

Reactions of the Ni(0) Compound Ni(PPh₃)₄ with Unactivated Alkyl Halides: Oxidative Addition Reactions Involving Radical Processes and Nickel(I) Intermediates

Ryley Kehoe, Markshun Mahadevan, Adeela Manzoor, Gillian McMurray, Patrick Wienefeld, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston ON K7L 3N6, Canada

Peter H. M. Budzelaar*

Department of Chemical Sciences, Federico II University of Naples, Napoli 80126, Italy

Supporting Information

ABSTRACT: Reactions of the nickel(0) compound NiL₄ (L = PPh₃) with alkyl halides RX involve initial inner-sphere halogen atom abstraction from the alkyl halides to form alkyl radicals R. and halonickel(I) metalloradical species $NiX(PPh_3)_{2,3}$. The radical pairs then undergo combination within the solvent cage to give the square planar nickel(II) compounds NiRX(PPh₃)₂. Radical intermediacy is demonstrated persuasively by observations that the relative rates vary in the orders tert-butyl > sec-butyl > n-butyl and RI > RBr > RCl, while density functional theory calculations indicate that the radical mechanism provides a lower energy pathway than do alternative, more conventional pathways. The product of the reaction of $Ni(PPh_3)_4$ with methyl iodide,



Mechanism of reaction of n-Bul with Ni(PPh₃)₄

NiMeI(PPh₃)₂, decomposes in solution to ethane and NiI(PPh₃)_{2,3}, but when RX = EtI, *n*-BuI, sec-BuI, tert-BuI, the alkyl-nickel products undergo rapid β -hydrogen elimination to give the hydride NiHI(PPh₃)₂ plus the corresponding alkene(s). Reactions also occur in which a portion of the alkyl radicals diffuses from the solvent cage and abstracts hydrogen from NiHI(PPh₃)₂ to form alkanes RH and Ni(I) species NiI(PPh₃)₂. As a result, NiHI(PPh₃)₂ is invariably a minor product while the major products are alkanes RH, alkenes R-H, and NiI(PPh₃)₂. Hydride NiHI(PPh₃)₂ is found to decompose to H₂ and NiI(PPh₃)₂ but is stable at low temperatures where it exhibits unusual NMR behavior because of exchange involving free PPh₃ and the bis- and trisphosphine species, $NiHI(PPh_3)_2$ and $NiHI(PPh_3)_3$. Present in all of the reactions are paramagnetic, substitution-labile Ni(I)metalloradical species. As a result, resonances of PPh₃, ethylene, and the smaller iodoalkenes are generally broad and shifted because of exchange between free and coordinated ligands.

INTRODUCTION

There has in recent years been considerable interest in the utilization of nickel compounds for the catalysis of crosscoupling of alkyl and aryl halides.¹ Driving this interest in part have been findings that cross-coupling reactions of secondary alkyl halides can be accomplished, including enantioselective reactions when appropriate ligands are utilized.¹ In related work, we have recently reported a catalytic and mechanistic investigation of the easily synthesized Ni(0) compound $Ni(PPh_3)_4$ which we find to be a very effective catalyst for representative Suzuki-Miyaura cross-coupling reactions of aryl halides with phenylboronic acid.^{2a} The mechanism is believed to involve a conventional catalytic cycle of the type pictured in Scheme 1.

 $Ni(PPh_3)_4$ was also found to be a very good catalyst for representative Heck-Mizoroki cross-coupling reactions such as those of aryl halides with styrene.^{2a}

Scheme 1. Conventional, Generic Two-Electron Ni(0)-Ni(II) Catalytic Cycle for Many Types of Cross-Coupling Reactions



A complementary NMR study^{2a} of the oxidative addition reaction of chlorobenzene to Ni(PPh₃)₄ found that the putative diamagnetic intermediate trans-NiPhCl(PPh₃)₂

Received: April 30, 2018



forms quickly and virtually quantitatively even at room temperature but that it decomposes surprisingly readily in the absence of free PPh₃ to biphenyl and NiCl(PPh₃)₃ (eq 1). This reaction involves PPh₃ dissociation and formation of a dinuclear intermediate such as Ni₂Ph₂Cl(PPh₃)₃(μ -Cl).

$$2trans-NiPhCl(PPh_3)_2 \rightarrow 2NiCl(PPh_3)_2 + Ph_2$$
(1)

The paramagnetic Ni(I) compounds NiCl(PPh₃)_{2,3}, as well as bromo and iodo analogues, were characterized for the first time by NMR spectroscopy. Their ¹H NMR spectra exhibit broad *meta* and *para* resonances at δ 9–11 and 3–4, respectively, and very broad *ortho* resonances at δ 4–6.^{2a} These chemical shifts are quite different from those of diamagnetic complexes of PPh₃, are very useful for detecting even low concentrations of Ni(I) species in solution, and have been utilized in this way in this work.

We have also found that simple alkyl halides react readily with $Ni(PPh_3)_4$, as indicated by rapid color changes, but that they do not partake in the types of cross-coupling processes observed for aryl halides. This was intriguing given the fact that nickel-based catalyst systems frequently do effect crosscoupling of alkyl halides,¹ and we have therefore carried out an NMR study to ascertain just how Ni(PPh₃)₄ does interact with various types of alkyl halides. We have found, interestingly, that Ni(PPh₃)₄ reacts readily below 250 K with methyl and ethyl iodides and with n-, sec-, and tert-butyl iodides and that most, if not all, of the reactions proceed via radical mechanisms. Although oxidative addition of alkyl/aryl halides to Ni(0) species is frequently assumed as a key step in many cross-coupling processes,^{1,2a} focused mechanistic studies of such oxidative addition reactions have only been notable for their rarity in the recent past.³

Finally, we also propose a non-conventional, two-electron but radical-based Ni(0)-Ni(II) catalytic cycle for crosscoupling reactions as an alternative to currently popular catalytic cycles involving Ni(I) species.

RESULTS AND DISCUSSION

Nature of the Experiments Carried Out. The Ni(0) compound Ni(PPh₃)₄ was prepared as previously described, via reduction of NiCl₂(PPh₃)₂ by zinc powder in the presence of excess PPh₃ in DMF.^{2a} The room temperature ¹H NMR spectrum (toluene- d_8) exhibits broad phenyl resonances at δ 7.34 and 6.93 but slowed exchange processes result in complex phenyl multiplets at 200 K.^{2a} A single resonance is observed at $\delta \sim 24$ in the ³¹P NMR spectrum (toluene- d_8) at room temperature, broadened by rapid dissociative exchange, while the spectrum at 200 K exhibits broad resonances at $\delta \sim -8$ and ~ 25 , attributed to free PPh₃ and Ni(PPh₃)₃, respectively.

As in our previous publication,^{2a} where we carried out an NMR investigation to better understand the reactions of Ni(PPh₃)₄ with halobenzenes, we describe here a similar NMR investigation of reactions of Ni(PPh₃)₄ with alkyl halides. Our initial experiments involved room temperature reactions of Ni(PPh₃)₄ with *tert*-butyl chloride, bromide, and iodide in addition to methyl, ethyl, *n*-butyl, and *sec*-butyl iodides. In all cases, the colors of the solutions changed rapidly from a deep red-brown to yellow, and complex ¹H NMR spectra were observed (as discussed below). Since it was clear that all of the reactions had already run their course by the time initial spectra were run, we adopted an experimental protocol in which the reactions were begun at ~200 K. We hoped to be

able to detect species not otherwise evident, and in this endeavor we were at least partially successful.

In typical experiments, NMR samples were prepared by adding an aliquot of an organic halide to an NMR tube containing a deep red-brown solution of Ni(PPh₃)₄ in toluene- d_8 cooled to 195 K. The tubes were then placed in the probe of a 600 MHz NMR spectrometer, precooled to 200 K or lower, and spectra were run at 200, 225, 250, 275, and 300 K. In each case, the temperature was allowed to equilibrate before a new spectrum was obtained, normally 10–15 min. However, in many cases 1D ³¹P NMR spectra and 2D COSY and ¹H–³¹P HMBC spectra were also run after thermal equilibrium had been reached and thus the time between ¹H spectra varied.

Common to all spectra, unless obscured by solute PPh₃ resonances, were the resonances of the residual protons of the solvent, toluene- d_8 , at δ 2.09 (-CHD₂) and δ 6.98, 7.02, and 7.10 (-C₆HD₄); the resonance at δ 2.09 was utilized as internal chemical shift standard in all spectra. Note also that paramagnetic Ni(I) species were generated in all of the reactions investigated here and that, as a consequence, all resonances were broadened, especially at lower temperatures. As a result, *J* couplings are rarely resolved and integrations are sometimes problematic because of overlap.

Reaction of Methyl lodide with $Ni(PPh_3)_4$. Addition of MeI to a deep red-brown solution of $Ni(PPh_3)_4$ at 200 K resulted in the solution becoming cloudy and its color becoming paler. Presented in Figure 1 is a stacked plot showing ¹H NMR



Figure 1. Stacked plot showing ¹H NMR spectra of reaction of Ni(PPh₃)₄ with excess MeI; * = unreacted MeI, # = ethane, \dagger = NiMeI(PPh₃)₂.

spectra for a reaction of Ni(PPh₃)₄ with a excess of MeI, run at 200, 225, 250, 275, and 300 K in that order at time intervals of 20–45 min. To facilitate discussion, full spectra are shown in the Supporting Information, Figure S1a–e, the corresponding ³¹P NMR spectra in Figure S1f–j.

The ¹H NMR spectrum at 200 K exhibits strong resonances of the diamagnetic Ni(PPh₃)₄ and weak PPh₃ resonances of a Ni(I) species at δ 10.7 and 3.4, but no resonances of methane

or ethane.⁴ There is, however, a weak resonance identified tentatively on the basis of its negative chemical shift^{5a,b} (δ –0.04) as NiMeI(PPh₃)₂, and thus one or more reactions had already begun. This conclusion was confirmed by a ³¹P NMR spectrum which exhibited a strong, broad resonance of Ni(PPh₃)_n at δ 25–27, a medium-intensity, broad resonance of PPh₃ at δ –7.43 and a medium-intensity, sharp resonance at δ 32.21 which we tentatively attribute to the above-mentioned NiMeI(PPh₃)₂ on the basis of a correlation in a ¹H–³¹P HMBC experiment. No resonances at 200 K or at the other temperatures could be attributed to the methyltriphenylphosphonium iodide, which forms but is insoluble in toluene and was the cause of the cloudiness mentioned above.

The ¹H NMR spectrum at 225 K is similar to that at 200 K, although the Ni(I) resonances are stronger and have shifted to δ 10.16 and 3.93; a weak ethane resonance is observed at δ 0.86,⁴ although again there is no resonance at δ 0.17 which can be attributed to methane.⁴ A medium intensity resonance at δ -0.08 is attributed to NiMeI(PPh₃)₂ as is a ³¹P resonance at δ 31.3 (¹H-³¹P HMBC). The ³¹P NMR spectrum also exhibits an extremely broad band centered at $\delta \sim 22$ but no resonance of free PPh₃, presumably because of exchange with paramagnetic Ni(I) species.^{2a}

The nickel(0) compound Ni(PPh₃)₄ had completely reacted by 250 K, and its ¹H NMR resonances are replaced by a broad swath of PPh₃ resonances of Ni(I) in the range δ 4.5–9.0. The resonance of the starting MeI has by this point decreased considerably and the resonance of ethane has increased significantly in intensity. The ¹H and ³¹P spectra now exhibit relatively strong resonances of NiMeI(PPh₃)₂ at δ –0.11 and δ 30.5, respectively, the latter broader than before. The ³¹P spectrum also exhibits an extremely broad band centered at δ ~ -5.

The ¹H NMR spectrum at 275 K exhibits a weakened methyl resonance of NiMeI(PPh₃)₂ at δ -0.13 in addition to an ethane resonance at δ 0.83 and strong, broad resonances at δ 8.13, 6.15, and 5.22. The latter are readily attributable to the *meta-, ortho-,* and *para*-hydrogens of iodonickel(I) PPh₃ species, the unusual chemical shifts and breadths of which have been rationalized previously.^{2a} The ³¹P NMR spectrum exhibits a broad resonance at δ 29.8, attributed to NiMeI-(PPh₃)₂ exchanging with inter alia free PPh₃ and Ni(I) species,^{2a} but little else of note.

There was little change in the ¹H NMR spectrum on going to 300 K although further evidence for exchange processes are apparent in the ³¹P NMR spectrum (Figure S1i). The methyl resonance of NiMeI(PPh₃)₂ at δ –0.16 in the ¹H NMR spectrum had weakened considerably, giving way to an ethane resonance at δ 0.82. The methyl compound thus is not thermally stable under these experimental conditions but apparently decomposes to ethane and NiI(PPh₃)₂ as in eq 2.

$$NiMeI(PPh_3)_2 \rightarrow 1/2C_2H_6 + NiI(PPh_3)_2$$
(2)

This reaction resembles the decomposition of *trans*-NiPhCl- $(PPh_3)_2$ to biphenyl and NiCl $(PPh_3)_2$, which proceeds via PPh₃ dissociation and formation of dinuclear intermediates.^{2a} Following this precedent, the mechanism of the reaction would be as in Scheme 2.

An earlier study 5c of the reaction of Ni(PPh₃)₄ with MeI in benzene at higher temperatures revealed the presence of methyltriphenylphosphonium iodide but not of the other products noted here.

Scheme 2. Suggested Mode of Decomposition of NiMeI(PPh₃)₂

 $2\text{NiMel}(\text{PPh}_3)_2 \longrightarrow \text{Ni}_2\text{Me}_2\text{I}(\text{PPh}_3)_3(\mu\text{-I}) + \text{PPh}_3 \longrightarrow \text{NiMe}_2(\text{PPh}_3)_2 + \text{NiI}_2(\text{PPh}_3)_2$

 $Ni(PPh_3)_2 + Me_2 + Nil_2(PPh_3)_2$

L.

