. Complex **5** formed rapidly, but no reduction was observed; yet when N,N-dimethylethylamine was added, reduction occurred immediately. Furthermore, the reduction rate increased with increased amine concentration.

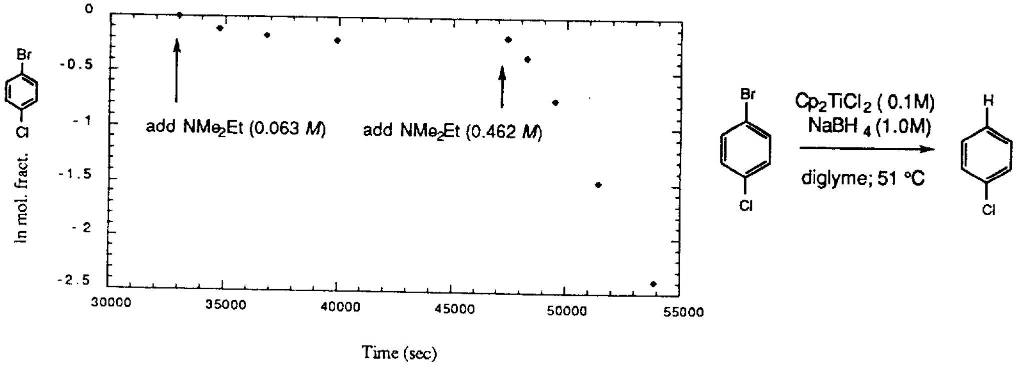


Figure 2. Reduction of aryl halides by **5** is promoted by the addition of an amine.

Relative rates for 4-bromochlorobenzene reduction using equimolar amounts of $NaBH_4$ and an amine were measured (Table III). Pseudo-first order rate constants depended on the structure of the added amine and showed an adverse effect of steric hindrance at nitrogen. For example, rates of reduction using pyridine, 2-picoline and 2,6-lutidine were 1.01; 0.3; 0.06, respectively. These pyridines react[20] with low steric demand Lewis acid BH_3 with heats of formation decreasing slightly: pyridine (-20.2 kcal/mole); 2-picoline (-19.7); and 2,6-lutidine (-16.4). They react[20] with more sterically demanding BMe_3 with heats of formation decreasing more significantly: pyridine (-21.4 kcal/mole); 2-picoline (-16.1); and 2,6-lutidine (> -9). Rate trends for reduction of 4-bromochlorobenzene seem to correlate with data for the interaction of BMe_3 with pyridines, suggesting that coordination of the pyridine might occur with the sterically bulky titanium center, rather than solely with a BH_3-derived unit.

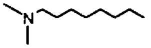
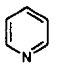
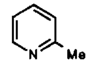
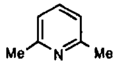
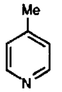
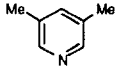
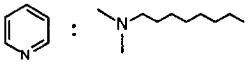
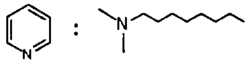
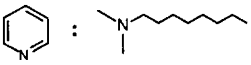
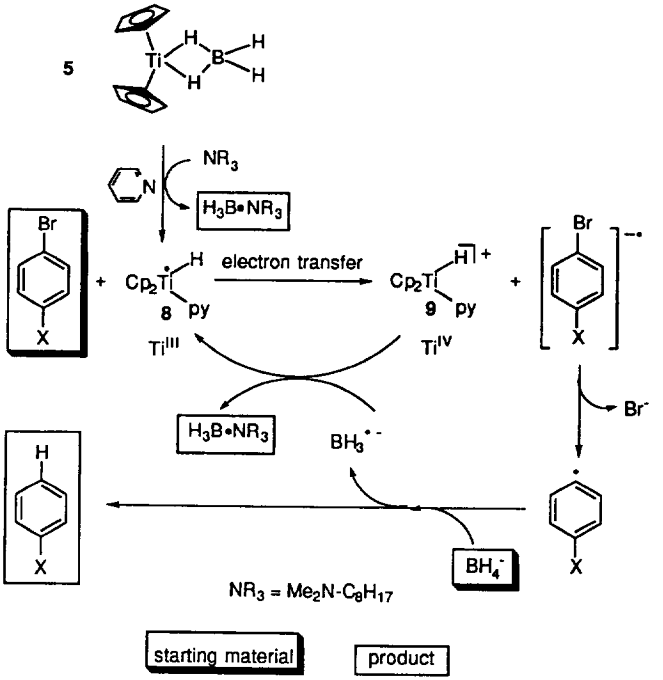
Amine (0.6 *M*)	k_{obs} (h^{-1})
	0.06
	1.01
	0.34
	0.03
	0.64
	0.84
 33% : 67%	1.13
 50% : 50%	1.40
 17% : 83%	0.90

Table III. Rates of aryl halide reduction depend on the structure of the added amine.

