CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201302539

Arene C−H Amination at Nickel in Terphenyl–Diphosphine Complexes with Labile Metal–Arene Interactions

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Abstract: The *meta*-terphenyl diphosphine, *m*-P_2, **1**, was utilized to support Ni centers in the oxidation states 0, I, and II. A series of complexes bearing different substituents or ligands at Ni was prepared to investigate the dependence of metal–arene interactions on oxidation state and substitution at the metal center. Complex (*m*-P_2)Ni (**2**) shows strong Ni^0–arene interactions involving the central arene ring of the terphenyl ligand both in solution and the solid state. These interactions are significantly less pronounced in Ni^0 complexes bearing L-type ligands (**2-L**: L = CH_3CN, CO, Ph_2CN_2), Ni^IX complexes (**3-X**: X = Cl, BF_4, N_3, $N_3B(C_6F_5)_3$), and [(*m*-P_2)$Ni^{II}Cl_2$] (**4**). Complex **2** reacts with substrates, such as diphenyldiazoalkane, sulfur ylides ($Ph_2S{=}CH_2$), organoazides (RN_3: R = *para*-C_6H_4OMe, *para*-$C_6H_4CF_3$, 1-adamantyl), and N_2O with the locus of observed reactivity dependent on the nature of the substrate. These reactions led to isolation of an η^1-diphenyldiazoalkane adduct (**2-Ph_2CN_2**), methylidene insertion into a Ni−P bond followed by rearrangement of a nickel-bound phosphorus ylide (**5**) to a benzylphosphine (**6**), Staudinger oxidation of the phosphine arms, and metal-mediated nitrene insertion into an arene C−H bond of **1**, all derived from the same compound (**2**). Hydrogen-atom abstraction from a Ni^I–amide (**9**) and the resulting nitrene transfer supports the viability of Ni–imide intermediates in the reaction of **1** with 1-azido-arenes.

Keywords: amination · arenes · C−H activation · group transfer · insertion reactions

Introduction

The design of ligands that support first-row-transition-metal complexes that can react with molecules such as organoazides, diazoalkanes, and nitrous oxide to form terminal multiply bound metal imides, carbenes, and oxo complexes active in group-transfer reactions has received significant attention recently as atom-efficient routes are sought for the functionalization of unreactive moieties, such as olefins and C−H bonds.[1–4] Examples of isolated complexes bearing imides (or nitrides) of late transition metals, such as Mn,[5] Fe,[6] Co,[7] and Ni,[8–10] have been reported and their group-transfer reactivity explored. Terminal copper nitrenes have been proposed as key reactive intermediates in Cu-catalyzed nitrene transfer/C−H amination.[11]

Notably, Hillhouse and co-workers have demonstrated that Ni, supported by bulky donating 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe) ligands, can form three-coordinate imides and carbenes from azide and diazoalkane precursors.[12–14] Warren has examined analogous reactions at Ni centers supported by β-diketiminate ligands.[9,10] In these cases, divergent types of group transfer was observed (e.g., aziridination versus C−H amination), depending on the coordination number and oxidation state of the metal center. Ni-mediated nitrene insertion into a strong aromatic C−H bond was not reported.[15]

We have investigated the chemistry of *trans*-spanning multidentate terphenyl diphosphine ligands wherein the central arene ring can act as a multihapto binding site and exhibit a range of versatile coordination and noninnocent behavior.[16,17] In this report, we describe the ability of a *meta*-terphenyl diphosphine (**1**) to support Ni centers in a variety of oxidation states [Ni^0, **2-L** (L = CH_3CN, CO, Ph_2CN_2); Ni^I, **3-X** (X = Cl, BF_4, N_3, N_3-$B(C_6F_5)_3$); Ni^{II}, **4** (X = Cl_2)] and detail the reactivity of these complexes towards a range of small molecules, such as azides, diazoalkanes, and nitrous oxide. A variety of reactivity modes was observed, including carbene coupling, Staudinger oxidation of phosphine arms, methylidene insertion into a P−C bond, and amination of an aromatic C−H bond. The role of the oxidation state, metal–arene interactions, and the substrate in these reactions are discussed in the context of functionalization of aromatic C−H bonds.

