A Practical Approach to PCB Cleanup Based Upon Molecular Architecture, Molecular Toxicology and Transition Metal Chemistry

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Abstract

Polychlorinated biphenyls (PCBs), as found in the environment, are complex mixtures of chlorinated aromatic chemicals which contain chlorine substituted in the ortho, meta and para positions of each aromatic nucleus of the biphenyl structure. The molecular toxicology of PCB congeners and the ability to attack and displace chlorine from the aromatic nucleus of individual PCB congeners are both a function of molecular architechture. Homogeneous nickel organophosphorus complexes, coupled with alkoxyborohydride reagents as a hydrogen source, mediate chlorine displacement by a process known as reductive dechlorination. The magnitude of chlorine displacement is a function of chlorine position and the shape and steric bulk of the organophosphorus-metal complex (i.e., the metal-ligand cone angle). The dioxin-like coplanar PCB congeners, which are meta-para chlorine substituted, undergo 99+ % conversion to a 99+ % yield to non-toxic, biodegradable biphenyl mediated by metal complexes containing ligands with medium cone angles ($120-145^0$). Orthogonal, ortho-substituted congeners (i.e., decachlorobiphenyl) require small cone angle complexes ($\sim120^0$), for conversion to biphenyl, which occurs at lower reaction rates.
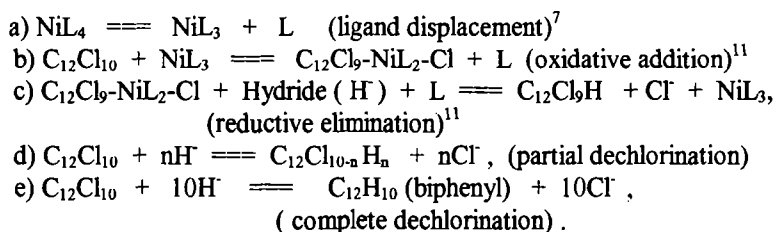
Because the transition metal complex and the hydride source are structurally modified with organic groups, both are soluble in solvents useful for PCB congener extraction from contaminated soils. Hence, a practical process for PCB removal from soil columns based upon one-step PCB extraction / PCB detoxification by use of subcritical fluid extraction and medium for catalysis has been demonstrated with model PCB congeners (orthogonal and dioxin-like coplanar congeners) and Aroclors.

Introduction and Specific Purpose of this Study

PCBs are ubiquitous in the global environment[1]. The toxiciology of the PCBs is dependent upon the size and shape of individual PCB congeners[2]. We have used this information to evolve an experimental approach to new methods for PCB detoxification based upon reductive dechlorination chemistry mediated by transition metal complexes and their ability to induce chlorine displacement as a function of PCB congener stereochemistry :

~ co-planar PCBs, meta-para substituted congeners which possess dioxin-like toxicity[2]
(3-MC [3-methylcholanthrene] responce, high complexation to the A_h receptor protein)
~ mono-ortho Cl, nearly coplanar PCBs, which show a mixed 3-MC / PB toxic responce[2]
~ orthogonal PCBs (i.e., decachlorobiphenyl) which show a low or zero toxic response[2]
(phenobarbitol [PB]- type ; induction of cytochrome P_{450})
~ conformationally-restricted PCB congeners[3], ortho-substituted congeners and
metabolites, the latter of which are biomimics of estradiol[3] and diethylstilbestrol[3] and
constitute a new class of toxicity, the so-called "environmental estrogens" [3].

Based upon some prior art[4-6], we have been examining the use of soluble, homogeneous nickel(II) and nickel (0) coordination compounds with organophosphorus ligands to initiate removal of chlorine from PCB congener mixtures as a function of molecular architecture and hence, molecular toxicology. The entire process, if successful, would be a new concept for detoxification of chlorinated organics, including PCBs. Simplified equations for this sequence of events are shown below using decachlorobiphenyl ($C_{12}Cl_{10}$) as a model PCB congener, and showing nickel insertion into the carbon-chlorine bonds :

a) $NiL_4 === NiL_3 + L$ (ligand displacement)[7]
b) $C_{12}Cl_{10} + NiL_3 === C_{12}Cl_9-NiL_2-Cl + L$ (oxidative addition)[11]
c) $C_{12}Cl_9-NiL_2-Cl + Hydride (H^-) + L == C_{12}Cl_9H + Cl^- + NiL_3$,
(reductive elimination)[11]
d) $C_{12}Cl_{10} + nH^- === C_{12}Cl_{10-n}H_n + nCl^-$, (partial dechlorination)
e) $C_{12}Cl_{10} + 10H^- === C_{12}H_{10}$ (biphenyl) $+ 10Cl^-$,
(complete dechlorination) .