Simple aliphatic amines are less effective catalyst promoters than are unhindered pyridines, even though the aliphatic amines are the stronger Brønsted bases. Pronounced synergism was noted when both an aliphatic amine and an aromatic amine were used to promote aryl halide reduction by **5**. For example, reduction rates (k_{obs}; h^{-1}) for 4-bromochlorobenzene used various amines at constant concentration and were: pyridine, 1.01; N,N-dimethyloctylamine, 0.06; N,N-dimethyloctylamine and pyridine (1:1), 1.4. ^{11}B NMR analysis of the reaction between **5** and pyridine showed a signal at -10.6 ppm, corresponding to BH_3•pyridine;[21] ^{11}B NMR analysis of the reaction between **5** and N,N-dimethyloctylamine showed a signal at -8.6 ppm, corresponding to BH_3•NMe_2(*n*-C_8H_{17});[21] but ^{11}B NMR analysis of the reaction between **5** and a 1:1 mixture of N,N-dimethyloctylamine and pyridine showed a signal only at -8.6 ppm, indicating preferential formation of BH_3•NMe_2(*n*-C_8H_{17}). Since catalytic rates do depend strongly on the structure of the added pyridine, we believed the measured synergism derives from coordination of the aliphatic amine with BH_3 and the pyridine with Cp_2TiH fragment formed concomitantly by cleavage of the borohydride ligand of **5**, which gives active species **8**, which catalyzes aryl halide reduction as shown in Scheme 4.



Scheme 4. The general scheme for catalyzed reduction of aryl halides.

Application to the reduction of polychlorinated biphenyls (PCBs). For reduction of a family of substituted bromobenzenes the less negative the reduction potential, the faster the reduction.[12] In the context of PCB treatment, phenyl group substitution in an aryl halide should facilitate reduction: Comparative $E_{1/2}$ data[14] show that *p*-phenyl or *p*-Cl group substitution have similar effects on the reduction potential of substituted *bromo*benzenes (-1.56V and -1.61V), and both substrates were reduced at comparable rates by the Cp_2TiCl_2-$NaBH_4$-amine system (1.11 vs. 1.01 h^{-1}). Based on electrochemical data for *p*-substituted bromo- and chlorobenzenes[14] the rate for reduction of 4-chlorobiphenyl was predicted to be *ca.* 0.2 h^{-1}, comparable to that of *p*-dichlorobenzene. Indeed, reduction of 4-chlorobiphenyl or *p*-dichlorobenzene occurred at nearly identical rates.

Monochlorobiphenyls have the most negative electrochemical reduction potentials of the PCB congeners,[22] suggesting that their chemical reduction rates should be limiting for overall reduction of a complex mixture of PCBs to biphenyl, itself. Since monochlorobiphenyls are readily reduced to biphenyl by the Cp_2TiCl_2-$NaBH_4$-amine system, chemical reduction of Aroclor® 1248 (Figure 3a), a common commercial mixture of PCBs which contains a substantial fraction of tetra- and pentachlorinated congeners,[1] was investigated. Under standard conditions for aryl halide treatment, complete reduction to biphenyl was noted after 24 h at 125 °C (Figure 3d).

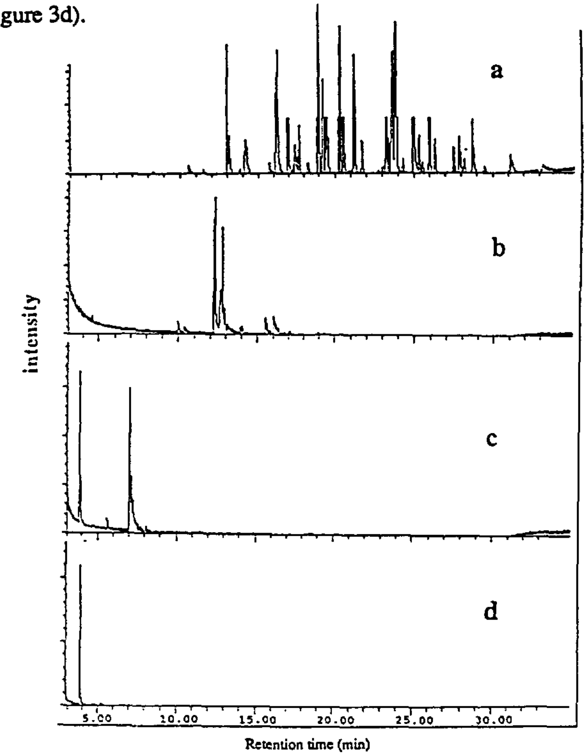


Figure 3. Reduction of Aroclor 1248® by Cp_2TiCl_2-$NaBH_4$-amine.