Results and Discussion

Ni complexes in oxidation states 0, I, and II were prepared by reaction of **1** with the appropriate Ni precursor

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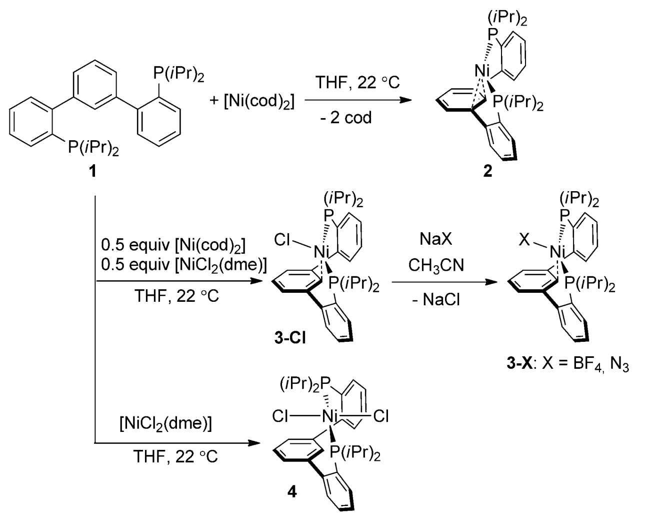
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201302539 and contains experimental details, NMR spectra, and crystallographic information for all compounds.

(Scheme 1). Treatment of diphosphine **1** with one equivalent of Ni^0 in the form of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) in THF gave the terphenyl-diphosphine Ni complex **2**, which was isolated as a red-brown solid. Treatment of **1** with $[NiCl_2(dme)]$ (dme = 1,2-dimethoxyethane) provided the terphenyl-diphosphine Ni complex **4** as a purple solid. Orange-colored Ni^I-chloride **3-Cl** was prepared by comproportionation of Ni^{II} and Ni^0 precursors by the reaction of **1** with 0.5 equivalents of $[Ni(cod)_2]$ followed by the addition of 0.5 equivalents of $[NiCl_2(dme)]$.[17] Salt metathesis of **3-Cl** provided access to structurally-related species with anions that have various electronic properties. The central arene of the terphenyl framework shows variable interactions with the metal center (in both solution and the solid state) as a function of the metal oxidation state and other coordinated ligands.



Scheme 1. Synthesis of Ni complexes **2**, **3-X**, and **4**.

The compounds described have been characterized by single-crystal X-ray diffraction. The central arene is bound η^2 to the metal center in **2** [Ni(1)–C(1) 1.973(2); Ni(1)–C(2) 2.133(2) Å], resulting in a localization of electron density within the central arene ring with concomitant lengthening of the distance between the two carbon atoms bound to Ni [**2**: C(1)–C(2) 1.425(2), C(2)–C(3) 1.441(3), C(3)–C(4) 1.371(3), C(4)–C(5) 1.418(3), C(5)–C(6) 1.373(3), C(6)–C(1) 1.435(2) Å].[16–18] Binding a σ-donor ligand, such as CH_3CN, to the Ni^0 center in **2** leads to an elongation of the Ni–C(arene) distances in the solid state [**2-CH$_3$CN**: Ni(1)–C(1) 2.0892(9) Å; Ni(1)–C(2) 2.427(1) Å; Figure 1]. The binding of more-π-acidic ligands has a similar effect. For example, in the CO adduct **2-CO**, the Ni(1)–C(1) distance is increased to 2.256(2) Å. Higher oxidation state complexes show significantly longer Ni–arene distances [**3-Cl**: Ni(1)–C(1) 2.562(1) Å;[17] **4**: Ni(1)–C(1) 2.775(1) Å]. To accommodate the significant change in ligand conformation, the P-Ni-P angle is more acute in the lower oxidation state complexes, with shorter Ni–arene contacts [139.06(2)° in **2**, 155.11(1)° in **3-Cl**, and 169.935(8)° in **4**].