↓ 2Nil(PPh₃)₂ + Me₂

The resonances which we attribute to iodonickel(I) species exhibit unusual behavior and, as very similar spectra are also observed during reactions of $Ni(PPh_3)_4$ with other alkyl iodides, the behavior of the Ni(I) resonances and the nature of the Ni(I) species involved will be discussed below.

Reaction of Ethyl lodide with $Ni(PPh_3)_4$. Presented in Figure 2 is a stacked plot showing ¹H NMR spectra for a



Figure 2. Stacked plot showing ${}^{1}H$ NMR spectra of a reaction of a Ni(PPh₃)₄ with excess EtI; * = unreacted EtI, # = ethane, \ddagger = ethylene.

reaction of Ni(PPh₃)₄ with a small excess of ethyl iodide, run at 200, 225, 250, 275, and 300 K in that order at time intervals of 20–45 min. To facilitate discussion, full spectra are shown in the Supporting Information, Figures S2a–e.

Spectra at 200 and 225 K in the phenyl region are rather similar to the corresponding spectra of the MeI series, with prominent resonances of Ni(PPh₃)₄ at both temperatures and weaker Ni(I) peaks being observed at δ 10.70 (br), 3.90 (vbr), and 1.37 (br) at 200 K, and at δ 10.18 (br), 3.92 (vbr), and ~2.0 (br) at 225 K. A resonance of ethane⁴ is also observed growing in at δ 0.92 and 0.87 at 200 and 225 K, respectively. The spectra at 250, 275, and 300 K also resemble somewhat their MeI counterparts, an exceedingly broad band of PPh₃ resonances at 250 K giving way to well separated *meta, ortho*, and *para* resonances of a Ni(I) species at the higher temperatures. An ethane resonance is present in each spectrum at δ 0.8–0.85, and an ethylene resonance is observed at δ 5.32⁴ at 300 K.

Interestingly, in a separate experiment involving somewhat different concentrations, the positions and line widths of the ethylene resonance were found to be temperature-dependent, as shown in Figure 3 where the contrast with the higher field ethane resonance is striking.

In this sequence of spectra, the ethylene resonance broadens and shifts from δ 5.31, which is already 0.06 ppm downfield



Figure 3. Stacked plot showing ¹H NMR of the ethylene and ethane resonances for an experiment similar to that shown in Figure 2.

from the position of free ethylene (δ 5.25), to δ 5.34. In contrast, the resonance of ethane remains narrow and unchanged at δ 0.83–0.84. Thus the ethylene appears to be interacting weakly with a paramagnetic Ni(I) species which behaves as a shift reagent toward it. The effect is much greater with the PPh₃, of course, but no such shifts were observed with the more sterically more encumbered alkenes discussed below. Indeed, we are aware of only a single previous report of alkenes undergoing exchange of this type with a paramagnetic metal ion.^{2g}

Note that although integration of the ethylene resonance at all temperatures is problematic because of overlap with the strong *ortho*-PPh₃ resonance, the ethylene and ethane resonances appear to have comparable intensities. Weak hydride resonances^{6a} were observed in the spectra at δ –23.7 (200 K), –22.7 (225 K), –19.9 (250 K), –18.0 (275 K), and –17.6 (300 K). The rather extreme temperature dependence of the chemical shifts will be discussed below. Unlike the situation with the methyl system, in no case was there an alkylnickel compound NiEtI(PPh₃)₂ detected.

Reaction of n-Bul with Ni(PPh₃)₄. Presented in Figure 4 is a stacked plot showing ¹H NMR spectra for a reaction of Ni(PPh₃)₄ with a slight excess of *n*-BuI in toluene- d_8 . To facilitate discussion, full spectra are shown in the Supporting Information, Figure S3a-g.

The phenyl regions of the ¹H NMR spectra at 200, 225, and 250 K are rather similar to those in the corresponding spectra of the EtI series, with prominent resonances of Ni(PPh₃)₄ evident at 200 and 225 K but disappearing by 250 K. In addition, weaker Ni(I) peaks in the ranges δ 10–11 and ~3.9 at 200 and 225 K converge at 250 K into a broad, strong band in the range δ 4.5–10.5 but separate at the higher temperatures



Figure 4. Stacked plot showing 1 H NMR spectra of a reaction of a Ni(PPh₃)₄ with a slight excess of *n*-BuI.

into well-defined *meta*, *ortho*, and *para* resonances. A ³¹P NMR spectrum at 200 K exhibited a strong resonance at δ 25.2 (Ni(PPh₃)_n) and weaker resonances at δ 26.3 and -7.6 (vbr, free PPh₃) while a ³¹P NMR spectrum at 225 K exhibited only a broad resonance at $\delta \sim 23.9$. Spectra at higher temperatures exhibited only weak or no ³¹P resonances because of exchange with paramagnetic Ni(I) species.^{2a}

The presence of weak Ni(I) resonances in spectra at 200 and 225 K indicate that a reaction of some kind had begun but, at first sight, there seems to be little other evidence in the spectra since the spectrum at 200 K exhibits only the resonances of *n*-BuI at δ 2.48, 1.18, 0.96, and 0.64 in the aliphatic region. That said, careful inspection of the vinyl region of this spectrum does reveal new, very weak vinyl resonances of 1-butene at δ 5.83 (m) and 5.07 (m), although the corresponding methyl and methylene resonance are obscured. Furthermore, at 225 K, a weak *n*-butane resonance appears at δ 0.92 in addition to the weak resonances of 1-butene at δ 5.82 and 5.04. In order to better assess changes in aliphatic region of the spectra and to facilitate discussion, we show in Figure 5 expansions of the aliphatic regions of the ¹H NMR spectra of Figure 4.

Significant changes are observed in the ¹H NMR spectrum run at 250 K, as shown in Figures 4, 5, and S3c.The intensities of the *n*-BuI resonances have decreased significantly relative to the solvent resonance at δ 2.09, and strong *n*-butane resonances at δ 1.32 and 0.92 are readily apparent. Weak 1butene resonances at $\delta \sim 5.0$ and 5.8 appear to reach maximum intensity at 250 K, and we also note for the first time strong Z-2-butene resonances at δ 5.51 and 1.55 and weak *E*-2-butene resonances at δ 5.39 and 1.62. Further reaction had occurred by the time that a spectrum was run at 275 K; the resonances of *n*-butane and the 2-butenes are now stronger than those of *n*-BuI, and, interestingly, the *E*-/Z-2-butene ratio has increased somewhat.



Figure 5. Stacked plot showing the aliphatic region of ¹H NMR spectra for a reaction of a Ni(PPh₃)₄ with a slight excess of *n*-BuI; * = unreacted *n*-BuI, # = n-butane, $\ddagger = E$ - and Z-2-butenes (see text).

The ¹H NMR spectrum at 300 K exhibits prominent resonances of *E*-2-butene and *Z*-2-butene, the former now being the dominant alkene, and there is also a hydride resonance at δ –17.6. A ¹H NMR spectrum run at 300 K the next day (after ~20 h) had changed very little, although the hydride resonance had disappeared and the *E*-/*Z*-2-butene ratio was now even greater. Interestingly, at 275 and 300 K, the sum of the 2-butene methyl resonance intensities now exceeds the intensity of the methyl resonance of *n*-butane, showing that the ratio *E*- + *Z*-2-butenes:*n*-butane becomes greater than unity as reactions proceed at higher temperatures.

Also very noticeable in Figure 5 is that all of the resonances of unreacted *n*-BuI shift to lower fields as the reaction progresses. The resonances of MeI and EtI exhibit similar behavior in Figures 1 and S1a-e and Figures 2 and S2a-e, respectively, and the behavior of all three alkyl iodide systems will be discussed below.

In a complementary experiment, a solution containing Ni(PPh₃)₄ and a slight excess of *n*-butyl iodide, prepared as above, was placed in the probe of the NMR spectrometer preset to 275 K. Sixteen spectra were obtained at 275 K over 90 min, during which time the pattern of broad PPh₃ resonances changed very little as did the relative intensities of the resonances of *n*-butane, *E*-2-butene, and *Z*-2-butene. It was also found that the sum of the intensities of the *E*- and *Z*-2-butene methyl resonances remained comparable with but somewhat higher than that of the *n*-butane methyl resonance, consistent with the results of the variable-temperature experiment, and that the ratio of the *E*- to *Z*-2-butene methyl resonances varied smoothly from ~0.6 to ~1.5, indicating isomerization of the kinetic product, *Z*-2-butene, to the thermodynamically more stable *E*-2-butene.

We note that in none of the spectra is there a group of resonances in the aliphatic region which can be attributed to the anticipated diamagnetic product of an oxidative addition reaction, Ni(*n*-Bu)I(PPh₃)₂. A weak resonance at δ 0.35 is of an impurity present at all temperatures, and the weak aromatic

resonance at δ 7.70 has also been observed in many spectra,^{2a} including that of Ni(PPh₃)₄. It is attributed to an as yet unidentified diamagnetic PPh₃ species, a COSY experiment showing that its other phenyl resonances are obscured by the solvent resonances.

Relatively weak hydride resonances were observed at δ –23.7 (200 K), –22.1 (225 K), –19.3 (250 K), –17.8 (275 K), and –17.6 at 300 K. These chemical shifts are very similar to those observed at the various temperatures in the EtI spectra and will be discussed below.

Reaction of sec-Bul with Ni(PPh₃)₄. Shown in the Supporting Information, Figure S4a-e, are ¹H NMR spectra for a reaction of a Ni(PPh₃)₄ and a slight deficiency of sec-BuI, run at 200, 225, 250, 275, and 300 K in that order. The phenyl regions of the ¹H NMR spectra at 200–250 K are similar to those in the corresponding spectra of the EtI and *n*-BuI series, with prominent resonances of Ni(PPh₃)₄ again evident at 200 and 225 K but disappearing by 250 K. Reasonably well-defined *meta, ortho,* and *para* resonances also ultimately appear in the 275 and 300 K spectra. A ³¹P NMR spectrum at 225 K exhibited a weak, sharp resonance at δ 25.2 and a very strong, broad resonance at $\delta \sim 22.9$.

In contrast to the EtI and *n*-BuI systems, however, the Ni(I) peaks in the ranges δ 9.5–11.5 and ~2.5–4.5 at 200 and 225 K are much stronger than in the corresponding spectra of the EtI and *n*-BuI systems, and thus a reaction was already well under way at 200 K. In agreement with this conclusion, a vinyl resonance of *Z*-2-butene was already evident at δ 5.56 at 200 K, and a very weak vinyl resonance of *Z*-2-butene could also be seen at δ 5.04 at 225 K. Furthermore, the α -CH resonance of the starting *sec*-BuI at δ ~3.5 is observed in the spectra at 200, and 225 K but has disappeared in the 250 K spectrum.

As with the *n*-BuI system, the aliphatic regions of the spectra are complex. As the spectra show, the amount of *n*-butane was already significant at 200 K, some Z-2-butene is apparent at 225 K but *E*-2-butene forms much more slowly. By 300 K, however, the thermodynamically more stable isomer is dominant, as is *n*-butane. Hydride chemical shifts are again strongly temperature dependent, the resonances being observed at δ -23.7, -22.7, -19.9, -18.0 and -17.6 in the range 200-300 K, very similar to the chemical shifts observed for the EtI and *n*-BuI series of spectra.

Thus *n*-BuI and *sec*-BuI react at different rates but ultimately produce essentially the same range of alkane-, alkene- and nickel-containing products. As with the EtI and *n*-BuI systems, in no case was the alkylnickel compound $NiI(sec-Bu)(PPh_3)_2$ detected.

Reaction of tert-Bul with $Ni(PPh_3)_4$: The Nature of the Hydride. Shown in the Supporting Information, Figure S5a-e, are ¹H NMR spectra for a reaction of a Ni(PPh₃)₄ and a slight deficiency of tert-BuI, run at 200, 225, 250, 275, and 300 K. Here again reaction was well underway at 200 K, with obvious resonances of a Ni(I) compound at $\delta \sim 10.7$, ~ 3.4 , and ~ 1.4 and a hydride resonance at δ –23.7 being readily observed. The patterns of Ni(I) resonances at the higher temperatures are similar to those in spectra of the *n*-BuI and sec-BuI series, although the hydrocarbons formed are obviously different. The chemical shifts of the methyl resonances of tert-BuI, isobutene, and isobutane are very similar, and therefore given the line broadening resulting from paramagnetism, these resonances cannot always be clearly distinguished. However, at 300 K, isobutene (δ 4.71, 1.60) and isobutane (δ 1.63, 0.86) are clearly present as is, interestingly, the resonance of H_2 at δ 4.51.⁴ Very weak H_2 resonances are also observed in the spectrum at 275 K and in the 300 K spectrum of the *sec*-BuI series if one looks carefully. As with the *n*- and *sec*-BuI systems, in no case was an alkylnickel compound NiI(*tert*-Bu)(PPh₃)₂ detected.

Hydride chemical shifts are again strongly temperature dependent, the resonances being observed at δ -23.7, -22.0, -19.0, -17.7, and -17.5 in the range 200-300 K and thus very similar to the chemical shifts observed for the *n*-BuI and *sec*-BuI series of spectra. In order to better understand these variations, an experiment was carried out in which spectra of a sample containing approximately equimolar amounts of Ni(PPh₃)₄ and *tert*-BuI were run first at 183 K and then at 10- or 15-degree increments 10-20 min apart up to 298 K. Stacked plots are shown in Figures 6 and S5f-h, and these give a more comprehensive visualization of the temperature dependences of the chemical shifts and line widths of the Ni(I)-PPh₃ and hydride resonances.



.17.5 .18.0 .18.5 .19.0 .19.5 .20.0 .20.5 .21.0 .21.5 .22.0 .22.5 .23.0 .23.5 .24.0

δ

Figure 6. Stacked plot showing the hydride region of ¹H NMR spectra for a reaction of a $Ni(PPh_3)_4$ with a comparable amount of *tert*-BuI.

