ORGANOMETALLICS

Catalysis of Cross-Coupling and Homocoupling Reactions of Aryl Halides Utilizing Ni(0), Ni(I), and Ni(II) Precursors; Ni(0) Compounds as the Probable Catalytic Species but Ni(I) Compounds as Intermediates and Products

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Supporting Information



ABSTRACT: Both Ni(0) and Ni(I) compounds are believed to exhibit cross-coupling catalytic properties under various conditions, and the compounds Ni(PPh₃)₄ and NiCl(PPh₃)₃ are compared as catalysts for representative Suzuki–Miyaura and Heck-Mizoroki cross-coupling reactions. The Ni(0) compound exhibits catalytic activities, for cross-coupling of chloro and bromoanisole with phenylboronic acid and of bromobenzene with styrene, yielding results which are comparable with those of many palladium-based catalysts, but our findings with $NiCl(PPh_3)_3$ are at this point unclear. It seems to convert to catalytically active Ni(0) species under Suzuki-Miyaura reaction conditions and is ineffective for Heck-Mizoroki cross-coupling. The paramagnetic Ni(I) compounds NiX(PPh₃)₃ (X = Cl, Br, I) are characterized for the first time by ¹H NMR spectroscopy and are found to exhibit broad *meta* and *para* resonances at δ 9–11 and 3–4, respectively, and very broad *ortho* resonances at δ 4–6; these resonances are very useful for detecting Ni(I) species in solution. The chemical shifts of NiCl(PPh₃)₃ vary with the concentration of free PPh₃, with which it exchanges, and are also temperature-dependent, consistent with Curie law behavior. The compound trans-NiPhCl(PPh₃)₂, the product of oxidative addition of chlorobenzene to Ni(PPh₃)₄ and a putative intermediate in cross-coupling reactions of chlorobenzene, is found during the course of this investigation to exhibit entirely unanticipated thermal lability in solution in the absence of free PPh₃. It readily decomposes to biphenyl and NiCl(PPh₃)₂ in a reaction relevant to the long-known but little-understood nickel-catalyzed conversion of aryl halides to biaryls. Ni(I) and biphenyl formation is initiated by PPh3 dissociation from trans-NiPhCl(PPh3)2 and formation of a dinuclear intermediate, a process which is now better defined using DFT methodologies.

C ross-coupling reactions involving aromatic halides and main group metal-based nucleophiles are currently utilized to form a wide variety of carbon-carbon and carbon-heteroatom bond types.¹ By and large, a significant proportion of these reactions are catalyzed by Pd(0)compounds of the type PdL_2 (L = phosphine ligand) via catalytic cycles which typically involve two-electron processes in which the metal alternates between the 0 and the II oxidation states as indicated in Scheme 1 (M = Pd) for a generic Suzuki-Miyaura cross-coupling reaction.

While very successful for aryl and vinyl halides, this type of cross-coupling turns out to be much less useful for alkyl halides containing β -hydrogen atoms; although, there have been reported a few examples of successful cross-coupling of primary alkyl halides and tosylates with e.g. organoboron reagents.²

Although lagging considerably behind the development of Pd-based catalysts, a number of Ni-based catalysts have also been investigated and found to catalyze rapid cross-coupling of

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Scheme 1. Two-Electron Catalytic Cycle for Suzuki– Miyaura Cross-Coupling Processes



alkyl halides.³ Interestingly, cross-coupling reactions of secondary alkyl halides have also been accomplished,⁴ including examples of stereoconvergent reactions in which both enantiomers of a racemic reactant are converted to a single resolved product.^{4j,l,m}

In many earlier investigations of Ni-based cross-coupling catalysts, it often seems assumed, implicitly or explicitly, that two-electron catalytic cycles of the type shown in Scheme 1 (M = Ni) are operational. However, stereoconvergent processes are incompatible with such two-electron catalytic cycles, which should result in the same configurational consequences for both enantiomers, and mechanisms involving catalysis by Ni(I) compounds and free radical intermediates have been proposed. A candidate one-electron process is shown in Scheme 2.^{30,p,u,v,4}

Scheme 2. Possible Catalytic Cycle for Suzuki–Miyaura Cross-Coupling Involving Ni(I)



This catalytic cycle begins with a halonickel(I) compound NiXL_n and differs from the catalytic cycle shown in Scheme 1 in that odd-electron intermediates⁵ are involved, and the metal alternates between the I and III oxidation states. Unambiguous mechanistic information has generally been difficult to come by, however, as many Ni-based catalysts are as yet very poorly defined. Indeed, very little is known about the possible roles of Ni(I) species as catalysts or catalytic intermediates, and there is a need for information on any kind concerning the chemistry of Ni(I) compounds.

Although drawing considerably less attention than Pd-based catalyst systems, a number of phosphine-stabilized, Ni-based catalysts have been investigated for coupling of aromatic electrophiles.^{6a-y} While most of such studies utilized Ni(II) precursors because of a dearth of useful Ni(0) candidates,^{3v} it seems generally to have been assumed that the actual catalytic species were Ni(0) species formed in some way in situ. The mechanism of Scheme 1 is commonly thought to apply, although again there is currently available very little information in most cases as to what the actual catalytic species are. Interestingly, and possibly complicating the issue, phosphine complexes of Ni(0) and Ni(II) can undergo comproportionation to Ni(I) species sufficiently readily that the presence of both during an activation stage or in a catalytic cycle can result

in the formation of Ni(I) compounds,⁷ which may or may not be involved in a catalytic cycle.

This paper describes the early stages of an investigation into the comparative use of Ni(0) and Ni(I) phosphine complexes as catalysts for representative cross-coupling catalytic processes of alkyl and aryl halides. In an attempt to address these issues, we have begun to map out potentially relevant catalytic Ni(0)and Ni(I) chemistry utilizing the Ni(0) compound Ni(PPh₃) $_{4}^{4}$ and the Ni(I) compound NiCl(PPh₃)₃.^{7a,9} While Suzuki-Miyaura cross-coupling reactions of aryl electrophiles have been catalyzed by a number of Ni-based catalyst systems, ^{6b-q,x,y,7d-f} including some containing PPh₃,^{6e,g,i,j,l-p} preformed Ni(PPh₃)₄ has in fact rarely been utilized 6n,o and thus the capabilities and potential advantages of this readily available catalyst are largely unknown. To our knowledge, very little is known also about the catalytic chemistry of NiCl(PPh₃)₃, although Ni(I) complexes of 1,1'-bis(diphenylphosphino)ferrocene (dppf) are receiving considerable attention.^{7d}

