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Organonickel chemistry in the catalytic hydrodechlorination of polychlorobiphenyls (PCBs): ligand steric effects and molecular structure of reaction intermediates

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Abstract

Soluble homogeneous organophosphorus–nickel complexes have been used to detoxify polychlorinated biphenyls (PCBs) by catalyzed hydrodechlorination using $NaBH_2(OCH_2CH_2OCH_3)_2$ as the hydrogen source. The reactions appear to proceed by NiL_3 oxidative addition into C–Cl bonds followed by hydrogenolysis of the metal–carbon bond. In model experiments with decachlorobiphenyl, the cone angle of the organophosphorus ligand L was shown to be a key factor controlling the magnitude and position of chlorine displacement. Hence, ligands leading to *para* displacement (e.g. $(o\text{-}MeC_6H_4O)_3P$), *meta–para* displacement (e.g. $(EtO)_3P$ and $(PhO)_3P$), and *ortho–meta–para* displacement (e.g. Me_3P and Et_3P) were found. Significantly, the highly toxic, coplanar dioxin precursor 3,3′,4,4′-tetrachlorobiphenyl, a *meta–para* chlorine-substituted congener, was dechlorinated quantitatively with the Et_3P catalyst system. Evidence for the presence of organonickel intermediates in the reaction mixtures was obtained by mass spectroscopic and X-ray diffraction studies. Of particular interest is the isolation of square planar complexes $p\text{-}C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ from the reaction of decachlorobiphenyl with $NaBH_2(OCH_2CH_2OCH_3)_2$–$(Et_3P)_2NiCl_2$ as the catalyst precursor and $m\text{-}C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ from decachlorobiphenyl–$Ni(1,5\text{-}C_8H_{12})_2$–$PEt_3$ at room temperature. All are oxidative addition intermediates and precursors for decachlorobiphenyl hydrodechlorination. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel complexes; Alkoxyborohydrides; Hydrogenolysis; Polychlorinated biphenyls; Catalysis; X-ray structures

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1. Introduction

Polychlorinated biphenyls (PCBs) [1] are ubiquitous in the global environment because of their biological and chemical stability and their historical widespread use in the power-generation industry. Because of the method of their manufacture, they exist in the environment as complex mixtures of chlorinated biphenyls referred to as congeners. In theory, 209 PCB congeners of the general formula $C_{12}H_xCl_{12-x}$ are possible. Their established toxicity to animals and man has been shown to be a function of molecular structure. Toxicological studies on PCB congener mixtures and individual PCB congeners have demonstrated a distinct correlation of toxicity with molecular structure. A simplified partitioning of PCB toxicity with molecular structure is as follows:

1. coplanar PCBs: *meta–para*-substituted congeners that possess dioxin-like toxicity (strong complexation to the A_h receptor protein and induction of cytochrome *P*448) and are known to bioaccumulate in the food chain;
2. orthogonal PCBs (e.g. decachlorobiphenyl) that show a low or zero toxic response (phenobarbital-type; induction of cytochrome *P*450);
3. conformationally restricted PCB congeners (*ortho*-substituted-congeners and metabolites) that are biomimics of estradiol and diethylstilbestrol and constitute a new type of toxic response, the so-called

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environmental estrogens or endocrine system disruptors.

Because of this complexity, PCBs have been the subject of numerous studies on catalytic and non-catalytic methods for detoxification by chlorine displacement from the biphenyl nucleus including stoichiometric displacement with bases, Wurtz reduction, and transition-metal-assisted hydrodehalogenation via hydrides.

2. Background

2.1. Heterogeneous transition-metal-assisted hydride reduction

Ordinarily, $NaBH_4$ will not reduce unactivated organic halides. However, in 1975 Dennis and Cooper [2] reported that the combination of a heterogeneous Ni_2B (boride) catalyst with sodium borohydride in alcohol hydrodechlorinated toxic polychlorinated hydrocarbon pesticides including the aliphatic substrates heptachlor, chlordane, and lindane and the aromatic substrates DDT and 2,4-D. In a comprehensive review of the extensive scope of transition-metal borides and aluminides for synthetically useful reactions, Ganem and Osby in 1986 [3] summarized the extensive literature including the scope of the studies on the reduction of halides. Combinations of $LiAlH_4$ with Co(II), Ni(II), Fe(II), Fe(III), Mn(II), Ti(III), Cr(III), and V(III) halides in THF were shown to be reducing agents for alkyl and aryl halides. Only Co, Ni and Ti were active in catalytic quantities.

