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Dinuclear Ni(I)—Ni(I) Complexes with Syn-Facial Bridging Ligands from Ni(I) Precursors or Ni(II)/Ni(0) Comproportionation

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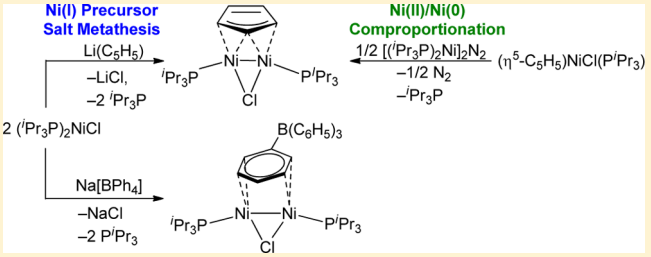
Supporting Information

ABSTRACT: The previously reported mononuclear d^9 complex $(^iPr_3P)_2NiCl$ (**1**) provides a convenient entry into a series of dinickel complexes with syn-facial bridging ligands. Cyclopentadienyllithium or indenyllithium react with **1** in in *n*-pentane to provide $[(^iPr_3P)Ni]_2(\mu\text{-Cl})(\mu\text{-}C_5H_5)$ (**3a**) and $[(^iPr_3P)Ni]_2(\mu\text{-Cl})(\mu\text{-}C_9H_7)$ (**3b**). Complexes **3a,b** are also accessible by comproportionation of the mononuclear Ni(II) complexes $(^iPr_3P)NiCl(\eta^5\text{-}C_5H_5)$ (**4a**) and $(^iPr_3P)NiCl(\eta^3\text{-}C_9H_7)$ (**4b**) with the Ni(0) precursor $[(^iPr_3P)_2Ni]_2(\mu\text{-}N_2)$ (**2**). The bulkier Ni(II) complex $(^iPr_3P)(\eta^5\text{-}C_5Me_4H)NiCl$ (**5**) does not undergo clean reaction with **2**, and the methyl complex $(^iPr_3P)(\eta^5\text{-}C_5H_5)Ni(CH_3)$ (**6**) does not react with **2**. Reaction of **1** with $NaBPh_4$ provided $[(^iPr_3P)Ni]_2(\mu\text{-Cl})(\mu\text{-}PhBPh_3)$ (**7**). The dinuclear complexes **3a,b** and **7** all feature structurally similar $[(P^iPr_3)Ni]_2(\mu_2\text{-Cl})$ fragments, with an approximate planar arrangement of the X and P^iPr_3 ligands and a perpendicular organic cyclopentadienyl, indenyl, or phenyl π system.



INTRODUCTION

The low cost of nickel in comparison to its heavier congeners provides an impetus to study its utilization in catalytic transformations.[1] Mononuclear transition-metal catalysts are vastly more widespread than dinuclear and polynuclear catalysts both in organic synthesis on a laboratory scale and in industrial homogeneous catalytic processes.[2] In contrast, biological redox transformations are commonly performed via multimetallic enzyme active sites.[3] The mechanisms of organonickel-catalyzed reactions are often assumed to involve mononuclear nickel intermediates in the oxidation states of +2 and 0. Although some mechanistic studies have proposed addition/elimination reaction sequences that require the presence of organometallic mononuclear Ni(III)[4] or Ni(IV),[5] such mechanisms are often difficult to verify, due to the relative paucity of model complexes in these oxidation states.[6] Inorganic complexes of Ni(I) have considerable precedent,[7] although organometallic hydrocarbyl-containing complexes are less common and are often overlooked as catalytic intermediates.[4,8]

The advantages of bimetallic systems in catalysis have been often discussed, though not always realized.[9] Several reports have shown the catalytic relevance of unusual dinuclear complexes of Pd[10] and Ni.[11] Dinuclear Ni complexes supported by phosphine ligands have also been reported that allow for catalytic C—C coupling chemistry.[12] These reports raise the interesting possibility of alternate mechanistic pathways for known reactions and new catalytic reactions based on group 10 bimetallic species displaying metal—metal bonds.

Although ligand design could play a role in the assembly of dinuclear complexes of Ni(I),[12a,b,13] oftentimes such complexes readily assemble as favored products.[14] Our group has recently isolated a number of dinuclear and polynuclear nickel complexes with unusual bonding and reactivity, which include dinuclear Ni(I) complexes that undergo isomerization by C—H bond activation,[15] asymmetric intermediates with formal Ni(I)—Ni(III) centers that are resting states in catalytic C—C activation and coupling,[16] formal Ni(I)—Ni(III) and Ni(I)—Ni(IV) clusters with silylene ligands,[17] and a pentanuclear Ni hydride complex that undergoes H/D exchange with benzene-d_6.[18] The mononuclear Ni(I) precursors $(^iPr_3P)_2NiCl$ (**1**) and the Ni(0) dinitrogen complex $[(^iPr_3P)_2Ni]_2$ $(\mu\text{-}N_2)$ (**2**) have been shown to serve as useful precursors to dinuclear Ni(I) complexes.[19] This report demonstrates how this synthetic approach can be extended to provide a simple entry into a family of novel bimetallic Ni(I)—Ni(I) complexes stabilized by interaction with π-conjugated rings and how dinuclear organometallic Ni(I) species could be unanticipated intermediates in a variety of catalytic systems from comproportionation of Ni(0) and Ni(II) complexes.

RESULTS AND DISCUSSION

Synthesis of Dinuclear Ni(I)—Ni(I) Complexes $[(^iPr_3P)Ni]_2(\mu_2\text{-Cl})(\mu\text{-}C_5H_5)$ (3a) and $[(^iPr_3P)Ni]_2(\mu\text{-Cl})(\mu\text{-}C_9H_7)$ (3b) via Nucleophilic Substitution or Comproportionation. Treatment of colorless $(^iPr_3P)_2NiCl$ (**1**) with a suspension of cyclopentadienyllithium or indenyllithium in *n*-pentane at 25 °C caused a color change to green. Subsequent filtration and crystallization of the product afforded the dinuclear Ni(I)

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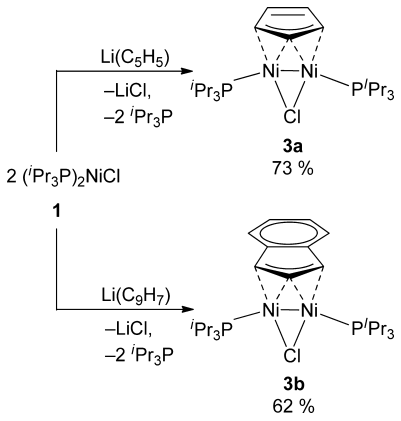
complex $[(^{i}Pr_3P)Ni]_2(\mu\text{-}Cl)(\mu\text{-}C_5H_5)$ (**3a**) and $[(P^{i}Pr_3)Ni]_2(\mu\text{-}Cl)(\mu\text{-}C_9H_7)]$ (**3b**) in 73% and 62% yields, respectively, as green-brown solids, as shown in Scheme 1.