As can be seen in Figure 6, the hydride resonance appears as a broad peak at δ –23.75 at 183 K that remains broad and shifts very little as the temperature is raised to 203 K. From 213 to 273 K, however, the resonance sharpens considerably and shifts downfield by ~6.5 ppm, at which point the resonance is observed at δ ~ –17.5 over 20 degrees. This behavior was found to be reversible. The nickel hydride, which we initially presumed to be *trans*-NiHI(PPh₃)₂,^{6b} appears to be undergoing an exchange process with the available free PPh₃ as shown in eq 3.

$$trans-NiHI(PPh_3)_2 + PPh_3 \rightleftharpoons NiHI(PPh_3)_3$$
 (3)

We suspect that the equilibrium being observed involves predominantly the tris-complex at low temperature, and that this dissociates as the temperature rises so that the higher temperature resonances are weighted averages of the two hydride complexes.

Although neither *trans*-NiHI(PPh₃)₂ nor NiHI(PPh₃)₃ appears to have been reported previously, diamagnetic Ni(II) hydride compounds are well known⁶ and the compound NiHBr(PPh₃)₃ has been reported although not characterized by ¹H NMR spectroscopy.^{6c,d} The chloro analogue has also been prepared by treating a solution of Ni(PPh₃)₄ with anhydrous HCl in toluene- d_8 at 195 K;^{6e} the species produced exhibited a broad hydride resonance at δ –29.4 at 213 K and decomposed to H₂ and a Ni(I) species on warming to room temperature.

The iodo hydride compound is also not stable at room temperature and appears to decompose to H_2 and NiI(PPh₃)₂, as in eq 4 and similar to the behavior of the chloro analogue.⁶⁶

$$2\text{NiHI}(\text{PPh}_3)_2 \rightarrow \text{H}_2 + 2\text{NiI}(\text{PPh}_3)_2 \tag{4}$$

This reaction also resembles the decomposition of NiMeI- $(PPh_3)_2$, described above, and the previously described decomposition of *trans*-NiPhCl(PPh₃)₂ to biphenyl and NiCl(PPh₃)₂.^{2a} Therefore, again a series of steps beginning with dissociation of PPh₃ from NiHI(PPh₃)₂ and formation of a dinuclear intermediate seems likely, much as in Scheme 2 (with H in lieu of Me).

Mechanisms of Reactions of Ni(PPh₃)₄ with Alkyl Halides: Nickel(I) Metalloradical and Alkyl Radical Involvement. We summarize in Scheme 3 the product distributions observed for reactions of Ni(PPh₃)₄ with MeI, EtI, *n*-BuI, sec-BuI, and *tert*-BuI.

While the reaction of Ni(PPh₃)₄ with MeI does produce some of the expected product of oxidative addition, NiMeI-(PPh₃)₂, this compound is unstable and decomposes readily to NiI(PPh₃)₂ and ethane as in eq 2 and Scheme 2. That said, Ni(I) is present at very low temperatures, in the early stages where ethane is not yet detected, and more than just a simple, conventional oxidative addition reaction must be occurring. These observations will be discussed further below.

A pattern of reaction products is clearly discernible for reactions of Ni(PPh₃)₄ with the iodoalkanes RI containing β hydrogen atoms; Ni(I), alkane RH, and alkene R–H are major products and the nickel hydride is a minor product. In no cases were either nickel alkyl compounds or dimer R₂ observed.

Our qualitative observations that Ni(PPh₃)₄ reacts more rapidly with *sec*-BuI and *tert*-BuI than with *n*-BuI were very interesting because the apparent relative rates correlate with the C–I bond strengths and the relative stabilities of alkyl radicals.⁷ Our complementary observations that Ni(PPh₃)₄ reacts rapidly at room temperature with all three *tert*-butyl halides added further interest because of the obvious novelty.

We therefore carried out competition experiments in attempts to obtain at least semiquantitative information on relative rates of the various reactions. In these experiments, deficiencies of Ni(PPh₃)₄ were added at room temperature to solutions containing comparable concentrations of two or three butyl halides for which relative rates were desired. Integrated ¹H NMR spectra of the alkyl halide solutions were acquired before and after addition of the Ni(PPh₃)₄, and relative rate data were deduced from the extents to which the

Scheme 3. Summary of Product Distributions Observed for Reactions of $Ni(PPh_3)_4$ with MeI, EtI, *n*-BuI, sec-BuI, and tert-BuI

 $Ni(PPh_3)_4 + Mel \rightarrow Nil(PPh_3)_n (major) + NiMel(PPh_3)_2 (minor) + C_2H_6 (major)$

 $Ni(PPh_3)_4 + EtI \rightarrow Nil(PPh_3)_n \text{ (major)} + NiHI(PPh_3)_2 \text{ (minor)} + C_2H_6 \text{ (major)} + C_2H_4 \text{ (major)}$

+ Z-CH₃CH=CHCH₃ (major) + E-CH₃CH=CHCH₃ (major) + *trans*-NiHI(PPh₃)₂ (minor)

 $Ni(PPh_3)_4 + sec-Bul \rightarrow Nil(PPh_3)_n \text{ (major)} + CH_3CH_2CH_2CH_3 \text{ (major)} + CH_2=CHCH_2CH_3 \text{ (minor)}$

+ Z-CH₃CH=CHCH₃ (major) + E-CH₃CH=CHCH₃ (major) + trans-NiHI(PPh₃)₂ (minor)

 $Ni(PPh_3)_4 + tert$ -Bul $\rightarrow Nil(PPh_3)_n$ (major) + HC(CH₃)₃ (major) + CH₂=C(CH₃)₂ (major) + trans-NiHI(PPh₃)₂ (minor)

relative intensities of the various alkyl halide resonances had changed. On the basis of results presented above, we assumed that all reactions would have proceeded to completion by the time an initial NMR spectrum was obtained; spectra run up to 30 min later exhibited no differences, and thus the assumption was shown to be reasonable. On the other hand, all of the resulting spectra in the region δ 0.5–1.7 contained paramagnetically broadened resonances of reactants and products. Thus there was much partial and even total overlap of resonances, and useful integrations were not always obtainable.

Three experiments were carried out utilizing *tert*-butyl halides, one in which all three halides were present, others involving mixtures of either iodide and bromide or bromide and chloride. The ¹H chemical shifts of *tert*-BuCl, *tert*-BuBr, and *tert*-BuI are δ 1.62, 1.49, and 1.34, respectively, and thus the three singlets are all well separated. Unfortunately, however, the methyl chemical shifts of the products isobutane (δ 1.63) and isobutene (δ 1.60) overlap significantly the methyl resonance of *tert*-BuI, and thus useful spectral integrations for this compound could not be obtained.

We show in Figure 7 the results of an experiment in which a deficiency of $Ni(PPh_3)_4$ was added to a solution containing *tert*-BuCl, *tert*-BuBr, and *tert*-BuI in the relative amounts shown.



Figure 7. Stacked plots of (lower) a room temperature solution of *tert*-BuCl (*), *tert*-BuBr (#), and *tert*-BuI (+) (molar ratios 1:2.6:1.9), and (upper) of the same solution after the addition of a deficiency of Ni(PPh₃)₄.

As can be seen, although the resonances of *tert*-BuCl and *tert*-BuBr are much broadened on reaction, useful integrations are possible, and one finds that *tert*-BuBr reacts faster by a factor of ~2. As can also be seen, and consistent with the expected presence of isobutane and isobutene, the broad resonance at $\delta \sim 1.62$ indicates the presence of at least two species, and it is impossible to integrate the *tert*-BuI resonance. If one assumes that one-third of the intensity is attributable to *tert*-BuI, then *tert*-BuI reacts fast than *tert*-BuBr by a factor of 2–3; this would be a lower limit since the amount of residual *tert*-BuI could be much lower. Similar conclusions were reached in experiments involving just the pairs of reactants, *tert*-BuCl vs *tert*-BuBr, and *tert*-BuBr vs *tert*-BuI.

Complementary experiments that were carried out involved reactions of deficiencies of Ni(PPh₃)₄ with (a) a mixture of sec-BuCl, sec-BuBr, and sec-BuI, (b) a mixture of sec-BuCl and sec-BuBr, and (c) a mixture of sec-BuBr and sec-BuI. In these cases there was considerable overlap between the α -CH multiplet resonances of sec-BuBr and sec-BuI and between the β -Me doublet resonances of these two compounds and CH₂ resonances. It was possible, however, to estimate that sec-BuI reacts faster than sec-BuBr by 10–20% and that sec-BuBr reacts faster than sec-BuCl by a factor of ~2.

We carried out two similar experiments, each in duplicate, to assess the influence of the alkyl groups on relative rates. In one we added deficiencies of Ni(PPh₃)₄ to solutions containing comparable amounts of *n*-BuI and *sec*-BuI, and in the other we added deficiencies of Ni(PPh₃)₄ to solutions containing comparable amounts of *sec*-BuI and *tert*-BuI. Although again resonance broadening and overlap were problematic, we were able to deduce that *sec*-BuI reacted faster than *n*-BuI by a factor of ~1.5 and that *tert*-BuI reacted faster than *sec*-BuI by a factor of ~3.

These results confirm that the orders of reactivities with $Ni(PPh_3)_4$ are *tert*-BuI > *sec*-BuI > *n*-BuI, *tert*-BuI > *tert*-BuBr > *tert*-BuCl, and *sec*-BuI > *sec*-BuBr > *sec*-BuCl. These trends all implicate, of course, processes involving radical formation.⁷

A possible mechanistic precedent for this chemistry was proposed many years ago by Tsou and Kochi^{3c} for oxidative addition reactions of aryl halides ArX (X = Cl, Br) to Ni(PEt₃)₄ (Scheme 4).

In this, a single-electron transfer (SET, or $S_{RN}1^8$) process yields a radical ion pair which can undergo combination within the solvent cage to give the square planar compounds NiArX(PEt₃)₂. These are observed and are, of course, identical to the products of oxidative addition via a conventional concerted process (Scheme 5).⁹

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

Scheme 4. Electron Transfer/Radical Pair Mechanism for Oxidative Addition of Aryl Halides to Ni(0) Compounds (L = PEt₃)



Scheme 5. Concerted Mechanism for Oxidative Addition of Aryl Halides to M(0) Species (M = Ni, Pd; L = Tertiary Phosphines)



solvent SH to give arene products, which are also observed. Thus, formation of all of the reaction products could be rationalized on the basis of the SET process shown.^{3c}

The Kochi mechanistic proposal has very recently been reassessed on the basis of DFT calculations on the reactions of phenyl halides with Ni(0) phosphine complexes.^{3f} Bisphosphine species NiL₂ were found to be too high in energy to be kinetically relevant for reactions with PhI, and SET from NiL₃ to PhX, as either an inner-sphere or an outer-sphere process, was ruled out as a route to Ni(I) products on the same basis. In addition, there was found no reaction path corresponding to the classical three-center oxidative addition of the Ph–X bond to Ni(0), as shown in Scheme 5. Instead, two competing reaction paths were found:

- 1. S_N2-like displacement of X⁻ by NiL₃ at the *ipso*-carbon, followed by phosphine loss and recombination to give *trans*-NiPhXL₂.
- 2. Halogen atom abstraction by NiL₃, leading to NiIL₃ and a phenyl radical (Scheme 6), with transition states for atom abstraction steps being located using an open-shell singlet (broken-symmetry) formalism.

Scheme 6. Inner-Sphere Oxidative Addition of Iodobenzene to Ni(0) Compound (L = PMe₃)

```
\mathsf{NiL}_3 + \mathsf{PhI} \longrightarrow [\mathsf{PhI} \rightarrow \mathsf{NiL}_3] \longrightarrow [\mathsf{Ph--I--NiL}_3] \longrightarrow [\mathsf{NiIL}_3 + \mathsf{Ph} \cdot] \longrightarrow \mathsf{NiPhIL}_2 + \mathsf{L}
```

The nickel- and carbon-centered radicals formed in this way through halogen abstraction can then combine within the solvent cage as shown or go on to the products of diffusion from the solvent cage, much as in Scheme 4.

An inner-sphere mechanism analogous to that shown in Scheme 6 could presumably apply to the reaction of $Ni(PPh_3)_4$ with, e.g., *n*-BuI, as shown in Scheme 7.

Here coordination of the *n*-BuI to the Ni(0) is followed by a halogen atom abstraction step to give Ni(I) metalloradicals and butyl radicals, which can presumably then couple within the solvent cage to give alkyl Ni(II) product Ni(*n*-Bu)I-(PPh₃)₂. The latter might well undergo subsequent β -H elimination to give *trans*-NiHI(PPh₃)₂ and 1-butene. Similar

Scheme 7. Inner-Sphere Oxidative Addition of *n*-Butyl Iodide to Ni(0) Compounds (L = PPh₃)

 $NiL_4 + Bul \longrightarrow \{Bul \rightarrow NiL_3\} \longrightarrow Bu---I--NiL_3$

 $NiIL_3 + Bu \cdot \longrightarrow NiBuIL_2 \longrightarrow NiHIL_2 + 1$ -butene

chemistry could result from reaction of Ni(PPh₃)₄ with *sec*-BuI, a difference being that the β -elimination step would presumably yield 1- and 2-butenes simultaneously although this could not be confirmed experimentally. Reaction of Ni(PPh₃)₄ with *tert*-BuI could in the same way result in formation of *trans*-NiHI(PPh₃)₂ and isobutene.

Formation of *trans*-NiHI(\overline{PPh}_3)₂ and 1-butene is indeed observed in the reactions of Ni(PPh_3)₄ with *n*- and *sec*-BuI, but in only very low concentrations in both cases. However, alkene isomerization is known to be catalyzed by nickel hydrides,^{6a} and it would not be surprising if 1-butene were to be catalytically isomerized to *E*- and *Z*-2-butenes by the nickel hydride present in solution. *Z*-2-Butene is also expected to be catalytically isomerized to *E*-2-butene, although the *E*/*Z* ratio never reaches the thermodynamic ratio of ~3:1, presumably because slow decomposition of the hydride results eventually in loss of catalytic activity.