The interaction between the Ni center and the central arene is also apparent in solution by NMR spectroscopy. The central arene C–H *ortho* to both flanking arene rings (denoted as $C{-}H_{Ni}$) is shifted considerably upfield (δ_{CH} = 5.18 ppm; C_6D_6, 22 °C) relative to other arene C–H resonances. The strong shielding of this resonance by the Ni^0 center is consistent with a significant metal–arene interaction in solution. In addition, the $^{13}C\{^1H\}$ NMR spectrum of **2** contains a triplet at $\delta = 68.6$ ppm ($J_{CP} = 3.6$ Hz) assigned to $C{-}H_{Ni}$ that shows coupling to the two phosphorus nuclei, further supporting an interaction between Ni and the arene in solu-

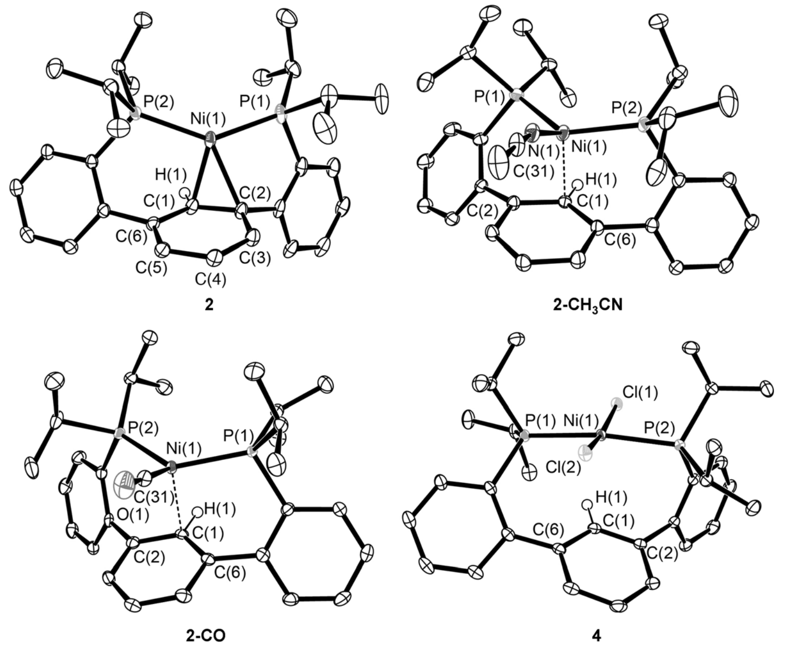


Figure 1. ORTEPs of **2**, **2-CH$_3$CN**, **2-CO**, and **4** with thermal ellipsoids shown at 50 % probability levels. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]. **2**: C(1)–Ni(1) 1.973(2), C(2)–Ni(1) 2.133(2), Ni(1)–P(1) 2.1777(5), Ni(1)–P(2) 2.1825(5), C(1)–C(2) 1.425(2), C(2)–C(3) 1.441(3), C(3)–C(4) 1.371(3), C(4)–C(5) 1.418(3), C(5)–C(6) 1.373(3), C(6)–C(1) 1.435(2); P(1)-Ni(1)-P(2) 139.06(2). **2-CH$_3$CN**: Ni(1)–C(1) 2.0892(9), Ni(1)–C(2) 2.4272(10), Ni(1)–N(1) 1.9131(9), Ni(1)–P(1) 2.1887(3), Ni(1)–P(2) 2.1854(3); P(1)-Ni(1)-P(2) 130.62(1), C(31)-N(1)-Ni(1) 164.70(9). **2-CO**: C(1)–Ni(1) 2.256(2), Ni(1)–P(1) 2.2123(6), Ni(1)–P(2) 2.1954(5), C(31)–Ni(1) 1.754(1) C(31)–O(1) 1.1565(2); P(1)-Ni(1)-P(2) 125.94(2), O(1)-C(31)-Ni(1) 178.2(1). **4**: Ni(1)–P(1) 2.2576(2), Ni(1)–P(2) 2.2424(2), Ni(1)–Cl(1) 2.1879(2), Ni(1)–Cl(2) 2.1805(2), C(1)–Ni(1) 2.775(1); P(1)-Ni(1)-P(2) 169.935(8), Cl(1)-Ni(1)-Cl(2) 167.570(8).

tion. Both the ^{1}H- and ^{13}C{^{1}H} NMR spectra of **2** are consistent with an average C_s-symmetric structure in solution at room temperature, indicating fast exchange, with the Ni center shuttling between the two sides of the pseudo mirror plane relating the two phosphine moieties on the timescale of the NMR experiments.