Scheme 1



Turquoise needles of **3a,b** were obtained by recrystallization from pentane solutions at −34 °C. Solid **3a** can be handled at room temperature for days without significant decomposition; however, solutions decompose over days at room temperature, with the deposition of a nickel mirror. Additionally, $(^{i}Pr_3P)_2NiCl_2$ and $(\eta^5\text{-}C_5H_5)_2Ni$[20] were both isolated as decomposition products from solutions of **3a** after extended periods in C_6D_6, presumably from a disproportionation reaction that liberates nickel metal. Complex **3b** decomposes in a similar manner in solution over time, as judged by the observation of $(^{i}Pr_3P)_2NiCl_2$, $Ni(C_9H_7)_2$,[21] $^{i}Pr_3P$, and a Ni mirror. The exact stoichiometry of the reagents is crucial for the formation of **3a,b**, and an excess of the lithium salts provided a drastic decrease in yield and a plethora of byproducts. The solid-state molecular structure of **3a** is shown in Figure 1. The

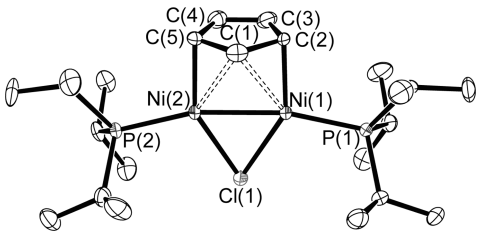


Figure 1. Depiction of the solid-state molecular structure of **3a** as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−C(2), 1.972(5); Ni(2)−C(5), 1.975(5); Ni(2)−C(1), 2.289(6); Ni(1)−C(1), 2.326(6); Ni(1)−Ni(2), 2.3995(10); C(1)−C(2), 1.444(9); C(1)−C(5) 1.429(8); C(2)−C(3), 1.418(9); C(3)−C(4), 1.328(9); C(4)−C(5), 1.435(9); Ni(1)−Cl(1), 2.1930(16); Ni(2)−Cl(1), 2.1919(17); Ni(1)−P(1), 2.1740(17); Ni(2)−P(2), 2.1716(16); P(1)−Ni(1)−Ni(2), 167.52(6).

complex features approximate C_s symmetry, with a Ni(1)−Ni(2) bond length of 2.3995(10) Å. The cyclopentadienyl ligand bridges in a symmetric manner, with short Ni(1)−C(2) and Ni(2)−C(5) distances of 1.972(5) and 1.975(5) Å, respectively, and longer Ni(2)−C(1) and Ni(1)−C(1) distances of 2.289(6) and 2.326(6) Å, respectively. Both the Ni(1)−C(3) and Ni(2)−C(4) distances of 2.616(6) and 2.639(6) Å, respectively, are significantly longer. This could be viewed as η^3 bonding of the cyclopentadienyl moiety to the Ni−Ni unit, which is consistent with the significant double-bond character suggested by the C(3)−C(4) distance of 1.328(9) Å.

The solid-state structure of **3b** is shown in Figure 2, and the complex is structurally similar to **3a**. The Ni(1)−C(3) and

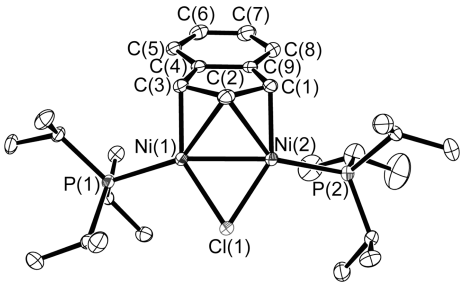


Figure 2. Depiction of the solid-state molecular structure of **3b** as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−Ni(2), 2.3918(8); Ni(1)−C(4), 2.847(3); Ni(1)−C(3), 1.945(3); Ni(1)−C(2), 2.151(3); Ni(1)−P(1), 2.1654(10); Ni(1)−Cl(1), 2.2045(9); Ni(2)−C(1), 1.948(3); Ni(2)−P(2), 2.1574(9); Ni(2)−C(2), 2.166(3); Ni(2)−Cl(1), 2.1947(8); P(1)−Ni(1)−Ni(2), 157.36(3); P(2)−Ni(2)−Ni(1), 163.26(3).

Ni(2)−C(1) distances are 1.945(3) and 1.948(3) Å, respectively. These are shorter than the Ni(1)−C(2) and Ni(2)−C(2) distances of 2.151(3) and 2.166(3) Å, respectively. The longer Ni(1)−C(4) and Ni(2)−C(9) distances of 2.847(3) and 2.878(3) Å, respectively, are consistent with an η^3 bonding of the indenyl moiety to the Ni−Ni unit. Closely related Pd analogues are known and have been structurally characterized.[22]

The $^{31}P\{^{1}H\}$ NMR spectra of **3a,b** have singlet resonances at δ 49.9 and 47.8, respectively. The ^{1}H NMR spectrum of **3a** features a cyclopentadienyl resonance at δ 5.07 as a broad singlet. Cooling solutions of **3a** in toluene-d_8 as low as 193 K did not result in decoalescence of this signal. Similarly, a single isopropyl methyl environment is observed as low as 193 K for **3a**, whereas two diastereotopic environments are expected for the pseudo-C_s symmetry structure observed in the solid state. This suggests that ring whizzing is rapid in **3b**, which exchanges the C_5H_5 environments, but a rapid sliding of the C_5H_5 moiety across the Ni−Ni bond must also occur to render the diastereotopic ^{i}Pr methyl groups chemically equivalent.