The most extensive investigation of the hydrodechlorination of PCBs and chlorinated pesticides using heterogeneous nickel systems has been conducted by Pittman and co-workers, who demonstrated that nickel species generated from $NiCl_2$ and alkoxyborohydride in THF at reflux (68°C) were very active reductants for Mirex [4], pentachlorophenols [5], γ-lindane [6], and 4-chlorobiphenyl [7]. An alkoxyborohydride was chosen as a stronger hydride donor than $NaBH_4$ and helped avoid phase-separation problems. Impressively, Aroclor 1016, a mixture of di-, tri-, and tetrachlorobiphenyls, was nearly quantitatively reduced with the above reagent to 2-chlorobiphenyl and biphenyl [6,7]. Pittman inferred that highly active colloidal nickel was produced and interacted with C–Cl bonds. Colloidal nickel agglomeration led to deactivation of the system for hydrogenolysis [7].

2.2. Homogeneous transition-metal-assisted hydride reduction

Homogeneous systems for hydrodehalogenation of aliphatic and aromatic halogenated compounds have been reported for nickel [8–14], palladium [10,15], titanium [16], ruthenium [17], and cobalt as vitamin B_{12} [18]. In 1979, Lin and Roth [9] reported that aryl bromides could be reduced with a homogeneous system generated from $(Ph_3P)_2NiCl_2$ with $NaBH_4$ in DMF or THF. The active catalyst was suggested to be $(Ph_3P)_3Ni^0$. In 1989, Carfagna et al. [10] reported on deuterium incorporation studies for the hydrodehalogenation of aryl halides using MgH_2 activated by Ni(0) and Pd(0) complexes, providing insights into the reaction mechanism. For homogeneous $Ni(PPh_3)_4$, 60% deuterium incorporation into benzene from chlorobenzene suggested oxidative addition of Ni(0) into the C–Cl bond followed by deuterium abstraction from MgD_2. A radical chain process was suggested where an aryl radical is formed and abstracts hydrogen from the reaction medium (40% d_0).

In 1994, Roth et al. [11] reported an extensive study on the hydrodechlorination of specific PCB congeners by $NaBH_4$ with homogeneous and heterogeneous nickel catalysts with emphasis on inter- and intramolecular reaction rate selectivity for homogeneous Ph_3P–Ni(0) complexes. Extensive hydrogenolysis occurred in dimethylformamide solvent even at room temperature. Intramolecular selectivities for the rate of Cl displacement for selected di- and trichlorobiphenyls with Ph_3P–Ni(0) complexes were shown to be *ortho* ≪ *para* < *meta*, similar to measurements on a $Pd(II)L_2Cl_2$–$NaBH_4$ system [15]. These results imply a potential ligand steric effect for Cl displacement as a function of its position on the biphenyl nucleus. Roth et al. [11] argued that the conversion of NiL_4 to coordinately unsaturated NiL_3 is a key step followed by $Ni(0)L_3$ oxidative addition to Ar–Cl and includes a one-electron transfer from Ni(0) to the C–Cl bonds, probably preceded by the formation of a charge-transfer or π-complex in accord with earlier work by Tsou and Kochi [13]. In addition Roth et al. [11] indicated that severe crowding of neighboring chloro and phenyl groups in the PCBs with the remaining Ph_3P ligands on Ni would force selection of the least crowded Cl when more than one is available.

Recently, Scrivanti et al. [12] have demonstrated highly improved catalyst efficiency for Ni(0)–phosphine–$NaBH_4$ in an ethanol–pyridine hydrodechlorination system illustrating the important role of the solvent.