In comparison with the solid-state structure of **2**, all of the yellow or orange Ni^{I} complexes, **3-X** [X = Cl, BF$_4$, N$_3$, N$_3$-B-(C$_6$F$_5$)$_3$], show longer metal–arene distances [Ni(1)−C(1): **3-Cl** 2.562(1), **3-BF$_4$** 2.4976(15), **3-N$_3$** 2.6182(8), **3-B(N$_3$)(C$_6$F$_5$)$_3$** 2.400(3) Å]. Comparing **3-BF$_4$** with **3-Cl** and **3-N$_3$**, the less coordinating anion results in a shorter Ni−C(arene) distance. Similarly, appending the strongly Lewis acidic tris(pentafluorophenyl)borane to the terminal nitrogen atom of the Ni-bound azide, by the addition of B(C$_6$F$_5$)$_3$ to a solution of **3-N$_3$**, renders the azido moiety a weaker donor, resulting in a shorter Ni(1)−C(1) contact in **3-B(N$_3$)(C$_6$F$_5$)$_3$** compared with **3-N$_3$** (Figure 2). Thus, the arene binds more strongly to the electron-rich Ni^{0} center in **2** by virtue of stronger metal-to-ligand backbonding compared with complexes of Ni^{I} and Ni^{II}. The labile interaction with the central arene is also sensitive to additional ligands, with more coordinating anions leading to weaker arene binding. With a better understanding of the ability of the pendant arene to satisfy the coordination requirements of various Ni complexes, the reactivity with group-transfer reagents was investigated.

The addition of a stoichiometric amount of diphenyldiazoalkane to a solution of **2** in hexanes resulted in the isolation of a 1:1 adduct (**2-Ph$_2$CN$_2$**; Scheme 2). Analysis of **2-Ph$_2$CN$_2$** by NMR spectroscopy revealed that the diagnostic central arene C−H resonances were found at much lower field (^{1}H: $\delta = 8.29$ ppm, ^{13}C{^{1}H}: $\delta = 108$ ppm; C$_6$D$_6$, assigned using the HSQC spectrum), suggesting weaker metal–arene interactions. Indeed, the solid-state structure of **2-Ph$_2$CN$_2$** confirmed this change in bonding (Figure 3). The Ni–carbon distance in **2-Ph$_2$CN$_2$** is considerably elongated compared with that in **2** [Ni(1)−C(1) 2.511(2) Å]. The diazoalkane moiety binds in an almost linear fashion [Ni(1)-N(1)-N(2) 160.5(2)°]. Interestingly, the Ni−N distance is significantly shorter [1.751(2) Å] compared with that of the terminal acetonitrile adduct **2-CH$_3$CN** [Ni(1)−N(1) 1.913(1) Å; Figure 1]. These features suggest contribution from a resonance structure involving multiple bonding between Ni and N. Notably, the Ni−N distance in **2-Ph$_2$CN$_2$** is only slightly longer than that of a tricoordinate Ni^{II}–imide reported by Hillhouse [1.702(2) Å].[12] Partial oxidation of the metal center is consistent with the deshielding of the C−H_{Ni} proton sitting below the metal, as observed by ^{1}H NMR spectroscopy (compare **2** with **4-Cl$_2$**).