Complex **3b** has a ^{1}H NMR spectrum consistent with its solid-state structure, with five sharp multiplets for the coordinated indenyl group. The signal at δ 3.59 integrated to one hydrogen, whereas the resonances at δ 4.22, 6.95, and 7.18 all integrated to two hydrogens. The ^{1}H NMR of **3b** features diastereotopic ^{i}Pr methyl groups, consistent with the pseudo-C_s symmetric structure observed in the solid state. The $^{13}C\{^{1}H\}$ NMR spectrum of **3b** showed five resonances for the indenyl group, with the most upfield shift at δ 36.4 for C_1/C_3 carbon atoms.

Comproportionation Routes to 3a,b. The ubiquity of organometallic Ni(0) and Ni(II) complexes and the relative paucity of Ni(I) hydrocarbyl complexes could be misconstrued to provide the erroneous hypothesis that comproportionation routes to **3a,b** would be thermodynamically unfavorable. In fact,

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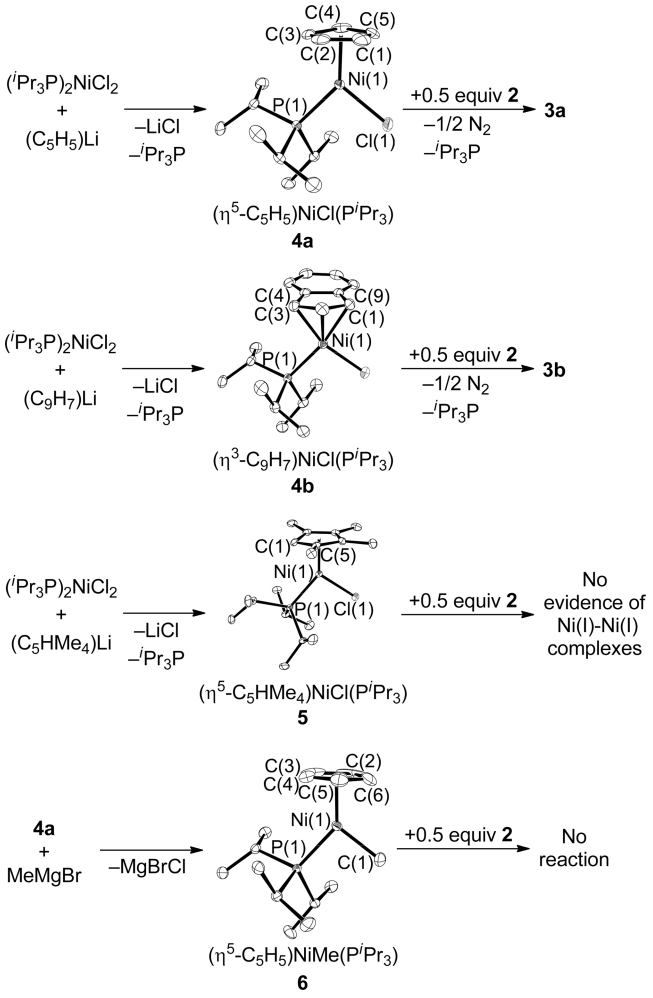
complexes **3a,b** are also accessible by the reaction of the mononuclear Ni(II) complexes (^{i}Pr$_3$P)NiCl(η^5-C$_5$H$_5$) (**4a**) and (^{i}Pr$_3$P)NiCl(η^5-C$_9$H$_7$) (**4b**) with the Ni(0) source [(^{i}Pr$_3$P)$_2$Ni]$_2$(μ-N$_2$) (**2**) over 30 min, as shown in the top two reactions of Scheme 2. The dark red mononuclear Ni(II)

Scheme 2



precursors (^{i}Pr$_3$P)NiCl(η^5-C$_5$H$_5$) (**4a**) and (^{i}Pr$_3$P)NiCl(η^3-C$_9$H$_7$) (**4b**) were prepared by the reaction of [(^{i}Pr$_3$P)$_2$NiCl$_2$] with cyclopentadienyllithium or indenyllithium in THF at 25 °C in yields of 73–79%.

The ^{31}P{^{1}H} NMR spectrum of **4a** has a singlet at δ 52.5. This shift is close to that observed for the structurally dissimilar **3a** and shows the potential dangers of structure assignment solely by ^{31}P NMR. Even the ^{1}H NMR spectrum of **4a** is similar to that of **3a**, with the η^5-C$_5$H$_5$ group singlet resonance at δ 5.08. The relative ^{1}H NMR integrals distinguish **4a** from **3a**, as do the ^{13}C{^{1}H} NMR spectra of **4a** and **3a**, which feature resonances at δ 92.9 and 80.3 for the η^5-C$_5$H$_5$ group, respectively. The ^{31}P{^{1}H} NMR spectrum of **4a** has a singlet at δ 49.2. The ^{1}H NMR spectrum of **4b** at 243 K is consistent with a C_1-symmetric molecule, with seven resonances for the indenyl moiety and diastereotopic methyl substituents. As the temperature was raised, a broadening and coalescence of peaks occurred, which is consistent with rotation about the Ni–indenyl centroid.

The solid-state molecular structures of **4a,b** were determined by X-ray crystallography. The Ni–C distances in the cyclopentadienyl derivative **4a** are similar (in the range of 2.11–2.15 Å),[23] whereas the indenyl ligand in **4b** appears to be η^3 bound, which can be attributed to both the tendency of d^8 complexes to form a 16-electron complexes and increased aromaticity.[24] The Ni–Cl distances are similar in both complexes and somewhat longer than the average of corresponding literature complexes.[25]

Ligand Effects on Comproportionation To Provide Dinuclear Ni(I)–Ni(I) Complexes. A more sterically bulky tetramethylcyclopentadienyl ligand was used to see if it would affect the formation of dinuclear Ni(I) complexes via comproportionation. The reaction of (^{i}Pr$_3$P)$_2$NiCl$_2$ with C$_5$Me$_4$HLi afforded red crystals of (^{i}PrP$_3$)NiCl(η^5-C$_5$Me$_4$H) (**5**) in 69% yield. The ^{1}H NMR spectrum of **5** is consistent with a C_s-symmetric complex. The ^{31}P{^{1}H} NMR chemical shift of δ 54.8 is similar to those of **4a,b**. Recrystallization from *n*-pentane solutions at 20 °C afforded crystals of **5** suitable for an X-ray structure determination. The reaction of **5** with **2** under conditions similar to those used to prepare **3a,b** from **4a,b** showed no NMR spectroscopic evidence for the formation of a related dinickel complex, as shown in Scheme 2. Evidence for disproportionation was obtained by the observation of NiCl(P^{i}Pr$_3$)$_2$; however, the observation of Ni(0) metal and a variety of unidentified byproducts detected by NMR indicate that no clean conversion occurred. It can be postulated that the greater steric bulk in the Cp backbone hindered the generation of the dinuclear complex analogous to **3a** and that the paramagnetic *mono*nuclear *mono*phosphine nickel(I) intermediate (^{i}PrP$_3$)Ni(C$_5$Me$_4$H) is not stable.