We have complemented our catalytic research by using NMR spectroscopy to characterize the paramagnetic Ni(I) compounds NiX(PPh₃)₃ (X = Cl, Br, I) and their very facile exchange processes with free PPh₃. To gain further mechanistic information, we have also carried out NMR studies of the oxidative-addition reactions of Ni(PPh₃)₄ with chloro and bromobenzene, reactions which give the Ni(II) products *trans*-NiPhX(PPh₃)₂ (X = Cl, Br).^{6k,n,p,s,10} Literature reports on the thermal stabilities of these compounds differ substantially,^{60,s,10b,e,h} and we now show that *trans*-NiPhCl(PPh₃)₂ is very stable in solution at room temperature in the presence of free PPh₃, but in the absence of added ligand, it decomposes smoothly and rapidly to biphenyl and the Ni(I) compound NiCl(PPh₃)₂. The latter finding has major mechanistic implications for Ni-catalyzed conversion of aryl halides to biaryls.^{8a,10d-f}

RESULTS AND DISCUSSION

Syntheses and Properties of Ni(0), Ni(I), and Ni(II) Coordination Compounds of PPh₃. The ligand PPh₃ was chosen for reasons given above but also, in part, because PPh₃ conveniently forms well-characterized nickel complexes in all three oxidation states of interest, Ni(PPh₃)₄, ⁸ NiX(PPh₃)₃ (X = Cl, Br, I),^{7a,9,10b,10j} and NiX₂(PPh₃)₂ (X = Cl, Br, I).¹¹ While a number of routes to Ni(0) and Ni(I) compounds have been described, Ni(I) materials containing apparent impurities and hence having significantly different colors have been reported, and we therefore describe in some detail the procedures which we have developed for synthesis and characterization.

The compounds $NiX_2(PPh_3)_2$ (X = Cl, Br, I) are readily prepared via reactions of the Ni(II) halides with PPh3; all assume pseudotetrahedral structures and are paramagnetic (two unpaired electrons) in solution and in the solid state.¹¹ Interestingly, and in spite of their paramagnetism, all exhibit useful ¹H NMR spectra; broad but readily identified resonances are observed at $\delta \sim 19$ (br), ~ 1 (vbr), and ~ -5.5 (br) and have been attributed on the basis of relative intensities, line widths, and mechanism of spin delocalization to the meta, ortho, and para hydrogens, respectively.¹² Thus the meta resonance shifts ~12 ppm downfield, and the ortho and para resonances shift ~6 and ~12.5 ppm upfield, respectively, from the corresponding chemical shifts of diamagnetic PPh₃ ($\delta \sim 7$), isotropic shifts which have been interpreted in terms of unpaired spin on the Ni(II) being delocalized into the ligand π system via a contact interaction.

The Ni(0) compound Ni(PPh₃)₄ was readily prepared via reduction of NiCl₂(PPh₃)₂ by zinc powder in the presence of excess PPh₃ in DMF (eq 1).^{8a}

$$NiX_2(PPh_3)_2 + Zn + 2PPh_3 \rightarrow Ni(PPh_3)_4 + ZnX_2$$
(1)

The orange-red, air-sensitive Ni(0) compound was characterized by broad phenyl resonances at $\delta \sim 7.0$ and ~ 7.8 in the ¹H NMR spectrum and a very broad resonance at $\delta \sim 24$ in the ³¹P NMR spectrum (toluene- d_8), in agreement with the literature.^{8h} The ³¹P resonance is broadened because Ni(PPh₃)₄ dissociates significantly to Ni(PPh₃)₃ plus free PPh₃, and the mixture engages in rapid exchange.^{8h}

The Ni(I) compounds NiX(PPh₃)₃ (X = Cl, Br, I) are best prepared via disproportionation reactions of Ni(PPh₃)₄ with NiX₂(PPh₃)₂ (eq 2).^{7a,9g,k,l}

$$Ni(PPh_3)_4 + NiX_2(PPh_3)_2 \rightarrow 2NiX(PPh_3)_3$$
(2)

Although the overall process from Ni(II) to Ni(0) to Ni(I) involves two steps, we find that it is not generally feasible to prepare Ni(I) compounds directly from Ni(II) precursors because mixtures of Ni(0) and Ni(I) are obtained.

The Ni(I) compounds NiX(PPh₃)₃ (X = Cl, Br, I) are also tetrahedral in the solid state although they are believed to dissociate in solution to the bis-phosphine species NiX-(PPh₃)₂.^{7a,9a} They are paramagnetic species with one unpaired electron,^{7,9d} a fact which has apparently discouraged others from pursuing NMR studies of them. However, while their ³¹P resonances are too broad to be observed, we find that all three can readily be characterized by their ¹H NMR spectra. As an example, the ¹H NMR spectrum of NiCl(PPh₃)₃ in toluene-*d*₈ (Figure 1) exhibits resonances at $\delta \sim$ 9.3 (br), ~5.2 (vbr), and



Figure 1. ¹H NMR spectrum of NiCl(PPh₃)₃ in toluene- d_{8i} * = solvent resonances. The weak resonance at δ 7.70 has also been observed in many spectra, including that of Ni(PPh₃)₄, and is attributed to an unidentified diamagnetic PPh₃ species. A COSY experiment showed that its other phenyl resonances are obscured by the solvent resonances; a sharp, weak resonance in ³¹P NMR spectra is also attributed to this minor species.

~3.7 (br), attributed to the *meta*, *ortho*, and *para* hydrogens, respectively, on the basis of relative intensities and line widths. The corresponding *meta*, *ortho*, and *para* resonances of NiBr(PPh₃)₃ and NiI(PPh₃)₃ are observed at δ 9–11, 4–5 and ~3, respectively, and thus the spectra exhibit characteristic resonances which are well outside the normal aromatic region for diamagnetic compounds. The spectra differ also from those of the Ni(II) species NiX₂(PPh₃)₂ (X = Cl, Br, I) (see above) and can be used to identify Ni(I) species in solution.^{7g,h}

That said, we note that $NiCl(PPh_3)_3$ has been shown to dissociate significantly in solution to the bis-phosphine Ni(I)

compound NiCl(PPh₃)₂ (eq 3).^{7a,9a} The degree of dissociation does not seem to be known precisely although the bisphosphine compound has been isolated and characterized crystallographically.^{9j}

$$NiX(PPh_3)_3 \rightleftharpoons NiX(PPh_3)_2 + PPh_3$$
(3)

Since the resonances of free PPh₃ are not observed in solution spectra of NiCl(PPh₃)₃, it follows that exchange between free and coordinated ligands must be rapid on the NMR time scale, and it seemed plausible that the chemical shifts might vary somewhat if the concentration of free PPh₃ varied. We therefore carried out an NMR study of NiCl(PPh₃)₃ in which 1 equivalent of PPh₃ had been added, finding that the spectrum now exhibited resonances at δ 8.0, 6.4, and 5.7. Thus all three averaged resonances shifted toward the chemical shifts of diamagnetic PPh₃ (δ 7.0–7.3), consistent with the exchanged process hypothesized in eq 3, and it seems clear that the broad resonances shown in Figure 3 are in fact weighted averages of the resonances of comparable amounts of free PPh₃ and the bis-phosphine compound NiCl(PPh₃)₂.

