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Electrocatalytic Coupling of Aryl Halides with (1,2-Bis(di-2-propylphosphino)benzene)nickel(0)

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Dibromo- and dichloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) is compared with tetrakis(triphenylphosphino)nickel(II) as an electrocatalyst for the reductive coupling of aryl halides. In many of the reactions examined, dehalogenation of the substrate predominated over coupling; however, preparative yields of biphenyls as high as 96% can be obtained with aryl chlorides and 2 mol % of the title catalyst in polar, coordinating solvents. Experimental factors governing the efficiency of these reactions are discussed, and possible mechanisms for coupling and catalyst deactivation are considered. Much better selectivity for aryl chlorides is attained in electroreductive couplings catalyzed by the title compound, whereas electrocatalysis with $(Ph_3P)_4NiCl_2$ allows for selective intra- and intermolecular coupling at aryl bromide and vinyl chloride sites. Modest yields of cyclization products can be attained with either electrocatalyst in the presence of appropriately functionalized aryl or vinyl halides.

Introduction

Nickel-Mediated Aryl Halide Coupling. Metals have been used to induce the coupling of aryl halides since the late nineteenth century.[1] The most well-known of these reactions, the Ullmann synthesis,[2-6] has been largely superceded by reactions which employ zero-valent nickel.[7-10] These reagents nonetheless pose significant limitations: aryl chlorides give poor yields (e.g., only 14% from chlorobenzene); air-sensitivity renders Ni(0) reagents difficult to manipulate; and a stoichiometric amount of nickel is required.

An alternative route uses transition metals to catalyze Grignard reactions. Initially copper salts[11,12] and later nickel complexes[13] were found to dramatically improve the yield and selectivity of cross-coupling reactions between Grignard reagents and aryl halides. It was surmised that a Ni(0) species, produced in situ from a relatively inexpensive and easy to handle nickel(II) precursor, functions as the catalytic agent in these reactions. Although the nickel-catalyzed Grignard reaction is very flexible, it requires the use of reagents that are sometimes awkward, and isolation of the product is often hampered by the presence of voluminous magnesium salts.

Kende developed a closely related technique in which a Ni(0) reagent is generated in situ from Ni(II) and a reducing metal (e.g., zinc),[14] thus greatly simplifying the coupling of aryl halides. This procedure can be rendered catalytic in nickel,[15] and Colon demonstrated that the use of a small excess of zinc (e.g., 2.2 mol for each mole of aryl halide) greatly enhanced coupling, claiming the procedure to be "superior to any current procedure for coupling aryl halides, especially aryl chlorides".[16]

As an additional refinement to the Ni(0)-catalyzed coupling of aryl halides, the reducing metal can be replaced with a cathode as the means for regenerating nickel(0).[17-19] By electrochemically recycling a nickel catalyst, it is possible to couple chlorobenzene to biphenyl in 90% yield. One shortcoming of these electrocatalyzed coupling reactions is the consumption of the promoter with each cycle (ca. 20%), so that fairly large amounts of catalyst are required to achieve high conversions.

Although an excellent mechanistic description of the steps involved in electrocatalyzed coupling of aryl halides by Ni(0)–phosphine complexes is now available,[19] neither the synthetic utility nor the cause of catalyst deactivation is clear. Efforts described herein, which employed a (1,2-bis(di-2-propylphosphino)benzene)nickel dichloride (1)[20] catalyst, have attacked this problem, achieving an improved catalytic turnover. Thus, the amount of catalyst required for high conversion has been reduced to 0.02 equiv (ca. 8-fold improvement over previously reported results for dppe-coordinated nickel).[19] This work also describes the factors that govern the utility of 1 to induce electrocatalytically the reductive coupling of aryl chlorides and defines the operational limitations of this electrocatalyst. We also compare this electrocatalyst with the more accessible $(Ph_3P)_4NiCl_2$ in order to highlight the effect of ligand perturbation. A rationale for the differences in catalytic activity between various coordinatively unsaturated nickel complexes with bidentate phosphine ligands is then offered.

Results and Discussion

Electrochemical Behavior of Dichloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) (1). A cyclic voltammogram of 1 in acetonitrile exhibits two irreversible, one-electron waves (Figure 1). The first wave ($E_p = -1.31$ V) is due to the Ni(II) → Ni(I) reduction, and the second ($E_p = -2.03$ V) arises from the Ni(I) → Ni(0) transfor-

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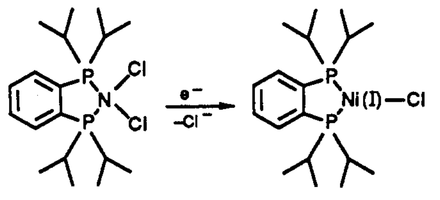
mation, eqs 1 and 2, respectively. The two reduction waves encompass equal areas (i.e., they involve an identical number of electrons), independent of scan rate.[21] The invariance of relative peak areas at slow scan rates is an indication that neither dimerization[22] nor disproportionation,[23] respectively, occur during the reduction of 1.



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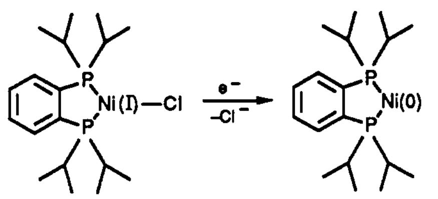


(2)

This electrochemical reduction is markedly affected by solvent. Upon reduction in acetonitrile, THF, DMF, or DMSO, the peak potentials of both waves consistently shift less negative as the dielectric constant of the solvent is increased (Table I), as would be expected with a build up of charge during each of the changes in oxidation state. Solvent also exerts a profound effect on the return oxidation of the Ni(0) complex. In acetonitrile, only a small return oxidation current can be observed in the reduction of 1 at 100 mV/s; when the scan rate is increased, the oxidation current also increases. The electrogenerated Ni(0) complex thus gradually undergoes a competitive irreversible reaction.[24] When 1 is reduced in DMF, the return oxidation current is slightly larger (indicating improved reversibility), and in DMSO, it is considerably more reversible.

Solvent effects on the reversibility of the reduction of 1 correlate well with the solvent's donor number (Table I), a relative indication of its ligating ability. The larger the donor number, the greater the reversibility, as would be expected if a coordinatively unsaturated Ni(0) complex is stabilized by solvent coordination.

The electrochemical behavior of dibromo(1,2-bis(di-2-propylphosphino)benzene)nickel(II) 2 is identical with that of 1, except that the two reduction peak potentials are shifted slightly positive (e.g., in DMSO, Ni(II) → Ni(I), $E_p = -1.15$ V; Ni(I) → Ni(0) $E_p = -1.60$ V).

Reduction of Chloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) in the Presence of Aryl Halides. The cyclic voltammogram of 1 in acetonitrile is greatly altered by the addition of bromobenzene (Figure 2) or chlorobenzene. As the halobenzene is added, a new wave at −2.3 V appears,[25] indicating the onset of a new redox process. When 1 is reduced to its Ni(0) analogue, it rapidly undergoes oxidative addition with bromobenzene (eq 3). The resulting Ni(II) complex (3) subsequently undergoes electrochemical reduction (eq 4).

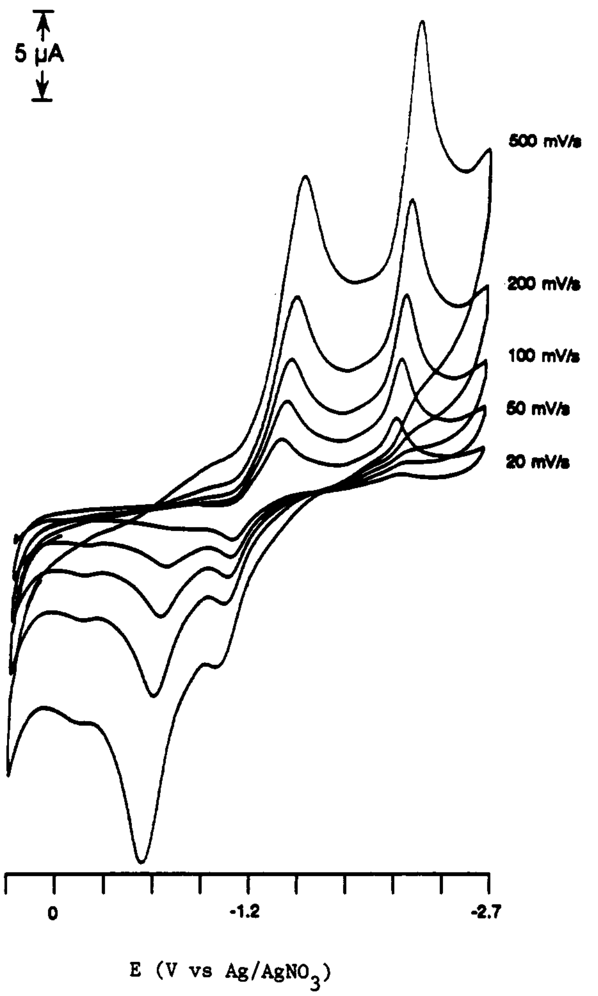
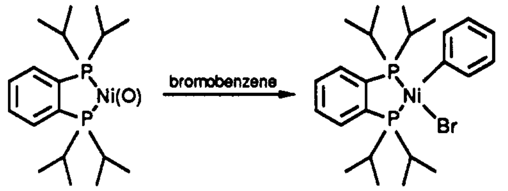


Figure 1. Cyclic voltammogram of dichloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) (1) at glassy carbon in acetonitrile, 25 °C, 0.2 M TBAP, 20, 50, 100, 200, and 500 mV/s.