The role of the chloride substituent in the propensity to form dinuclear Ni(I) complexes via comproportionation was also examined. Mononuclear **4a** was treated with MeMgCl in diethyl ether at –34 °C. After 15 min the methyl complex (^{i}PrP$_3$)Ni(Me)(η^5-C$_5$H$_5$) (**6**) was obtained in 75% yield as dark brown cubic crystals. The ^{1}H NMR spectrum of **6** featured a doublet at δ –0.58 ($^3J_{PH}$ = 5.1 Hz) in the ^{1}H NMR spectrum and a ^{13}C{^{1}H} resonance at δ –39.2 (d, $^2J_{PC}$ = 28.1 Hz) for the Ni–CH$_3$ moiety. Recrystallization from *n*-pentane at –34 °C afforded single crystals of **6** suitable for X-ray crystallography. Both mononuclear molecular structures **5** and **6** demonstrate geometric features common to all of the mononuclear structures in this paper and previous reports.[26] Attempts to obtain a dinuclear complex similar to **3a,b** via comproportionation of **6** with **2** failed to yield any conversion of **6**, even under reflux conditions in benzene.

Tetraphenylborate as a Bridging Ligand for Dinuclear Ni(I) Complex Formation. The propensity for cyclopentadienyl and indenyl to support dinuclear Ni(I) complexes such as **3a,b** suggest that other modestly sized anionic π systems should also react with **1** to provide dinuclear complexes. The reaction of NaBPh$_4$ with 2 equiv of (^{i}Pr$_3$P)$_2$NiCl (**1**) in diethyl ether provided the dinickel compound [(^{i}Pr$_3$P)Ni]$_2$(μ_2-Cl)(μ_2-η^2:η^2-C$_6$H$_5$BPh$_3$) (**7**) in 73% yield as a green powder, as shown in Scheme 3.

Crystals suitable for structural characterization by X-ray crystallography were obtained by the reaction of pentane solutions of **1** with NaBPh$_4$, which provided large green crystals of **7** directly from the reaction mixture. The solid-state molecular structure of **7** was determined by X-ray crystallography, and an ORTEP depiction is shown in Figure 3. Solid **7** was stable under N$_2$ up to 70 °C. Complex **7** features a BPh$_4$

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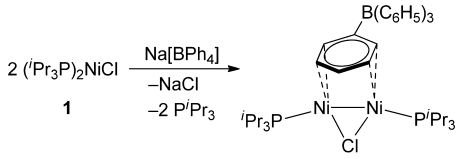
Scheme 3



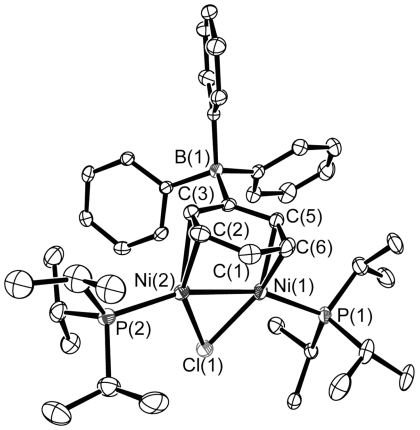


Figure 3. Depiction of the solid-state molecular structure of **7** as determined by X-ray crystallography with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−Ni(2), 2.4255(9); Ni(1)−Cl(1), 2.1983(15); Ni(1)−P(1), 2.2118(14); Ni(1)−C(5), 2.025(5); Ni(1)−C(6), 2.154(5); Ni(2)−Cl(1), 2.1689(14); Ni(2)−P(2), 2.2201(15); Ni(2)−C(1), 2.504(6); Ni(2)−C(2), 2.008(5); Ni(2)−C(3), 2.144(5); C(1)−C(2), 1.414(8); C(1)−C(6), 1.370(8); C(2)−C(3), 1.407(7); C(3)−C(4), 1.417(7); C(4)−C(5), 1.418(6); C(5)−C(6), 1.430(7); P(1)−Ni(1)−Ni(2), 162.07(5); Cl(1)−Ni(1)−Ni(2), 55.69(4); Cl(1)−Ni(1)−P(1), 108.16(5); P(2)−Ni(2)−C(1), 121.69(15).

anion coordinated by as a bridging ligand, with two nickels bound to one of the phenyl rings, and a short Ni(1)−Ni(2) distance of 2.4255(9) Å. Similar to the case for complexes **3a,b**, an additional chloride bridges the metal centers. Steric crowding between the $^{i}Pr_3P$ ligand associated with P(1) and the propeller arrangement of the BPh_3 backbone appears to cause the π-coordinated phenyl ring to twist slightly toward P(1). The C−C bond lengths of the π-coordinated η^2:η^2-phenyl ring range from 1.370(8) to 1.430(7) Å, with two relatively short and two slightly elongated Ni−C bond lengths: Ni(1)−C(5) = 2.025(5) Å, Ni(1)−C(6) = 2.154(5) Å, Ni(2)−C(2) = 2.008(5) Å, and Ni(2)−C(3) = 2.144(5) Å.

The $^{31}P\{^{1}H\}$ NMR spectrum of **7** has a single resonance at δ 28.1. The ^{1}H NMR spectrum has distinctive signals for the bridging phenyl ring at δ 5.29, 5.84, and 6.38 observed for the *para*, *meta*, and *ortho* hydrogens, respectively, which are upfield from the three chemically equivalent noncoordinated Ph substituents.