The ¹H chemical shifts of the Ni(I) compounds are also temperature dependent, the *meta* resonance at $\delta \sim 9$ shifting upfield, and the *ortho* and *para* resonances at $\delta \sim 5$ and ~ 3 shifting downfield as the temperature increases. A plot of the chemical shifts of NiCl(PPh₃)₃ vs T⁻¹ are shown in Figure 2, where the linearity expected of Curie law behavior¹³ is observed.



Figure 2. Curie law plot for the phenyl resonances of NiCl(PPh₃)₃ in toluene- d_8 ($\blacklozenge = meta$, $\blacksquare = ortho$, $\blacktriangle = para$).

The observed Curie law behavior suggests that dimerization to spin-paired $[NiCl(PPh_3)_2]_2$ is not significant over the temperature range studied and that the extent of dissociation remains essentially constant, and therefore presumably complete. Thus the concentrations of free PPh₃ and NiCl- $(PPh_3)_2$ in solutions of NiCl(PPh₃)₃ are essentially identical, and the intrinsic chemical shifts of the *meta*, *ortho*, and *para* hydrogens of NiCl(PPh₃)₂ should be $\delta \sim 11.3, \sim 3.4$, and ~ 0.4 , respectively. We shall say more on this issue below.

The patterns of chemical shifts and line widths for the Ni(I) compounds resemble those discussed above for the corresponding tetrahedral Ni(II) compounds NiX₂(PPh₃)₂, and it seems very likely that the same mechanism for π electron delocalization into the ligand π orbitals of the tetrahedral Ni(I) species pertains, with *meta*, *ortho*, and *para* isotropic shifts being \sim 3, \sim -2, and \sim -4 ppm, respectively. These shifts are considerably less than the isotropic shifts observed for the

Ni(II) compounds and are qualitatively consistent with the fact that the Ni(II) compounds contain two unpaired electrons, whereas the Ni(I) compounds contain only one and that there is less unpaired-electron spin available for delocalization in the latter.

An EPR spectrum of a solid sample was run at 77 K and found to exhibit a resonance at $g \approx 2.22$ (Figure 3), which is consistent with the presence of Ni(I).^{7,9k,m}



Figure 3. EPR spectrum of NiCl(PPh₃)₃ at 77 K.

Catalytic Cross-Coupling Utilizing Ni(PPh₃)₄ and NiCl-(PPh₃)₃. We have carried out an investigation of the catalytic effectiveness of Ni(PPh₃)₄ for a representative Suzuki–Miyaura cross-coupling reaction between phenylboronic acid and 4bromoanisole (eq 4); the latter was chosen to distinguish between the desired product 4-methoxybiphenyl and biphenyl, the sometimes observed homocoupling product of phenylboronic acid.

$$PhB(OH)_{2} + MeO - He - Br - He - OMe \quad (4)$$

Duplicate or more runs were carried out in all cases, and reaction profiles were generated by monitoring the loss of starting compound and conversion to product by GC. Shown in Figure 4 are representative reaction profiles for the formation of 4-methoxybiphenyl from 4-chloro and 4-bromoanisole utilizing Ni(PPh₃)₄ as catalyst.

As can be seen, there was generally good mass balance between reactant and product. Our reaction profiles also provide information on the time scale over which the crosscoupled products are formed. Most publications in the area of catalytic cross-coupling reactions report isolated yields, obtained on termination of reactions after arbitrary periods of time.¹⁻⁴ In such studies, little distinction can be made between catalytic reactions which are still proceeding at the point of termination and those whose rates have decreased to zero before the point of termination. Indeed, the advantages of reactions which are completed within a relatively short time span, well before the point of termination, likewise remain unappreciated. Thus use of isolated yields in comparisons of various catalysts and ligand systems can be misleading.

Interestingly, catalysis of the Suzuki–Miyaura reaction by Ni(PPh₃)₄ is approximately as effective as is catalysis by the Pd(0) analogue, Pd(PPh₃)₄, investigated previously under comparable conditions albeit with somewhat lower catalyst loadings.^{14a} Indeed, Ni(PPh₃)₄ is almost as effective for this cross-coupling reaction as is the very good catalyst Pd-[PBut₃]₂.^{14a} suggesting that catalysis by nickel may be more broadly useful than is commonly thought.

Shown in Figure 5 for purposes of comparison are analogous reaction profiles for the same reaction utilizing NiCl(PPh₃)₃ as catalyst. Experiments involving use of NiBr(PPh₃)₃ as catalyst gave similar results, but use of $NiCl_2(PPh_3)_2$ or a combination of NiCl₂(PPh₃)₂ and zinc powder produced no product after 24 h. In addition, no usefully successful cross-coupling reactions involving alkyl halides were found using either $Ni(PPh_3)_4$ or $NiCl(PPh_3)_3$. The apparent near equivalence of Ni(0) and Ni(I) catalyst precursors surprised us, as we anticipated significant differences in activities. We therefore utilized ¹H NMR spectroscopy in attempts to determine the nature of the species present in live catalytic mixtures.^{7h} Aliquots from crosscoupling reactions involving Ni(0) and Ni(I) catalysts were periodically removed, taken to dryness, and extracted with toluene-d₈. NMR spectra run immediately exhibited no resonances attributable to Ni(I) species, and thus we assume that in all cases catalysis involved Ni(0) as in Scheme 1. We have been unable to determine just how the change in oxidation state might have been effected, but we note that facile interconversion between oxidation states has also been noted in the analogous dppf catalyst system.^{7d}

Figure 6 shows an analogous reaction profile for the Heck–Mizoroki reaction of bromobenzene with styrene to give *trans*stilbene (eq 5). Reactions were again carried out in duplicate and monitored by GC.

$$PhBr + PhCH=CH_2 \xrightarrow{Ni(PPh_3)_4} (5)$$

Again, excellent mass balance is observed, and again, catalysis by Ni(PPh₃)₄ essentially matches that by Pd[PBu^t₃]₂,^{14b} although, perhaps surprisingly in view of effective catalysis of Suzuki–Miyaura coupling by NiCl(PPh₃)₃, Heck–Mizoroki



Figure 4. Formation of 4-methoxybiphenyl and decay of 4-chloroanisole (a) and of 4-bromoanisole (b) using Ni(PPh₃)₄ as catalyst.