CONCLUSIONS

Reduction of aryl halides by sodium borohydride promoted by titanium catalysts in various solvents was investigated, and we found that reduction reaction mechanisms are strongly solvent dependent. In DMF, a new species, $NaBH_3(OCH_2NMe_2)$, is formed autocatalytically; only the induction period, and not the rate of aryl halide reduction, depends on the concentration of titanium species added. This new species reduces and dimethylaminates organic halides by a non-radical, likely nucleophilic pathway. The simple change of solvent from DMF to DMA gives rise to a completely different reduction system in which reaction occurs by an outer sphere electron transfer pathway, and the rate of reduction depends on the concentration of titanium complex added. Aryl halides are reduced by an electron transfer process, leading to an intermediate aryl radical. Reduction of aryl halides is promoted by amines in ethereal solvents, in which the amine cleaves $Cp_2Ti(BH_4)$ to give borane-amine and titanium-amine adducts. A synergic effect was noted for a mixture of aliphatic and aromatic amines, and the active species for aryl halide reduction is likely a (Cp_2TiH)-amine adduct. Close to stoichiometric amounts of amine and $NaBH_4$ and 0.01-0.05 equiv Ti can be used for efficient aryl halide reduction. This system easily reduces complex mixtures of PCB congeners to biphenyl. Reasonable estimates of comparative PCB congener reduction rates can be made on the basis of available electrochemical data. Finally, in this last context, since hydrolyzed reduction reaction mixtures yield only biodegradable organic components and NaCl, TiO_2 and sodium borate by-products, this new titanium catalyzed reduction procedure might be environmentally, as well as chemically, benign.

EXPERIMENTAL SECTION

General Methods. Operations were performed using either standard Schlenk techniques under dry N_2, or in a Vacuum Atmospheres dry box, or under air. Dimethylformamide, dimethylacetamide, N-methylpyrrolidinone and tetramethylurea were used as received. Dry dimethylacetamide was obtained by distillation over CaO under N_2. All amines were used as received, or were dried with activated molecular sieves. GC yields were determined using an internal standard. ^{11}B NMR spectra were recorded on a Bruker WM-250 NMR spectrometer using an internal capillary reference of $BF_3 \bullet OEt_2$.

Reduction of 2-bromophenyl allyl ether by $NaBH_4$-Cp_2TiCl_2-DMF. A flask was charged with $NaBH_4$ (1.135 g, 30 mmol), Cp_2TiCl_2 (75 mg 0.3 mmol) and DMF (30 ml), and the mixture was heated at 95 °C for 90 min. 2-Bromophenyl allyl ether (153 mg, 0.072 mmol) was added, and the reaction mixture was heated at 75 °C for 2 hr. After standard workup, phenyl allyl ether was obtained as the only reduction product (10%).

Gas formation measurements for the $NaBH_4$-Cp_2TiCl_2-DMF system. A flask was charged with $NaBH_4$ and Cp_2TiCl_2 in DMF and was attached through a water-cooled condenser to a gas buret. The flask was heated at 87 °C. The volume of gas evolved was monitored, and GC-MS analysis showed the formation of trimethylamine as a major component of the gas phase; tetramethyldiaminomethane was present in the condensed phase. Similar measurements were made in the absence of titanium complex.

Competitive reduction of substituted aryl bromides by the $NaBH_4$-Cp_2TiCl_2-DMA system. A flask was equipped with a magnetic stir bar and was charged in the dry box with 4-bromochlorobenzene (384 mg, 2.01 mmol), 4-bromofluorobenzene (367 mg, 2.10 mmol), sodium borohydride (150 mg, 4.0 mmol) and Cp_2TiCl_2 (125 mg, 0.5 mmol). Freshly distilled DMA (5 ml) was added under N_2, and the reaction mixture was heated at 75 °C for 5 hours. The reaction mixture was cooled to 0 °C and quenched with water. The organic products were extracted into diethyl ether, and octane was added as an internal standard. GC analysis showed the formation of chlorobenzene (0.74 mmol) and fluorobenzene (0.48 mmol). Relative reactivities were obtained from product ratios corrected for relative concentrations of starting materials and were compared with the rate for bromobenzene reduction. Similar experiments were conducted with other bromobenzenes.