2.3. Homogeneous Ni(II) macrocycles as biomimics of factor F430 in hydride reducing systems/biotic reductive dechlorination

There is abundant evidence that hydrodechlorination of PCBs occurs in natural sediments containing methanogenic bacteria. The enzyme, which may be involved in hydrodechlorination, is factor F430, a nickel–hydrocorphinoid that undergoes redox reactions and electron transfer at the metal center, all reactions important to hydrodechlorination. Hence, there are numerous reports of studies on nickel–macrocycle–porphyrin-like complexes in combination with reducing agents as homogeneous biomimics for halogenated hydrocarbon reduction. For example, Stiles [8] has reported recently evidence for a radical chain mechanism in the quantitative hydrodebromination of 2,6-dibromobiphenyl to biphenyl at 25°C using a Ni(II) tetraazamacrocycle–$NaBH_4$ catalyst system. Stolzenberg and Zhang [19] reported more recently on an investigation of F430 biomimetic modeling chemistry using Ni(II) macrocycles as catalysts for the reduction of alkyl halides and methyl coenzyme M by $NaBH_4$. Eight Ni(II)–macrocycle complexes were shown to catalyze the dehalogenation of cyclohexyl bromide by $NaBH_4$ homogeneously. The facility of the reaction varied markedly with the solvent composition and the structure of the ligand. Again, a ligand steric factor is implied to influence reaction specificity.

Because the toxicology of the PCBs and their tendency to undergo Cl displacement by hydrodechlorination are both dependent upon the molecular architecture of individual PCB congeners, we have evolved an experimental approach to PCB detoxification based upon hydrodechlorination chemistry mediated by homogeneous transition metal complexes and alkoxyborohydrides. Their ability to induce Cl displacement as a function of PCB congener stereochemistry and the stereochemistry and molecular architecture of the homogeneous nickel–ligand complexes is described in this paper.

3. Results and discussion

Based upon this prior art, we have been examining the use of soluble, homogeneous Ni(II) and Ni(0) coordination compounds with organophosphorus ligands to initiate the removal of Cl from PCB congener mixtures as a function of molecular architecture and, hence, molecular toxicology. Simplified equations for this sequence of events are shown below using decachlorobiphenyl ($C_{12}Cl_{10}$) as a model PCB congener, and showing Ni insertion into the C–Cl bonds:

1. Ligand displacement:

$$NiL_4 \rightarrow NiL_3 + L$$

2. Oxidative addition:

$$C_{12}Cl_{10} + NiL_3 \rightarrow C_{12}Cl_9NiL_2Cl + L$$

3. Reductive elimination:

$$C_{12}Cl_9NiL_2Cl + H^- + L \rightarrow C_{12}Cl_9H + Cl^- + NiL_3$$

4. Partial dechlorination:

$$C_{12}Cl_{10} + nH^- \rightarrow C_{12}Cl_{10-n}H_n + nCl^-$$

5. Complete dechlorination

$$C_{12}Cl_{10} + 10H^- \rightarrow C_{12}H_{10}(\text{biphenyl}) + 10Cl^-$$

These equations predict the generation of partially chlorinated PCB congeners and biphenyl. Hence, this is a redox reaction with electron transfer mediated by nickel–ligand and hydride intermediates. Owing to the stereochemistry of the chlorinated biphenyls, with *ortho*, *meta* and *para* Cl substitution, the insertion of a nickel–ligand fragment into a C–Cl bond is also predicted to be influenced greatly by the nickel–ligand cone angle [20] (i.e. metal–ligand stereochemistry) based upon molecular mechanics computer modeling. Hence, we have designed soluble metal complexes that mediate Cl displacement from each of the toxicity classes cited above, based upon the molecular architecture of the organometallic reactions.

3.1. Orthogonal PCB detoxification

Decachlorobiphenyl (DCBP) was chosen as a model PCB congener to test the ligand–cone angle hypothesis on the stereochemical course of reductive dechlorination because it contains Cl in all positions of the biphenyl system and is readily synthesized in the pure state. Results of this systematic examination of hydrodechlorination of DCBP are shown in Table 1 expressed as percentage Cl displacement versus the ligand cone angle [20] for seven NiL_2Cl_2 complexes used to

Table 1
Percentage chlorine displacement and product distribution from DCBP as a function of the phosphine and phosphite ligand cone angle for NiL_2Cl_2 and NiL_4 homogeneous complexes