Figure 5. Formation of 4-methoxybiphenyl and decay of 4-chloroanisole (a) and 4-bromoanisole (b) using NiCl(PPh₃)₃ as catalyst.



Figure 6. Formation of *trans*-stilbene and decay of bromobenzene using $Ni(PPh_3)_4$ as catalyst.

coupling was not affected by NiCl(PPh₃)₃. We also assessed the possibility of using NiCl(PPh₃)₃ and NiCl₂(PPh₃)₂ in the presence of zinc dust, which would reduce both to Ni(0) species. Reaction profiles of these reactions were very similar to that shown in Figure 6, indicating that catalysis of this Heck–Mizoroki reaction does not require the use of preformed Ni(PPh₃)₄. The reaction profiles are shown in the Supporting Information (SI), Figures S1 and S2.

An NMR Study of the Oxidative-Addition Reactions of Aryl Halides to Ni(PPh₃)₄ and of the Decomposition of trans-NiPhCl(PPh₃)₂. As shown above, $Ni(PPh_3)_4$ is an excellent catalyst for cross-coupling of aryl halides, presumably via the type of catalytic cycle shown in Scheme 1 and involving an oxidative step to yield an aryl-nickel intermediate. In contrast, as mentioned above, Ni(PPh₃)₄ is found not to catalyze cross-coupling of representative alkyl halides, and thus this catalyst system differs fundamentally from nickel catalyst systems reported elsewhere.^{3,4} The difference lies not in lack of reactivity, however, as we have actually found that primary, secondary, and even tertiary alkyl halides all react readily with Ni(PPh₃)₄; they just do not give the anticipated alkyl-nickel products. In an attempt to better understand these differences in chemistry, we have carried out extensive NMR studies of reactions of Ni(PPh₃)₄ with representative aryl and alkyl halides. Our results with aryl halides are described below and then related to catalytic biaryl formation. Reactions with alkyl halides turned out to proceed in a very different fashion, however, and will be described elsewhere.¹

The oxidative addition of chlorobenzene to $Ni(PPh_3)_4$ is reported to proceed as in eq 6.^{10a,g}

$$Ni(PPh_3)_4 + PhCl \rightarrow trans-NiPhCl(PPh_3)_2 + 2PPh_3$$
(6)

Presented in Figure 7 is a stacked plot showing representative ¹H NMR spectra for an oxidative-addition



Figure 7. Stacked plot of the course of an oxidative-addition reaction of a 4-fold excess of chlorobenzene to $Ni(PPh_3)_4$.

experiment involving reaction of Ni(PPh₃)₄ with a 4-fold excess of chlorobenzene in toluene- d_8 and monitored at 30 min intervals for 8 h. The data presented in Figure 7 are for the Ni(PPh₃)₄ starting material alone and for the reaction mixture at 10, 30, 60, 180, and 360 min after initiation. Note that the resonances of unreacted chlorobenzene are observed at δ 6.8–6.85 (m) and 7.04–7.08 (m) and remain unchanged throughout the reaction. Also shown is the CHD₂ resonance of the solvent at δ 2.09, useful as an internal standard for chemical shift and relative intensity measurements.

As can be seen, the resonances of Ni(PPh₃)₄ at δ 6.93 and 7.35 disappear quickly as resonances of *trans*-NiPhCl(PPh₃)₂ appear at δ 6.23, 6.33, and 7.72. The other Ni-Ph and PPh₃ resonances of *trans*-NiPhCl(PPh₃)₂ occur at δ 6.95 and 7.0– 7.1, respectively (COSY), and overlap significantly with the chlorobenzene multiplet resonance at δ 7.04–7.08 and a broad resonance of free PPh₃ at δ ~7.0. These result in the broad, irregular feature observed in the region δ 6.9–7.1 in the earliest spectra. The intensities of the three resonances of *trans*-NiPhCl(PPh₃)₂ at δ 6.23, 6.33, and 7.72 cease growing within the first hour, indicating that the oxidative-addition reaction was completed as in eq 6. Furthermore, little change was noted in the intensities or chemical shifts of the resonances of *trans*-NiPhCl(PPh₃)₂ over several hours, and thus this compound is reasonably stable under these conditions.

That said, the resonances of the free PPh₃, 2 equivalents of which are expected to be present on the basis of the stoichiometry of eq 6, are identified as the broad resonances at δ 7.05 and 7.29 in the spectrum obtained at 10 min, slightly shifted from the positions of free PPh₃ at δ 7.03 (br, o-H) and 7.32 (br, m-, p-H). This difference may seem only marginally significant, but the trends apparently continue and, within 6 h these resonances had shifted to δ 7.14 and 7.23 and were sufficiently separated from other resonances that they could be shown to have intensities comparable both to each other and, as expected, to that of the resonance of trans-NiPhCl(PPh3)2 at δ 7.72 (all 12H). In addition, as time progressed, a triplet with intensity about half those of the others and hence attributable to the *p*-H emerged from around δ 7.0 and shifted upfield to δ 6.90 after 6 h. Thus the free PPh₃ in solution was undergoing rapid exchange with a species, of very low initial but growing concentration, and presumably of Ni(I), for which the *m*-H lies downfield and the *o*- and *p*-H upfield of the positions of the free ligand. A ³¹P NMR spectrum run after 6 h exhibited only a single sharp resonance, at δ 21.6, attributable to *trans*-NiPhCl(PPh₃)₂; there was no resonance visible for free PPh₃.

A variable-temperature NMR experiment was therefore carried out on a fresh solution of *trans*-NiPhCl(PPh₃)₂ containing 2 equivalents of free PPh₃, formed like the sample considered in Figure 7 by reaction of Ni(PPh₃)₄ with chlorobenzene. A room-temperature ¹H NMR spectrum of the sample was as in Figure 7, but a spectrum run at 223 K did indeed exhibit weak, broad resonances at δ 10.20, 4.27, and 2.70. These chemical shifts compare well with the lowtemperature chemical shifts shown in Figure 2, and thus the resonances are attributed to NiCl(PPh₃)₃. Consistent with the exchange process discussed above, the three resonances were much broader at 233 K and had shifted toward the corresponding diamagnetic positions and were not observed at higher temperatures.

Complementing these ¹H NMR data, a ³¹P NMR spectrum run at room temperature revealed only the sharp singlet of *trans*-NiPhCl(PPh₃)₂, with no resonance of PPh₃ being apparent. On cooling the sample to 243 K and then to 233 K, however, a broad resonance of free PPh₃ did appear and then narrow somewhat, and at 223 K, the spectrum exhibited sharp resonances of comparable intensity for *trans*-NiPhCl(PPh₃)₂ at δ 22.7 and for free PPh₃ at δ –7.12 (Figure 8).