A few examples where BPh_4^- binds in a mononuclear η^6 fashion are known for Os,[27] Rh,[28] and Ru.[29] Recently Zargarian et al. described a closely related nickel complex with a similar twisted BPh_4 coordination mode, but with a bridging PPh_2 ligand instead of a chloro ligand.[30] The mechanism of formation of this latter complex is complicated, and details remain unclear. The reaction we present here from **1** provides a direct and synthetically useful entry into these complexes.

CONCLUSIONS

We have shown a convenient entry to a series of dinuclear Ni(I) complexes which are easily obtained by simple nucleophilic substitution of the *mono*chloro Ni(I) precursor with the corresponding Li/Na organics. The exact stoichiometry is crucial for the formation of the reported dinuclear complexes. An alternative method of comproportionation of the corresponding mononuclear complexes in the presence of a Ni(0) source was also demonstrated. It also appears that the decomposition of many of these compounds proceeds by disproportionation, to give nickel metal and products such as $(^{i}Pr_3P)_2NiCl_2$, $Ni(Cp)_2$, $Ni(Ind)_2$, **4a,b**, and free phosphine ligand.

An examination of the various factors that influence dinuclear Ni(I) complex formation showed the importance of both the bridging π system and halide. Complex **5**, which contained the sterically more bulky tetramethylcyclopentadienyl ligand, still reacted with the Ni(0) complex **2**, presumably via disproportionation, but provided $(^{i}Pr_3P)_2NiCl$ and a complex product mixture rather than a dinuclear Ni(I) complex. Replacement of the chloride ligand in **3a** with a methyl ligand in **6** provided a complex that did not react via disproportionation. In view of the catalysis and reactivity exhibited by some Pd(I)−Pd(I) dimers[31] and the promising study of cross-coupling reactions with dinuclear nickel complexes,[12a,13b] future studies are planned to probe the reactivities of these dinuclear Ni(I)−Ni(I) complexes toward a variety of substrates. Although the work presented in this paper suggests that organometallic dinuclear Ni(I) complexes may be present in a number of catalytic systems that feature nickel catalysts that cycle between Ni(II) and Ni(0), it remains to be determined if these Ni(I) complexes play an active role in catalysis.[32]

EXPERIMENTAL SECTION

General Procedures. Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glovebox. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas; toluene and hexanes were further deoxygenated using a Grubbs type column system.[1] Benzene-d_6 was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure and then trap-to-trap distilled and freeze−pump−thaw degassed three times. Toluene-d_8 was purified in an analogous manner by heating at reflux over Na. THF-d_8 was purified in an analogous manner by heating at reflux over K. ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra were recorded on a Bruker AMX spectrometer operating at 300 or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in hertz. ^{1}H NMR spectra were referenced to residual protons (C_6D_5H, δ 7.15; C_7D_7H, δ 2.09; C_4D_7HO, δ 1.73) with respect to tetramethylsilane at δ 0.00. $^{31}P\{^{1}H\}$ NMR spectra were referenced to external 85% H_3PO_4 at δ 0.00. $^{13}C\{^{1}H\}$ NMR spectra were referenced relative to solvent resonances (C_6D_6, δ 128.0; C_7D_8, δ 20.4; C_4D_8O, δ 25.37). $^{29}Si\{^{31}P\}$ NMR spectra were referenced to an external sample of 50% $Si(CH_3)_4$ in C_6D_6 at δ 0.0. Infrared spectra (IR) were recorded on a Bruker Tensor 27 instrument operating from 4000 to 400 cm^{-1}. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario. $NiCl_2(P^{i}Pr_3)_2$, $NiCl(P^{i}Pr_3)_2$ (**1**), and $[(^{i}Pr_3P)_2Ni]_2(\mu\text{-}N_2)$ (**2**) were synthesized according to literature methods.[19] The compounds benzene-d_6, toluene-d_8, and THF-d_8 were purchased from Cambridge Isotope Laboratory. The compounds lithium bis(trimethylsilyl)amide, indenyllithium, cyclopentadienyllithium, tetramethylcyclopentadienyllithium, sodium tetraphenylbo-

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rate, and methylmagnesiumbromide (3.0 M) were purchased from Aldrich and used as received. Triisopropylphosphine was purchased from Strem and used as received.

Synthesis and Characterization of 3a. *Method 1.* A solution of $(^{i}Pr_3P)_2NiCl$ (164 mg, 0.39 mmol) in 5 mL of *n*-pentane was combined with a suspension of cyclopentadienyllithium (14 mg, 0.19 mol) in 5 mL of *n*-pentane. After the mixture was stirred for 3 h, the volatiles were removed under vacuum, which afforded a brown-green residue. The residue was extracted with *n*-pentane (2 × 10 mL). Green-turquoise needles of **3a** suitable for analysis by X-ray crystallography were isolated from concentrated *n*-pentane solutions at −34 °C and dried under vacuum (77 mg, 73% yield).

Method 2. A solution of $[(^{i}Pr_3P)_2Ni]_2(\mu\text{-}N_2)$ (157 mg, 0.20 mmol) in 5 mL of *n*-pentane was added to a stirred solution of $(\eta^5\text{-}C_5H_5)NiCl(P^{i}Pr_3)$ (**4a**; 128 mg, 0.40 mmol) at −34 °C. After 5 min the reaction mixture turned blue-green, and after the mixture was stirred for an additional 30 min, the volatiles were removed under vacuum, which afforded a dark brown oil. The oil was taken up in 5 mL of *n*-pentane and cooled to −34 °C, which provided turquoise needles of **3a** (112 mg, 52% yield). ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.26 (dd, $^3J_{PH}$ = 12.3 Hz, $^3J_{HH}$ = 6.9 Hz, 36H, $P(CH(CH_3)_2)_3$); 1.95 (m, $^3J_{HH}$ = 6.9 Hz, 6H, $P(CH(CH_3)_2)_3$); 5.07 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 20.2 (s, $P(CH(CH_3)_2)_3$); 24.5 (vt, $^1J_{PC}$ + $^4J_{PC}$ = 16.6 Hz, $PCH(CH_3)_2)_3$); 80.3 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 49.9 (s). IR (Nujol, KBr): ν (cm^{-1}) 3059 w, 2721 w, 1655 vw, 1590 vw, 1379 s, 1366 s, 1298 w, 1235 m, 1156 w, 1093 m, 1057 s, 1024 s, 966 w, 923 w, 883 s, 801 m, 753 s, 723 s, 655 vs, 613 w, 598 w, 570 s, 523 vs, 477 w, 432 w. Anal. Calcd for $C_{23}H_{47}ClNi_2P_2$ (538.41): C, 51.31; H, 8.80; Found: C, 51.48; H, 9.18.