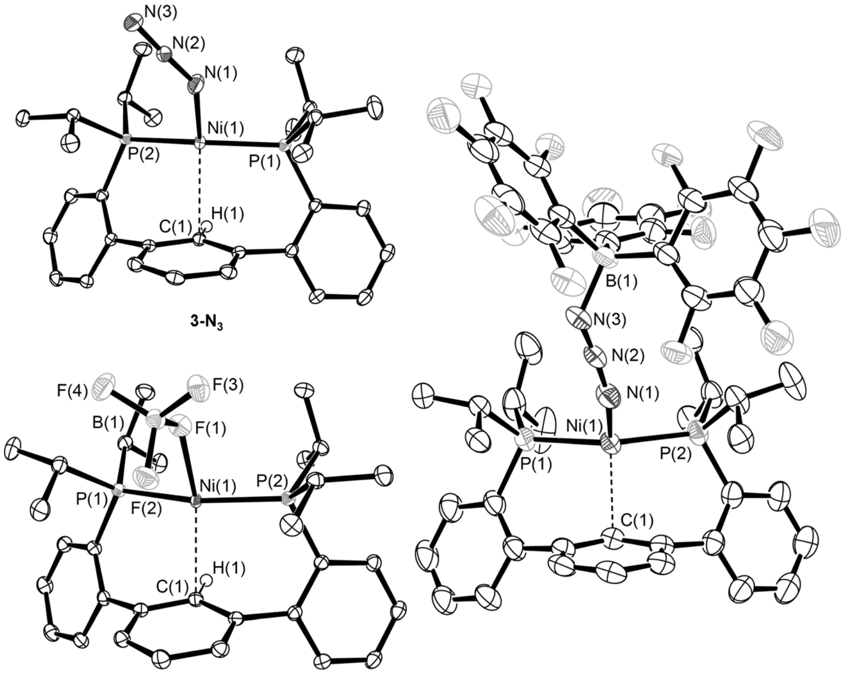
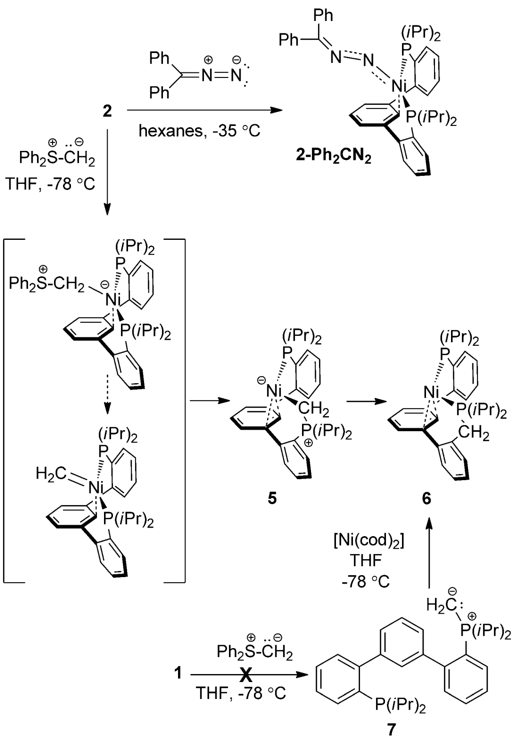


Figure 2. ORTEPs of **3-BF$_4$**, **3-N$_3$**, and **3-B(N$_3$)(C$_6$F$_5$)$_3$** with thermal ellipsoids shown at 50 % probability levels. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **3-BF$_4$**: Ni(1)−P(1) 2.2665(4), Ni(1)−P(2) 2.2634(4), Ni(1)−F(1) 2.1852(11), C(1)−Ni(1) 2.4976(15); P(1)-Ni(1)-P(2)158.487(15), B(1)-F(1)-Ni(1) 128.78(10). **3-N$_3$**: Ni(1)−P(1) 2.2687(3), Ni(1)−P(2) 2.2449(3), Ni(1)−N(1) 1.9746(10), N(1)−N(2) 1.1852(13), N(2)−N(3) 1.1696(13), C(1)−Ni(1) 2.6182(8); P(1)-Ni(1)-P(2) 155.207(10), Ni(1)-N(1)-N(2) 140.29(8), N(1)-N(2)-N(3) 177.13(11). **3-B(N$_3$)(C$_6$F$_5$)$_3$**: Ni(1)−P(1) 2.2625(9), Ni(1)−P(2) 2.2673(8), Ni(1)−N(1) 1.970(3), N(1)−N(2) 1.160(4), N(2)−N(3) 1.191(4), C(1)−Ni(1) 2.400(3), N(3)−B(1) 1.591(4); P(1)-Ni(1)-P(2) 153.27(3), Ni(1)-N(1)-N(2) 153.8(3), N(1)-N(2)-N(3) 173.9(3), N(2)-N(3)-B(1) 124.8(2).