Thus the free PPh₃ was undergoing ligand exchange with a species which was evidently not *trans*-NiPhCl(PPh₃)₂ since its ¹H and ³¹P resonances remained sharp and unshifted throughout. The exchange partner was clearly of a nature which could induce the pronounced line broadening observed and is almost certainly the paramagnetic Ni(I) species NiCl(PPh₃)₃ for which the ³¹P resonance is too broad to be observed. Participation of the latter compound as the emerging exchange partner would result in the assignments noted in



Figure 8. 31 P NMR spectra of a 1:2 mixture of NiPhCl(PPh₃)₂ and PPh₃ at 223, 233, and 243 K.

Figure 7, since each of the three resonances is shifting toward the resonance positions of NiCl(PPh₃)₃ as time progresses.

A similar result has been reported for the ³¹P NMR spectrum of *trans*-NiPhCl(PPh₃)₂ in the chlorobenzene in which it was prepared from Ni(PPh₃)₄.⁶ⁿ A broadened resonance of the free ligand was observed in this instance, and the broadening was attributed to exchange with unreacted Ni(PPh₃)₄. This rationale seems unlikely, however, given the presence of a large excess of chlorobenzene and the rapidity with which the oxidative-addition reaction occurs.

We now address the issue of the source of the Ni(I) species, which was clearly present from the beginning and then slowly increased in concentration. Conventional wisdom has long held that oxidative-addition reactions of aryl halides to compounds of Ni(0) and Pd(0) proceed via a concerted process similar to that shown in Scheme 3.¹⁶

Scheme 3. Concerted Mechanism for Oxidative Addition of Aryl Halides to M(0) Species



This process would not, of course, result in the formation of paramagnetic intermediates or products.

An alternative mechanism for oxidative addition of aryl halides ArX (X = Cl, Br) to Ni(PEt₃)₄ that does involve paramagnetic intermediates and products was proposed in 1979 by Tsou and Kochi (Scheme 4).^{17a} In this, a single-electron

Scheme 4. Electron-Transfer/Radical-Pair Mechanism for Oxidative Addition of Aryl Halides to M(0) Species

NiL₄
$$\longrightarrow$$
 NiL₃ + L (L = PEt₃) Preequilibrium
NiL₃ + ArX \longrightarrow [NiL₃* + ArX•⁻] Electron transfer
[NiL₃* + ArX•⁻] \longrightarrow NiArXL₂ + L Collapse within solvent cage
NiL₃* + ArX•⁻] \longrightarrow NiArXL₂ + L Collapse within solvent cage
NiL₃* + ArX•⁻] \longrightarrow NiArXL₂ + Ar• Reactions following diffusion from solvent cage

transfer (SET) process yields a radical-ion pair which can undergo combination within the solvent cage to give NiArX(PEt₃)₂, which were observed and which are, of course, identical to the products of oxidative addition via a concerted process.

Alternatively the radical species can diffuse from the solvent cage to give Ni(I) products $NiX(PEt_3)_3$, which were observed, and aryl radicals which abstract a hydrogen atom from the solvent SH to give arene products, which were also observed.

This paper has been much cited in the literature as evidence for possible roles of Ni(I) species as intermediates for e.g. the chemistry outlined in Scheme 2,^{3,4} and somewhat similar observations have also been made for a dppf-Ni(0) system.^{7f} Although we had no a priori reason to suspect that our observed oxidative addition of chlorobenzene to Ni(PPh₃)₄ to give *trans*-NiPhCl(PPh₃)₂ did not proceed via the type of concerted process shown in Scheme 3, the NMR studies discussed above in connection with Figures 7 and 8 seemingly required that a small amount of Ni(I) species was present from the beginning. The Ni(I) could result from competitive processes involving concerted and radical mechanisms, as in Schemes 3 and 4, or it could result from a very slow secondary reaction involving the Ni(II) product, *trans*-NiPhCl(PPh₃)₂.

Tsou and Kochi reported also that the Ni(I)/Ni(II) product ratios decreased drastically in the order I > Br > Cl,¹⁷ h and we therefore examined reactions of Ni(PPh₃)₄ with bromo and iodobenzene. Under reaction conditions analogous to those used for chlorobenzene, we found that bromobenzene reacts smoothly to give a good yield of trans-NiPhBr(PPh₃)₂₁ identified by ¹H NMR resonances at δ 6.32 (1H, p-H of Ni-Ph), 6.22 (2H, m-H of Ni-Ph), and 7.74 (12 H, m, PPh), all very similar to the corresponding resonances of trans-NiPhCl(PPh₃)₂ and justifying the assignments. Interestingly, the intensities of the resonances of trans-NiPhBr(PPh₃)₂ remained unchanged over several hours at 0 °C, although the resonances of the free PPh3 were again clearly exchanging with an unobserved species, presumably NiBr(PPh₃)₃. Thus the chloro and bromo systems were very similar in their tendencies to form diamagnetic species trans-NiPhX(PPh₃)₂ rather than paramagnetic Ni(I) compounds NiX(PPh₃)₃.

In the case of the reaction of Ni(PPh₃)₄ with iodobenzene, however, a resonance attributable to the NiPh group of NiPhI(PPh₃)₂ was observed at δ 6.24 in the first spectrum run, but it was too broad for J-coupling to be observed. All of the other resonances in the spectrum were broadened as well, and the resonances of the free PPh₃ diverged from the diamagnetic positions much more than was the case with the chloro and bromobenzene systems. All of these observations, taken together, indicate the presence of higher concentrations of paramagnetic Ni(I) species and hence possibly a higher propensity to the type of SET process shown in Scheme 4.

Thus both Ni(PEt₃)₄ and Ni(PPh₃)₄ undergo oxidativeaddition chemistry to yield both adducts of the type *trans*-NiPhXL₂ and Ni(I) halo compounds with proclivities to Ni(I) increasing in the orders PhCl \leq PhBr < PhI and Ni(PPh₃)₄ < Ni(PEt₃)₄. However, formation of Ni(I) species occurs concurrently with oxidative addition with Ni(PEt₃)₄ but not necessarily with Ni(PPh₃)₄.