The equations predict the generation of partially chlorinated PCB congeners and biphenyl. Hence, this is a redox reaction[4.5] with electron transfer mediated by nickel / ligand and hydride intermediates. Owing to the stereochemistry of the chlorinated biphenyls, with ortho, meta and para chlorine substitution[1], the insertion of a nickel / ligand fragment into a carbon-chlorine bond is also predicted to be greatly influenced by the nickel / ligand cone angle[7], based upon molecular mechanics computer modeling. Hence, we have designed soluble metal complexes which mediate chlorine displacement from each of the toxicity classes cited above, based upon the molecular architechture of the organometallic reactions.

Experimental Methods
Orthogonal PCB congeners (decachlorobiphenyl, 2-chlorobiphenyl and 2,6 dichlorobiphenyl) were prepared by literature methods[8] and purified by fractional crystallization. Co-planar PCB congeners[2] (3,3'4,4'-tetrachlorobiphenyl) were prepared by the benzidine literature method[8]. A Capillary Column Gas Chromatograph (CCGC) with a Ni-63 Electron Capture Detector (ECD) was used to confirm the purity of individual congeners and to monitor the progress of metal-complex-mediated reductive dechlorination using relative retention time data[8] .
Nickel (II) bis-ligand complexes were prepared by published methods[9] for seven distinct ligands including trimethylphosphine, triethylphosphine, triphenylphosphine and

tricyclohexylphosphine to test the ligand cone-angle parameter[7]. Phosphite ligands included triethyl phosphite, triphenyl phosphite and tri-orthotolyl phosphite, all with a wide variation of the cone angle parameter[7]. The borohydride reducing agent was prepared from commercial sodium borohydride with commercial 2-methoxyethanol by the method of Pittman[4].

Reductive dechlorination experiments were conducted as follows[4] : under a nitrogen atmosphere, a three-necked flask fitted with a dropping funnel and a reflux condenser was charged with DCBP (0.6 mm) and 5.0 ml of tetrahydrofuran (THF). A 5.0 ml THF solution of $Na^+ BH_2(OCH_2CH_2OCH_3)_2$ (6 mm), prepared in a separate reaction flask, was added to the DCBP solution and heated to reflux (68^0C). The refluxing solution was treated dropwise with a THF solution (10 ml) of the NiL_2Cl_2 complex (0.3-6.0 mm). Smaller quantities of NiL_2Cl_2 complex were used to confirm catalytic activity. Hydrogen gas evolution was instantaneous[4,5] and was believed to cause in-situ reduction of the nickel (II) complex[4,5] to nickel(0)$L_2(THF)_2$, which is the low valent form reactive with carbon-halogen bonds[4-6]. The borohydride / H^- source is a stoichiometric source of hydrogen[4,5] and is used in excess. Aliquots of the reaction product were removed with time, taken to dryness under vacuum and treated with aqueous sulfuric acid to destroy the nickel complex[4]. The mixture was treated with dichloromethane (CH_2Cl_2) to extract the PCB reaction products[4]. The CH_2Cl_2 phase was taken to dryness under vacuum and the organic residues dissolved in n-hexane[4] for CCGC / ECD and CCGC / mass spectrometry analyses.

One-step PCB extraction / PCB detoxification experiments were conducted as follows: a conventional Soxhlet apparatus with a thimble insert was assembled, to which was added a large excess of silica (10 gms) as a "synthetic soil", followed by a model PCB congener or Aroclor mixture corresponding to a 100-500 ppm soil contamination level. The NiL_2Cl_2 / $Na^+ (RO)_2BH_2^-$ complexes were added directly to the Soxhlet thimble in small amounts of THF. These components were completly absorbed by the silica matrix. THF in the reboiler section of the Soxhlet apparatus was heated to reflux and continuously recycled in the extractor compartment. Samples were removed from the reboiler section and treated with acid, CH_2Cl_2, hexane as described above and analyzed by CCGC / ECD methods.