Ligand	Cone angle (°)	% Cl displaced	Biphenyl (yield %)	Predominant congeners produced	Chlorine position
Me_3P	118	70	Yes (25)	Di, tri, tetra	*o*
Et_3P	120	65	Yes (30)	Di, tri, tetra	*o*
Ph_3P	145	30	No	Penta, hexa	*o/m/p*
Cx_3P	180	0	No	No reaction	No reaction
$(EtO)_3P$	110	40	No	Tetra, penta	*o/m/p*
$(PhO)_3P$	128	30	No	Penta, hexa	*o/m/p*
(*o*-TolO)$_3$P	164	15	No	Octa, nona	*o/m*

Table 2
Percentage chlorine displacement and product distribution using $(Et_3P)_2NiCl_2$–$NaBH_2(OCH_2CH_2OCH_3)_2$ in THF at 68°C

Congener or aroclor	Reaction time (h)	% Cl displaced	Biphenyl (yield %)	Predominant congeners produced	Chlorine position
DCBP	6	65	Yes (25)	Di, tri, tetra	*Ortho*
TCBP 'coplanar PCB'	<1	99+	Yes (99)	Biphenyl	Complete displacement
Aroclor 1221	6	50	Yes (25)	Not determined	*Ortho*
Aroclor 1232	6	75	Yes (35)	Not determined	*Ortho*
Aroclor 1254	6	75	Yes (50)	Not determined	*Ortho*
2-CBP	12	99	Yes (99)	Biphenyl	Complete displacement
2,6-DCBP	12	99	Yes (99)	Biphenyl	Complete displacement

mediate chlorine removal using $NaBH_2(OCH_2CH_2OCH_3)_2$ as the hydride source and a reducing agent for Ni(II). All complexes were extremely active for chlorine displacement, except $(Cx_3P)_2NiCl_2$ containing the very bulky Cx_3P ligand (Cx = cyclohexyl). The gas chromatograms were very complex, but discrete patterns of reactivity were discernible, and were approximately related to the ligand cone angle parameter, particularly the observations made at the extremes of this steric-bulk variable. Product distribution to lower-molecular-weight congeners is also given in Table 1, including biphenyl, the complete dechlorination product.

The data in Table 1 indicate clearly that the magnitude and position (*o*/*m*/*p*) of Cl displacement is related to the nickel–ligand cone angle parameter, particularly for phosphine ligands. Thus by varying the nickel–ligand cone angle parameter, complexes for *para* Cl displacement ($(o\text{-}MeC_6H_4O)_3P$), *meta–para* Cl displacement (Et_3P and Ph_3P) and *ortho–meta–para* Cl displacement (Me_3P, Et_3P, and $(EtO)_3P$) were realized (Table 1). In addition, *no* Cl displacement was observed for the ligand with largest cone angle, Cx_3P. Molecular mechanics computer modeling of the stereochemical course of this organometallic reaction also confirmed semi-quantitatively that the ability to insert into a C–Cl bond is a function of the Cl position on the biphenyl nucleus and the stereochemical size of the NiL_n fragment, which is governed by the metal–ligand cone angle. Clearly, homogeneous metal–complex-mediated reductive dechlorination is a function of molecular architecture and the stereochemical course of the organometallic transformation.

The ligand cone angle parameter was defined previously by Tolman [20], who demonstrated that the magnitude of ligand dissociation for a series of soluble $Ni(0)L_4$ complexes (i.e. $NiL_4 \rightarrow NiL_3 + L$) was governed predominantly by the size of the ligand and the volume subtended by the ligand when complexed with a transition metal. The relative magnitude of the ligand displacement constant increased by a factor of 10^8 from $(PhO)_3P$–Ni(0) to $(o\text{-}MeC_6H_4O)_3P$–Ni(0), meaning the latter complex exists in solution as predominantly the coordinately unsaturated NiL_3. The chemical and industrial significance of this observation was revealed by King et al. [21], who demonstrated that the NiL_3 complex optimized the kinetics for the hydrocyanation of 3-pentenenitrile to adiponitrile, an important nylon-66 precursor [22]. In combination with Lewis acid catalysis, the yield of *anti*-Markovnikov addition product was also optimized to 96% [21,23]. Hence, steric control of a catalytic reaction by optimizing the ligand displacement reaction via the ligand cone angle was shown to control the reaction rate and the product distribution. Steric factors to optimize reaction rate and product selectivity have also been shown to be important for the trimerization of butadiene [24], the hydroformylation of olefins to aldehydes [25], and the use of water-soluble transition metal complexes for catalytic reactions and asymmetric synthesis [26].