We are left, then, with the presumably related problems of rationalizing the very low concentrations in all cases of the hydride, NiHI(PPh₃)₂, and the formation in high yields of butanes. Although *trans*-NiHI(PPh₃)₂ does decompose thermally to H₂ and NiI(PPh₃)₃, that process occurs on the time scale of hours. It cannot account for the fact that the concentration of the hydride is extremely low from the beginning while the amounts of butanes formed are generally comparable to those of the total alkenes.

To answer these questions, we must consider the possibility that NiI(PPh₃)₃ and the butyl radical can, in addition to coupling, diffuse from the solvent cage. This would rationalize the formation of NiI(PPh₃)₃, and one needs then to consider the fates of the butyl radicals which would result. As is well known, alkyl radicals readily undergo self-reactions,¹⁰ as exemplified for the *n*-butyl radical in Scheme 8.

Scheme 8. Self-Reactions of the *n*-Butyl Radical



Thus *n*-butyl radicals can undergo disproportionation to equal amounts of 1-butene and *n*-butane, reasonably consistent with our findings, or couple to give *n*-octane. The ratio of the rate constants, k_c/k_d , is ~7, essentially independent of solvent,¹⁰ and thus *n*-octane would be the major product if the self-reaction were important in the nickel chemistry described here. We have, however, examined by ¹H NMR spectroscopy and GC the product distributions of several experiments involving the reaction of Ni(PPh₃)₄ with *n*-BuI. None of the samples contained detectable amounts of *n*-octane, and therefore butyl radical self-reactions are not a factor in the reaction of Ni(PPh₃)₄ with *n*-BuI.

Alternative reactions yielding *n*-butane would involve D atom abstraction from the methyl group of the toluene- d_8 solvent or hydridic H atom abstraction from *trans*-NiHI-(PPh₃)₂ as in eq 5. The latter reaction is, of course, appealing

because it also results in the formation of $NiI(PPh_3)_{2}$, a relatively important product at all times and in all cases.

$$Bu \cdot + NiHI(PPh_3)_2 \rightarrow BuH + NiI(PPh_3)_2$$
(5)

Both atom abstraction reactions should be feasible thermodynamically,^{6a,7} the latter more so since the nickelhydride bond strength $(50-60 \text{ kcal/mol})^{6a}$ is expected to be significantly lower than $C-H^7$ bond strengths. On the other hand, the concentration of *trans*-NiHI(PPh₃)₂ is always much lower than the solvent concentration, and therefore bimolecular atom abstraction from the solvent could be kinetically preferred, all else being comparable.

Kinetics studies of hydrogen abstraction reactions of free radicals with both toluene $^{11a-c}$, and metal hydrides 12 have been reported. Thus, methyl, ethyl, and *tert*-butyl radicals abstract a methyl hydrogen atom from toluene with secondorder rate constants of ~ 17 , ~ 219 (both extrapolated to ~ 20 °C), and ~14 M^{-1} s⁻¹ (48 °C), respectively, although a kinetic isotope effect might lower such rate constants significantly in the case of toluene- d_8 .^{11d} The metal hydride studies have involved abstraction reactions of primary, secondary, tertiary, and trityl radicals with metal hydride complexes containing various combinations of CO, Cp, Cp*, and phosphine ligands.¹² Rate constants are found to vary enormously $(10^1-10^{10} \text{ M}^{-1} \text{ s}^{-1})$, with both steric and electronic (M-H bond dissociation energies) effects being important. Although no good precedent seems to exist for abstraction of the hydridic hydrogen of trans-NiHI(PPh₃)₂ by the alkyl radicals postulated here, one can reasonably anticipate that this type of reaction could be comparable to or faster than abstraction from toluene-*d*₈.

Indeed, our experimental evidence suggests that the nbutane does form via hydridic hydrogen atom abstraction from the hydride as in eq 5. Supporting evidence includes the apparent absence among the reaction products of *n*-butane-d₁, the product anticipated from D atom abstraction by the butyl radical from the deuterated solvent. The ratio of integrated intensities of the *n*-butane methyl and methylene resonances is 6:4, not 5:4. In addition, each component of the ¹H resonance of the -CH₂D group of CH₃CH₂CH₂CH₂D would be a 1:1:1 triplet $(J_{\text{H-D}} \approx 1 \text{ Hz})$ and would be shifted upfield of the CH₃ resonance by ~0.015 ppm^{13} (~9 Hz), giving rise to considerable asymmetry in the combined methyl resonance multiplet. This resonance is shown in Figure 8, and, although broad because of the paramagnetism, it clearly does not exhibit significant asymmetry to the high-field side of the multiplet or evidence of coupling to deuterium in the center peak.

Reactions of $Ni(PPh_3)_4$ with sec-butyl iodide and tert-butyl iodide probably proceed similarly to the processes shown in



Scheme 7 and eq 5 since, as mentioned above, radical formation would be more facile with these substrates. Values of k_c/k_d for secondary and tertiary radicals are ~1 and ~0.16, respectively,¹⁰ and therefore dimeric products of radical coupling should again be readily apparent. They are not: while inspection of ¹H NMR spectra of reaction mixtures (Figures S4e and S5e) does reveal weak unassigned peaks in the aliphatic regions, by far the strongest peaks are those attributed to *n*-butane and *E*- and *Z*-2-butenes in the case of *n*-BuI and *sec*-BuI reactions, and to isobutane and isobutene for the *tert*-BuI reaction. Thus, reactions of Ni(PPh₃)₄ with *n*-BuI, *sec*-BuI, and *tert*-BuI all appear to proceed as in Scheme 7, and a similar conclusion can probably also be reached for the EtI system.

On the basis of analogous palladium oxidative addition chemistry,^{14,15} MeI might well be expected to react via an S_N^2 -type mechanism. Indeed, it should be the most likely of all of the alkyl iodides studied here to react in this way and the one least likely to react via the type of radical processes discussed above. That said, however, the low-temperature formation of Ni(I) (Figure 1) clearly suggests the relevance of a radical process analogous to those discussed above. Indeed, indirect support for this conclusion may be found in early work,^{3a} which demonstrated that oxidative addition of (*R*)-PhCHDCl to Ni(PPh₃)₄ proceeds with racemization at the benzylic carbon,^{3a} in contrast to the analogous palladium chemistry.¹⁴ Thus, even benzyl chloride reacts with Ni(PPh₃)₄ via a radical process, although such a mechanism was not proposed and Ni(I) products were not identified (or considered, apparently).

Also, as discussed above, oxidative addition reactions of aryl halides, which contain relatively strong carbon–halogen bonds, to Ni(PPh₃)₄ clearly involve halogen atom abstraction^{2a,3f} and one can ask just how general might such processes be during oxidative addition to Ni(0). Relatively few detailed mechanistic studies of Ni(0) oxidative addition reactions appear to have been carried out, but radical processes are apparent in oxidative addition reactions of alkyl halides with Ni-(PHPh₂)₄,^{3b} Ni(PCy₃)₂,^{3d} and Ni(PEt₃)₄.^{3e} In the case of Ni(PHPh₂)₄, ^{3b} formation of compounds of the type NiRX-(PHPh₂)₂ was postulated, but these were thought to undergo Ni-R homolysis to give alkyl radicals in order to rationalize certain of the alkene and alkane products observed.

In the cases of the Ni(PCy₃)₂ system,^{3d} organic and Ni(I) product distributions consistent in large part with those described here were observed although it was again thought that radical formation resulted from homolysis of Ni–C bonds; the type of process shown in Scheme 7 had not at the time been conceived. A similar conclusion was reached (by the same authors) for oxidative addition reactions of Ni(PEt₃)₄.^{3e} Thus, in spite of the paucity of firm evidence, it seems quite possible that reactions of Ni(0) phosphine complexes with organic halides generally involve halogen abstraction processes.

Can one expect the putative alkylnickel compounds to be viable species, and are they feasible intermediates? Very few estimates of Ni–C bond dissociation energies (BDEs) are available, but the BDEs of the species NiMe and Ni⁺-Me have been estimated as 55 and 45 kcal/mol, respectively,^{16a} and that of *cis*-NiMe₂(PH₃)₂ as 51.1 kcal/mol.^{16b} Reasonably consistent with these data, we note that the enthalpy change in eq 2 gives an upper limit of the Ni-R BDE as half of the C–C BDE of R₂. For NiMeI(PPh₃)₂, this translates to half of the C–C bond strength in ethane, i.e., ~45 kcal/mol,^{7d} reassuringly similar to the data for NiMe and Ni⁺-Me.

The corresponding Ni–C BDEs for the ethyl- and butyl-Ni compounds discussed above should be lower by perhaps up to 5–10 kcal/mol and may be expected to decrease in the order Me > Et > *n*-Bu > *sec*-Bu > *tert*-Bu,^{7d,16} but it seems likely that all of the alkylnickel compounds would be sufficiently robust that they would be stable at room temperature in the absence of non-homolytic degradative processes such as β -elimination. We say more on this issue below in connection with a DFT study.

DFT Investigations. DFT calculations were employed to assess both the thermodynamics and the mechanism(s) of the reactions of NiL_n with alkyl halides, using PMe₃ as a model for PPh₃ as has been done elsewhere.^{3f} The reactions studied include both neutral and charge-separated species; to ensure a balanced description of these, all geometry optimizations were carried out including a continuum solvent model (Gaussian:¹⁷ B3LYP^{18,19}/PCM(toluene)²⁰/SVP,²¹LANL2DZ²²). The level used for final electronic energies (Gaussian: M06²³/PCM-(toluene)/cc-pVTZ^{24,25}) is the same as the preferred method in our previous report^{2a} on ArCl oxidative addition to "Ni(PPh₃)₄". Broken-symmetry solutions were checked for and were found to be relevant only for X atom abstraction from RI by tris-phosphine species Ni(PMe₃)₃. All energies cited below are free energies (298 K, 1 bar).

 $Ni(PMe_3)_4$ is coordinatively saturated and unreactive. Dissociation of one PMe₃ costs 17.2 kcal/mol at the level of theory applied (see below), but dissociation of a second PMe₃ costs another 13.4 kcal/mol and is unlikely to contribute to a competitive reaction path. For the bulkier ligand PPh₃, however, the dominant species in solution is $Ni(PPh_3)_3^{26}$ and hence it is conceivable that formation of $Ni(PPh_3)_2$ is kinetically relevant. Therefore, we include $Ni(PMe_3)_2$ in the DFT study.

Thermodynamics of Halogen Atom Abstraction. DFT calculations were carried out to assess, in the first instance, the free energy changes for halogen atom abstraction reactions from chloro-, bromo-, and iodoalkanes shown in eqs 6 and 7 (X = Cl, Br, I; R = Me, Et, *n*-Bu, *sec*-Bu, *tert*-Bu; L = PMe₃).

$$NiL_2 + RX \to NiXL_2 + R. \tag{6}$$

$$NiL_3 + RX \rightarrow NiXL_3 + R \cdot$$
⁽⁷⁾

Trends in these energies are of course dominated by trends in R–X bond strengths (or, viewed differently, in Rstabilities). We show in Table 1 the free energy changes for halogen atom abstraction reactions from chloro-, bromo-, and iodoalkanes by Ni(PMe₃)₂ and Ni(PMe₃)₃.

For Ni(PMe₃)₃, abstraction is exergonic for all alkyl halides, with magnitudes ranging from -2.0 (MeCl, barely exergonic) to -10.3 (*tert*-BuI, significantly exergonic). Only for phenyl are the reactions endergonic. Abstraction becomes easier, in steps of 1-2 kcal/mol, in both sequences Me \approx Et \approx *n*-Bu > *sec*-Bu > *tert*-Bu and Cl > Br > I. Abstraction by Ni(PMe₃)₂ is clearly more exergonic than abstraction by Ni(PMe₃)₃, but this minitrend reverses when the initially required dissociation of two phosphine ligands from Ni(PMe₃)₄ is included. Curiously, the trend in variation with X is somewhat attenuated relative to the Ni(PMe₃)₃ reactions.

These data represent only the abstraction step itself, of course, not the overall free energy change for whatever net reactions ultimately occur. To determine the reactant side correctly relative to Ni(PMe₃)₄, 17.2 kcal/mol would have to be added to every value to account for the cost of dissociation

Table 1. Free Energies of Halogen Atom Abstraction from	n
RX by Ni(PMe ₃) ₂ and Ni(PMe ₃) ₃ (kcal/mol) as in Eqs 6	
and 7	

RX	$Ni(PMe_3)_2^a$	$Ni(PMe_3)_3^b$
MeCl	-8.7	-2.0
MeBr	-8.5	-2.9
MeI	-7.3	-3.2
EtCl	-9.9	-3.2
EtBr	-10.6	-5.0
EtI	-10.2	-6.1
n-BuCl	-9.2	-2.5
<i>n</i> -BuBr	-9.8	-4.2
n-BuI	-9.3	-5.2
sec-BuCl	-10.3	-3.6
sec-BuBr	-11.7	-6.1
sec-BuI	-12.0	-7.9
tert-BuCl	-11.6	-4.9
tert-BuBr	-13.5	-7.9
tert-BuI	-14.4	-10.3
PhCl	1.3	8.0
PhBr	0.0	5.6
PhI	0.0	4.1

"Relative to Ni(PMe₃)₂; add 30.6 kcal/mol for values relative to Ni(PMe₃)₄. ^bRelative to Ni(PMe₃)₃; add 17.2 kcal/mol for values relative to Ni(PMe₃)₄.

of one PMe₃, and this would make all abstractions endergonic. On the other hand, the initially formed alkyl radicals will form more stable species as outlined above. Consideration of these factors would presumably render every abstraction exergonic, even relative to Ni(PMe₃)₄, and more so for the Ni(PPh₃)₄ system for which the dominant species is the tris-complex.

Based on these results, a halogen atom abstraction mechanism for reactions of Ni(PPh₃)₄ (actually Ni(PPh₃)₃²⁶) with alkyl halides certainly seems thermodynamically feasible with the proclivities as found experimentally, *tert*-Bu > *sec*-Bu > *n*-Bu and RI > RBr > RCl. Halogen atom abstraction from *aryl* halides appears to be less favorable but is known to proceed readily.^{2a,3c} For the larger phosphine PPh₃, while dissociation to form Ni(PPh₃)₂ or Ni(PPh₃)₃ is easier,²⁶ the actual abstraction step might become more hindered sterically and the overall net effect would be difficult to predict.