Results and Discussion

Decachlorobiphenyl (DCBP) was chosen as a model PCB congener to test the ligand-cone angle hypothesis[7] on the stereochemical course of reductive dechlorination because it contains chlorine in all positions of the biphenyl system. Results of this systematic examination of reductive dechlorination are shown in Table I expressed as percent chlorine displacement versus the ligand cone angle for seven NiL_2Cl_2 complexes used to mediate chlorine removal using $(CH_3OCH_2CH_2O)_2BH_2^-$ Na^+ as the hydride source and in-situ nickel(II)L_2Cl_2 reductant[4,5]. All complexes were extremely active for chlorine displacement, except the very bulky tricyclohexylphosphine. CCGC / ECD patterns were very complex, but discrete patterns of reactivity were discernable, and were approximately related to the ligand cone angle parameter[7], particularly the observations made at the extremes of this steric-bulk variable. Product distribution to lower molecular weight congeners is also given in Table I, including biphenyl, the complete dechlorination

product. The predominant position of chlorine in the reaction products is also given, based upon congener assignments via retention times relative to decachlorobiphenyl[8].

Table I: Percent Chlorine Displacement and Product Distribution from DCBP as a Function of the Phosphine and Phosphite Ligand Cone Angle for NiL_2Cl_2 Complexes

Ligand	P(Me)₃	P(Et)₃	P(Ph)₃	P(Cy)₃	P(OEt)₃	P(OPh)₃	P(o-ortho tolyl)₃
Cone Angle	118°	120°	145°	180°	110°	128°	164°
%Cl Displace	70%	65%	30%	0 %	40%	30%	15%
Biphenyl (Yield %)	Yes (25%)	Yes (30%)	No	No	No	No	No
Congener Produced	Di, Tri, Tetra	Di, Tri, Tetra	Penta, Hexa	No Reaction	Tetra, Penta	Penta, Hexa	Octa, Nona
Cl Position	Ortho	Ortho	o/m/p	No Reaction	o/m/p	o/m/p	o/m

The magnitude of chlorine displacement is related to the nickel-ligand cone angle parameter[7], particularly for phosphine ligands. These results imply a stereochemical effect on the course of reductive dechlorination related to the steric bulk of the ligand. Most importantly, our observations predicted that several complexes should be highly active for meta-para chlorine displacement from PCB congeners which are in the class of the co-planar PCBs (toxicologically the most potent[2] and precursors to the most toxic furans and dioxins)[1,2]. In addition, the observation of biphenyl as a reaction product implied that attack at the ortho position of the biphenyl ring was also occuring. These nickel complexes should be active for chlorine displacement from the pure orthogonal, conformationally restricted PCBs[3], some of which are precursors to the "endocrine disruptors" [3].

Hence, complexes for para-chlorine displacement (tri-orthotolylphosphite), meta-para chlorine displacement (triethyl and triphenylphosphines) and ortho-meta-para chlorine displacement (trimethyl and triethylphosphines) were realized. No chlorine displacement was observed for the largest cone angle ligand, tricyclohexylphosphine. Although this is a completely negative result, this observation can be explained by the steric bulk/cone angle correlation. Molecular mechanics computer modeling of the stereochemical course of this organometallic reaction also confirmed semi-quantitatively that the ability to insert into a carbon-chlorine bond is a function of the chlorine 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 results for decachlorobiphenyl predicted that several complexes had been uncovered that should induce chlorine displacement from the most toxic, dioxin-like PCB congeners, the so-called "co-planar" PCBs [2]. This was confirmed for the co-planar PCB congener 3,3'4,4'-tetrachlorobiphenyl. Reactions of 3,3'4,4'-tetrachlobiphenyl with