3.2. Coplanar PCB detoxification

The results for DCBP suggested several Ni complexes that should induce Cl displacement from the most toxic, dioxin-like PCB congeners, namely the so-called coplanar PCBs. This was confirmed for the coplanar PCB congener 3,3′,4,4′-tetrachlorobiphenyl. Thus reactions of 3,3′,4,4′-tetrachlorobiphenyl with $(Et_3P)_2NiCl_2$ and excess $NaBH_2(OCH_2CH_2OCH_3)_2$ as the nickel reductant and hydride source led to extensive hydrodechlorination at 68°C (Table 2). Essentially quantitative (~ 99%) conversion of 3,3′,4,4′-tetrachlorobiphenyl was observed routinely with a 99% yield of non-toxic, biodegradable biphenyl, which was identified by CCGC–ECD retention time and GC–mass spectrometry. The reductive dechlorination of 3,3′4,4′-tetrachlorobiphenyl even proceeds at room temperature (25°C), where lower-molecular-weight tri-Cl and di-Cl congeners are produced. No biphenyl was observed at room temperature. The $NaBH_2(OCH_2CH_2OCH_3)_2$ was also examined as a nucleophilic hydride source in the absence of added nickel, since related borohydrides are known [27] to be excellent reagents for S_N2 reactions of a wide variety of aliphatic substrates, including *n*-octyl chloride, bromide and iodide although unreactive with aromatic halogen compounds. No hydrodechlorination was observed with $NaBH_2(OCH_2CH_2OCH_3)_2$ and 3,3′,4,4′-tetrachlorobiphenyl in the absence of Ni, thereby confirming the importance of nickel–ligand complexes to induce Cl displacement from PCB congeners at low temperatures. The borohydride is believed to be a nucleophilic hydride source, which proceeds by nucleophilic attack on the transition-metal–organometallic intermediate ($RNiL_2Cl$), at the transition-metal center.

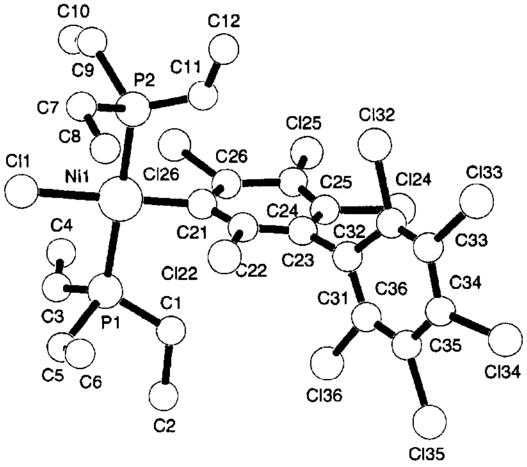

Fig. 1. CHARON ball-and-stick diagram of m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$. Selected bond distances (Å) and angles (°): Ni(1)–Cl(1), 2.18(2); Ni(1)–P(1), 2.24(2); Ni(1)–P(2), 2.21(2); Ni(1)–C(21), 1.88(4); Cl(1)–Ni(1)–P(1), 90.0(6); Cl(1)–Ni(1)–P(2), 89.8(7); P(2)–Ni(1)–C(21), 91(1); P(2)–Ni(1)–C(21), 89(1); P(1)–Ni(1)–P(2), 174.8(8); Cl–Ni(1)–C(21), 179(1). Torsion angles (°): P(1)–Ni(1)–C(21)–C(22), −87(5); C(22)–C(23)–C(31)–C(36), 90(6).