Paths for Reaction of Mel with NiL_n ($L = PMe_3$). Since Ni(PMe₃)₄ is coordinatively saturated, at least one phosphine has to dissociate for a reaction to occur; in what follows, we use Ni(PMe₃)₃ as the reference point for relative energies. Reactions involving interactions of MeI with Ni(PMe₃)₂ and Ni(PMe₃)₃ are summarized in Scheme 9; information about energies and geometric details are provided in the Supporting Information.

As can be seen, the first step starting from Ni(PMe₃)₃ involves formation of a weakly bound complex via interaction with the metal of either a hydrogen atom ($\Delta G = 0.0$ kcal/mol) or the iodine atom ($\Delta G = -4.4$ kcal/mol) of the MeI. The former possibility (Figure 9, left) leads to the S_N2-like transition state for displacement of I⁻ by Ni(PMe₃)₃, with an effective barrier for this process of 14.0 kcal/mol above Ni(PMe₃)₃. From there the reaction proceeds in a highly exergonic process to [NiMe(PMe₃)₃]⁺I⁻.

Alternatively, coordination of MeI to $Ni(PMe_3)_3$ via the iodine atom leads in a closed-shell calculation to a three-center transition state for side-on oxidative addition, with a higher

Scheme 9. Free Energy Profile for Reaction of NiL_4 with MeI (L = PMe₃), with the Preferred Halogen Abstraction Path Highlighted in Red





Figure 9. Main transition states (TS) for reactions of $Ni(PMe_3)_3$ with MeI: (left) S_N2 -like TS; (right) halogen abstraction TS.

barrier of 20.0 kcal/mol (Scheme 9). On the other hand, a broken-symmetry solution is much lower in energy, and geometry optimization on this potential-energy surface (in red in Scheme 9) completely avoids geometries corresponding to S_N2 and three-center oxidative addition processes. Instead we locate a transition state for iodine atom abstraction at a much lower energy of 5.9 kcal/mol (Figure 9, right), and this collapses readily to doublet NiI(PMe₃)₃ and a methyl radical. These could be expected to recombine but, at the computational level used, the hypothetical five-coordinate product NiMeI(PMe₃)₃ is not a local minimum. A few plausible scenarios (not studied computationally) for the fate of the highly reactive methyl radical would involve (a) direct displacement of L from NiI(PMe₃)₃ to give square-planar NiMeI(PMe₃)₂, (b) reaction of the methyl radical with NiI(PMe₃)₂ (easily formed by loss of L from NiI(PMe₃)₃) to also give NiMeI(PMe₃)₂, and (c) reaction with Ni(PMe₃)₃ to give NiMe(PMe₃)₃. Ultimately, we find that a reasonable Ni(II) methyl product, [NiMe(PMe₃)₃]⁺I⁻, is stable by 21.5 kcal/mol relative to the Ni(PMe₃)₃ and MeI starting points.

A similar radical-type halogen abstraction transition state on the broken-symmetry surface has been reported previously for oxidative addition of *aryl* halides,^{3f} and our added results reinforce the idea that halogen abstraction might well be a general feature of oxidative addition reactions of nickel(0) compounds. Even an S_N2-type process for the reaction of MeI involves a significantly higher barrier as does the side-on oxidative-addition transition state, which in any case seems to an artifact of restriction to the closed-shell energy surface; we consider neither any further. The preferred path for reaction of Ni(PMe₃)₃ with MeI is identified as a radical-type halogen atom abstraction process.

We also considered paths beginning with further dissociation of phosphine to the bis-phosphine species $Ni(PMe_3)_{2}$, although the latter lies some 13.4 kcal/mol higher in energy than does $Ni(PMe_3)_3$, and therefore all alternatives discussed below are unlikely to be competitive with the process shown in red in Scheme 9. The $Ni(PMe_3)_2$ reaction again begins with a weakly bound complex, but we could not locate an S_N 2-like transition state analogous to that discussed above for the trisphosphine system. We also, surprisingly, could not locate a

Table 2. Free Energies of Important Transition States and Intermediates for Reactions of Ni(PMe₃)₂ and Ni(PMe₃)₃ with RI (kcal/mol)

step		MeI	EtI	<i>n</i> -BuI	sec-BuI	tert-BuI
1	Ni(PMe ₃) ₃	(0)	(0)	(0)	(0)	(0)
2	Ni(PMe ₃) ₃ (I-bound RI)	-4.4	n.d.	n.d.	n.d.	n.d.
3	TS for I atom abstraction	5.9	4.9	5.7	3.9	2.0
4	$NiI(PMe_3)_3 + R \cdot$	-3.2	-6.1	-5.2	-7.9	-10.3
5	Ni(PMe ₃) ₃ (H-bound RI)	0.0	-0.8	-1.4	-0.9	-1.0
6	S _N 2-like TS	14.0	15.0	13.1	17.9	21.9
7	$Ni(PMe_3)_2$	13.4	13.4	13.4	13.4	13.4
8	Ni(PMe ₃) ₂ (I-bound RI)	10.4	10.7	10.7	10.9	9.8
9	$NiI(PMe_3)_2 + R \cdot$	6.1	3.2	4.1	1.4	-1.1
10	cis-NiRI(PMe ₃) ₂	-13.3	-11.5	-11.0	-10.3	-9.2
11	trans-NiRI(PMe ₃) ₂	-21.5	-18.7	-19.5	-12.8	-8.1

^{*a*}All data relative to separated $L_3Ni + RI$. nd = not detected.

low-energy broken-symmetry solution leading to halogen abstraction even though such abstraction is thermodynamically favorable as noted above: NiI(PMe₃)₂ + Me[•] is 7.3 kcal/mol below Ni(PMe₃)₂ + MeI. Instead, a modest deformation of the I-bound MeI complex leads to a low-energy oxidative-addition transition state (only 2.4 kcal/mol above Ni(PMe₃)₂) which then proceeds to give *cis*-NiMeI(PMe₃)₂ and thence the more stable *trans* isomer. Note that *trans*-NiMeI(PMe₃)₂ corresponds to the PPh₃ analogue, which we believe is observed during the reaction of Ni(PPh₃)₄ with MeI and is of the same energy as [NiMe(PMe₃)₃]⁺T⁻, the ultimate product shown in the Ni(PMe₃)₃ manifold of Scheme 9.

All in all, halogen atom abstraction appears to be the lowestenergy path for the reaction of MeI with $Ni(PMe_3)_4$. Caution should of course be exercised when trying to extrapolate this conclusion to reactive species involving the much larger but poorer donor ligand PPh₃, but halogen abstraction is also likely to be the least sterically demanding reaction of the alternatives considered and so is likely the preferred path for reactions involving PPh₃ also.

Transition-State Calculations for Reactions of RI with $Ni(PMe_3)_{2,3}$ (R = Et, n-Bu, sec-Bu, tert-Bu). Paths for reactions of primary, secondary, and tertiary alkyl iodides with $Ni(PMe_3)_2$ and $Ni(PMe_3)_3$ were also explored. Table 2 compares the calculated relative energies of various transition states and intermediates for the series MeI, EtI, *n*-BuI, sec-BuI, tert-BuI; energies and geometries are provided in the Supporting Information.

In most cases for the tris-phosphine system, we did not find local minima for weakly iodine-bound complexes containing iodine-coordinated RI (step 2). The $Ni(PMe_3)_3$ and RI fragments simply drifted apart during geometry optimization, but this makes no difference to the expected kinetics.

Going from primary to secondary to tertiary alkyls, the barrier for abstraction of an iodine atom by Ni(PMe₃)₃ (step 3) becomes lower by a few kcal/mol (*n*-Bu, 5.7; *sec*-Bu, 3.9; *tert*-Bu, 2.0 kcal/mol), compared with 10.0 kcal/mol for PhI,^{3f} and the abstraction (step 4) also becomes more exergonic (-5.2, -7.9, and -10.3 kcal/mol). At the same time, while weakly bound complexes formed via interactions of the metal a hydrogen atom of RX are slightly stabilized, the barrier for S_N2-like displacement (step 6) is large for MeI and increases substantially for the higher alkyls (13.1, 17.9, and 21.9 kcal/mol), presumably because of steric effects. It seems clear that if halogen abstraction already dominates for MeI, it will certainly do so for the higher alkyl iodides.

Reaction paths involving Ni(PMe₃)₂ rather than Ni(PMe₃)₃ were also examined. Formation of iodine-bound species Ni(PMe₃)₂(RI) from Ni(PMe₃)₂ is slightly exergonic for all alkyl iodides, but we could not locate oxidative addition transition states for Ni(PMe₃)₂ in combination with *sec*-BuI and *tert*-BuI. The potential-energy surface appears to be very flat for these reactions, which seem to be nearly barrierless starting from the weakly I-bound Ni(PMe₃)₂(RI) adducts. However, the 13.4 kcal/mol cost of dissociating the second ligand from Ni(PMe₃)₃ to form Ni(PMe₃)₂ appears to largely negate any potential advantages of reactions involving Ni(PMe₃)₂ relative to iodine abstraction by Ni(PMe₃)₃. Similar conclusions have been reached elsewhere.^{3f}

As mentioned above, subsequent reactions of alkyl radicals (formed by abstraction) leading to more stable compounds would result in even somewhat endergonic halogen abstraction reactions proceeding to completion, and an example of this is represented by steps 10 and 11, coupling of the alkyl radicals with the metalloradical NiI(PMe₃)₂ to give four-coordinated Ni(II) alkyl compounds NiRI(PMe₃)₂ (R = Me, Et, *n*-Bu). The corresponding *sec*-Bu and *tert*-Bu complexes are less stable, presumably because of steric interactions and intrinsically weaker Ni–C bonds.

In this context, we note that the calculated Ni-Me dissociation energy for the compound *trans*-NiMeI(PMe₃)₂ is the difference between steps 9 and 11 of Table 2, i.e., 27.6 kcal/mol. This fits in reasonably well with the rather wide limit set by eq 2 which, as is noted above, gives an upper limit of the Ni-Me BDE energy of NiMeI(PPh₃)₂ as ~45 kcal/mol. Thus the Ni-Me BDE of NiMeI(PPh₃)₂ seems to be greater than that of NiMeI(PMe₃)₂ by ~17 kcal/mol or less.

We note that the compounds *trans*-NiRI(PMe₃)₂ (step 11) constitute a series of relatively stable alkyl nickel compounds of the type postulated in Scheme 7, thereby strengthening the cases made above that such species are viable products and for the identification of *trans*-NiMeI(PPh₃)₂ as a product of the reaction of Ni(PPh₃)₄ and MeI. Relevant to this point, we note also that each step in the calculated energy profile for the reaction of PhI with Ni(PPh₃)₄ differs only by 2–3 kcal/mol from the corresponding steps involving Ni(PMe₃)₄.^{3f}

Precedents for the Types of Radical Reactions Postulated Here. We note several reports, analogous to those discussed here, of reactions of organic halides with coordination compounds of metal ions in low oxidation states to produce alkyl metal compounds in a higher oxidation states via electron or halogen atom transfer processes (eq 8-10).^{27a,b,c,d}

$$2[Co(CN)_{5}]^{3-} + RX[CoR(CN)_{5}]^{3-} + [CoX(CN)_{5}]^{3-}$$
(8)
$$2[Cr(en)_{5}(H_{5}O)]^{2+} + [CrR(en)_{5}(H_{5}O)]^{2+}$$

+
$$[CrX(en)_2(H_2O)]^{2+}$$
 (9)

$$2[Ni(TMC)]^{+} + RX[NiR(TMC)]^{+} + [NiX(TMC)]^{+}$$

(10)

where R = alkyl, benzyl; X = Cl, Br, I; en = ethylenediamine; TMC = a tetradentate N_4 macrocycle.

While some of the thus-formed alkylmetal compounds undergo subsequent reactions which differ from those observed here, experimental evidence in most cases suggests initial coordination of the alkyl halides to the substitutionlabile metal reactants and points clearly to the involvement of radical processes and intermediates. Of particular relevance, relative rates follow the trends *tert*-alkyl > *sec*-alkyl > *n*-alkyl and RI > RBr > RCl.

Perhaps more closely related, oxidative addition of alkyl bromides to elemental zinc to form alkylzinc bromides (eq 11)^{27e} probably proceeds via electron transfer, much as postulated by Kochi for Ni(PEt₃)₄ (Scheme 4).^{3c}

$$RBr + Zn \to RZnBr \tag{11}$$

Here again relative rates follow the trends *tert*-alkyl > *sec*-alkyl > *n*-alkyl.

Nature of the Paramagnetic Ni(I) lodo Species. We have previously reported NMR spectral properties of NiCl- $(PPh_3)_2$ and of mixtures of PPh₃ and NiCl $(PPh_3)_2$ which are in exchange with small proportions of NiCl $(PPh_3)_3$.^{2a} Room-temperature ¹H NMR spectra exhibit averaged resonances at $\delta \sim 9-10$ (br, meta-H), $\sim 4-5$ (vbr, ortho-H), and $\sim 2-4$ (br,

para-H); similar resonances are also observed in ¹H NMR spectra of bromonickel(I) and iodonickel(I) species,^{2a} and we have utilized this information to identify Ni(I) iodo species formed during reactions with alkyl halides.