Ni[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ and excess (CH$_3$OCH$_2$CH$_2$O)$_2$BH$_2^-$ Na$^+$ as nickel reductant[4,5] and hydride source[4,5] confirmed extremely high reactivity at 68^{0}C at < 3 hrs. reaction time. Ninety-nine percent conversion of 3,3',4,4'-tetrachlorobiphenyl was routinely observed with a 99% yield of non-toxic[1], biodegradable[1] biphenyl. The biphenyl structure was confirmed by CCGC/ECD retention time and GC/mass spectrometry. The reductive dechlorination of 3,3'4,4'-tetrachlorobiphenyl even proceeds at room temperature (25^{0}C), where lower molecular weight tri-Cl and di-Cl congeners are produced. No biphenyl was observed at room temperature. The (CH$_3$OCH$_2$CH$_2$O)$_2$BH$_2^-$ Na$^+$ complex was also examined alone as a nucleophilic hydride (H$^-$) source, since such compounds are known[10] to be excellent reagents for S$_n$2 (binary nucleophilic displacement) reactions of a wide variety of aliphatic substrates, including n-octyl chloride, bomide and iodide. They are reported to be unreactive with aromatic halogen compounds[10]. No reductive dechlorination activity was observed with the borohydride reagent and 3,3'4,4'-tetrachlorobiphenyl, confirming the importance of nickel-ligand complexes to induce chlorine displacement from PCB congeners at low temperatures. The borohydride is believed to be a nucleophilic hydride (H$^-$) source whose chemistry proceeds by nucleophilic attack on the transition metal-organometallic intermediate (RNiL$_2$Cl), at the transition metal center. Experiments are in progress to confirm this interesting hypothesis.

Transition and actinide metals in the form of organophosphorus-metal complexes can be recovered and recycled by liquid extraction technology. This is a commercial scale fact for at least two large scale processes : (1) the recovery of Ni(0)L$_4$ and excess ligand as practiced by E. I. DuPont de Nemours and Co. in their homogeneous catalytic process for the hydrocyanation of olefins[11] to nylon intermediates and (2) the recovery of uranium, neptunium and plutonium as ActinideL$_3$Cl$_2$ complexes in the PUREX process[12] as practiced by the U.S. Department of Energy. We have used this prior art[11,12] to speculate that a soil matrix contaminated with PCB congeners could be subjected to PCB removal and simultaneous PCB congener chlorine displacement (detoxification) by liquid extraction technology, owing to the solubility properties and low temperature reactivity of the NiL$_2$Cl$_2$ /(CH$_3$OCH$_2$CH$_2$O)$_2$BH$_2^-$ Na$^+$ complexes useful for reductive dechlorination. This one-step simultaneous PCB extraction/ PCB reductive dechlorination / PCB detoxification sequence has been confirmed for model PCB congeners and Arochlor compositions, tested to date, with (CH$_3$OCH$_2$CH$_2$O)$_2$BH$_2^-$ Na$^+$ and Ni[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ complexes added to a soil matrix prior to liquid extraction in a Soxhlet apparatus. THF was used as extractant and medium for catalysis. Decachlorobiphenyl undergoes extensive chlorine displacement to lower molecular weight congeners and biphenyl in a CCGC/ECD pattern analogous to the semi-batch reactions. The lower molecular weight congeners are believed to be primarily ortho-substituted products since the nickel complex is most active for meta-para chlorine displacement. Co-planar 3,3'4,4'-tetrachlorobiphenyl underwent 99% conversion with a 90% yield to biphenyl, somewhat analogous to the semibatch results. Arochlor 1221, primarily low molecular weight, ortho-substituted congeners, was converted to an even lower molecular weight product distribution. Control experiments in the Soxhlet apparatus confirmed that THF is an excellent solvent for extraction of model PCB congeners and Aroclors, resulting in chemically unmodified PCB congeners. Similar observations were made when the (CH$_3$OCH$_2$CH$_2$O)$_2$BH$_2^-$ Na$^+$ reagent and the PCB congeners were subjected to Soxhlet extraction from a soil matrix. This again confirms the

unique role of soluble nickel complexes for induction of chlorine displacement from PCB congeners.

Conclusions

Homogeneous nickel(II) and nickel(0) complexes coordinated to organophosphorus ligands, coupled with borohydride reagents, are active for the reductive dechlorination of PCB congeners. Their reactivity is a function of the position of chlorine on the biphenyl nucleus and the stereochemical bulk / cone angle of the nickel-ligand complex (i.e., the molecular architecture of the organo-metallic transformation).

Complete chlorine 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 $Ni[P(C_2H_5)_3]_2Cl_2$, a soluble complex, highly reactive for meta-para chlorine displacement.

A potentially practical process, applicable to PCB soil decontamination and based upon simultaneous PCB liquid extraction/ PCB reductive dechlorination, has been demonstrated in a Soxhlet solid / liquid extractor with contaminated soil-like matrices containing PCB model congeners and Aroclors. THF was the subcritical fluid extractant and medium for nickel-ligand-complex induced reductive dechlorination, in the presence of an organic-modified borohydride reagent as the source of hydrogen.

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