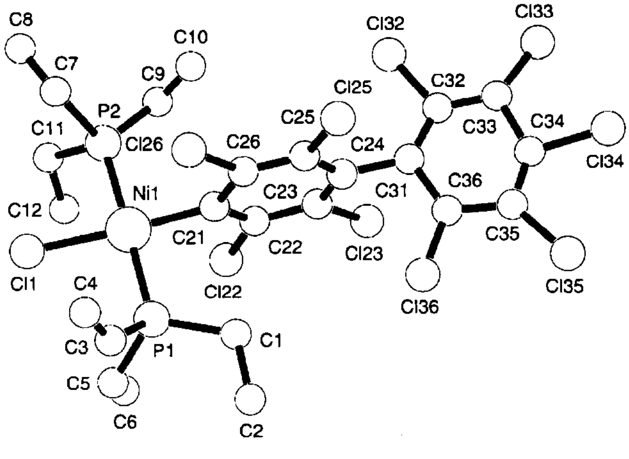

Fig. 2. CHARON ball-and-stick diagram of p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$. Selected bond distances (Å) and angles (°): Ni(1)–Cl(1), 2.187(7); Ni(1)–P(1), 2.223(7); Ni(1)–P(2), 2.203(7); Ni(1)–C(21), 1.86(2); Cl(1)–Ni(1)–P(1), 89.8(3); Cl(1)–Ni(1)–P(2), 89.1(3); P(2)–Ni(1)–C(21), 89.5(6); P(2)–Ni(1)–C(21), 91.8(6); P(1)–Ni(1)–P(2), 176.8(7); Cl–Ni(1)–C(21), 175.9(7). Torsion angles (°): P(1)–Ni(1)–C(21)–C(22), 90(2); C(23)–C(24)–C(31)–C(36), −88(3).

Table 3
X-ray data on m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ and p-$C_6Cl_5C_6Cl_4$-$Ni(PEt_3)_2Cl$

	Meta isomer	*Para* isomer
Empirical formula	$C_{24}H_{30}Cl_{10}NiP_2$	$C_{24}H_{30}Cl_{10}NiP_2$
Molecular weight	793.68	793.68
Crystal dimensions (mm³)	0.3 × 0.3 × 0.4	0.3 × 0.3 × 0.4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (no. 14)	$P2_1/a$ (no. 14)
a (Å)	16.706(5)	14.040(5)
b (Å)	10.132(5)	12.108(5)
c (Å)	20.657(5)	19.917(5)
β (°)	105.86(3)	97.97(3)
V (Å³)	3364(2)	3353(2)
F(000)	1608	1608
μ(Cu-K_α) (cm^{-1})	1.481	1.486
$D_{calc.}$ (g cm^{-3})	1.567	1.572
Z	4	4
Total reflections	10561	6463
Observed reflections	1079	2742
Octants collected	$+h, +k, \pm l$	$+h, +k, \pm l$
R	0.1273	0.1178
R_w	0.1530	0.1234

3.3. Structural evidence for the reaction mechanism based upon mass spectroscopy and X-ray diffraction

Evidence for the presence of organonickel intermediates in the reaction mixtures was obtained by mass spectroscopic and X-ray diffraction studies. Of particular interest is the isolation in low yields of the crystalline square planar complexes p-$C_6Cl_5C_6Cl_4$-$Ni(PEt_3)_2Cl$ from the reaction of decachlorobiphenyl with $NaBH_2(OCH_2CH_2OCH_3)_2$–$(Et_3P)_2NiCl_2$ and m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ from a DCBP–Ni(1,5-$C_8H_{12})_2$–PEt_3 mixture. The $Ni(PEt_3)_2C_{12}Cl_{10}$ stoichiometries for these two isomeric Ni complexes were indicated by the observation of molecular ions in their mass spectra combined with ions arising from successive loss of the first two Cl atoms with all of the observed ions exhibiting the expected complicated isotopic patterns. Both m- and p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ are oxidative addition intermediates and precursors for nickel catalysts for C–Cl hydrodechlorination.

Figs. 1 and 2 show the CHARON ball-and-stick diagrams of the m- and p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ structures, respectively. Details of the X-ray structure determinations are presented in Table 3. Since hydrodechlorination of DCBP was observed in both experiments where $C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ products were isolated in low yields, there is a distinct possibility that atom positions in mixed crystal systems containing $RNi(PEt_3)_2Cl$ derivatives with various degrees of replacement of perchlorobiphenyl chlorines with hydrogens are actually being measured, thereby accounting for the high R factors and large thermal factors when attempts are made to refine the structures as completely chlorinated $C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ derivatives. Despite these major limitations, these structural results are informative since they demonstrate insertion of Ni into a C–Cl bond, square planar Ni geometry, and orthogonal biphenyl arene rings with the plane of the Ni-bonded arene ring orthogonal to the plane of the $Ni(PEt_3)_2Cl$ fragment. We believe that these products are the first oxidative addition adducts of PCBs with Ni(0) resulting in square planar Ni(II) complexes that lend support to the interpretation of the reaction sequence proposed above. In addition, the structures of the two $C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ derivatives are consistent with those of the octafluorobiphenyl-nickel complex (4,4′-$C_{12}F_8H$)$Ni(PMePh_2)_2Br$ reported by Hunter and coworkers [28] and the biphenylyl–nickel complex (p-$C_6H_5C_6H_4$)$Ni(PEt_3)_2Br$ reported by Fugi and Yamamoto [29].