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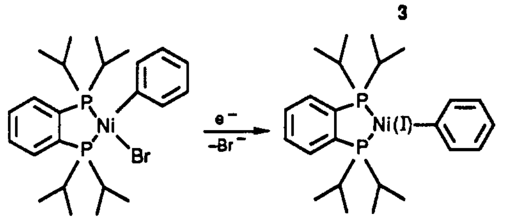

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(4)

There are two additional noteworthy features in Figure 2. First, as bromobenzene is added, the height of the first reduction wave (Ni(II) → Ni(I), −1.31 V) changes very little. This is an indication that Ni(I) complex of 1 is unreactive toward bromobenzene, and, therefore, an addition reaction between the two probably does not occur. Second, as the concentration of bromobenzene is increased, the third wave, which is attributed to the reduction of 3, also increases. At high concentrations of bromobenzene, the height of the third wave becomes considerably greater

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[21] Areas for the Ni(II) → Ni(I) and the Ni(I) → Ni(0) waves remained equal over the entire range of scan rates which were experimentally possible with the equipment used (10–2000 mV/s).

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[24] Irreversible behavior is often an indication that a compound will perform poorly as an electrocatalyst.

[25] The new wave at −2.3 V is largely obscured because it is sandwiched between the Ni(I) → Ni(0) reduction for 3 and the direct reduction of bromobenzene (−2.03 and −2.52 V, respectively).

Table I. Dependence of Electrochemical Peak Reduction Potential (E_p) on Solvent

	E_p (V vs Ag(AgNO$_3$ ± 50 mV)[a]							
	THF (donor no. 20.0) (ϵ = 7.6)		DMF (donor no. 26.6) (ϵ = 37)		CH_3CN (donor no. 14.1) (ϵ = 37)		DMSO (donor no. 29.8) (ϵ = 47)	
substrate	Ni(II/I)	Ni(I/0)	Ni(II/I)	Ni(I/0)	Ni(II/I)	Ni(I/0)	Ni(II/I)	Ni(I/0)
1	-1.53	-2.25	-1.50	-2.17	-1.31	-2.03	-1.30	-1.64
2							-1.15	-1.60
3							-1.15	-1.60
5							-1.15	-1.60
8							-1.15	-1.60
	Ni(II)ArX → NiAr		Ni(II)ArX → NiAr		Ni(II)ArX → NiAr		Ni(II)ArX → NiAr	
1/C_6H_5Cl	-2.48		-2.45		-2.25		-2.15	
3/C_6H_5Cl							-2.15	
1/C_6H_5Br	-2.45[b]		-2.40		-2.25		-2.35	
1/p-$ClC_6H_4CH_3$							-2.01	
3/p-$ClC_6H_4CH_3$							-2.40	
1/p-ClC_6H_4Cl							-2.07	
1/p-$ClC_6H_4OCH_3$							-2.39	
1/o-ClC_6H_4Cl							-2.12	
	ArX → ArX^{-}[c]		ArX → ArX^{-}[c]		ArX → ArX^{-}[c]		ArX → ArX^{-}[c]	
2/C_6H_5Cl	-2.55		-2.40		-2.37		-2.85	
1/C_6H_5Cl	-2.65[b]		-2.60		-2.52		-2.55	
3/p-$ClC_6H_4CH_3$							-2.45	
4/p-ClC_6H_4Cl							-2.55	
6/o-ClC_6H_4Cl							-2.40	
5/p-$ClC_6H_4OCH_3$							-2.40	

[a] Peak potentials determined by cyclic voltammetry: glassy carbon, 25 °C, 0.2 M $TBABF_4$, 100 mV/s. [b] Contains HMPA. [c] Onset potentials for 0.05 M concentration of ArX. Peak potentials would be slightly more negative.

than either of the two preceding peaks, a feature characteristic of electrocatalysis.

When 1 is reduced in THF containing chlorobenzene, electrocatalysis is even more readily apparent. Reduction in the presence of an equal molar volume of chlorobenzene produces three waves of approximately equal area. Because the first two waves are one-electron processes, the third wave therefore also arises from a one-electron reduction as is consistent with eq 6. As in Figure 2, the cyclic voltammogram changes when 1 is reduced in the presence of a large excess of chlorobenzene. Under those conditions, the third reduction wave becomes noticeably larger than the first two waves, as is consistent with an ECE mechanism entering into a catalytic cycle.[19] Since in the presence of excess chlorobenzene a cycle continuously regenerates the species being reduced, the amount of current passed at the potential of the third wave is controlled by the rate of diffusion and of the rate-limiting step in the cycle. As a result, the relative heights of the first two waves, compared to the third wave, are strongly dependent on the scan rate: at very slow scan rates (e.g., 10 mV/s), the third reduction wave dwarfs the first two.

In order to effectively couple aryl halides with complexes 1 and 2, however, it is necessary to select conditions under which the catalytic cycle can propagate at a potential that is significantly positive of direct reduction of the substrate (e.g., aryl halide). Several variables may thus be adjusted in order to optimize coupling conditions: substrate type (e.g., aryl halide), solvent polarity and temperature. Table I also summarizes the potentials of the three reduction waves observed for 1, 2, and the diphos complex for a variety of solvent/aryl halide combinations and the potentials for direct reduction of several aryl halides (i.e., conversion to the radical anion). The most promising conditions for aryl halide coupling will require the greatest difference between the potentials for the Ni(II)ArX → Ni(I)Ar conversion and aryl halide reduction.

Upon examination of Table I, two trends are apparent. Solvents with a high dielectric constant shift the third reduction wave (and presumably the onset of electrocatalysis) to more positive potentials.[26] The typically more negative reduction potentials of the aryl chlorides than of the corresponding aryl bromides makes it reasonable to expect that aryl chlorides should couple more cleanly than bromides, via electrocatalysis by 1, in a very polar solvent. For example, the cyclic voltammogram for 2 in DMSO containing chlorobenzene shows three clearly defined waves in which the third (electrocatalysis at -2.15 V) is well-removed from direct reduction of the aryl halide (-2.85 V). These conditions should therefore support an effective coupling reaction.

Temperature elevation may also be used to increase the effectiveness of an electrocatalytic coupling reaction. An increase in temperature will alter the dielectric constant of the solvent and accelerate the catalytic cycle. The cyclic voltammogram of 1 in DMSO containing bromobenzene at 65 °C exhibits a third reduction wave about twice as large (in proportion to the first two waves) as that observed at 25 °C.

An ideal electrocatalyst will be stable in each of the oxidation states required to complete a catalytic cycle. Spectroelectrochemical measurements of absorption spectra recorded during the reduction of 1 in DMSO (with no aryl halide present) indicate that the Ni(0) complex may be at least partially unstable, since no isosbestic point is evident. Thus, a partially nonreversible reaction follows reduction.[27] When chlorobenzene was added, however, the reduction of 1 occurs with clearly defined isosbestic points at 340 and 410 nm, indicating that Ni(0) reacts cleanly with the aryl halide, thereby avoiding catalyst deactivation. Thus, effective electrocatalytic coupling of aryl halides will be possible under carefully chosen conditions and with some expected limitations (e.g., a limited number of catalyst turnovers before deactivation occurs).

Preparative Electrocatalytic Reduction of Aryl Halides. Several reactions in which aryl halides are electrocatalytically coupled by reduced 1 were carried out

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(26) The dielectric constant of the solvent affects the potential of the third reduction wave in much the same manner as it affects the first two waves, presumably for the same reason. Charge separation accompanies the transition.

(27) The reaction is probably oxidative insertion of Ni(0) in the ligand P–C bond.