Reduction of 2-bromophenyl allyl ether by $NaBH_4$-Cp_2TiCl_2-DMA. A flask was charged in the dry box with 2-bromophenyl allyl ether (153 mg, 0.72 mmol), $NaBH_4$ (255 mg, 6.7 mmol) and Cp_2TiCl_2 (140 mg, 0.56 mmol). DMA (6 ml) was added, and the reaction mixture was heated at 75 °C for 4 hr. After standard workup, 3-methyldihydrobenzofuran (57%) was obtained as the sole reduction product; GC analysis showed no phenyl allyl ether was produced. No reduction of 2-bromophenyl allyl ether was observed in 24 h in a control experiment performed without Cp_2TiCl_2.

^{11}B NMR studies of reactions between Cp_2TiBH_4 and amines. (a) A quartz NMR tube was charged with $Cp_2Ti(BH_4)$ (20 mg) and 0.5 ml of THF-d_8 in the dry box, and a capillary containing BF_3 etherate was inserted. Pyridine (30 µl) was added, and the reaction mixture was heated at 75 °C for 5 min; ^{11}B NMR analysis at 25 °C showed a signal at -10.4 ppm, corresponding to $H_3B{\bullet}$pyridine;[21] (b) similarly, N,N-dimethyloctylamine (30 µl) was added, and the reaction mixture was heated at 75 °C for 5 min; ^{11}B NMR analysis at 25 °C showed a signal at -8.6 ppm, corresponding to $H_3B{\bullet}NMe_2$(*n*-octyl);[21] (c) a (1:1) mixture of pyridine and N,N-dimethyloctylamine (total 30 µl) was added to a similar preparation of $Cp_2Ti(BH_4)$, and the reaction mixture was heated at 75 °C for 5 min; $^{11}B\{^1H\}$ NMR analysis at 25 °C showed a signal at -8.6 ppm, corresponding to $H_3B{\bullet}NMe_2$(*n*-octyl).

Reduction of Aroclor® 1248 by $NaBH_4$-Cp_2TiCl_2-Amine. Aroclor® 1248 (1.0 gm; 13.7 mmol chlorine; Figure 3a) was treated with Cp_2TiCl_2 (171 mg; 0.687 mmol; 0.05 equiv.), $NaBH_4$ (622 mg; 16.44 mmol; 1.2 equiv.), pyridine (0.68 ml ; 8.4 mmol; 0.61 equiv.) and N,N-dimethyloctylamine (1.73 ml ; 8.4 mmol; 0.61 equiv.) at 125 °C in triglyme. After 12 min, a mixture was obtained consisting only of dichlorobiphenyls (80%) and trichlorobiphenyl (20%) (Figure 3b). After further heating at 125 °C (2 hours), the products were biphenyl (50%) and monochlorobiphenyl (Figure 3c). After 24 hrs, only biphenyl remained (Figure 3d).

Acknowledgements. The authors acknowledge support for this work given by Texas Eastern Transmission Corporation and by the National Science Foundation.

REFERENCES AND NOTES

1. For a general overview, see, Waid, J. S., Ed. *PCBs and the Environment*; CRC Press: Boca Raton, FL. 1986; D'Itri, F. M.; Kamrin, M. A., Eds. *PCBs: Human and Environmental Hazards*; Butterworth Publishers: Boston. 1983.
2. For examples, see, Roth, J. A.; Dakoji, S. R.; Hughes, R. C.; Carmody, R. E. *Environ. Sci. Technol.* **1994**, *28*, 80; Dennis, W. H., Jr.; Chang, Y. H.; Cooper, W. J. *Bull. Environ. Contam. Toxicol.* **1979**, *22*, 750. Because the catalyst formed under the reported reaction conditions is insoluble, its removal from treated soils or other solids would be problematic. Contamination of the treated materials with nickel would likely result, and many nickel compounds are classified as hazardous.
3. See, Sittig, M. , Ed. *Handbook of Toxic and Hazardous Chemicals and Carcinogens, Second Edition*; Noyes Publications: Park Ridge, NJ. 1985; p. 639.
4. Meunier, B. *J. Organomet. Chem.* **1981**, *204*, 345.
5. (a) Ganem, B.; Osby, J. O. *Chem. Rev.* **1986**, *86*, 763; (b) Strohmeier, W.; Steigerwald, H. *Z. Naturforsch. B: Anorg. Chem., Biochem., Biophys., Biol.* **1977**, *32b*, 111; (c) Babler, J. H.; Invergo, B. J. *Tetrahedron Lett.* **1981**, *22*, 11; (d) Entwhistle, E. D.; Boehm, P.; Johnstone, R. A. W.; Telford, R. P. *J. Chem. Soc. Perkin Trans. I.* **1980**, 27; (e) *Morton Intl. Sodium Borohydride Digest*, **1992**, 6.