4. Experimental

4.1. Methods

The X-ray structure determinations were conducted on an Enraf–Nonius-Delft single-crystal diffractometer, computer controlled by a DEC Microvax II unit. The mass spectroscopic measurements were conducted on a Finnigan 4000 GC–MS spectrometer with direct probe insertion for low volatility samples. A Hewlett–Packard 5890A Capillary Column Gas Chromatograph with a ^{63}Ni electron capture detector (ECD) and a Supelco PB-Octyl capillary column was used for the PCB congener analyses.

4.2. Materials

Orthogonal PCB congeners (decachlorobiphenyl, 2-chlorobiphenyl and 2,6-dichlorobiphenyl) were prepared by literature methods [30] and purified by fractional crystallization. The co-planar PCB congener [31] 3,3′,4,4′-tetrachlorobiphenyl was prepared by the benzidine literature method [30]. Capillary column gas chromatography (CCGC) with an electron capture detector (ECD) was used to confirm the purity of individual congeners and to monitor the process of metal–complex-mediated reductive dechlorination using relative retention time data.

The L_2NiCl_2 complexes of Ni(II) were prepared by published methods [32] for the four phosphines Me_3P, Et_3P, Cx_3P, and Ph_3P. In addition, Ni(0) complexes of the three phosphite ligands $(EtO)_3P$, $(PhO)_3P$, and (o-$MeC_6H_4O)_3P$ were obtained commercially or prepared by standard methods [33,34]. The $NaBH_2(OCH_2CH_2OCH_3)_2$ reductant was prepared in THF solution from stoichiometric amounts of $NaBH_4$ and 2-methoxyethanol [6].

4.3. Reductive dechlorination experiments

The reductive dechlorination experiments were conducted under a N_2 atmosphere in a three-necked flask fitted with a reflux condenser and dropping funnel. Using this apparatus 5.0 ml of a THF solution of $NaBH_2(OCH_2CH_2OCH_3)_2$ (6 mmol), prepared in a separate reaction flask from $NaBH_4$ and 2-$CH_3OCH_2CH_2OH$, was added to a solution of decachlorobiphenyl (0.6 mmol, 6.0 mmol in total Cl) and 5.0 ml of THF at the boiling point (68°C). The refluxing solution was treated dropwise with a THF solution (10 ml) of the NiL_2Cl_2 complex (0.3–6.0 mmol). The evolution of H_2 gas was instantaneous. Smaller quantities of the NiL_2Cl_2 complex were used to confirm catalytic rather than stoichiometric activity. The $NaBH_2(OCH_2CH_2OCH_3)_2$ provides a stoichiometric source of hydrogen and was used in excess. Aliquots of the reaction product were removed with time, evaporated to dryness under vacuum, and treated with aqueous H_2SO_4 to destroy the Ni complex. The mixture was treated with CH_2Cl_2 or Et_2O to extract the PCB reaction products. The organic phase was taken to dryness under vacuum and the organic residues dissolved in n-hexane for CCGC–ECD and CCGC–MS analyses. Control experiments were conducted with the borohydride reagent alone to confirm the importance of the transition metal complexes in the hydrogenolysis process.

4.4. Isolation of organonickel intermediates

The m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ was isolated in low yield from the reaction of decachlorobiphenyl with $Ni(1,5\text{-}C_8H_{12})_2$ in stoichiometric amounts, along with two equivalents of Et_3P in Et_2O at room temperature in the absence of any borohydride. The reaction product was chromatographed on alumina using hexane as the eluent. The concentrated eluate was refrigerated for 14 days, leading to the separation of a small amount of crystals used for the X-ray diffraction and mass spectroscopic studies. The p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ was isolated in low yield after chromatography of a $(Et_3P)_2NiCl_2$–$NaBH_2(OCH_2CH_2OCH_3)_2$–DCBP reaction product with the reactants in stoichiometric rather than catalytic proportions.