Synthesis and Characterization of 3b. *Method 1.* A solution of $(^{i}Pr_3P)_2NiCl$ (200 mg, 0.48 mmol) in 5 mL of *n*-pentane was combined with a suspension of indenyllithium (29 mg, 0.24 mmol) in 5 mL of *n*-pentane. After the mixture was stirred for 3 h, the volatiles were removed under vacuum, which afforded a brown-green residue. The oil was taken up in 5 mL of *n*-pentane and filtered through Celite. Turquoise needles of **3b** suitable for analysis by X-ray crystallography precipitated via slow evaporation over 2 days at −34 °C and were isolated and dried under vacuum (88 mg, 62% yield).

Method 2. A solution of **4b** (89 mg, 0.24 mmol) was combined at −34 °C with a solution of $[(^{i}Pr_3P)_2Ni]_2(\mu\text{-}N_2)$ (94 mg, 0.12 mmol) dissolved in 5 mL of *n*-pentane. After 5 min the reaction mixture turned blue-green, and after the mixture was stirred for an additional 30 min, the volatiles were removed under vacuum, which afforded a dark brown oil. The oil was taken up in 5 mL of *n*-pentane, and cooling to −34 °C afforded turquoise needles of **3b** (54 mg, 38% yield). ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.10 and 1.17 (overlapping m, 36H total, $P(CH(CH_3)_2)_3$); 1.97 (m, $^3J_{HH}$ = 7.0 Hz, 6H, $P(CH(CH_3)_2)_3$); 3.59 (coincident tt, $^3J_{HH}$ = 4.2 Hz, $^3J_{HP}$ = 4.0 Hz, 1H, H_2); 4.22 (td, $^3J_{PH}$ = 9.3 Hz, $^3J_{HH}$ = 4.2 Hz, 2H, H_1/H_3); 6.95 (second order m, 2H, H_5/H_8); 7.18 (second order m, 2H, H_6/H_7). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 19.8 and 20.3 (s, $P(CH(CH_3)_2)_3$); 24.9 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 17.8 Hz, $PCH(CH_3)_2)_3$); 36.4 (second order m, C_1/C_3); 53.1 (t, $^2J_{PC}$ = 6.6 Hz, C_2); 122.3 (s, C_4/C_9); 122.6 (s, C_5/C_8); 148.1 (s, C_6/C_7). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 47.9 (s). IR (Nujol, KBr): ν (cm^{-1}) 3062 m, 3038 w, 3038 m, 1911 vw, 1876 vw, 1696 vw, 1589 m, 1366 s, 1338 vw, 1315 m, 1315 m, 1294 m, 1279 s, 1241 s, 1198 s, 1157 s, 1093 m, 1056 s, 1031 s, 1019 s, 955 m, 921 s, 906 w, 882 vs, 849 vw, 822 m, 786 m, 744 vs, 722 m, 659 vs, 615 vs, 574 s, 525 vs, 473 s, 430 m. Anal. Calcd for $C_{27}H_{49}ClNi_2P_2$ (588.47): C, 55.11; H, 8.39; Found: C, 55.50; H, 7.99.

Synthesis and Characterization of 4a. To an ice-cold solution of $(^{i}Pr_3P)_2NiCl_2$ (450 mg, 1.0 mmol) in 10 mL of THF was added a solution of cyclopentadienyllithium (72 mg, 1.0 mmol) in 3 mL of THF. Immediately, the solution turned from dark red to pink. After the mixture was stirred for 1 h at room temperature, the volatiles were removed in vacuo, the residue was extracted with *n*-pentane (2 × 10 mL), and the extracts were filtered through a plug of Celite. Over the course of 5 h at room temperature, wine red plates deposited. The crystals were filtered off and the mother liquor reduced by half its volume under vacuum, and a second crop of **4a** was obtained. The combined yield afforded 252 mg (79%) of analytically pure **4a**. ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.07 (dd, $^3J_{PH}$ = 13.8 Hz, $^3J_{HH}$ = 7.2 Hz, 18H, $P(CH(CH_3)_2)_3$); 1.71 (m, $^3J_{HH}$ = 7.2 Hz, 3H, $P(CH(CH_3)_2)_3$); 5.08 (s, 5H, Cp-*H*). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 19.5 (s, $P(CH(CH_3)_2)_3$); 24.4 (d, $^1J_{PC}$ = 21.8 Hz, $PCH(CH_3)_2)_3$); 92.9 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 52.5 (s). Anal. Calcd for $C_{14}H_{26}ClNiP$ (319.48): C, 52.63; H, 8.20. Found: C, 52.31; H, 7.89.

Synthesis and Characterization of 4b. To an ice-cold solution of $(^{i}Pr_3P)_2NiCl_2$ (450 mg, 1.0 mmol) in 10 mL of THF was added a solution of indenyllithium (122 mg, 1.0 mmol) in 3 mL of THF. Immediately, the solution turned from dark red to pink. After the mixture was stirred for 1 h at room temperature, all volatiles were removed in vacuo, the residue was extracted with *n*-pentane (2 × 10 mL), and the extracts were filtered through a plug of Celite. Over the course of 5 h at room temperature, wine red plates deposited. The crystals were filtered off and the mother liquor reduced by half its volume under vacuum, and a second crop of **4b** was obtained. The combined yield afforded 252 mg (73%) of analytically pure **4b**. ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 0.97 (dd, $^3J_{PH}$ = 13.8 Hz, $^3J_{HH}$ = 7.2 Hz, 18H, CH_3); 1.75 (m, $^3J_{HH}$ = 7.2 Hz, 3H, $P(CH(CH_3)_2)_3$); 4.15 (br s, $W_{1/2}$ = 90 Hz, 1H, H_1); 5.57 (br s, W = 90 Hz, 1H, H_3); 6.39 (t, $^3J_{HH}$ = 3.3 Hz, 1H, H_2); 6.89 (br s, $W_{1/2}$ = 45 Hz, 2H, H_6/H_7); 7.02 (br s, $W_{1/2}$ = 90 Hz, 2H, H_5/H_8). ^{1}H NMR (193 K, C_7D_8, 500 MHz): δ 0.97 (br, 18H, $P(CH(CH_3)_2)_3$); 1.75 (br, 3H, $P(CH(CH_3)_2)_3$); 3.99 (br, 1H, H_1); 5.77 (br, 1H, H_3); 6.40 (br, 1H, H_2); 6.83 (br, 1H, H_6); 6.95 (br, 1H, H_7); 7.12 (br, 1H, H_5); 7.33 (br, 1H, H_8). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 19.4 (s, $PCHMe_2$); 24.9 (d, $^1J_{PC}$ = 19.5 Hz, PCH); 59.9 (br s, $W_{1/2}$ = 150 Hz, C_1 or C_3); 89.2 (br s, $W_{1/2}$ = 150 Hz, C_3 or C_1); 102.7 (s, C_2); 119.3 (br s, $W_{1/2}$ = 75 Hz); 125.6 (br s, $W_{1/2}$ = 75 Hz); 130.6 (br s, $W_{1/2}$ = 75 Hz). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 49.2 (s). Anal. Calcd for $C_{18}H_{28}ClNiP$ (369.54): C, 58.50; H, 7.64. Found: C, 58.12; H, 7.90.