6. Liu, Y.; Schwartz, J. *J. Org. Chem.* **1993,** *58,* 5005.
7. Golden, J. H.; Schreier, C., Singarma, B.; Williamson, S. M. *Inorg. Chem.* **1992,** *31,* 1533.
8. Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985,** *107,* 4594.
9. (a) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964,** *86,* 1807; (b) Kerber, R. C.; Urry, G. W.; Kornblum, N. *J. Am. Chem. Soc.* **1964,** *86,* 3904; (c) Barltrop, J. A.; Bradbury, D. *J. Am. Chem. Soc.* **1973,** *95,* 5085; (d) Groves, J. T.; Ma, K. W. *J. Am. Chem. Soc.* **1974,** *96,* 6527.
10. Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992,** *114,* 4983.
11. See, Sittig, M., Ed. *Handbook of Toxic and Hazardous Chemicals and Carcinogens, Second Edition*; Noyes Publications: Park Ridge, NJ. 1985; p. 646.
12. Liu, Y.; Schwartz, J. *J. Org. Chem.* **1994,** *59,* 940.
13. March, J. *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*; John Wiley & Sons: New York. 1992; 280.
14. Measured in DMF versus Ag/AgBr. See Sease, J. W.; Burton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968,** *90,* 2595. These data measure half-wave reduction potentials, $E_{1/2}$, and not E^0_{redox}. A quantitative correlation with E^0_{redox} would be required for a definitive proof of an outer sphere pathway. Obtaining E^0_{redox} for aryl halides from simple electrochemical studies can be difficult. Although $E_{1/2}$ depends on E^0_{redox}, it is also affected by variable electron transfer rates from the electrode to the substrate and the rate of halide loss from the radical anion intermediate (See, Savéant, J. M., *Adv. Phys. Org. Chem.* **1990,** *20,* 1). These complications can be handled for our series of strongly similar substrates through analysis of $E_{1/2(X)} - E_{1/2(H)}$, the difference between $E_{1/2}$ for a substituted bromobenzene and the parent bromobenzene, assuming that electron transfer rates from the electrode to variously *para*-substituted bromobenzenes and rates of halide loss from the radical anion intermediates are similar: $\Delta E^0_{(X)} = E^0_{(X)} - E^0_{(H)} \approx E_{1/2(X)} - E_{1/2(H)}$. See Bockris, J. O. M.; Khan, S. U. M. *Surface Electrochemistry. A Molecular Level Approach*; Plenum Press: New York. 1993; Ch. 6. The good correlation obtained between $\log(k_X/k_H)$ and $E^0_X - E^0_H$ suggests that an outer sphere process does indeed exist.
15. Tsou, T. T. and Kochi, J. K. *J. Am. Chem. Soc.* **1979,** *101,* 6319.
16. Aryl radicals photochemically generated from aryl halides react with BH_4^- by H· abstraction to give $BH_3^{\dot{-}}$. See, Barltorp, J. A.; Bradbury, D. *J. Am. Chem. Soc.* **1973,** *95,* 5085. Analogous H· abstraction from $(Ti^{IV})BH_4$ would give a $(Ti^{III})BH_3$ species.
17. Nöth, H.; Hartwimmer, R. *Chem. Ber.* **1960,** *93,* 2238.
18. (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976,** *98,* 7024. (b) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988,** *21,* 206.
19. Liu, Y.; Schwartz, J. Cavallaro, C. submitted.
20. Brown, H. C. *Boranes in Organic Synthesis*; Cornell University Press: Ithaca, NY. 1972.
21. Nöth H.; Wrackmeyer, B. *Nuclear Resonance Spectroscopy of Boron Compounds*, in *NMR Basic Principles and Progress*, Diehl, P.; Fluck, E.; Kosfled, R., Eds. Springer-Verlag: New York, 1978. Chapter 7, p. 88; Table LXV, p. 311.
22. Wiley, J. R.; Chen, E. C. M.; Chen, E. S. D.; Richardson, P.; Reed, W. R.; Wentworth, W. E. *J. Electroanal. Chem.* **1991,** *307,* 169.

(*Received* 25 *August* 1994)