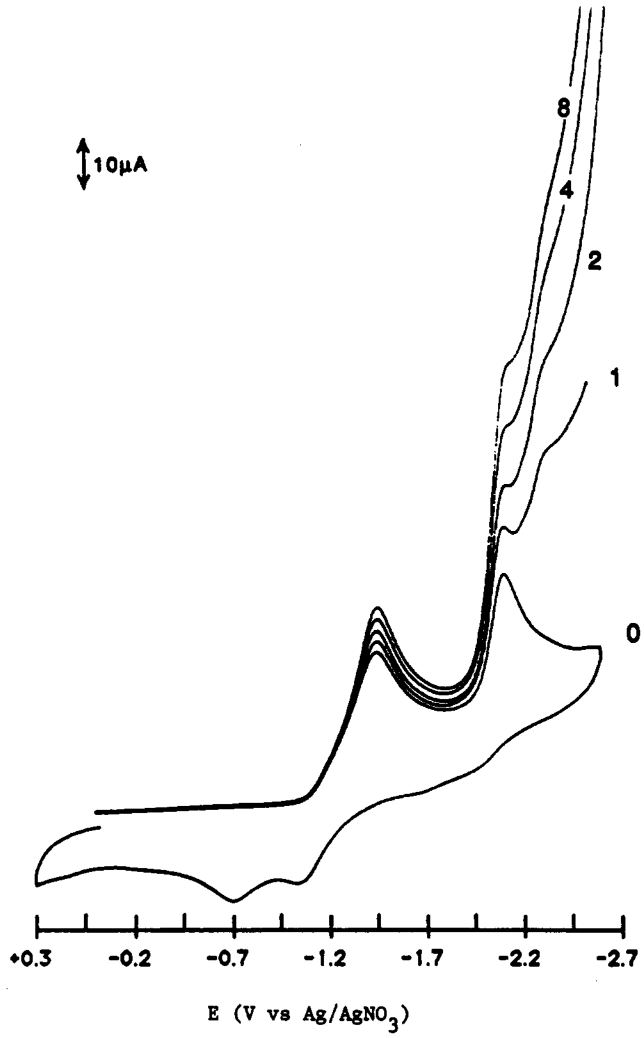

Figure 2. Cyclic voltammogram of dichloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) (1) with 0, 1, 2, 4 and 8 molar equiv of bromobenzene at a glassy carbon electrode in acetonitrile, 25 °C, 0.2 M TBAP, 100 mV/s.

(Table II). The yield of coupling of these aryl halides varied widely with substrate, but reasonable yields could be attained for those aryl halides whose reduction potentials were consistent with the requirements outlined in the previous section.

A. Dehalogenation. Bromobenzene could not be coupled effectively, presumably because at the potential necessary for the reduction of the catalyst, mediated electron transfer gave direct reduction. In DMF, the reaction proceeded almost exclusively by dehalogenation of the substrate. In DMSO, the yield of biphenyl was slightly improved but remained far lower than the production of benzene.

B. Aryl Coupling. Chlorobenzene reduces at a more negative potential than bromobenzene and proved to be less prone to dehalogenation. In DMF and THF, chlorobenzene underwent coupling as inefficiently as bromobenzene. In DMSO, however, coupling was the predominant process (38% coupling vs 6% dehalogenation), eq 5, although the attainable yield remained low at room temperature.

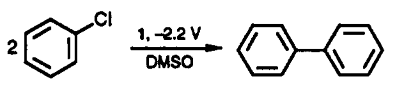

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Table II. Electrocatalytic Coupling of Aryl Halides with (1,2-Bis(di-2-propylphosphino)benzene)nickel(0) (1)

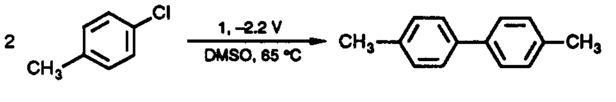
substrate	reaction conditions[a]	products (yield, %)
bromobenzene	1.0% 1, DMF, 25 °C, −2.6 V	14% benzene, trace of biphenyl
bromobenzene	1.0% 1, DMSO, 25 °C, −2.3 V	18% benzene, 2.8% biphenyl
chlorobenzene	1.0% 1, THF, 25 °C, −2.5 V	rapid catalyst deactivation
chlorobenzene	1.0% 1, DMF, 25 °C, −2.4 V	13% benzene, trace of biphenyl
chlorobenzene	1.0% 1, DMSO, 25 °C, −2.2 V	6% benzene, 38% biphenyl
chlorobenzene	1.0% 2, DMSO, 65 °C, −2.2 V	80% biphenyl[c]
4-chlorotoluene	1.0% 1, DMSO, 65 °C, −2.2 V	3% toluene, 91% 4,4′-dimethylbiphenyl
4-chlorotoluene	2.0% 1, THF, 65 °C, −2.2 V	2% toluene, 96% 4,4′-dimethylbiphenyl 0.5% 4,2′-dimethylbiphenyl[d]
1,4-dichlorobenzene	3.0% 1, DMSO, 65 °C, −2.2 V	quantitative conversion to polyphenylene
1,2-dichlorobenzene	1.0% 1, DMSO, 65 °C, −2.2 V	rapid catalyst deactivation
benzyl chloride	2.0% 1, DMSO, 65 °C, −1.75 V	18% toluene, 40% bibenzyl

[a] The percentage of catalysts precursor is based on the molar concentration of the substrate; all on glassy carbon; conditions as in Table I. [b] Yields determined by gas chromatography are based on percent conversion of the starting substrate. [c] Yield was lowered by the evaporation of substrate during reaction. [d] The substrate 4-chlorotoluene contained a small amount of 2-chlorotoluene as an impurity. [e] Conversion based on the disappearance of substrate. The product was insoluble.

There are two reasons for DMSO's superior ability to support the electrocatalytic coupling of chlorobenzene. First, the Ni(0) catalyst is most stable in solvents with large donor numbers. Second, the potentials at which direct reduction of the aryl halide and propagation of the catalytic cycle occur are widely separated (0.78 V). Therefore, the catalyst is sufficiently stable to undergo multiple turnovers, and catalysis need not compete with aryl halide dehalogenation.

Conducting the reaction at higher temperatures enhances both the selectivity and the yield of these reactions. The efficiency of coupling for chlorobenzene in DMSO (with 1 mol % of catalyst) improved from 38% at 25 °C to 80% at 65 °C. This represents an increase of 100% in catalytic turnover (19 → 40 turnovers). Thus, warming the reaction mixture favors catalysis over deactivation. The reaction composition is a monotonic function of coulombic charge for the reaction of chlorobenzene in DMSO at 65 °C: a Faradaic efficiency greater than 80% for this reaction was realized.[28] This measured value represents a lower limit for the actual Faradaic efficiency, for at 65 °C the vapor pressure of chlorobenzene is significant. As a result, the substrate slowly evaporated from the reaction media and the operative catalysis was starved, producing a lower efficiency for coupling.

The coupling of 4-chlorotoluene in DMSO (65 °C) was also very effective (eq 6). Using 1.0 mol % of catalyst, the reaction coupled 91% of the substrate before deactivation (45 turnovers). Because 4-chlorotoluene has an appreciably higher boiling point than chlorobenzene, volatilization of the substrate was a less significant problem, and the plot exhibits the linearity expected for a clean conversion to 4,4′-dimethylbiphenyl.



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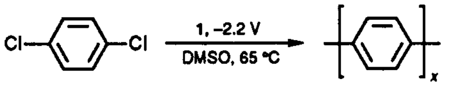
[28] In determining Faradaic efficiency, no attempt was made to substract the background current or the charge required to activate the catalyst (2 mol of e per mole of catalyst precursor 3).

The coupling of two dichlorobenzenes was also attempted. The electrocatalytic coupling of 1,4-dibromobenzene with 10 mol % of Ni(0) diphos has been successfully carried out by Fauvarque,[29] eq 7, producing poly-1,4-phenylene with a degree of polymerization of 9. In our hands, the reaction of 1,4-dichlorobenzene and 1 in DMSO proceeded to a high conversion based on the charge passed (eq 7). The product, an off-white powder, precipitated from solution during the reaction.[30] An infrared spectrum of the solid gave three principal bands at 807, 766, and 693 cm^{-1}, characteristic of poly-1,4-phenylene.[29]



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In an attempt to prepare biphenylene, 1,2-dichlorobenzene was reacted with 1 in DMSO. This reaction, however, failed to produce coupling products. Current flow ceased soon after passage of four electrons per catalyst precursor had been transferred. Activation of the catalyst (Ni(II) → Ni(0)) would consume two electrons.