Synthesis and Characterization of 5. A solution of $(^{i}Pr_3P)_2NiCl_2$ (220 mg, 0.48 mmol) in 10 mL of THF was combined at −34 °C with tetramethylcyclopentadienyllithium (63 mg, 0.48 mmol). After the mixture was warmed to ambient temperature, the solvent was removed under vacuum, the solid was extracted with *n*-pentane (2 × 10 mL), and the extracts were filtered through a plug of Celite. The pink filtrate was left to slowly evaporate at room temperature, and wine red plates deposited over the course of 16 h that were suitable for analysis by X-ray crystallography (126 mg, 69% yield). ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.13 (dd, $^3J_{PH}$ = 13.8 Hz, $^3J_{HH}$ = 6.9 Hz, 18H, $PCHMe_2$); 1.45 (d, J_{PH} = 2.7 Hz, 6H, C_5Me_4H); 1.88 (m, 3H, PC*H*); 1.92 (s, 6H, C_5Me_4H); 3.65 (d, $^3J_{PH}$ = 3.1 Hz, 1H, C_5Me_4H). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 9.62 (s, C_5Me_4H); 11.9 (s, C_5Me_4H); 19.8 (s, $PCHMe_2$); 25.3 (d, $^1J_{PC}$ = 20.6 Hz, PCH); 72.5 and 106.1 (s, C_5Me_4H); 110.3 (d, $^2J_{PC}$ = 4.5 Hz, C_5Me_4H). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 54.8 (s). Anal. Calcd for $C_{18}H_{34}ClNiP$: C, 57.56; H, 9.12. Found: C, 57.29; H, 8.90.

Synthesis and Characterization of 6. A solution of MeMgBr in diethyl ether (3.0 M, 0.18 mL, 0.55 mmol) was slowly added dropwise to a stirred solution of $(\eta^5\text{-}C_5H_5)NiCl(P^{i}Pr_3)$ (**4a**; 178 mg, 0.55 mmol) in diethyl ether at −34 °C. The temperature was maintained, and after 2 min, the reaction mixture turned dark brown. Stirring was stopped after 15 min, and all volatiles were removed in vacuo. The dark brown residue was extracted with *n*-pentane (2 × 5 mL) and filtered through a plug of Celite. Crystals deposited at −34 °C and were separated from the solution by decantation, and the residual solvent was removed using vacuum. The dark brown cubic crystals suitable for analysis by X-ray crystallography were washed with cold *n*-pentane and dried under vacuum to provide **6** (125 mg, 75% yield). Complex **6** is reasonably thermally stable after isolation. ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ −0.58 (d, $^3J_{PH}$ = 5.1 Hz, 3H, Ni−CH_3); 1.06 (dd, $^3J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 7.2 Hz, 18H, $PCHMe_2$); 1.68 (m, $^3J_{HH}$ = 7.2 Hz, 3H, PC*H*); 5.35 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ −39.2 (d, $^2J_{PC}$ = 28.1 Hz, Ni-CH_3); 19.5 (s, $PCHMe_2$); 24.5 (d, $^1J_{PC}$ = 20.8 Hz, PCH); 90.3 (s, C_5H_5). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 64.7 (s). IR (Nujol, KBr): ν

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Table 1. Data and Structure Refinement Parameters for Complexes 3−7

	3a	3b	4a	4b
empirical formula	$C_{23}H_{47}P_2\ ClNi_2$	$C_{27}H_{49}P_2ClNi_2$	$C_{14}H_{26}PClNi$	$C_{18}H_{28}PClNi$
fw	538.42	588.47	319.48	369.53
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic
a (Å)	7.7246(15)	16.456(3)	7.7760(9)	14.641(3)
b (Å)	11.666(2)	8.1490(16)	14.0565(17)	16.122(3)
c (Å)	29.958(6)	22.477(5)	14.5394(17)	16.613(3)
α (deg)	90	90	96.640(2)	90
β (deg)	90	95.00(3)	96.441(2)	107.60(3)
γ (deg)	90	90	90.256(2)	90
V (Å^3)	2699.7(9)	3002.8(10)	1568.3(3)	3737.9(13)
space group	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Z	4	4	4	8
D_{calcd} (g/cm^3)	1.325	1.302	1.353	1.313
μ(Mo Kα) (mm^{-1})	1.620	1.463	1.488	1.259
temp (K)	173(2)	173(2)	173(2)	173(2)
$2\theta_{max}$ (deg)	51	52.7	50	52.7
total no. of rflns	27198	31161	15428	39692
no. of unique rflns; R_{int}	5005; 0.1056	6123; 0.0475	5518; 0.0507	7656; 0.0874
abs cor	multiscan	multiscan	multiscan	multiscan
transmissn factors	0.88−0.60	0.94−0.73	0.86−0.72	0.93−0.84
no. of variables	265	313	319	415
rflns/params	18.8	19.5	22.3	18.4
GOF on F^2	1.003	1.040	0.998	1.010
R1; wR2 ($I \geq 2\sigma$)	0.0522; 0.1042	0.0368; 0.0839	0.051; 0.094	0.0533; 0.1013
R1; wR2 (all data)	0.0711; 0.1132	0.0500; 0.0954	0.0796; 0.106	0.0959; 0.1207
residual density (e/Å^3)	0.809; −0.370	0.78; −0.28	0.618; −0.368	0.61; −0.32