Intrinsic Instability of *trans*-NiPhCl(PPh₃)₂ and the Relevance Thereof to Catalytic Biaryl Formation. Paramagnetic Ni(I) species may also arise as products of a secondary reaction following the oxidative-addition step, and we note that the experiments described in Figures 7 and 8

involved studies of *trans*-NiPhCl(PPh₃)₂ in the presence of 2 molar equivalents of PPh₃. We therefore ran a room-temperature ¹H NMR spectrum of a sample of large, visually pure orange crystals of *trans*-NiPhCl(PPh₃)₂ which had been grown at -30 °C in a toluene/hexanes mixture containing free PPh₃. The NMR solution contained no added PPh₃, however, and to our surprise, a spectrum run immediately after mixing (Figure 9) exhibited, in addition to the resonances of *trans*-



Figure 9. ¹H NMR spectrum of a solution containing *trans*-NiPhCl(PPh₃)₂ (observable resonances denoted by arrows; others obscured by solvent resonance at δ 6.99), biphenyl (#), and an apparent Ni(I) species (see text); * = solvent resonances.

NiPhCl(PPh₃)₂, relatively intense resonances of biphenyl at δ 7.40, 7.20, and ~7.10 and broad new resonances at δ ~10.6 (br), 4.1 (vbr and hence, barely perceptible above the baseline), and 1.86 (br).

The new, broad resonances resemble those of NiCl(PPh₃)₃ (Figure 1) in that an apparent *meta* resonance ($\delta \sim 10.6$) is broad and shifted to low field, an apparent *para* resonance ($\delta \sim 1.86$) is comparably broad and shifted to high field, and an apparent *ortho* resonance ($\delta \sim 4.1$) is much broader and is shifted upfield from the diamagnetic positions. These chemical shifts differ significantly from the averaged chemical shifts of NiCl(PPh₃)₃, i.e. of a 1:1 mixture of NiCl(PPh₃)₂ and PPh₃, shown in Figure 1 ($\delta \sim 9.3$, ~ 5.2 , and ~ 3.7), and we believe that the new Ni(I) species appearing in Figure 9 is actually NiCl(PPh₃)₂. The chemical shifts agree reasonably well with those calculated above on the assumption of averaged chemical shifts for NiCl(PPh₃)₃.

Of significance to discussions of catalytic biaryl formation,^{83,10d–1} the resonances of *trans*-NiPhCl(PPh₃)₂ shown in Figure 9 disappeared from the spectrum within 1 h as the resonances of biphenyl intensified. Thus while *trans*-NiPhCl-(PPh₃)₂ decomposes to biphenyl and Ni(I) extremely slowly at 298 K in toluene solution in the presence of PPh₃, conversion is complete within minutes in its absence. Although the broad, sometimes overlapping resonances in ¹H NMR spectra render accurate integrations difficult, the changes seem consistent with the stoichiometry of the decomposition reaction being as in eq 7.

 $2trans-NiPhCl(PPh_3)_2 \rightarrow 2NiCl(PPh_3)_2 + Ph_2$ (7)

These observations differ radically from those reported for the very similar compounds *trans*-NiPhX(PEt₃)₂ (X = Cl, Br), which seemingly are indefinitely stable in solution at room temperature,¹⁷ but which, unlike *trans*-NiPhCl(PPh₃)₂, react rapidly with aryl halides via a radical-chain process to give biaryls and NiX(PEt₃)₂.^{17a} Our observations do, however, seemingly rationalize several apparently incongruent observations in the literature concerning *trans*-NiPhCl(PPh₃)₂ and confirm others. For instance, Hidai et al.^{10a} report the original syntheses of *trans*-NiPhCl(PPh₃)₂ and *trans*-NiPhBr(PPh₃)₂ via oxidative additions of chloro and bromobenzene to Ni(PPh₃)₄ but make no mention of latent instability of the products at room temperature in solution. This paper is frequently cited as the preferred route to the compounds *trans*-NiPhX(PPh₃)₂ (X = Cl, Br), but apparently on the basis of this report, it seems frequently assumed that the compounds are thermally stable in solution.

Confusing the issue, while several authors prepare *trans*-NiPhX(PPh₃)₂ by allowing oxidative-addition reaction mixtures to stir for many hours, it is also been reported that the isolated products inexplicably undergo decomposition to biphenyl within minutes.^{60,s,10b,e,h} These apparent incongruities have received little attention but are now readily rationalized. Products maintained in reaction mixtures can be stable for many hours because of the free PPh₃, which remains in solution, and isolated products contaminated with free PPh₃ will likewise seem stable if the PPh₃ contaminant is not recognized as being present. Alternatively, as our Figure 9 shows, pure *trans*-NiPhCl(PPh₃)₂ is very unstable in solution at room temperature. Consistent with our findings, Ni(I) species are also cited as products of decomposition of NiPhX-(PPh₃)₂,^{65,10h} although just how the Ni(I) species were identified is not always reported.

Related to the chemistry of eqs 6 and 7, reactions of aryl halides with Ni(0) compounds such as Ni(PPh₃)₄ have often been cited as good catalytic routes to biaryls at 50–80 °C.^{8a,10d-f} The reactions are generally believed to involve conversion of a Ni(0) catalyst to an aryl-nickel(II) intermediate followed somehow by reductive elimination of biaryl to regenerate the Ni(0) catalyst. In some cases, the active Ni(0) species is generated from Ni(II) precursors either electrochemically or via reduction by zinc metal.

Several mechanisms have been considered for biaryl formation, including radical-chain processes, reductive elimination from diaryl Ni(II) and diaryl Ni(IV) compounds, and homolysis to aryl radicals which couple.^{10e,f,18a,b} The last mentioned seems very unlikely in the present case because the aryl radicals would certainly abstract hydrogen from the deuterated solvent toluene to yield benzene rather than biphenyl. To our knowledge, the inhibitory effect of added PPh₃ on the clean conversion of *trans*-NiPhCl(PPh₃)₂ to Ni(I) and biphenyl has not been noted and related to mechanistic considerations, and it seems reasonable to interpret our observations in terms of a mechanism in which PPh₃ dissociation to give NiPhCl(PPh₃) is followed by reaction of the latter with a molecule of *trans*-NiPhCl(PPh₃)₂ to give chloride-bridged dinuclear species (Scheme 5).

The dinuclear species could in principle eliminate biphenyl directly and produce Ni(I), or it could undergo metathesis to give $NiPh_2(PPh_3)_2$ and $NiCl_2(PPh_3)_2$, followed by the reductive elimination and comproportionation steps shown. The system could be made catalytic in nickel if carried out in the presence of zinc dust, which would convert the Ni(I) product to Ni(0) catalyst. We have carried out DFT calculations to assess the feasibility of these processes.