The chemical shifts of NiCl(PPh₃)₂ mixtures are temperature-dependent, consistent with Curie law behavior,^{2b-f} which results in the chemical shifts varying linearly with T⁻¹ and therefore shifting toward the chemical shifts of diamagnetic PPh₃ at δ 7.0–7.3 (and narrowing) as the temperature rises. Although NiCl(PPh₃)₃ is in facile equilibrium with NiCl-(PPh₃)₂ and free PPh₃, dissociation is extensive but the bisphosphine complex appears not to dimerize significantly to [NiCl(PPh₃)₂]₂.^{2a}

As is shown above, reactions of Ni(PPh₃)₄ with alkyl iodides produce initially low concentrations of Ni(I) species as indicated in ¹H NMR spectra by the presence of weak, broad resonances. The resonances move between 200 and 225 K toward the chemical shifts of free PPh₃, apparently consistent with Curie law behavior^{2b-f} although the available data are sparse, and then merge into a very broad band at ~250 K, quite unlike the behavior of the chloro system.^{2a} On raising the temperature to 275 K and then 300 K, the very broad band separates into well-defined *meta, ortho,* and *para* resonances with chemical shifts similar to those of the chloro system.^{2a} Interestingly, these three resonances exhibit what might be thought of as anti-Curie law behavior, diverging as the temperature rises and thereby suggesting complex exchange processes.

By analogy with the chloro system,^{2a} the major species present in solutions is probably NiI(PPh₃)₂, but free PPh₃ is definitely present in reaction mixtures as may be also NiI(PPh₃)₃ and the dimer, [NiI(PPh₃)₂]₂. Although the bisphosphine chloro analogue is monomeric,^{2a} the larger iodide ligands may well facilitate dimerization via bridging iodides. Unfortunately ³¹P NMR spectroscopy is of no help identifying any of the Ni(I) species because ³¹P NMR spectra of solutions containing significant amounts of paramagnetic species are broadened beyond recognition. Thus at this point we have insufficient information to identify either the iodo species present or the nature of the exchange process(es).

Coordination of Alkyl lodides. In several of the experiments discussed above, we note unusual chemical shifts for the resonances of unreacted alkyl iodides as the reactions progressed. For instance, in the MeI system (Figures 1 and S1a-e), the resonance of the unreacted MeI shifts 0.22 ppm downfield during the reaction, from δ 1.26 at 200 K to δ 1.48 at 300 K, the chemical shift of free MeI at this temperature. Similarly, in the EtI system over the same temperature range (Figures 2, S2a-e), the methylene resonance shifts downfield 0.18 ppm from δ 2.40 to δ 2.58, the methyl resonance 0.14 ppm from δ 1.21 to δ 1.35. The methylene and methyl chemical shifts of free EtI at 300 K are δ 2.58 and δ 1.54, respectively.

For the *n*-BuI system (Figures 4, 5), the resonances of the hydrogens on C(1), C(2), C(3), and C(4) of unreacted *n*-BuI shift downfield ~0.2, ~0.2, ~0.12, and ~0.01 ppm, respectively, in the temperature range 200–300 K, the ultimate chemical shifts being very close to those of free *n*-BuI. In a complementary experiment, a solution Ni(PPh₃)₄ with a slight excess of *n*-butyl iodide was prepared at 275 K and spectra were run at this temperature over 90 min; as mentioned above, the Ni(PPh₃)₄ had all reacted from the beginning. Of interest here, however, the chemical shift of the ICH₂ group remained

constant as throughout the experiment, did the chemical shifts of the phenyl resonances of the Ni(I) species, suggesting a constant concentration of Ni(I) species during this time period.

Similar data were obtained for *sec*-BuI in the temperature range 200–250 K, although data could not be obtained at higher temperatures because all of the *sec*-BuI had been consumed.

In contrast, the methyl resonances of *n*-butane and *E*- and *Z*-2-butenes all shift slightly (~0.05 ppm) upfield in the temperature range 200–300 K, and thus the behaviors of the MeI, EtI, *n*-BuI, and *sec*-BuI resonances seem anomalous. We suggest tentatively that the observed downfield shifts are a result of coordination to the ever-increasing amounts of paramagnetic Ni(I) species and rapid exchange between free and coordinated alkyl iodide.²⁸

Possible Relevance of This Investigation to Mechanisms of Nickel-Catalyzed Cross-Coupling Reactions. A great deal is known of the utility of nickel-based catalysts for cross-coupling chemistry¹ and it is now well established that, in contrast to most palladium-based catalysts, many nickel-based catalyst systems can readily catalyze cross-coupling of alkyl halides.¹ Interestingly, use of appropriately enantioenriched chiral ligand templates has also resulted in the discovery of a number of enantioconvergent reactions in which both enantiomers of a racemic alkyl halide reactant are converted to a resolved cross-coupled product.²⁹ Enantioconvergent processes of this type have been thought to be incompatible with the type of conventional, two-electron catalytic cycle shown in Scheme 1 (RX instead of ArX), which is generally expected to result in identical configurational consequences for both enantiomers. Therefore mechanisms involving catalysis by Ni(I) compounds and free radical intermediates have been proposed, such as that shown in Scheme 10.^{1,29}

Scheme 10. Two-Electron Ni(I)-Ni(III) Catalytic Cycle for Cross-Coupling Reactions



This catalytic cycle begins with a halonickel(I) compound $NiXL_n$ containing some number n (often 3) of neutral ligands L. Transmetalation (alkylation) yields alkyl-Ni(I) species NiR'L_n which, when n = 3, are 17-electron metalloradicals, a class of compounds expected to abstract halogen atoms from alkyl halides RX to give the Ni(II) species NiR'XL, plus an organic radical R· as in the second step in Scheme 10.30 Subsequent combination of NiR'XL_n and R· then constitutes the second of two SET steps in what amounts to oxidative addition of RX to NiR'L_n to form NiRR'XL_n, and reductive elimination from the latter yields the coupled product R-R' and regenerates the catalyst species $NiXL_n$. When $NiXR'L_n$ contains an enantioenriched chiral ligand template L_n enantioconvergent reactions can result because one prochiral face of R. couples preferentially to the nickel. Such observations are usually taken as evidence that a mechanism as in Scheme 1 cannot apply and that a Ni(I)–Ni(III) catalytic cycle must pertain. $^{29,31}\,$

However, as indicated in Scheme 7, we now have the potential feasibility of the Ni(0)-Ni(II) catalytic cycle which also involves radical intermediates, as in Scheme 11.

Scheme 11. Non-conventional, Two-Electron but Radical-Based Ni(0)–Ni(II) Catalytic Cycle for Cross-Coupling Reactions



Here the oxidative addition step proceeds via two oneelectron steps, much as in Scheme 10 but beginning with a Ni(0) species, with the second step involving one or the other face of \mathbb{R} coupling possibly preferentially to the nickel(I) if L_n constitutes an enantioenriched, chiral manifold. Thus, with a proper choice of ligands L, cross-coupling via an *overall* twoelectron Ni(0)–Ni(II) mechanism may apply, and enantioconvergent reactions could possibly occur without involvement of a Ni(I)–Ni(III) process as in Scheme 10.

Pursuing this theme further, recent work has shown that some nickel compounds can catalyze cross-coupling reactions involving tertiary alkyl halides.³² Again the identities of the catalytic species are not known and radical mechanisms as in Scheme 10 are usually favored. Confounding progress in understanding and development of the new catalyst systems, however, are occasional observations that the order of crosscoupling catalysis of alkyl halide conversion is primary > secondary > tertiary, or that reactions of tertiary alkyl chlorides and bromides are too slow to be useful. In addition, the presence of potential byproducts such as alkenes is rarely considered.

The results reported here, however, suggest that a closer look at even simple Ni(0)-phosphine systems might prove useful since the order of reactivity of Ni(PPh₃)₄ is tertiary > secondary > primary alkyl halides. Indeed, as we have also shown, Ni(PPh₃)₄ reacts with *tert*-BuI very rapidly even at 200 K and with *tert*-BuCl at room temperature. Thus this particular nickel-phosphine system appears to be more reactive than many of the ligand systems currently under investigation, ^{1,29,32} and the only problem is that the presumed alkylnickel products undergo rapid β -elimination.

Since β -elimination requires a vacant site on the nickel to which the hydrogen can migrate, a strategy to render feasible alkylnickel intermediates of the type NiRXL₂ (R = primary, secondary, tertiary alkyl group containing one or more β hydrogen atoms) would be to utilize ligands which dissociate less readily than does PPh₃ and which therefore can inhibit β -H elimination reactions. Cis-chelating diphosphines may well be worth investigating in this way, and we note that most of the successful ligand systems reported to date have involved chelating diamine ligands.^{1,29,32} Indeed, β -hydrogen elimination reactions should be relatively slow in intermediates of the types NiRX(diphosphine) and NiRR'(diphosphine).

A number of diphos-nickel compounds have been utilized for cross-coupling reactions of aryl halides^{32i,33a-j} and therefore, given the reactivity of Ni(PPh₃)₄, activation of even secondary and tertiary alkyl halides may well be feasible utilizing diphos ligand systems. Coordinatively saturated, sterically encumbered compounds of the type Ni(diphos)₂ may well prove unrewarding, but Ni(0) compounds of the types Ni(diphos)L (L = labile ligand such as PPh₃, alkenes)^{33k} are worth investigating and, if experiments prove successful, investigations of chiral diphosphines may prove to be very rewarding.

Summary. This paper describes a variable-temperature NMR investigation of reactions of the nickel(0) compound Ni(PPh₃)₄ with methyl, ethyl, *n*-butyl, *sec*-butyl, and *tert*-butyl halides RX (X = Cl, Br, I). The reactions all appear to involve inner sphere, direct halogen atom transfer within the solvent cage from the alkyl halides to the metal to form alkyl radicals R· and halonickel(I) metalloradical species, and these subsequently undergo radical combination within the solvent cage to give the square planar compounds NiRX(PPh₃)₂. Radical intermediacy is demonstrated by observations that the relative rates vary in the orders *tert*-Bu > *sec*-Bu > *n*-Bu and RI > RBr > RCl. In addition, DFT calculations on the halogen transfer and coupling reactions generally support and shed considerable light on the mechanism proposed.

Formation of the methyl compound, $NiMeI(PPh_3)_2$, is indicated by the appearance of a methyl resonance with a negative chemical shift in the ¹H NMR spectra of reaction mixtures and demonstrates that radical combinations are feasible although this compound is surprisingly unstable and decomposes in solution to ethane and $NiI(PPh_3)_2$. The phenyl analogues $NiPhX(PPh_3)_2$ have been previously shown to be formed in much the same way,^{2a} thus also demonstrating the feasibility of nickel- and carbon-based radical coupling.

When R = Et, *n*-Bu, *sec*-Bu, *tert*-Bu, on the other hand, the alkyl-nickel products are not observed because of rapid β -H elimination to give hydrides NiHX(PPh₃)₂ and the corresponding alkenes. Also occurring are secondary reactions in which a proportion of the alkyl radicals does not couple with the associated Ni(I) species but rather diffuses from the solvent cage and abstracts hydrogen from NiHX(PPh₃)₂. As a result, the hydrides are invariably a minor product while the major products are alkanes RH and alkenes R–H (in comparable amounts) and Ni(I) species.

The hydride species NiHI(PPh₃)₂ decomposes to H₂ and NiI(PPh₃)₂, in chemistry similar to that of the corresponding methyl and phenyl analogues, and also exhibits unusual NMR spectra. The hydride chemical shifts vary from about δ -23 (broad) below 200 K to about -17.5 (sharp) above 274 K, changes rationalized on the basis of exchange between bis- and trisphosphine species, NiHI(PPh₃)₂ and NiHI(PPh₃)₃.

Present in all of the reactions are paramagnetic, presumably substitution-labile Ni(I) metalloradical species, and thus PPh₃ resonances are generally broad and exhibit large contact shifts because of exchange between free and coordinated ligands. Interestingly, resonances of ethylene (but not of more sterically hindered alkenes) and of the smaller iodoalkanes also exhibit broadening and changes in chemical shifts, indicating that these compounds also coordinate to the Ni(I) products.

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

Organometallics

column of BASF copper catalyst and then dried by passing through a column of 4 Å 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.

As a general procedure, NMR solutions of 0.48 mg Ni(PPh₃)₄ (43 μ mol) in toluene- d_8 were made up under nitrogen in a glovebox and then placed in a dry ice-acetone bath and treated with 1–4 equiv of alkyl halide. Samples were then placed in an NMR probe preset to 180–200 K, and reactions were monitored by ¹H NMR spectroscopy over a range of temperatures.

Computational Methods. Geometries were optimized using Gaussian 09¹⁷ coupled to the external Baker optimizer³⁴ via the BOpt package;³⁵ at this stage we used the B3LYP functional^{18,19} in combination with the SVP basis²¹ (LANL2DZ with corresponding ECP at Ni, Br, and I^{22}) and a solvent correction (PCM = toluene²⁰). 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, the M06 functional,²³ the cc-pVTZ basis set²⁴ obtained from the EMSL library,²⁵ and the PCM solvent correction. Phosphine dissociation energies are fairly sensitive to the choice of functional and correlation treatment; in our previous paper we found that for this type of system M06 produces more reasonable results than the add-on Grimme DFT-D3 correction.³⁶ To obtain final free energies, thermal corrections from the B3LYP/SVP vibrational analysis (enthalpy and entropy, 298 K, 1 bar) were added to the above-mentioned final electronic energies; the entropy contribution was scaled by 0.67 to account for reduced freedom in solution.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00244.

Optimized geometries (XYZ)

NMR spectra for all experiments described (Figures S1– S5) and a table (Table S1) showing total and relative free energies of various relevant species studied by DFT (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: bairdmc@chem.queensu.ca.

*E-mail: petrushenricusmaria.budzelaar@unina.it.

ORCID 🔍

Michael C. Baird: 0000-0002-1497-3511

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

M.C.B. and P.H.M.B. acknowledge financial support from NSERC.