4.5. X-ray structure determinations

Crystals of p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ were removed from the very thick syrup of residual solvent and reaction products. The crystals could not be cleaned of residual syrup and remained sticky throughout the data collection. A selected crystal was mounted on a glass fiber and analyzed on a Nonius CAD-4 diffractometer using Mo–K_α radiation. The orientation matrix and cell dimensions were determined from 25 centered reflections obtained from a random search procedure. Diffraction maxima were measured automatically from 0 to 25° θ. A ψ-scan was measured for three top reflections for later use in absorption correction. Crystals of m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ were also removed from a solvent–product syrup and were also quite sticky. A crystal of m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ was treated in a manner similar to the *para* isomer, except that the maximum θ was increased to 30°. A ψ-scan was not obtained because the crystal was lost before it could be accomplished. Table 3 lists cell dimensions and other pertinent information concerning the data collection.

The structure of the *para* isomer was solved using SIR-92 included in the TEXSAN suite of crystallographic programs [35]. Isotropic refinement with an application of an absorption correction [36] proceeded reasonably well but anisotropic refinement indicated large thermal displacement factors, especially for the chlorine atoms on the distant ring. Also, carbon atoms were very poorly behaved as anisotropic atoms and were finally treated only isotropically. After numerous least-square cycles, the R value only reached 12%. Despite the relatively large R value and high thermal displacement factors, the structure of p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ was clearly discernible.

In the case of m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$, the crystal was more weakly diffracting than that of p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$, thus providing considerably less data for the analysis. The lack of an absorption correction also worked against a successful refinement. Thus, with structure solution and refinement proceeding as in the *para* isomer case, the R value only reached about 15%. Again, quite large and unreasonable thermal displacement parameters were observed for the distant ring chlorine atoms and carbon atoms had to be treated isotropically only. During the review process, it was suggested that using DIFABS corrections might provide an adequate absorption correction and permit a somewhat better refinement. However, application of DIFABS absorption corrections led to a final refinement in which the structure became meaningless chemically. Another suggestion was made that raising the refinement σ cutoff from 3.0 to (perhaps) 5.0 would certainly improve the agreement values, even though some data would be lost. Also, two large outliers, 0 0 1 and 1 2 −4, were removed from the data completely. That refinement result, with $R = 13\%$, is the one reported here. Additional information concerning the refinement is given in Table 3.

5. Conclusions

Homogeneous Ni(II) and Ni(0) complexes coordinated with organophosphorus ligands, coupled with borohydride reagents, are active for the hydrodechlorination of PCB congeners. Their reactivity is a function of the position of Cl on the biphenyl nucleus and the stereochemical bulk of the nickel–ligand complex (i.e. the nickel–ligand cone angle). Catalysts for *para*, *meta–para*, and *ortho–meta–para* Cl displacement from the biphenyl nucleus were discovered. Hydrodechlorination is catalytic in the homogeneous Ni complex and stoichiometric in the borohydride reagent.

Complete Cl displacement of the most toxic forms of the PCBs, the dioxin-like, co-planar structures, has been confirmed by the complete conversion of 3,3′,4,4′-tetrachlorobiphenyl to non-toxic, biodegradable biphenyl mediated by $(Et_3P)_2NiCl_2$, a soluble complex which is highly reactive for *meta–para* Cl displacement when used with $NaBH_2(CH_2CH_2OCH_3)_2$.

Crystal structures were determined for p-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$ and m-$C_6Cl_5C_6Cl_4Ni(PEt_3)_2Cl$, which confirmed that oxidative addition of low-valent Ni and insertion into the C–Cl bond of a PCB model congener had occurred by two independent reaction pathways. Both complexes appear to be reaction intermediates and plausible precursors to hydride transfer to complete the catalytic hydrodehalogenation process.

6. Supplementary material

Crystallography data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Deposit numbers are CCDC 136934 for *para* isomer; CCDC 136935 for the *meta* isomer. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +1-44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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