With diazoalkane adduct **2-Ph$_2$CN$_2$** in hand, thermal extrusion of dinitrogen was attempted in order to access a Ni carbene.[14] However, extensively heating solutions of **2-Ph$_2$CN$_2$** in benzene or toluene (80–110 °C) over several days slowly regenerated **2** with no observable intermediates. The diazoalkane fragment was converted under these conditions into three detectable products: tetraphenylethylene, 1,2-bis(diphenylmethylene)hydrazine, and *N*-(diphenylmethylene)-1,1-diphenylmethanamine, in a 50:40:10 ratio (GC). Control reactions that consisted of heating solutions of diphenyldiazomethane at equivalent concentrations for the same period of time yielded the hydrazine exclusively in our hands. Addition of the Lewis acid, Sm(OTf)$_3$, to the reaction mixture in an attempt to assist N$_2$ extrusion[14] increased the proportion of the tetrasubstituted olefin to 60 % of the observed products. Mechanisms involving dissociated and metal-bound diphenyl-



Scheme 2. Reactivity of **2** towards diphenyldiazoalkane and methylidene transfer reagents.

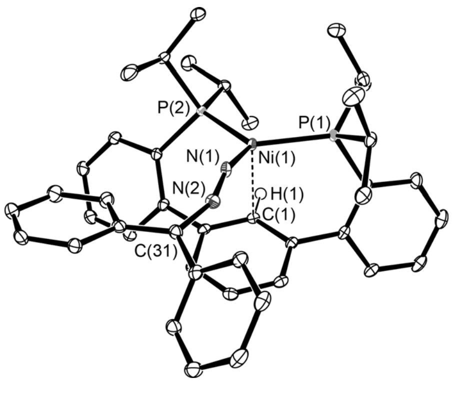


Figure 3. ORTEP of **2-Ph$_2$CN$_2$** with thermal ellipsoids shown at 50% probability levels. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)−Ni(1) 2.511(2), Ni(1)−P(2) 2.1947(6), Ni(1)−P(1) 2.1975(6), Ni(1)−N(1) 1.7514(17), N(1)−N(2) 1.190(2), C(31)−N(2) 1.327(2); P(2)-Ni-P(1) 122.43(2), N(2)-N(1)-Ni(1) 160.5(2), N(1)-N(2)-C(31) 152.7(2).

diazomethane moieties are feasible, and the generation of short-lived metal-carbene species is not required for the observed reactivity.

We therefore turned to an alternative method for preparing metal carbenes. "Transylidation" of a carbenoid fragment from in situ generated sulfur ylides was reported by Milstein and co-workers who demonstrated this method's utility in preparing a range of late-metal carbenes, such as Grubbs' catalyst.[19] Deprotonation of diphenylmethylsulfonium tetraphenylborate with lithium hexamethyldisilazide at −78 °C gave the methylidene-bearing sulfur ylide, which was added to a solution of **2** in THF (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum collected immediately upon warming the resulting solution exhibited two doublets ($\delta_P = 48.4$, 39.0 ppm; $J_{P,P} = 9$ Hz), indicating inequivalent magnetic environments for the phosphines of the ligand coupling weakly to one another. The ^1H NMR spectrum contained a resonance consistent with insertion of a methylidene into a Ni−P bond to yield a phosphine/phosphine-ylide ligand environment about Ni (**5**; $\delta_H = 0.45$ ppm; dd, $J = 18.4$, 6.8 Hz).