Finally, benzyl chloride was catalytically coupled in DMSO to bibenzyl in 40% yield, in competition with dehalogenation to toluene (18%). Thus, electrocatalytic coupling is not exclusively limited to aryl chlorides.[31]

C. Optimization of Coupling. The coupling of 4-chlorotoluene was thus chosen as a prototype for optimization. With a catalyst (1) concentration of 2 mol % of the substrate, conversions as high as 96% were achieved. In the initial stages of the reaction, the current decreases rapidly as the catalyst precursor (1) is reduced and enters the catalytic cycle. The slope of the remaining curve then remains very shallow until nearly all of the aryl halide has been consumed, whereupon there is a steep drop to essentially zero current. The slope of the curve during reaction was independent of the concentration of aryl halide, an indication that the gradual drop in current was due to catalyst deactivation and not to a decrease in substrate access. Furthermore, the addition of fresh 4-chlorotoluene to a completed reaction failed to restore the initial value for the passage of current.

D. Catalyst Deactivation Mechanism. If deactivation of the catalyst were predominantly occurring in the Ni(0) state (i.e., insertion of nickel into a carbon–phosphorus bond),[32] increasing the relative concentration of the aryl halide might suppress deactivation by increasing the rate of oxidative addition to form the more stable Ni(II) aryl halide adduct. When the concentration of 4-chlorotoluene was increased, however, only a very small change in the number of catalyst turnovers was observed (48 turnovers was the observed maximum). Alternatively, catalyst deactivation might occur by decoordination and precipitation of Ni(0).[23] Following reaction, the carbon working electrode was removed and examined for Ni(0) deposits by photoelectron spectroscopy. No metallic nickel could be detected. A remaining possibility, involving C–P oxidative insertion, was therefore assumed to be likely.

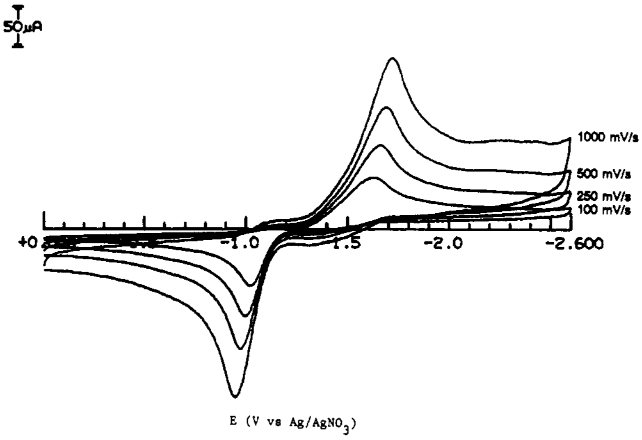
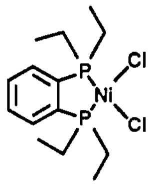


Figure 3. Cyclic voltammogram of dichloro(1,2-bis(diethylphosphino)benzene)nickel(II) (4) at glassy carbon in DMSO, 25 °C, 0.2 M TBAP, 100, 250, 500, and 1000 mV/s.

Structural Effects in the Electrocatalyst: Other Coordinatively Unsaturated Ni(0) Catalysts. The perethyl-substituted analogue of 1, dichloro(1,2-bis(diethylphosphino)benzene)nickel(II) 4, was also evaluated as a potential electrocatalyst for coupling aryl halides. Because 4 is less bulky than 1, the possibility that it might propagate catalysis more rapidly was considered feasible.



4

The cyclic voltammetry of 4 in DMSO radically differs from that of 1 (Figure 3). The reduction of 4 occurs in a single wave at −1.6 V and involves only one electron per nickel atom (as determined by coulometry). The return oxidation, also a single electron wave, is separated from the reduction wave by 600 mV. Variation of the scan rate (20–2000 mV/s) had little effect on the peak position or the relative areas of the anodic and cathodic waves. The constant parity of anodic and cathodic waves is an indication that the reduction of 4 appears to occur without a following chemical reaction, producing a fairly stable product. Unless a species of different aggregation exhibited redox chemistry identical to that of its monomer precursor, this observation excludes the possible formation of a dimeric Ni(I) species being formed in the electroreduction of 4. Unlike 1, when complex 4 is reduced, a clean conversion (with a sharp isobestic point) from starting material to a single product is observed by spectroelectrochemical techniques.

Frequently, when a single reduction wave occurs where two would normally have been expected, disproportionation is involved. This route, however, may be ruled out with 4. Since at high scan rates (e.g., 2000 mV/s), a second reduction wave, which would have appeared at a potential more negative than the pre-existing wave, was absent. In addition, when 4 is reduced in the presence of 4-chlorotoluene, no evidence for a reaction between Ni(0) and the aryl halide was detected. If the Ni(0) analogue of 4 were being electrolytically generated, it would undoubtably undergo oxidative addition with 4-chlorotoluene.

Any mechanism which is proposed for the reduction of 4 must explain why it is reduced in a single wave, why the reduction product is more stable than that for 1, and why the reduction product is inert toward 4-chlorotoluene. A

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(29) Fauvarque, J. F.; Petit, M. A.; Pfluger, F.; Jutand, A.; Chevrot, C. *Makromol. Chem., Rapid Commun.* 1983, *4*, 455.

(30) Precipitation of the polymer onto the electrode surface began after only 40% conversion of the substrate.

(31) Several potential substrates for coupling catalyzed by the electroreduction of 1 could be screened out, however, by the criterion that the potential for direct reduction of the substrate (i.e., $ArX \rightarrow Ar^{\bullet +}X^-$) be more negative than the potential for propagating catalytic coupling (e.g., $ArNiX \rightarrow ArNi^+X^-$): 4-chloroanisole; 2-bromo-2-methylpropane; and most aryl bromides. The direct reduction of benzyl chloride does not occur at the potential of this catalyzed coupling reaction.

(32) Garrou, P. E. *Chem. Rev.* 1985, *85*, 171.

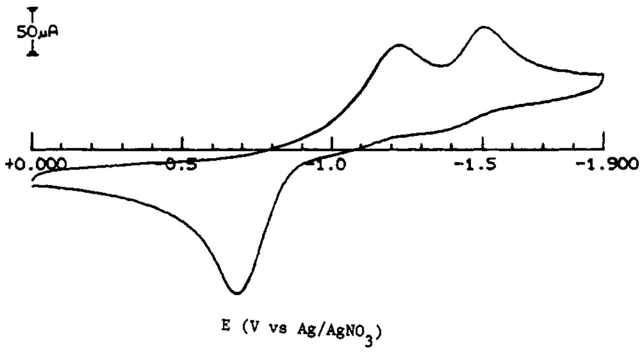
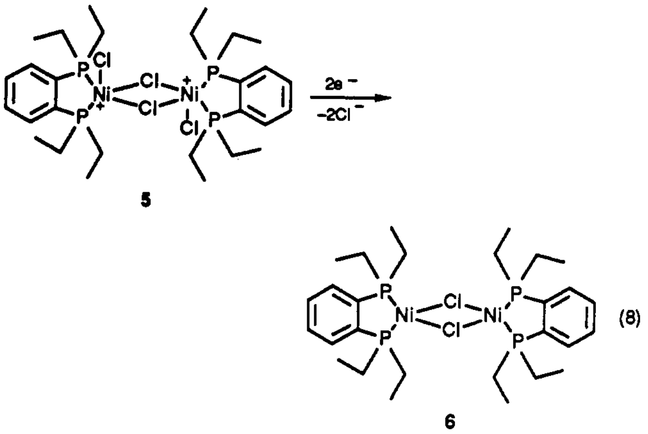


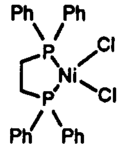
Figure 4. Cyclic voltammogram of dichloro(1,2-bis(diphenylphosphino)ethane)nickel(II) (7) at glassy carbon in DMSO, 25 °C, 0.2 M TBAP, 500 mV/s.

possible scenario is that 4 exists in solution as dimer, 5. As a dimer, 5 would reduce to 6 (one electron per nickel), which is also a dimer (eq 8).



Because the metal centers in 6 are enclosed by a strong ligand field and are coordinatively saturated, they are fairly inert. The X-ray crystal structure for a bimetallic complex with bonding similar to 5 has been reported.[33] Presumably 1 would exhibit behavior similar to 4, if not for the large steric bulk of the phosphine ligand, which inhibits dimerization.