DFT Calculations on the Oxidative Addition of PhCl to Ni(PPh₃)₄ and the Conversion of *trans*-NiPhCl(PPh₃)₂ to

Scheme 5. Dinuclear Route to Biaryls via Nickel Catalysis (L = PPh₃)







^aCalculated relative free energies per Ni atom (298 K) in kcal/mol. Thick blue arrows indicate oxidative-addition transition states. In either case, the final product is *trans*-NiPhClL2.

explored using closed-shell restricted density-functional methods: optimization with Turbomole,¹⁹ b-p^{20,21}/SV(P),²² singlepoint energies at Gaussian 09²³ M06²⁴/cc-pVTZ,^{25–27} and PCM(THF). For Ni(II) species, triplet states were considered as well (energies included in the SI) but were in most cases found to be higher in energy. No broken-symmetry solutions were found for dimeric Ni(II) compounds. We found that some form of dispersion correction is essential and that different choices (DFT-D3,²⁸ M06, M06L²⁴) produce rather different results. Here we report data based on M06 results; a motivation is provided in the SI. Due to this method sensitivity, it seems likely that the error margins in the results are larger than usual for DFT studies. Numbers mentioned below and in the figures are free energies.

In view of the SET mechanism proposed by Kochi,^{17a} we also briefly explored potential SET intermediates using triplet and open-shell singlet electronic structures, but no plausible intermediates could be located. This does not rule out SET as a reaction mechanism, but in our opinion it suggests that involvement of long-lived SET intermediates is not very likely.

Paths for PhCl oxidative addition are shown in Scheme 6. The first dissociation step from NiL₄ (L = PPh₃) is facile; in fact, with a calculated dissociation energy of only ~2 kcal/mol, solutions of NiL₄ should already contain a significant amount of NiL₃. After this dissociation, a transition state exists for direct C–Cl oxidative addition without going through an intervening arene complex; although, the barrier calculated for this is rather high (38 kcal/mol). A lower-energy path goes through NiL₂ and its arene complex, with an effective barrier of 27 kcal/mol.



^{*a*}Calculated relative free energies (298 K) in kcal/mol. From species C on, energies are per pair of Ni atoms. Thick red arrows indicate reductive-elimination transition states. No calculations were attempted for species D and G.

Scheme 7 summarizes plausible reaction paths leading from the initial oxidative-addition product *trans*-NiPhClL₂ (**A**) to biphenyl and Ni(I) species. Since this scheme involves binuclear species, starting from **C**, energies are given per two Ni atoms, relative to **A**.

For biphenyl formation to occur, some form of Ph/Cl exchange is needed. Complex A can dissociate one phosphine ligand (B), bind to a second molecule of A giving singly bridged dimer C, and lose one more phosphine to form a doubly bridged dimer in one of two ways. The preferred dimer (E) has two chloride bridges, but forming this is nonproductive. The alternative is a Cl/Ph bridged dimer (F), which then can

open up (G), trap a phosphine ligand (H), and break apart into L_2NiCl_2 and $LNiPh_2$ (I). Biphenyl formation, indicated by bold red arrows in Scheme 7, can take place at this stage or after first binding a second phosphine molecule (J). Alternatively, reductive elimination could proceed directly from asymmetric dimer F. Our results suggest that all three variations are possible, although the path via J is likely preferred.

Geometries of the three relevant transition states are shown in Figure 10. Mononuclear elimination from 14-e⁻ intermediate I proceeds with a barrier of only 5 kcal/mol, while elimination from 16-e⁻ J has a somewhat higher barrier of 6 kcal/mol, which is still a very fast reaction at room temperature. We conclude that any L_nNiPh₂ species formed from trans-NiPhClL₂ will not survive for long. Even elimination from asymmetric dimer F has a barrier of only 11 kcal/mol. Thus under conditions where *trans*-NiPhClL₂ undergoes intermolecular Cl/ Ph exchange, fast formation of biphenyl would be expected. This explains the role of free PPh₃ in stabilizing solutions of trans-NiPhClL₂; it opposes dissociation of L, which is the first step toward Cl/Ph exchange. In particular, the main effect is not conversion of LNiPh₂ to potentially more stable L₂NiPh₂: our results show that even L2NiPh2 would eliminate rapidly once formed.

The last statement, concerning the very low thermal stability of NiPh₂(PPh₃)₂, gives pause for thought. We have noted above the very significant differences in chemistry between the Ni-PEt₃ and Ni-PPh₃ systems, and note also that Ni(II) compounds of the type NiAr₂(2,2-bipyridine) were shown some years ago to be too thermally stable to participate in known cross- and homocoupling catalytic cycles involving bipytype ligands.^{3c} This latter finding was shortly thereafter conflated to infer that "reductive elimination from diorgano– Ni complexes is a facile process when the formal oxidation state of the metal is...not two",^{3e} a conclusion which is clearly incorrect. Nickel chemistry can readily involve formal oxidation states 0–IV and which couple(s) is(are) involved in any particular catalytic process may depend to a very great extent on the ligand system(s) used.

SUMMARY

The Ni(0) compound Ni(PPh₃)₄ is found to be a surprisingly interesting catalyst for representative Suzuki–Miyaura and Heck–Mizoroki cross-coupling reactions such as the cross-coupling of chloro and bromoanisole with phenylboronic acid to give 4-methoxybiphenyl and of bromobenzene with styrene



Figure 10. Geometries of transition states for C-C coupling from NiPh₂L₁ NiPh₂L₂ and [NiPhClL]₂; bond lengths in Å.

to give trans-stilbene. This catalytic system can also be generated by treating the air-stable $NiCl_2(PPh_3)_2$ with zinc dust and works well for Heck-Mizoroki but not Suzuki-Miyaura cross-coupling reactions utilizing phenylboronic acid; the latter may react preferentially with the zinc. A mechanistic NMR study of the oxidative-addition reaction of chlorobenzene to $Ni(PPh_3)_4$ shows that the diamagnetic, putative crosscoupling intermediate trans-NiPhCl(PPh₃)₂ forms quickly and virtually quantitatively, but a small amount of paramagnetic species also forms and slowly increases in concentration. The latter turns out to be the paramagnetic Ni(I) compound $NiCl(PPh_3)_{3}$, which is prepared separately and characterized for the first time by NMR spectroscopy. Its ¹H NMR spectrum exhibits broad meta and para resonances at $\delta \sim 9.3$ and ~ 3.7 , respectively, and a very broad *meta* resonance at $\delta \sim 5.2$, resonances which are well-separated from normal chemical shifts of diamagnetic complexes of PPh₃ and hence are very useful for detecting this and similar Ni(I) species in solution. The compound trans-NiPhCl(PPh₃)₂ is found to exhibit entirely unanticipated thermal lability in solution in the absence of free PPh₃. It readily decomposes to biphenyl and $NiCl(PPh_3)_3$ in a reaction relevant to the long-known but little understood nickel-catalyzed conversion of aryl halides to biaryls. Biphenyl formation is initiated by PPh₃ dissociation from Ni(PPh₃)₄ and formation of a dinuclear intermediate, a process which is now better defined using DFT methodologies. The fact that the analogous compound *trans*-NiPhCl(PEt₃)₂ is stable¹⁷ is probably to be related to the fact that the smaller, better donor ligand PEt₃ does not dissociate significantly under the same conditions.