Over time, these resonances disappeared while two new ^{31}P doublets grew in, showing considerably larger coupling ($\delta_P = 58.4$, 35.8 ppm; $J_{P,P} = 86$ Hz). These resonances were accompanied by the appearance of two multiplets in the ^1H NMR spectrum assigned to benzylic protons coupling both to one another and to the phosphorus nuclei of the ligand ($\delta_H = 3.00$ ppm, 1H, dd, $^2J_{HH} = 13.2$, $^2J_{HP} = 5.7$ Hz; 2.85 ppm, 1H, ddd, $^2J_{HH} = 13.2$, $^{2,3}J_{HP} = 9.9$, 3.5 Hz). These data suggest rearrangement of monoylide **5** to benzylphosphine **6**. This rearrangement is reminiscent of the phosphorus analogue of the Stevens rearrangement,[20] of which a limited number of examples have been reported to proceed at high temperatures[21] and mediated by low-valent metals, such as Ni^0.[22] This rearrangement could be reproduced by adding an equivalent of $[Ni(cod)_2]$ to the independently prepared monoylide of **1** (**7**, Scheme 2). Triphenylmethylenephosphorane does not transfer a methylidene fragment to **2** and rather is isomerized to benzyldiphenylphosphine. No reaction was observed between diphosphine **1** and triphenylmethylenephosphorane in the absence of Ni. This suggests that the Ni center is involved in the methylene-transfer reaction, although the intermediacy of a Ni-methylidene adduct may not be required. The observed attack of phosphine on the methylene carbon atom suggests that the putative Ni-methylidene (or Ni-methylidene/diphenylsulfide adduct) is electrophilic.[23]

This unusual rearrangement to generate **6** (Figure 4) suggests that although initial binding may occur at the Ni center, the final locus of reactivity in **2** can be the phosphine arms, which may or may not dissociate in the process. Indeed, when treated with an oxygen-atom-transfer agent,

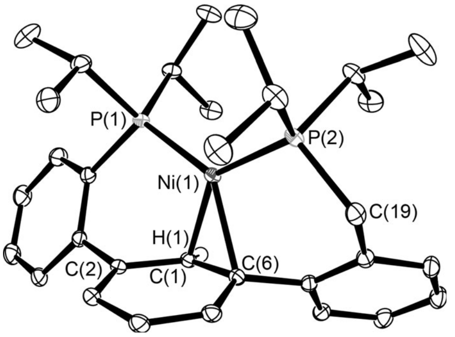
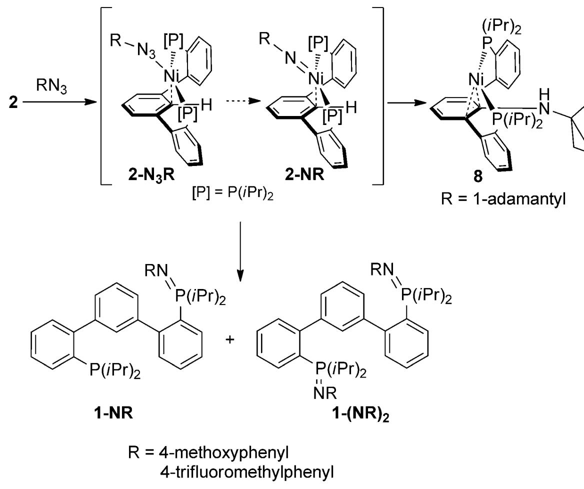


Figure 4. ORTEP of **6** with thermal ellipsoids shown at 50% probability levels. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)−Ni(1) 1.9614(9), C(6)−Ni(1) 2.0614(10), Ni(1)−P(1) 2.1813(3), Ni(1)−P(2) 2.1519(3), C(19)−P(2) 1.865(1), C(1)−C(6) 1.430(1); P(2)-Ni(1)-P(1) 129.07(1).

such as N_2O, oxidation of a phosphine arm and loss of the metal was observed. Similarly, **2** reacted with arylazides 1-azido-4-methoxybenzene and 1-azido-4-(trifluoromethyl)-benzene to give Staudinger oxidation products (oxidation of the phosphine arms to phosphoranimines) and loss of the metal (Scheme 3). A mixture of bis-oxidized and mono-oxidized products was observed when one equivalent of arylazide was used, even when the reaction was carried out at low temperature (−35 °C). Different modes of reactivity have been described stemming from the activation of organic azides by a metal center, including formal fragment insertion into metal–phosphine bonds.[24–26]



Scheme 3. Reactivity of **2** towards organoazides.