REFERENCES

(1) For general reviews of nickel-based cross-coupling catalysts, see: (a) Netherton, M. R.; Fu, G. C. Nickel-;catalyzed cross-couplings of unactivated alkyl halides and pseudohalides with organometallic compounds. *Adv. Synth. Catal.* **2004**, *346*, 1525. (b) Terao, J.; Kambe, N. Cross-Coupling Reaction of Alkyl Halides with Grignard Reagents Catalyzed by Ni Pd or Cu Complexes with π -Carbon Ligand(s). *Acc. Chem. Res.* **2008**, *41*, 1545. (c) Phapale, V. B.; Cárdenas, D. J. Nickelcatalysed Negishi cross-coupling reactions: scope and mechanisms. *Chem. Soc. Rev.* **2009**, *38*, 1598. (d) Hu, X. Nickel-catalyzed cross coupling of non-activated alkyl halides: a mechanistic perspective. Chem. Sci. 2011, 2, 1867. (e) Jana, R.; Pathak, T. P.; Sigman, M. S. Advances in Transition Metal (PdNiFe)-Catalyzed Cross-Coupling Reactions Using Alkyl-organometallics as Reaction Partners. Chem. Rev. 2011, 111, 1417. (f) Jahn, U. Radicals in transition metal catalyzed reactions? Transition metal catalyzed radical reactions? A fruitful interplay anyway: part 3: catalysis by group 10 and 11 elements and bimetallic catalysis. Top. Curr. Chem. 2011, 320, 121. (g) Han, F.-S. Transition-metal-catalyzed Suzuki-Miyaura crosscoupling reactions: a remarkable advance from palladium to nickel catalysts. Chem. Soc. Rev. 2013, 42, 5270. (h) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. Nature 2014, 509, 299. (i) Iwasaki, T.; Kambe, N. Ni-Catalyzed C-C Couplings Using Alkyl Electrophiles. Top. Curr. Chem. 2016, 374, 65. Hazari, N.; Melvin, P. R.; Beromi, M. M. Well-defined nickel and palladium precatalysts for cross-coupling. Nat. Rev. Chem. 2017, 1, 0025 DOI: 10.1038/s41570-017-0025. (k) Bhat, V.; Welin, E. R.; Guo, X.; Stoltz, B. M. Advances in Stereoconvergent Catalysis from 2005 to 2015: Transition-Metal-Mediated Stereoablative Reactions Dynamic Kinetic Resolutions and Dynamic Kinetic Asymmetric Transformations. Chem. Rev. 2017, 117, 4528. (1) Choi, J.; Fu, G. C. Transition metal-catalyzed alkyl-alkyl bond formation: Another dimension in cross-coupling chemistry. Science 2017, 356 (6334), 152. (m) Taylor, B. L. H.; Jarvo, E. R. Construction of enantioenriched tertiary stereogenic centers by nickel- and palladium-catalyzed cross-coupling reactions of alkyl electrophiles. Synlett 2011, 2011, 2761.

(2) (a) Manzoor, A.; Wienefeld, P.; Baird, M. C.; Budzelaar, P. M. H. 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. Organometallics 2017, 36, 3508. (b) Keller, H. J.; Schwarzhans, K. E. Magnetic resonance of paramagnetic complexes. Angew. Chem., Int. Ed. Engl. 1970, 9, 196. (c) Kaupp, M.; Köhler, F. H. Combining NMR spectroscopy and quantum chemistry as tools to quantify spin density distributions in molecular magnetic compounds. Coord. Chem. Rev. 2009, 253, 2376. (d) Köhler, F. H. Paramagnetic complexes in solution: The NMR approach. Encyclopedia of Magnetic Resonance, Online 2011; DOI: 10.1002/9780470034590.emrstm1229. (e) La Mar, G. N.; Sherman, E. O. Proton nuclear magnetic resonance investigation of the kinetics of tetrahedral-planar isomerization of bis(n-alkyldiphenylphosphine) nickel(II) dihalides. J. Am. Chem. Soc. 1970, 92, 2691. (f) La Mar, G. N.; Sherman, E. O.; Fuchs, G. A. Proton NMR investigation of $\mathrm{d}\pi\mathrm{d}\pi$ bonding in low-valent cobalt and nickel complexes with alkyldiphenylphosphines. J. Coord. Chem. 1972, 1, 289. (g) Zelonka, R. A.; Baird, M. C. Olefin and acetylene complexes of divalent copper. J. Organomet. Chem. 1971, 33, 267.

(3) (a) Stille, J. K.; Cowell, A. B. The oxidative addition of benzyl halides to tetrakis(triphenylphosphine)nickel(0). J. Organomet. Chem. **1977**, *124*, 253. (b) Weston, C. W.; Verstuyft, A. W.; Nelson, J. H.; Jonassen, H. B. Reactions of the Zerovalent Compound Ni[HP- $(C_6H_5)_2]_4$. Inorg. Chem. **1977**, *16*, 1313. (c) Tsou, T. T.; Kochi, J. K. Mechanisms of Oxidative Addition. Reaction of Nickel(0) Complexes with Aromatic halides. J. Am. Chem. Soc. **1979**, *101*, 6319. (d) Morvillo, A.; Turco, A. Reactions of Organic Halides and cyanides with bis(tricyclohexylphosphine)nickel(0). J. Organomet. Chem. **1981**, 208, 103. (e) Morvillo, A.; Turco, A. Reactions of methyl and ethyl halides with the complexes Ni[P(C_2H_5)_3]_4 and Ni(X)[P- $(C_2H_5)_3$]_3. J. Organomet. Chem. **1982**, 224, 387. (f) Funes-Ardoiz, I.; Nelson, D. J.; Maseras, F. Halide Abstraction Competes with Oxidative Addition in the Reactions of Aryl Halides with [Ni-(PMe_nPh_{(3-n)})_4]. Chem. - Eur. J. **2017**, 23, 16728.

(4) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents Organics and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176. (5) (a) Green, M. L. H.; Smith, M. J. Stable Methylnickel Complexes containing Tertiary Phosphine Ligands. J. Chem. Soc. A **1971**, 639. (b) Yamamoto, T.; Takamatsu, M.; Yamamoto, A. Preparation of Alkylnickel(II)-Phosphine Complexes by Reactions of Ni(acac)₂ with Alkylaluminums in the Presence of Teriary Phosphines. Bull. Chem. Soc. Jpn. **1982**, 55, 325. (c) Le Page, M. D.; Patrick, B. O.; Rettig, S. J. James Br R. 2-Pyridyl-phosphine and -diphosphine complexes of nickel(0) their reactivity (including aqueous solution chemistry) and some related incidental methylphosphonium iodides. Inorg. Chim. Acta **2015**, 431, 276–288.

(6) (a) Eberhardt, N. A.; Guan, H. Nickel Hydride Complexes. *Chem. Rev.* **2016**, *116*, 8373. (b) The hydride *trans*-NiHI(PPh₃)₂ appears not to have been reported previously, but tris-PPh₃ nickel hydride complexes have.^{6c,d} (c) Nesmeyanov, A. N.; Isaeva, L. S.; Morozova, L. N.; Petrovskii, P. V.; Tumanskii, B. L.; Lokshin, B. V.; Klemenkova, Z. S. Interaction of Nickel Acetylacetonate with Diethylaluminum Chloride. *Inorg. Chim. Acta* **1980**, *43*, 1. (d) Nesmeyanov, A. N.; Isaeva, L. S.; Drogunova, G. I.; Morozova, L. N. A new cationic hydride complex of nickel [(Ph₃P)₃Ni(H)-(CH₃CN)]BF₄. *J. Organomet. Chem.* **1980**, *195*, C15. (e) D'Aniello, M. J.; Barefield, E. K. Mechanistic Studies on the Catalysis of Isomerization of Olefins by (PPh₃)₃NiX. *J. Am. Chem. Soc.* **1978**, *100*, 1474.

(7) (a) Colussi, A. J. Thermochemistry of Free Radicals. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, USA, 1988; Vol. 1, p 25. (b) Hioe, J.; Zipse, H. Radical stability and its role in synthesis and catalysis. *Org. Biomol. Chem.* **2010**, *8*, 3609. (c) Zipse, H. Radical stability - a theoretical perspective. *Top. Curr. Chem.* **2006**, 263, 163. (d) Blanksby, S. J.; Ellison, G. B. Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* **2003**, 36, 255.

(8) (a) Rossi, R. A.; Pierini, A. B.; Santiago, A. N. Aromatic substitution by the SRN1 reaction. *Organic Reactions* **1999**, *54*, 1. (b) Terme, T.; Crozet, M. P.; Maldonado, J.; Vanelle, P. Mechanistic approach to electron transfer reactions. *Electron Transfer Reactions in Organic Synthesis*; Research Signpost, 2002; p 1 (c) Pierini, A. B.; Penenory, A. B.; Baumgartner, M. T. Formation of carbon-carbon and carbon-heteroatom bonds by electron transfer nucleophilic substitution of alkyl halides. *Electron Transfer Reactions in Organic Synthesis*; Research Signpost, 2002; p 63 (d) Rossi, R. A.; Postigo, A. Recent advances in radical nucleophilic substitution reactions. *Curr. Org. Chem.* **2003**, *7*, 747.

(9) (a) Sundermann, A.; Uzan, O.; Martin, J. M. L. Computational study of a new Heck reaction mechanism catalyzed by palladium(II/IV) species. *Chem. - Eur. J.* 2001, 7, 1703. (b) Senn, H. M.; Ziegler, T. Oxidative Addition of Aryl Halides to Palladium(0) Complexes: A Density-;Functional Study Including Solvation. *Organometallics* 2004, 23, 2980. (c) Ahlquist, M.; Norrby, P.-O. Oxidative Addition of Aryl Chlorides to Monoligated Palladium(0): A DFT-;SCRF Study. *Organometallics* 2007, 26, 550. (d) Bajo, S.; Laidlaw, G.; Kennedy, A. R.; Sproules, S.; Nelson, D. J. Oxidative Addition of Aryl Electrophiles to a Prototypical Nickel(0) Complex: Mechanism and Structure/Reactivity Relationships. *Organometallics* 2017, 36, 1662–1672.

(10) (a) Sheldon, R. A.; Kochi, J. K. Pair Production and Cage Reactions of Alkyl Radicals in Solution. J. Am. Chem. Soc. **1970**, 92, 4395. (b) Alfassi, Z. B. Combination and Disproportionation of Alkyl Radicals. In Chemical Kinetics of Small Organic Radicals; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, USA, 1988; Vol. 1, p 129.

(11) (a) Dütsch, H. R.; Fischer, H. Nucleophilic Character of the *tert*-Butyl Radical. Absolute Rate Constants for the Reactions with Substituted Toluenes. *Int. J. Chem. Kinet.* **1982**, *14*, 195. But, see: (b) Lomas, J. S.; Briand, S.; Fain, D. Reactions of Thermally Generated *tert*-Butyl and Di(*tert*-alkyl)ketyl Radicals in Toluene: Cage Effects and Hydrogen Transfer. *J. Org. Chem.* **1991**, *56*, 166. (c) Zhang, H.-X.; Ahonkhai, S. I.; Back, M. H. Rate constants for abstraction of hydrogen from benzene toluene and cyclopentane by methyl and ethyl radicals over the temperature range 650–770 K. *Can. J. Chem.* **1989**, *67*, 1541. (d) Luzhkov, V. B. Theoretical study of

deuterium kinetic isotope effect in peroxidation of phenol and toluene. Chem. Phys. 2005, 320, 1.

(12) (a) Kinney, R. J.; Jones, W. D.; Bergman, R. G. Synthesis and Reactions of (η^{5} -Cyclopentadienyl)tricarbonylhydridovanadate. A Comparative Mechanistic Study of its Organic Halide Reduction Reactions with those of Tri-n-butyltin Hydride. J. Am. Chem. Soc. **1978**, 100, 7902. (b) Ash, C. E.; Hurd, P. W.; Darensbourg, M. Y.; Newcomb, M. Competing Nucleophilic Displacement and Radical Chain Reduction in Reactions of Transition-Metal Hydride Anions with Alkyl bromides. J. Am. Chem. Soc. **1987**, 109, 3313. (c) Eisenberg, D. C.; Lawrie, C. J.; Moody, A. E.; Norton, J. R. Relative Rates of H-Transfer from Transition-Metal Hydrides to Trityl Radicals. J. Am. Chem. Soc. **1991**, 113, 4888. (d) Franz, J. A.; Linehan, J. C.; Birnbaum, J. C.; Hicks, K. W.; Alnajjar, M. S. Absolute Rate Constants for Hydrogen Atom Abstraction from Molydenum Hydrides to Carbon-Centered Radicals. J. Am. Chem. Soc. **1999**, 121, 9824.

(13) (a) Batiz-Hernandez, H.; Bernheim, R. A. Isotope Shifts. Prog. Nucl. Magn. Reson. Spectrosc. 1967, 3, 63. (b) Hansen, P. E. Isotope Effects on Nuclear Shielding. Annu. Rep. NMR Spectrosc. 1984, 15, 105.

(14) For early seminal studies, see: (a) Lau, K. S. Y.; Wong, P. K.; Stille, J. K. Oxidative Addition of Benzyl Halides to Zero-Valent Palladium Complexes. Inversion of Configuration at Carbon. *J. Am. Chem. Soc.* **1976**, *98*, 5832. (b) Stille, J. K.; Lau, K. S. Y. Mechanisms of Oxidative Addition of Organic Halides to Group 8 Transition-Metal Complexes. *Acc. Chem. Res.* **1977**, *10*, 434. (c) Becker, Y.; Stille, J. K. Stereochemistry of oxidative addition of benzyl- α -d chloride and bromide to tris(triethylphosphine);palladium(0). Direct observation of optical activity in a carbon-palladium σ -bonded complex. *J. Am. Chem. Soc.* **1978**, *100*, 838.

(15) For recent reviews, see: (a) Netherton, M. R.; Fu, G. C. Palladium-catalyzed cross-coupling reactions of unactivated alkyl electrophiles with organometallic compounds. *Top. Organomet. Chem.* 2005, 14, 85. (b) Kambe, N.; Iwasaki, T.; Terao, J. Pd-catalyzed cross-coupling reactions of alkyl halides. *Chem. Soc. Rev.* 2011, 40, 4937. (c) Labinger, J. A. Tutorial on Oxidative Addition. *Organometallics* 2015, 34, 4784.