EXPERIMENTAL SECTION

General Procedures. All syntheses were carried out under a dry, deoxygenated argon or nitrogen atmosphere with standard Schlenk line techniques. Argon was deoxygenated by passage through a heated column of a BASF copper catalyst and then dried by passing through a column of 4A molecular sieves. Handling and storage of air-sensitive compounds were carried out in an LC Technology LCBT-1 benchtop purged glovebox. NMR spectra were recorded on Bruker AV500 or AV600 MHz spectrometers with ¹H NMR data being referenced to TMS via the residual proton signals of the deuterated solvent, and EPR spectra were run on powder samples at 77 K on a Bruker EMX spectrometer equipped with a Bruker-8/2.7 electromagnet and a Bruker ER4119HS resonant cavity. GC experiments were carried out using a Varian 3900 GC equipped with a CP 8400 autosampler, 0.32 mm Varian fused silica column, and an FID; the injector temperature was set at 250 degrees, the initial column temperature was at 140 degrees, and the detector temperature was at 250 degrees. Hexadecane was added as an internal standard, and GraphPad Software Prism Version 3.02 was used for curve fitting. The compounds Ni(PPh₃)₄, $NiX(PPh_3)_3$ (X = Cl, Br, I), ^{7a,9,10b} $NiX_2(PPh_3)_2$ (X = Cl, Br, I), ¹¹ and trans-NiPhCl(PPh₃)₂^{10g} were prepared as in the literature.

NMR Study of Oxidative Addition of Chlorobenzene to Ni(PPh₃)₄. In a typical procedure, a solution of 48 mg of Ni(PPh₃)₄ (43 μ mol) in 0.7 mL of toluene- d_8 was transferred into an NMR tube; the tube was sealed by a septum and parafilm, and 25 μ L of chlorobenzene (0.16 mmol, 4.0 equiv) was added. The sample was shaken briefly, and NMR spectra were run at various temperatures using as internal standard the toluene- d_8 signal at δ 2.09. Although ¹H and ³¹P data have been reported for diamagnetic *trans*-NiPhCl(PPh₃)₂ in CD₂Cl₂, ^{10g} we have carried out all of our reactions in toluene- d_8 , in which the chemical shifts are different and thus needed to be determined. The resonances of the *p*- and *m*-H of the Ni-Ph group are observed at δ 6.33 (t, J = 7.5 Hz) and 6.23 (t, J = 7.5 Hz), respectively, while the resonance of the corresponding *o*-H was obscured by stronger PPh₃ resonances but was determined via a COSY experiment

to be at δ 6.95. A prominent 12H resonance at δ 7.72 (br) is assigned to the coordinated PPh₃ of *trans*-NiPhCl(PPh₃)₂, with the other PPh₃ resonances overlapping at δ 7.0–7.1. Similar experiments were carried out at lower temperatures and, at room temperature, with bromobenzene.

General Experimental Methodologies for Suzuki–Miyaura Reactions. 4-Bromoanisole (0.187g, 1.0 mmol) in 3 mL of dioxane was added under argon to a mixture of 0.107 g of Ni(PPh₃)₄ (0.1 mmol), 0.18 g of phenylboronic acid (1.5 mmol), and 0.625 g of Cs_2CO_3 (2 mmol). The mixture was stirred at 60 °C for 4 h. Stirring was stopped periodically to allow the undissolved base to settle, and aliquots of 0.1 mL were taken, diluted by 10 mL of solvent and analyzed by GC. Hexadecane was used as an internal standard. A similar procedure was used for studies of *trans*-NiPhCl(PPh₃)₂, NiCl(PPh₃)₃, and NiBr(PPh₃)₃.

General Experimental Methodologies for Heck–Mizoroki Reactions. Pyridine and acetonitrile were dried overnight over molecular sieves. Ni $(PPh_3)_4$ (0.11g, 0.1 mmol) was added under argon to a mixture of 0.16 g of bromobenzene (1 mmol), 0.42 g of styrene (4 mmol), and 0.32 g of pyridine (4 mmol) in 3 mL of acetonitrile; the mixture was stirred at 65 °C for 4 h. Aliquots of 0.1 mL were taken at specified intervals, diluted by 10 mL of acetonitrile and analyzed by GC. Naphthalene was used as an internal standard.

NMR Studies of Suzuki–Miyaura Reactions. A mixture of 0.18 g of phenylboronic acid (1.5 mmol), 0.088 g of NiCl(PPh₃)₃ or 0.107 g of Ni(PPh₃)₄ (both 0.1 mmol), and 0.625 g Cs₂CO₃ (2 mmol) in a test tube sealed with a septum was purged with argon. A solution of 0.187 g of 4-bromoanisole (1 mmol) in 3 mL of dioxane was added, and the mixture was stirred at 60 °C. Stirring was stopped periodically to allow the undissolved base to settle, and aliquots of 0.5 mL were taken, pumped down to dryness, dissolved in deuterated toluene, and analyzed by ¹H NMR spectroscopy. A similar experiment was carried out using 0.69 g of *trans*-NiPhCl(PPh₃)₂ (0.1 mmol) in the presence of 0.026 g of PPh₃ (0.1 mmol).

Methods—Computational. Geometries were optimized using Turbomole¹⁹ coupled to the external Baker optimizer^{29,30} via the BOpt package;³¹ at this stage we used the Turbomole b-p functional^{20,21} in combination with the def-SV(P) basis²² and the RI approximation.³² The nature of all stationary points was checked using a vibrational analysis (no imaginary frequencies for minima, exactly one for transition states). Improved single-point energies were then calculated using Gaussian 09,²⁵ the M06 functional,²⁴ and the cc-pVTZ basis set^{25–27} obtained from the EMSL library.^{33,34} The PCM method^{35–38} was used for modeling the solvent (THF). To obtain final free energies, thermal corrections from the b-p/SV(P) vibrational analysis (enthalpy and entropy, 298 K, 1 bar) were added to the abovementioned final electronic energies; the entropy contribution was scaled by 0.67 to account for reduced freedom in solution.^{39,40}

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00446.

Figures S1 and S2; a brief discussion of the computational methodologies tested and utilized; tables of the free energies of various relevant species calculated at different levels (Table S1); tables of the contributions to final free energies (Table S2) (PDF)

Cartesian coordinates for all of the calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

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