Dichloro(1,2-bis(diphenylphosphino)ethane)nickel(II) (7) was also investigated as a catalyst precursor. This complex has already been confirmed as a catalyst for coupling aryl halides.[18,29,34]



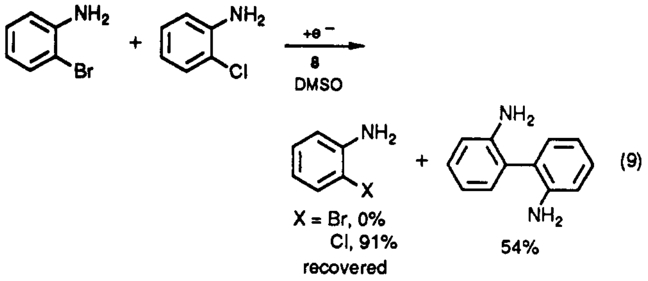
7

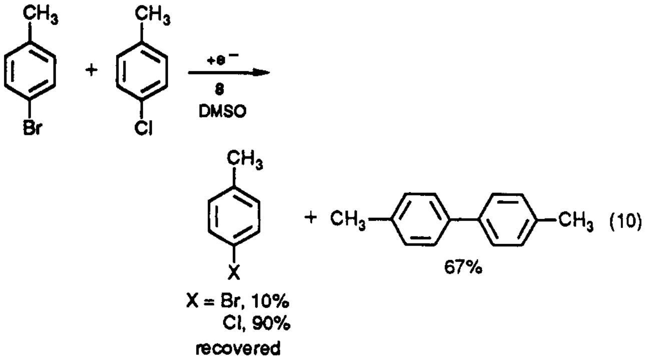
The cyclic voltammogram of 7 in DMSO is in many ways similar to 1 (Figure 4). This complex reduces in two steps (−1.2 and −1.5 V) and is quasi-reversibly oxidized from the Ni(0) state. Unlike 1, however, the relative area for the two reduction waves is highly dependent upon the scan rate. At fast scan rates (e.g., 500 mV/s), the two peaks appear approximately equal in intensity, but when the scan rate is reduced (20 mV/s), the first wave becomes much larger than the second. The dependence of relative height of the two peaks on scan rate can probably be attributed to dimerization. At slow scan rates, the first wave becomes larger than the second, not because it is augmented, but because the second wave is diminished. The first wave never deviates from a one electron event (as determined by coulometry), which is consistent with the formation of a Ni(I) dimer.

In the presence of 4-chlorotoluene, 7 exhibits electrocatalytic behavior similar to that described in Figure 2. The appearance of a third reduction wave (−2.2 V) corresponds with the production of a Ni(II)–aryl halide complex and its subsequent reduction. The relative height of the third wave was also found to vary with the scan rate. At slow scan rates (20 mV/s) the catalyst tends to dimerize, and because the dimer is unreactive toward aryl halide, the height of the third wave also decreases.

An attempt was made to use 7 for the preparative coupling of 4-chlorotoluene. When the same reaction conditions found to be effective for 1 were used (0.5 mol % catalyst, DMSO, 65 °C), the catalyst was completely deactivated after less than three turnovers. Thus, 7 is much less effective than 1 as an electrocatalyst because of its greater proclivity for dimerization.

Halide Selectivity in Intermolecular Coupling. Although both 4 and 7 proved to be less effective than 1 in the electrocatalytic intermolecular coupling of aryl chlorides, the simplest analogous nickel–phosphine complex, $(Ph_3P)_4NiCl_2$ 8, can provide reasonable yields of coupling of aryl halides, although much better yields are obtained with aryl bromides and iodides than chlorides, i.e., with reversed selectivity compared with 1. For example, when 8 (20 mol %) was electrolyzed in the presence of an equimolar mixtures of 2-bromoaniline and 2-chloroaniline and excess triphenylphosphine, unreacted 2-chloroaniline was recovered in 91% yield, in contrast to the nearly complete consumption of 2-bromoaniline (2% remaining), which produced 2,2′-diaminobiphenyl[35] in 54% yield (eq 9). Similarly, when 8 was electrolyzed under the same conditions with a 1:1 mixture of 4-chlorotoluene and 4-bromotoluene, 4,4′-dimethylbiphenyl was formed in 67% yield, with 90% of 4-chlorotoluene being recovered (eq 10).





These results are in agreement with previous reports of the coupling of 4-bromo-1-chlorobenzene catalyzed by a nickel-containing complex reducing agent to produce

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[33] Dunitz, J. D.; Mez, H. C.; Mills, O. S.; Shearer, M. M. *Helv. Chim. Acta* **1962**, *45*, 647.

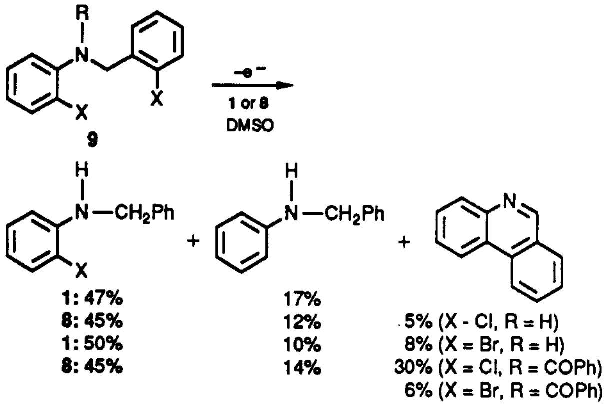
[34] Schiavon, G.; Bontempelli, G.; Magno, F.; Daniele, S. *J. Electroanal. Chem.* **1982**, *91*, 140.

[35] Moore, R. E.; Furst, A. *J. Org. Chem.* **1958**, *23*, 1504.

4,4′-dichlorobiphenyl (63%) under the same conditions.[36] Clearly, different aryl halides can be selectively catalytically coupled depending on the catalyst employed.

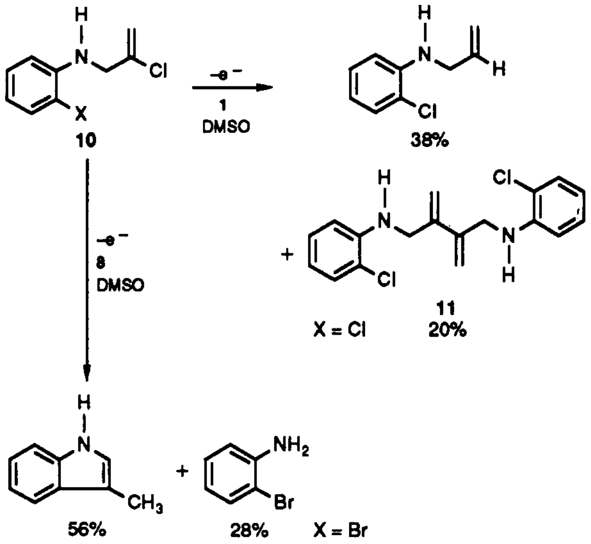
Intramolecular Reductive Coupling. Although many examples exist for intermolecular coupling of aryl halides catalyzed by zero-valent nickel, examples employing these catalysts for intramolecular coupling remain rare. Since 1 can effectively catalyze intermolecular couplings of aryl chlorides and 8 can similarly catalyze the coupling of bromides, we sought to define the applicability of these catalysts in electrocatalysis of intramolecular couplings, i.e., cyclizations.

The coupling of 9 (X = Cl) employing 1 as electrocatalyst produced small amounts (ca. 5%) of phenanthridine[37] along with reduction products 2-chloro-*N*-benzylaniline[38] and *N*-benzylaniline[39] (eq 11). Similarly, with 9 (X = Br) catalyzed by electroreduction of 8, the major products (2-bromo-*N*-benzylaniline and *N*-benzylaniline) result from simple reduction. Nonetheless, 8% of phenanthridine could also be isolated. The yield of intramolecular cyclization product derived from 1-catalyzed coupling of 9 (X = Cl) could be improved by substitution on nitrogen: under the same conditions, 9 (R = COPh) gave 30% of phenanthridine. In the electrocatalytic reduction of 8 in the presence of 9 (X = Br, R = COPh), however, only 6% of phenanthridine was formed. Possibly, the enhanced steric demand of the larger bromine atoms, together with the bulky triphenylphosphino functionalities held close to the catalytic nickel center cause this lower yield of cyclization product.[40]



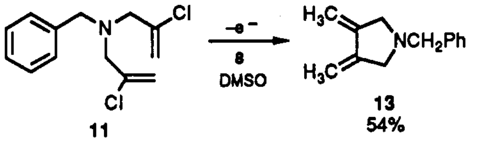
(11)

Similar intramolecular cross coupling was attempted between an aryl halide and a vinyl chloride. Compound 10 (X = Cl), for example, yielded reduction product (2-chloro-*N*-(2-propenyl)aniline, 38%) and dimerization product 11 (20%) without cyclization (eq 12). The major product (56%) isolated from the 8-electrocatalyzed reaction of 10 (X = Br) is 3-methylindole,[41] which is the aromatized tautomer of the initially formed coupling product, together with smaller amounts of 2-bromoaniline (25–30%).