	5	6	7
empirical formula	$C_{18}H_{34}ClNiP$	$C_{15}H_{29}PNi$	$C_{42}H_{62}BP_2ClNi_2$
fw	375.58	299.06	792.54
cryst syst	monoclinic	orthorhombic	Monoclinic
a (Å)	7.4557(15)	8.8699(18)	34.726(7)
b (Å)	17.270(3)	10.142(2)	11.609(2)
c (Å)	16.264(5)	17.693(4)	21.980(4)
α (deg)	90	90	90
β (deg)	108.57(3)	90	112.26(3)
γ (deg)	90	90	90
V (Å^3)	1985.1(8)	1591.6(5)	8201(3)
space group	$P2_1/c$	$P2_12_12_1$	$C2/c$
Z	4	4	8
D_{calcd} (g/cm^3)	1.257	1.248	1.284
μ(Mo Kα) (mm^{-1})	1.186	1.300	1.089
temp (K)	173(2)	173(2)	130(2)
$2\theta_{max}$ (deg)	54	52.7	51
total no. of rflns	22050	16836	40712
no. of unique rflns; R_{int}	4372; 0.0715	3253; 0.0296	7778; 0.0927
abs cor	multiscan	multiscan	multiscan
transmissn factors	0.94−0.84	0.73−0.59	0.94−0.81
no. of variables	200	161	445
rflns/params	21.8	20.2	17.5
GOF on F^2	1.040	1.062	1.037
R1; wR2 ($I \geq 2\sigma$)	0.0444; 0.0956	0.0332; 0.0840	0.0647; 0.1475
R1; wR2 (all data)	0.0628; 0.1112	0.0350; 0.0852	0.1039; 0.1677
residual density (e/Å^3)	0.58; −0.39	1.01; −0.48	1.371; −0.597

(cm^{-1}) 3098 m, 1510 w, 1459 vs, 1407 w, 1382 s, 1366 m, 1298 w, 1242 s, 1144 s, 1113 w, 1092 w, 1056 m 1018 m, 985 w, 928 w, 883 s, 837 w, 773 vs, 657 s, 632 m, 618 m, 571 w, 531 s, 479 w, 449 vw. Anal. Calcd for $C_{15}H_{29}NiP$ (299.06): C, 60.24; H, 9.77. Found: C, 59.97; H, 10.17.

Synthesis and Characterization of 7. To a solution of (^{i}Pr$_3$P)$_2$NiCl (**1**); 210 mg, 0.50 mmol) in 5 mL of diethyl ether was added finely powdered $NaBPh_4$ (86 mg, 0.25 mmol) at 20 °C. The heterogeneous mixture was stirred vigorously for 4 h, and when a green solid was formed, stirring was stopped and the solution was decanted from the remaining solid. The solvent was removed in vacuo, the green residue was extracted with toluene (2 × 5 mL), and the extracts were filtered through a plug of Celite. Removal of the solvent gave **7** as a viscous oil (146 mg, 73% yield) that was reasonably pure

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by ^{31}P and ^{1}H NMR spectroscopy. Complex **7** was obtained as a green crystalline solid by evaporation of a benzene/hexamethyldisiloxane solution. Alternatively, crystalline **7** can be prepared by the reaction of $NiCl(P^iPr_3)_2$ (45 mg, 0.1 mmol) with sodium tetraphenylborate (17 mg, 0.05 mmol) in 3 mL of *n*-pentane without stirring at room temperature. Complex **7** is sparingly soluble in pentane and soluble in toluene. If the precursor **1** contains significant amounts of $(^iPr_3P)_2NiCl_2$ as an impurity, complex **7** appears to rapidly decompose. ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 0.62 (br dd, $^{3}J_{PH}$ = 13.5 Hz, $^{3}J_{HH}$ = 5.1 Hz, 18H, $P(CH(CH_3)_2)_3$); 1.05 (br dd, $^{3}J_{PH}$ = 13.5 Hz, $^{3}J_{HH}$ = 5.1 Hz, 18H, $P(CH(CH_3)_2)_3$); 1.67 (sept(br), $^{3}J_{HH}$ = 7.2 Hz, 6H, $P(CH(CH_3)_2)_3$); 5.29 (br t, $^{3}J_{HH}$ = 7.5 Hz, 1H, *para*-H_1); 5.84 (br apparent t, $^{3}J_{HH}$ = 3.1 Hz, 2H, *meta*-H_2/H_6); 6.38 (br d, $^{3}J_{HH}$ = 3.1 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, *ortho*-H_3/H_5); 7.28 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H, *para*-*H*); 7.38 (apparent t, $^{3}J_{HH}$ = 6.9 Hz, 6H, *meta*-*H*); 7.97 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H, *ortho*-*H*), $^{13}C\{^{1}H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 18.8 (s, $P(CH(CH_3)_2)_3$); 19.2 (s, $PCHMe_2$); 24.9 (virtual t, $^{1}J_{PC} + {}^{4}J_{PC}$ = 15.8 Hz, PCH); 82.1 (s, C_2/C_6); 87.3 (br s, C_1); 97.5 (s, C_3/C_5); 102.1 (s, BC_{ipso}); 123.1 (s, BC_{ipso}); 131.3 (s, C_{para}); 137.1 (s, C_{meta}); 139.4 (s, C_{ortho}). $^{31}P\{^{1}H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 28.1 (s). Anal. Calcd for $C_{42}H_{62}BClNi_2P_2$ (792.54): C, 63.65; H, 7.89. Found: C, 63.82; H, 8.35.

X-ray Crystallography. The X-ray structures were obtained at low temperature, with the crystals covered in Paratone and placed rapidly into the cold N_2 stream of the Kryo-Flex low-temperature device. The data were collected using SMART[33] software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected using a counting time of 10−30 s per frame. Data reductions were performed using SAINT[34] software, and the data were corrected for absorption using SADABS.[35] The structures were solved by direct or Patterson methods using SHELXS-97[36] and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELX-97[36] and the WinGX[37] software package, and thermal ellipsoid plots were produced using ORTEP32.[38] Crystallographic parameters are given in Table 1.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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