(16) (a) Martinho Simões, J. A.; Beauchamp, J. L. Transition metalhydrogen and metal-carbon bond strengths: the keys to catalysis. *Chem. Rev.* **1990**, *90*, *629*. (b) Macgregor, S. A.; Neave, G. W.; Smith, C. Theoretical studies on C-heteroatom bond formation via reductive elimination from group 10 $M(PH_3)_2(CH_3)(X)$ species (X = CH3 NH2 OH SH) and the determination of metal-X bond strengths using density functional theory. *Faraday Discuss.* **2003**, *124*, 111.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morukuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Ciolowski, J.; Fox, D. J. Gaussian 09, B.01; Gaussian, Inc.: Wallingford, CT, 2009.

(18) (a) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. A new mixing of Hartree-Fock and local-density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372.

(19) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

(20) (a) Miertus, S.; Tomasi, J. Approximate evaluations of the electrostatic free energy and internal energy changes in solution

Organometallics

processes. *Chem. Phys.* **1982**, *65*, 239. (b) Miertus, S.; Scrocco, E.; Tomasi, J. Electrostatic interaction of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects. *Chem. Phys.* **1981**, *55*, 117. (c) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. Chem. Rev. **2005**, *105*, 2999. (d) Scalmani, G.; Frisch, M. J.; et al. Electronic excitation energies in solution at equation of motion CCSD level within a state specific polarizable continuum model approach. J. Chem. Phys. **2010**, *132*, 084102.

(21) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets for atoms lithium to krypton. *J. Chem. Phys.* **1992**, 97, 2571.

(22) (a) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements sodium to bismuth. *J. Chem. Phys.* **1985**, *82*, 284. (b) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms scandium to mercury. *J. Chem. Phys.* **1985**, *82*, 270.

(23) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry thermochemical kinetics noncovalent interactions excited states and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215.

(24) (a) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. **1989**, 90, 1007. Woon, D. E.; Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. J. Chem. Phys. **1993**, 98, 1358. (c) Balabanov, N. B.; Peterson, K. A. Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements Sc-Zn. J. Chem. Phys. **2005**, 123, 064107.

(25) (a) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L. S.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. Basis Set Exchange: A Community Database for Computational Sciences. *J. Chem. Inf. Model.* **2007**, *47*, 1045. (b) Feller, D. The role of databases in support of computational chemistry calculations. *J. Comput. Chem.* **1996**, *17*, 1571.

(26) (a) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. Triarylphosphine and Ethylene Complexes of Zerovalent Nickel Palladium and Platinum. *J. Am. Chem. Soc.* **1972**, *94*, 2669. (b) Tolman, C. A.; Seidel, W. C.; Gosser, L. Formation of Three-Coordinate Nickel(0) Complexes by Phosphorus Ligand Dissociation from NiL₄ W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

(27) (a) Halpern, J.; Chock, P. B. The Reactions of Pentacyanocobaltate(II) with Some Organic Halides. J. Am. Chem. Soc. 1969, 91, 582. (b) Kochi, J. K.; Powers, J. W. The Mechanism of Reduction of Alkyl Halides by Chromium(II) Complexes. Alkylchromium Species as Intermediates. J. Am. Chem. Soc. 1970, 92, 137. (c) Bakac, A.; Espenson, J. H. Kinetics and mechanism of the alkylnickel formation in one-electron reductions of alkyl halides and hydroperoxides by a macrocyclic nickel(I) complex. J. Am. Chem. Soc. 1986, 108, 713. (d) Ram, M. S.; Bakac, A.; Espenson, J. H. Freeradical pathways to alkyl complexes of a nickel tetraaza macrocycle. Inorg. Chem. 1986, 25, 3267. (e) Guijarro, A.; Rosenberg, D. M.; Rieke, R. D. The Reaction of Active Zinc with Organic Bromides. J. Am. Chem. Soc. 1999, 121, 4155. This paper provides an extremely useful overview of the type of chemistry in question here.

(28) For previous reports of coordination of alkyl halides to transition metals see (a) Cheng, T. Y.; Szalda, D. J.; Hanson, J. C.; Muckerman, J. T.; Bullock, R. M. Four-Electron-Donor Hemilabile η^3 -PPh₃ Ligand that Binds through a C=C Bond Rather than an Agostic C-H Interaction and Displacement of the C=C by Methyl Iodide or Water. *Organometallics* **2008**, *27*, 3785. (b) Pathak, D. D.; Adams, H.; White, C. Enantioselective alkylating reagents; crystal structure of [Ru{ $\eta^5 C_5 H_4(C_{10}H_{19})$ }(dppe)(IEt)]CF₃SO₃[dppe = PPh₂CH₂CH₂PPh₂ C₁₀H₁₉=(+)-neomenthyl]. *J. Chem. Soc., Chem. Commun.* **1994**, 733. (c) Conroy-Lewis, F. M.; Redhouse, A. D.; Simpson, S. J. Molecular iodoalkane complexes: preparation of the complexes [$(\eta^5-C_5H_5)$ Ru(PPh₃)(CN^tBu)(IR)]PF₆, (R = CH₃,

CH₂SiMe₃), and the crystal structures of $[(\eta^5-C_5H_5Ru(PPh_3)-(CN^tBu)I]$ and $[(\eta^5-C_5H_5)Ru(PPh_3)(CN^tBu)(ICH_3)]PF_6$. J. Organomet. Chem. **1989**, 366, 357. (d) Winter, C. H.; Arif, A. M.; Gladysz, J. A. A general class of stable alkyl halide complexes: synthesis structure and reactivity of alkyl iodide complexes of the formula $[(\eta 5-C5H5)Re(NO)(PPh3)(IR)]+BF4^-$. J. Am. Chem. Soc. **1987**, 109, 7560. (e) Burk, M. J.; Segmuller, B.; Crabtree, R. H. Coordination chemistry of methyl iodide. Organometallics **1987**, 6, 2241.

(29) For early examples, see: (a) Caeiro, J.; Sestello, J. P.; Sarandeses, L. A. Enantioselective nickel-catalyzed cross-coupling reactions of trialkynylindium reagents with racemic secondary benzyl bromides. *Chem. - Eur. J.* **2008**, *14*, 741. (b) Saito, B.; Fu, G. C. Enantioselective Alkyl-Alkyl Suzuki Cross-Couplings of Unactivated Homobenzylic Halides. *J. Am. Chem. Soc.* **2008**, *130*, 6694. (c) Smith, S. W.; Fu, G. C. Nickel-Catalyzed Asymmetric Cross-Couplings of Racemic Propargylic Halides with Arylzinc Reagents. *J. Am. Chem. Soc.* **2008**, *130*, 12645. (d) Lu, Z.; Fu, G. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 6676. (e) Wilsily, A.; Tramutola, F.; Owston, N. A.; Fu, G. C. New Directing Groups for Metal-Catalyzed Asymmetric Carbon-Carbon Bond-Forming Processes: Stereoconvergent Alkyl-Alkyl Suzuki Cross-Couplings of Unactivated Electrophiles. *J. Am. Chem. Soc.* **2012**, *134*, 5794.

(30) (a) Baird, M. C. Seventeen-electron metal-centered radicals. *Chem. Rev.* **1988**, *88*, 1217. (b) Brown, T. L. Atom transfer reactions and radical chain processes involving atom transfer. In *Organometallic Radical Processes*; Trogler, W. C. Ed.; Elsevier: New York, 1990; p 67. (31) For recent, very useful critiques of current mechanistic considerations and conundrums, see: (a) Lucas, E. L.; Jarvo, E. R. Keeping Track of Electrons. *Acc. Chem. Res.* **2018**, *51*, 567. Balcells, D.; Nova, A. Designing Pd and Ni Catalysts for Cross-Coupling Reactions by Minimizing Off-;Cycle Species. *ACS Catal.* **2018**, *8*, 3499.

(32) (a) Dudnik, A. S.; Fu, G. C. Nickel-Catalyzed Coupling Reactions of Alkyl Electrophiles Including Unactivated Tertiary Halides To Generate Carbon-Boron Bonds. J. Am. Chem. Soc. 2012, 134, 10693. (b) Zultanski, S. L.; Fu, G. C. Nickel-Catalyzed Carbon-Carbon Bond-Forming Reactions of Unactivated Tertiary Alkyl Halides: Suzuki Arylations. J. Am. Chem. Soc. 2013, 135, 624. (c) Zhao, C.; Jia, X.; Wang, X.; Gong, H. Ni-Catalyzed Reductive Coupling of Alkyl Acids with Un-activated Tertiary Alkyl and Glycosyl Halides. J. Am. Chem. Soc. 2014, 136, 17645. (d) Yotsuji, K.; Hoshiya, N.; Kobayashi, T.; Fukuda, H.; Abe, H.; Arisawa, M.; Shuto, S. Nickel-Catalyzed Suzuki-Miyaura Coupling of a Tertiary Iodocyclopropane with Wide Boronic Acid Substrate Scope: Coupling Reaction Outcome Depends on Radical Species Stability. Adv. Synth. Catal. 2015, 357, 1022. (e) Chu, C. K.; Liang, Y.; Fu, G. C. Silicon-Carbon Bond Formation via Nickel-Catalyzed Cross-Coupling of Silicon Nucleophiles with Unactivated Secondary and Tertiary Alkyl Electrophiles. J. Am. Chem. Soc. 2016, 138, 6404. (f) Zhou, Q.; Cobb, K. M.; Tan, T.; Watson, M. P. Stereospecific Cross Couplings To Set Benzylic All-Carbon Quaternary Stereocenters in High Enantiopurity. J. Am. Chem. Soc. 2016, 138, 12057. (g) Rezazadeh, S.; Devannah, V.; Watson, D. A. Nickel-Catalyzed C-;Alkylation of Nitroalkanes with Unactivated Alkyl Iodides. J. Am. Chem. Soc. 2017, 139, 8110. (h) Ariki, Z. T.; Maekawa, Y.; Nambo, M.; Crudden, C. C. Preparation of Quaternary Centers via Nickel-Catalyzed Suzuki-Miyaura Cross-Coupling of Tertiary Sulfones. J. Am. Chem. Soc. 2018, 140, 78. (i) Wang, J.-L.; Li, H.-J.; Wang, M.; Wang, J.-H.; Wu, Y.-C. A six-step synthetic approach to marine natural product (+)-aureol. Tetrahedron Lett. 2018, 59, 945.

(33) (a) Tamao, K.; Sumitani, K.; Kumada, M. Asymmetric homogeneous hydrosilylation with chiral phosphine-palladium complexes. J. Am. Chem. Soc. **1972**, 94, 4374. (b) Percec, V.; Bae, J.-Y.; Hill, D. H. Aryl Mesylates in Metal Catalyzed Homocoupling and Cross-Coupling Reactions. 2. Suzuki-Type Nickel-Catalyzed Cross-Coupling of Aryl Arenesulfonates and Aryl Mesylates with Arylboronic Acids. J. Org. Chem. **1995**, 60, 1060. (c) Saito, S.; Sakai, M.; Miyaura, N. Tetrahedron Lett. **1996**, 37, 2993. (d) Indolese, F. Suzuki-type coupling of chloroarenes with arylboronic acids catalysed by nickel complexes. Tetrahedron Lett. 1997, 38, 3513. (e) Saito, S.; Oh-tani, S.; Miyaura, N. Synthesis of Biaryls via a Nickel(0)-Catalyzed Cross-Coupling Reaction of Chloroarenes with Arylboronic Acids. J. Org. Chem. 1997, 62, 8024. (f) Galland, J.-C.; Savignac, M.; Genêt, J.-P. Cross-coupling of chloroarenes with boronic acids using a water-soluble nickel catalyst. Tetrahedron Lett. 1999, 40, 2323. (g) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. Synthesis of Biaryls via a Nickel(0)-Catalyzed Cross-Coupling Reaction of Chloroarenes with Arylboronic Acids. J. Org. Chem. 2004, 69, 3447. (h) Bronstein, H. A.; Luscombe, C. K. Externally Initiated Regioregular P3HT with Controlled Molecular Weight and Narrow Polydispersity. J. Am. Chem. Soc. 2009, 131, 12894. (i) Zhao, Y.-L.; Li, Y.; Li, S.-M.; Zhou, Y.-G.; Sun, F.-Y.; Gao, L.-X.; Han, F.-S. A Highly Practical and Reliable Nickel Catalyst for Suzuki-Miyaura Coupling of Aryl Halides. Adv. Synth. Catal. 2011, 353, 1543. (j) Kampmann, S. S.; Skelton, B. W.; Wild, D. A.; Koutsantonis, G. A.; Stewart, S. G. An Air-Stable Nickel(0) Phosphite Precatalyst for Primary Alkylamine C-N Cross-Coupling Reactions. Eur. J. Org. Chem. 2015, 2015, 5995. (k) Brunker, T. J.; Blank, N. F.; Moncarz, J. R.; Scriban, C.; Anderson, B. J.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Sommer, R. D.; Incarvito, C. D.; Rheingold, A. L. Chiral Palladium(0) trans-Stilbene Complexes: Synthesis Structure and Oxidative Addition of Phenyl Iodide. Organometallics 2005, 24, 2730.

(34) (a) Baker, J. *PQS 2.4*; Parallel Quantum Solutions: Fayetteville, AR, 2001;. (b) Baker, J. An algorithm for the location of transition states. *J. Comput. Chem.* **1986**, *7*, 385.

(35) Budzelaar, P. H. M. Geometry optimization using generalized chemically meaningful constraints. J. Comput. Chem. 2007, 28, 2226.

(36) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-;Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(37) (a) Raucoules, R.; de Bruin, T.; Raybaud, P.; Adamo, C. Theoretical Unraveling of Selective 1-Butene Oligomerization Catalyzed by Iron–Bis(arylimino)pyridine. *Organometallics* **2009**, 28, 5358. (b) Tobisch, S.; Ziegler, T. Catalytic Oligomerization of Ethylene to Higher Linear α -Olefins Promoted by the Cationic Group 4 [(η 5-Cp-(CMe2-bridge)-Ph)MII(ethylene)2]+ (M = Ti Zr Hf) Active Catalysts: A Density Functional Investigation of the Influence of the Metal on the Catalytic Activity and Selectivity. *J. Am. Chem. Soc.* **2004**, 126, 9059.