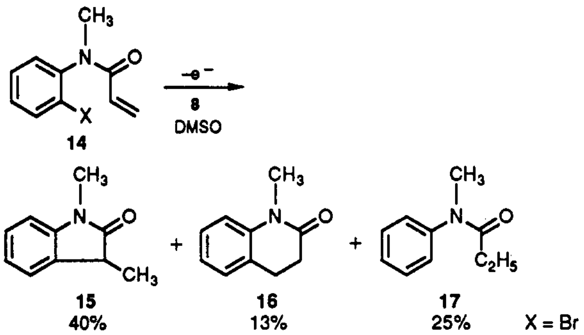
(12)

The analogous intramolecular coupling of bis(vinyl chloride) 12 was achieved with similar efficiency upon electrocatalysis by 8, producing diene 13 (eq 13).



(13)

The intermediate formed via oxidative insertion of Ni(0) into the aryl halide might also be trapped by an α,β-unsaturated amide (eq 14). The cyclization of 14 (X = Br), for example, to produce ring-closed products (15[42] and 16,[43] 53%) and reduction product 17[44] (25%) could be catalyzed by the electroreduction of 8. With 1, direct electroreduction to 17, i.e., of both the aryl bromide and α,β-unsaturated amide, became the dominant process.



(14)

In our hands, the chlorinated analogue 14 (X = Cl) gave no detectable cyclization with 8, despite a previous report that exo- and endo-ring closed products were produced by electrocatalysis by 8.[38] That better cyclization yields were obtained from the aryl bromide than the chloride implies smoother reaction under these conditions. Thus, vinyl chlorides and aromatic bromides, being more reactive, can be selectively coupled in the presence of aromatic chlorides upon electrocatalysis by 8. The intramolecular coupling of aryl chloride, which can be achieved via electrocatalysis by 1, albeit in moderate yield, can be a useful route to certain heterocyclic compounds.

Conclusions

The catalyst (1,2-bis(di-2-propylphosphino)benzene)-nickel(0), generated electrolytically in situ from dichloro-

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[36] Lourak, M.; Vanderesse, R.; Fort, Y.; Caubere, P. *J. Org. Chem.* **1989**, *54*, 4840.

[37] It is assumed that dihydrophenanthridine, the expected coupled product, was oxidized during work-up, since approximate 20% of dihydrophenanthridine in chloroform was oxidized to phenanthridine 19 in one day at room temperature: Wooten, W. C.; Makee, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 2946.

[38] Mori, M.; Ban, Y. *Tetrahedron Lett.* **1976**, 1807.

[39] Sprinzak, Y. *J. Am. Chem. Soc.* **1956**, *78*, 3207.

[40] Berndt, A.; Schemper, E. O. *Acta Crystallogr.* **1982**, *B38*, 2493.

[41] Wenkert, E.; Udelhofen, J. H.; Bhattacharyya, N. K. *J. Am. Chem. Soc.* **1959**, *81*, 3763.

[42] Wolfrom, M. L.; George, L. W.; Soltzberg, S. *J. Am. Chem. Soc.* **1934**, *56*, 1794.

[43] Morfat, A.; Carta, M. *Synthesis* **1987**, 515.

[44] Hammel, M.; Levine, R. *J. Org. Chem.* **1950**, *15*, 162.

(1,2-bis(di-2-propylphosphino)benzene)nickel(II) (1) under carefully chosen conditions is an effective electrocatalyst for the coupling of aryl chlorides. These conditions include use of a polar solvent with a large donor number (e.g., DMSO), a substrate which is not easily reduced directly (e.g., chlorobenzene), and a slightly elevated reaction temperature (ca. 65 °C).

Preparative yields of biphenyls as high as 96% with Faradaic efficiencies of greater than 97% were achieved using 2 mol % 1. These results compare very favorably with previously reported reactions employing (1,2-bis(diphenylphosphino)ethane)nickel(0) as the catalyst. In those reactions, 10 mol % of catalyst was required in order to achieve high yields of coupling products (i.e., five turnovers or less). Since 40–50 turnovers could be attained routinely with 1, the electrocatalyst could be present at an initial concentration about 1 order of magnitude lower than the previously described catalyst.

Although 1 is an effective catalyst in several reactions, it is by no means a panacea for the coupling of organic halides. Most organic halides undergo competitive direct reduction (and subsequently, dehalogenation) in parallel with, or instead of, coupling. In addition, the catalyst gradually deactivates under even the most favorable conditions, probably via oxidative insertion of Ni(0) into ligand phosphorus–carbon bond: dimerization and decoordination appear unlikely. These coupling reactions appear to proceed via a route consistent with the mechanism previously proposed by Amatore and Jutand. With 1, however, it appears unlikely that a reaction between Ni(I) and aryl halide competes with activation through Ni(0).

One reason that 1 may be a more effective catalyst is that its bulky phosphine ligands suppress dimerization. Dimerization via a Ni(I) species has been identified as a principal mode of deactivation in reactions with diphos Ni(0). The less bulky ethyl-substituted analogue 4, for example, was ineffective at coupling aryl halides. The relative catalytic inactivity of 4 is also attributed to dimerization. Nickel complexes of 1,2-bis(diphenylphosphino)ethane 7 were less effective than 1 in these electrocatalyses.

Intramolecular coupling products can be isolated in modest yield from aryl and vinyl chlorides upon catalytic reduction of 1 or from aryl bromides and vinyl chlorides from the more accessible 8.

Experimental Section

General. Phosphorus-31 NMR spectra were obtained on either a Varian FT80 and proton and carbon spectra were recorded on a General Electric QE-300 or GN-500 spectrometer. Chemical shifts are given in parts per million relative to phosphoric acid (^{31}P) or tetramethylsilane (^{1}H and ^{13}C). Gas–liquid chromatographic (GC) analyses were obtained using a Hewlett-Packard 5890 programmable chromatograph equipped with a capillary column and flame ionization detector. Peak intensities were monitored with a Hewlett-Packard 3390A integrator. Quantitative analyses by GC were made against biphenyl or 4,4′-dimethylbiphenyl as an internal standard. GC/MS analyses were performed on a Finnegan 700 mass spectrometer equipped with an ion trap detector.

The electrochemical experiments were performed on a Bioanalytical Systems BAS-100 electrochemical analyzer equipped with a Houston Instruments DMP-40 digital plotter or a Princeton Applied Research (PAR) electrochemical apparatus (Model 173 potentiostat, a Model 176 universal programmer, a Model 179 coulometer, and Houston Instruments Model 2000 x-y-t recorder). Cyclic voltammetry (CV) was performed in a single compartment cell equipped with a glassy carbon disk working electrode, a silver–silver nitrate reference electrode, and a platinum auxiliary electrode. Electrolyte solutions (0.2 M tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetrafluoroborate (TBABF$_4$)) were prepared just prior to use and were deaerated by bubbling argon. After recording a cyclic voltammogram of the electrolyte to ensure the absence of any electroactive impurities, the nickel complex was added ($\approx 10^{-3}$ M). Positive feedback was utilized in all CV experiments to compensate for IR drop between the working and reference electrodes.

Spectroelectrochemical experiments employed the use of a flow cell. A Waters HPLC pump was used to continuously circulate electrolyte between an electrochemical cell and a quartz cuvette. A Hewlett-Packard 8154A diode array spectrophotometer permitted continuous monitoring over a range of wavelengths during bulk electrolysis experiments.

Solvents and Reagents. All commercially available chemicals employed were reagent grade. Acetonitrile and HMPA were further purified by distillation from phosphorus pentoxide and subsequently stored under argon over 3A molecular sieves. Similarly, DMF, THF, and DMSO were distilled from calcium hydride and analogously stored. The supporting electrolytes (Southwestern Analytical Chemicals) were recrystallized from a mixture of acetone/diethyl ether and dried under vacuum (50 °C, 0.1 Torr, 24 h). Stock solutions of electrolyte (0.3 M TBAP or TBABF$_4$) in one of the above solvents were prepared prior to electrochemical experiments. The solutions were maintained under dry N$_2$ or Ar and were used within 48 h of preparation.

Unless noted otherwise, all manipulations involving phosphines were conducted under a dry or argon atmosphere, and compounds were used as received (Fisher Scientific, Mallinckrodt, Lancaster Synthesis, and Aldrich Chemicals).

Dichloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) (1).[45] Into a 50-mL round-bottom flask equipped with a stir bar and a septum were combined 460 mg (1.9 mmol) of $NiCl_2 \cdot 6H_2O$ and 25 mL of MeOH. The solution was degassed with bubbling argon, and a solution of 590 mg (1.9 mmol) of 1,2-bis(di-2-propylphosphino)benzene[20] in 15 mL of CH_2Cl_2 was added via cannula. After 30 min, the solution was cooled to 0 °C and filtered to isolate an orange crystalline product. The crystals were rinsed with cold MeOH and dried under vacuum: yield 0.64 g (75%); mp 277–285 °C dec; ^{31}P (CDCl$_3$) δ 78.0 ppm (s).

Dichloro(1,2-bis(diethylphosphino)benzene)nickel(II) (4).[45] Into a 50-mL round-bottom flask equipped with a stir bar and a septum were combined 950 mg (4.0 mmol) of $NiCl_2 \cdot 6H_2O$ and 25 mL of MeOH. The solution was degassed with bubbling argon, and a solution of 1.0 g (4.0 mmol) of 1,2-bis(diethylphosphino)benzene[20] in 15 mL of CH_2Cl_2 was added via cannula. After 30 min, the solution was cooled to 0 °C and filtered to isolate a yellow crystalline product. The crystals were rinsed with cold MeOH and dried under vacuum: yield 0.76 g (36%); mp 333–340 °C dec; ^{31}P (CDCl$_3$) δ 72.21 ppm (s).

General Procedure for the Preparative Electrocatalytic Coupling of Aryl Halides. A two-compartment electrochemical cell was rendered free of air and moisture by flushing with argon for at least 10 min while externally heating the vessel with a hot air gun. The cell was equipped with a freshly cleaned lithium wire anode (anode compartment), a carbon cloth cathode, ca. 3 cm × 4 cm (cathode compartment), and a Ag/AgNO$_3$ reference electrode with a DMSO/TBABF$_4$ bridge (cathode compartment). The cell was then filled with a 0.3 M solution of TBABF$_4$ in DMSO (ca. 25 mL in cathode compartment), immersed in a 65 °C oil bath, and purged with bubbling argon. A potential of −2.2 V was then applied (for ca. 5 min) in order to eliminate contaminants from the working electrode until a background current of about 30–80 μA was attained. The electrodes were then disconnected and withdrawn from the reaction mixture. The catholyte was poured into 150 mL of water, and the cathodic compartment was washed with 10 mL of water. The mixture was extracted ether or ethyl acetate and the organic layer was washed with 30 mL of water. After drying over anhyd Na$_2$SO$_4$ and filtration, the residue was concentrated on a rotary evaporator and purified by silica gel chromatography on a column and/or a Chromatotron plate. Where known compounds were involved, products were identified by comparison of spectroscopic properties and gas chromatographic retention times with authentic samples. Spectral information follows for previously unknown compounds.

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[45] Liu, S.-T. Ph.D. Dissertation, University of Texas at Austin, March, 1985.

The specific procedure is illustrated for the catalytic reduction of 4-chlorotoluene. To the cathodic compartment were added 1 mL (8.5 mmol) of 4-chlorotoluene, 74 mg (2 mol %) of catalyst precursor, and 6.5 mg (0.004 mmol) of biphenyl (internal standard for GLC analysis). When the solution had become homogeneous, electrolysis was begun at −2.2 V. Care was taken to demonstrate that in no case was the applied potential sufficient to initiate direct reduction of the halogenated substrate itself, i.e., the reported reactions represent electroreductions initiated by catalyst reduction. During the passage of the first 30 C of charge (ca. 2 electrons per molecule of catalyst), the reaction mixture's color changed from orange to yellow. After 50 C had passed, and every 100 C thereafter, a 0.1-mL sample was withdrawn from the cathode compartment and analyzed by GLC. After 820 C had passed (ca. 6 h), the current had decayed to 3 mA and the reaction was halted. GLC analysis of the final reaction mixture indicated that 96% of the starting substrate had been coupled to 4,4′-dimethylbiphenyl. The solution from the cathode compartment was then poured into 100 mL of diethyl ether, filtered, and extracted with two 50-mL portions of water. The ether layer was dried over sodium sulfate, filtered, and concentrated to isolate the desired product, 4,4′-dimethylbiphenyl: yield 0.60 g (82%); mp 117–119 °C.

Electrolysis of *N*-(2-Chlorobenzyl)-2-chloroaniline [9 (X = Cl, R = H)].[46] Electrolysis of 1 in the presence of 252 mg of **9** (X = Cl, R = H) gave 115 mg *N*-benzyl-2-chloroaniline. Yields of *N*-benzylaniline and phenanthridine were determined by GC and CG/MS, and the identity of the cyclization product was verified by isolation.

Electrolysis of *N*-(2-Bromobenzyl)-2-bromoaniline [9 (X = Br, R = H)].[47] From the electrolysis of 8 in the presence of 341 mg **9** (X = Br, R = H) were isolated 117 mg of *N*-benzyl-2-bromoaniline, 22 mg (12%) of *N*-benzylaniline, and 14 mg (8%) of phenanthridine.

Electrolysis of *N*-(2-Chlorobenzyl)-*N*-(2-chlorophenyl)benzamide [9 (X = Cl, R = COPh)]. To a stirred solution of **9** (X = Cl, R = H, 2.56 g) in 50 mL of methylene chloride and triethylamine (1.5 g) was added dropwise benzoyl chloride (1.24 g) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 3 h at room temperature. The mixture was poured into water and extracted with methylene chloride. The extract was dried over anhydrous $MgSO_4$. After concentration on a rotary evaporator, the crude product was recrystallized from ether to give 3.02 g (85%) of **9** (X = Cl, R = COPh): white solid; mp 87–88 °C; ^1H NMR ($CDCl_3$) δ 4.73 (d, *J* = 15.0 Hz, 1 H), 5.77 (d, *J* = 15.0 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.92 (dd, *J* = 7.0, 8.0 Hz, 1 H), 7.04–7.35 (m, 10 H), 7.56 (d, *J* = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 48.8, 126.8 , 127.1, 127.6, 127.7, 128.8, 128.9, 129.3, 129.9, 130.1, 131.2, 131.5, 132.8, 134.1, 134.2, 135.6, 139.5, 170.9; IR (KBr) 3070, 3033, 2959, 2927, 2870, 1661, 1590, 1482, 1447, 1379, 1307, 1094, 1074, 1053, 1005, 706 cm^{-1}; MS CI (M + 1/e), $C_{20}H_{16}Cl_2NO$ calcd 356.0609, found 356.0562.

After electrolysis of 1 in the presence of 356 mg of **9** (X = Cl, R = COPh), the catholyte was poured into 30 mL of 10% KOH in 1:1 mixture of methanol and water.[48] The mixture was stirred for 30 min and neutralized with NH_4Cl. The mixture was extracted with ether and dried over anhydrous Na_2SO_4 to give 108 mg of *N*-benzyl-2-chloroaniline and 54 mg of phenanthridine. The yield of *N*-benzylaniline was determined by GC and GC/MS.

Electrolysis of *N*-(2-Bromobenzyl)-*N*-(2-bromophenyl)benzamide [9 (X = Br, R = COPh)]. To a stirred solution of **9** (R = H, X = Br) in 5 mL of methylene chloride and triethylamine (0.2 g) was added dropwise benzoyl chloride (124.5 mg) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 3 h at room temperature. The mixture was poured into water, extracted with methylene chloride, and dried over anhyd $MgSO_4$. After filtration, the filtrate was concentrated on a rotary evaporator. The crude product was purified by recrystallization over ether to give 340 mg (76%) of the desired product **9** (X = Br, R = COPh): white solid; mp 130–131 °C; ^1H NMR ($CDCl_3$) δ 4.84 (d, *J* = 15.0 Hz, 1 H), 5.99 (d, *J* = 15.0 Hz, 1 H), 6.90–7.64 (m, 13 H); ^{13} C NMR ($CDCl_3$) δ 51.0, 123.5, 124.3, 127.4, 127.6, 127.7, 129.0, 129.1, 129.6, 131.2, 131.8, 132.5, 133.3, 135.5, 135.7, 140.6, 170.6; IR (KBr) 3069, 3001, 2971, 2941, 4879, 1660, 1578, 1490, 1451, 1381, 1300, 1074, 1001 cm^{-1}; MS CI (M + 1/e) $C_{20}H_{16}Br_2NO$ calcd 443.9599, found 443.9588.

After electrolysis of 8 in the presence of 341 mg of **9** (X = Br, R = COPh) and basic workup,[48] yields of *N*-benzyl-2-bromoaniline, *N*-benzylaniline, and phenanthridine were obtained by GC.

Electrolysis of *N*-(2-Chloro-2-propenyl)-2-chloroaniline [10 (X = Cl)]. To a stirred suspension of 2-chloroaniline (12.7 g, 0.1 mol) and potassium carbonate (10 g) was added 2,3-chloro-1-propene (17 g, 0.16 mol) at room temperature. The mixture was stirred at 90 °C for 12 h under N_2. After having been cooled to room temperature, the reaction mixture was poured into 100 mL of water and extracted with diethyl ether. After having been dried over anhyd Na_2SO_4, the filtrate was concentrated on a rotary evaporator. The residue was purified by vacuum distillation to give 3 g (15%) of **10** (X = Cl): bp 105 °C (0.2 Torr); ^1H NMR ($CDCl_3$) δ 3.95 (s, 2 H), 4.55 (br s, 1 H), 5.28 (s, 1 H), 5.33 (s, 1 H), 6.48–6.80 (m, 2 H), 7.00–7.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 49.6, 111.5, 112.4, ,118.1, 119.2, 127.8, 129.2, 138.4, 142.6; IR (neat) 3429, 3071, 2926, 1645, 1599, 1514, 1462, 1443, 1360, 1323, 1294, 1236, 1163, 1130, 1087, 1035, 925, 889, 808, 745 cm^{-1}; MS *m*/*e* calcd for $C_9H_9Cl_2N$ 201.0112 and 203.0083, found 201.0091 and 203.0088.

From the electrolysis of 8 in the presence of **10** (X = Cl) (201.8 mg) were isolated 63.5 mg of *N*-allyl-2-chloroaniline and 33.3 mg of dimer **11**. **11**: mp 121 °C; ^1H NMR ($CDCl_3$) δ 3.98 (s, 4 H), 4.52 (br s, 2 H), 5.23 (s, 4 H), 6.50–6.59 (m, 4 H), 7.02–7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 46.7, 111.4, 113.3, 117.4, 119.1, 128.8, 129.1, 141.7, 143.6; IR (KBr) 3424, 3075, 3022, 2933, 2864, 1597, 1514, 1460, 1445, 1433, 1383, 1323, 1296, 1273, 1235, 1159, 1129, 1076, 1032, 891 cm^{-1}; MS *m*/*e* calcd for $C_{18}H_{18}Cl_2N_2$ 332.0847, found, 332.0824.

Electrolysis of *N*-(2-Chloro-2-propenyl)-2-bromoaniline [10 (X = Br)]. To a stirred suspension of 2-bromoaniline (2.4 g, 14 mmol) and K_2CO_3 (2 g) was added 2,3-dichloro-1-propene (2.2 g, 19 mmol) at room temperature. The mixture was stirred for 12 h at 90 °C under N_2. After being cooled to room temperature, the reaction mixture was poured into 100 mL of water and extracted with diethyl ether. After drying over anhyd Na_2SO_4, the fitrate was concentrated on a rotary evaporator. The residue was purified by silica gel column chromatography (5% ethyl acetate/hexane) to give 680 mg (20%) of the desired product **10** (X = Br); ^1H NMR ($CDCl_3$) δ 3.95 (d, *J* = 5 Hz, 2 H), 4.82 (br s, 1 H), 5.28 (s, 1 H), 5.35 (s, 1 H), 6.56–6.62 (m, 2 H), 7.15 (m, 1 H), 7.41 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 49.9, 109.8, 111.7, 112.4, 118.7, 128.4, 132.5, 138.6, 143.7; IR (neat) 3420, 3069, 2924, 1645, 1597, 1512, 1458, 1441, 1429, 1360, 1321, 1292, 1263, 1165, 1126, 1086, 1047, 1020, 889, 744 cm^{-1}; MS *m*/*e* calcd for C_9H_9BrCl 244.9607 and 246.9577, found 244.9579 and 246.9589.

From the electrolysis of 8 in the presence of 123.5 mg of **10** (X = Br) was isolated 37 mg of 3-methylindole.

Electrolysis of *N*,*N*-Bis(2-chloro-2-propenyl)benzylamine (12). To a stirred suspension of benzylamine (5.4 g, 50 mmol) and powered potassium hydroxide (4 g) was added 2,3-dichloro-1-propene (15 g, 130 mmol). The mixture was stirred at 90 °C for 12 h, poured into water, and extracted with ether. The ethereal solution was washed with water and dried over anhyd Na_2SO_4. After filtration, the filtrate was concentrated on a rotary evaporator. The residue was purified by silica gel column chromatography (hexane) to give 5.0 g of **13**: ^1H NMR ($CDCl_3$) δ 3.30 (s, 4 H), 3.71 (s, 2 H), 5.34 (s, 2 H), 5.51 (s, 2 H), 7.24–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 57.0, 59.4, 114.2, 127.2, 128.3, 128.5, 138.3, 139.5; IR (neat) 3079, 3050, 3011, 2905, 2860, 2762, 1611, 1591, 1478, 1449, 1347, 1323, 1225, 1159, 1084, 1054, 1017, 945, 862, 727 cm^{-1}; MS *m*/*e* calcd for $C_{13}H_{15}Cl_2N$ 255.0582 and 257.0552, found 255.0578 and 257.0550.

From the electrolysis of 8 in the presence of 256 mg of **12** was isolated 100 mg (54%) of diene **13** as a viscous oil after purification on silica gel (15% ethyl acetate/hexane) **13**: ^1H NMR ($CDCl_3$) δ 3.32 (s, 4 H), 3.65 (s, 2 H), 4.91 (s, 2 H), 5.38 (s, 2 H), 7.18–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 59.8, 60.5, 103.3, 127.1, 128.2, 128.8, 138.4, 144.6; IR ($CDCl_3$) 3088, 3067, 3032, 2926, 2789, 1663, 1530,

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1497, 1455, 1426, 1372, 1329, 1298, 1248, 1142, 1028, 876 cm^{-1}; MS *m/e* calcd for $C_{13}H_{15}N$ 185.1205, found 185.1194.

Electrolysis of *N*-(2-Bromophenyl)-*N*-methyl-2-propenamide [14 (X = Br)].[49] From the electrolysis of 8 in the presence of 120 mg of 14 were isolated 63 mg of 15, 16, and 17 in a 1.6:0.5:1 ratio.

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Supplementary Material Available: ^{13}C NMR spectra of 9 (X = Cl, R = COPh), 9 (X = Br, R = COPh), 10 (X = Cl), 10 (X = Br), 12, and 13 (7 pages). Ordering information is given on any current masthead page.

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Electrochemical Cyclopropanation of Alkenes Using Dibromomethane and Zinc in CH_2Cl_2/DMF Mixture

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An efficient electrosynthesis of cyclopropanes from *gem*-dibromoalkanes and alkenes is achieved in a one-compartment cell fitted with a sacrificial zinc anode. The part played by the anodically generated Zn(II) in the coupling reaction is pointed out, and evidence for the existence of an organozinc species as intermediate is presented.

Introduction

The occurrence of the cyclopropane ring in many natural products and the utility of cyclopropanes as intermediates for ring expansions and chain elaborations[1] makes the cyclopropanation of a carbon–carbon double bond a highly useful operation in organic synthesis.

The Simmons–Smith reaction[2] is the most convenient method for the synthesis of these derivatives. An organozinc reagent is prepared from diiodomethane and zinc metal activated by preparation of zinc/copper or zinc/silver couples.[3] However, the reaction mixture is heterogeneous and long reaction time is required.

Some useful modifications of the reaction conditions have subsequently appeared. Diethylzinc, in Furukawa's method,[4] or triethylaluminum, in Yamamoto's one,[5] can be used as reductant instead of zinc metal. But the pyrophoric character of these compounds restricts the usefulness of these methods. Recently, Molander[6] reported the convenience of samarium–mercury amalgam to generate samarium carbenoids from diiodomethane for the efficient cyclopropanation of allylic alcohols.

Although dibromomethane is considerably less expensive, and more easy to store than diidomethane, only few works have been reported about its use in the Simmons–Smith reaction. In fact, the Zn/Cu couple needs a special activation to react with CH_2Br_2, such as ultrasound irradiation[7] or $TiCl_4$ catalysis.[8] The metal powder can also be prepared by Rieke's method.[9]

Electrosynthesis with sacrificial anodes has been successfully used as a substitute for many organometallic reactions,[10] and the applicability of this method in the field of cyclopropanation had to be investigated. The already described electrocatalytic process using nickel catalyst and zinc anode in DMF as solvent[11] was applied to dibromomethane with the aim of generating the desired organozinc reagent. This procedure enabled the cyclopropanation of cyclooctene, but with 1-octene rapid isomerization of the starting olefin occurred. Consequently, the nickel catalyst was excluded and direct reduction of CH_2Br_2 was attempted; cyclopropanes were obtained in high yield from a variety of alkenes, using a sacrificial zinc anode in a one-compartment cell supplied with constant current.

The scope of this electrochemical cyclopropanation reaction using various alkenes and dihalo compounds was examined and the role played by electrogenerated zinc(II) salts in the eventual formation of an organozinc species discussed.

Results and Discussion

The effects of the solvent and electrolysis conditions on the product cyclopropane yield were determined. Cyclopropanation of either cyclooctene or crotyl alcohol (eq 1) has served as a model to optimize the coupling reaction. The criteria were not only the chemical yield of isolated cyclopropane but also the amount of CH_2Br_2 used for total

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