As the oxidation of **1** by 1-azidoarenes proceeds in the absence of Ni to yield a bis(phosphorane), the less reactive 1-azidoadamantane (N_3Ad) was investigated, as it does not oxidize **1**.[27] The reactivity of **2** with 1-azido-adamantane was different from that observed with 1-azido-arenes (Scheme 3). Treatment of **2** with 1-azido-adamantane at −35 °C led to only a slight shift of the $^{31}P\{^1H\}$ resonance of **2** from $\delta = 40.8$ to 40.4 ppm, consistent with the phosphines remaining bound to a Ni^0 center. ^1H NMR spectroscopic analysis indicated complete consumption of 1-azido-adamantane and also the disappearance of the resonance assigned to the central arene $C{-}H_{Ni}$ *ortho* to both flanking aryl rings of the terphenyl backbone. The solid-state structure of the product **8** revealed that an azide-derived adamantylnitrene had inserted into the central C−H bond of **2** (Figure 5). The aminated Ni^0 product **8** retains close metal–arene contacts [Ni(1)−C(1) 2.053(6); Ni(1)−C(2) 2.198(7) Å].

No reaction was observed between N_3Ad and **3-Cl** or **3-BF$_4$**, indicating that the Ni^I center is not reactive enough, owing either to steric constraints or to the metal center not being sufficiently reducing. Furthermore, no reaction was observed between N_3Ad and the benzyl phosphine Ni^0 complex, **6**, likely as a consequence of the increased steric crowding of the metal center in **6** compared with that in **2**, as the increased flexibility of the benzylphosphine arm allows the metal center to bind closer to the central arene with a more acute P-Ni-P angle [129.073(12)°; compare with **2**: 139.06(2)°].

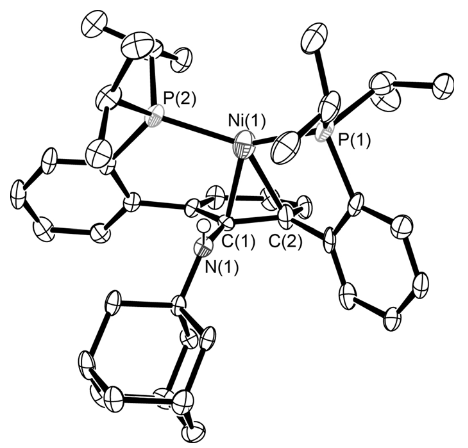
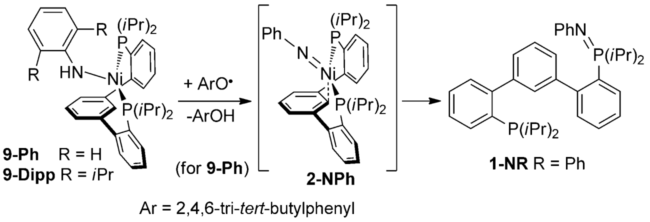


Figure 5. ORTEP of **8** with thermal ellipsoids shown at 50 % probability levels. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)−Ni(1) 2.053(6), C(2)−Ni(1) 2.198(7), Ni(1)−P(1) 2.125(2), Ni(1)−P(2) 2.216(2), C(1)−N(1) 1.415(8); P(1)-Ni(1)-P(2) 137.95(8).

Assembling these observations, we propose that, as observed for the diazoalkane adduct **2-Ph$_2$CN$_2$**, azide reagents may initially bind to the metal center on the opposite side to the activated C−H bond and above the central arene (Scheme 3, **2-N$_3$R**). Direct isomerization at Ni or isomerization via dissociation of a phosphine arm allows the azide (**2-N$_3$R**) or putative imide (**2-NR**) to move to the coordination site proximal to $C{-}H_{Ni}$. This process could lead to oxidation of a phosphine arm to give **1-NR** or **1-(NR)$_2$** when the reagent is sufficiently oxidizing (e.g., 1-azido-arenes or N_2O). Dissociation of a phosphine arm may be involved in the conversion of **2** to **6** (Scheme 2). In this case, attack of a phosphine arm on the proposed Ni-methylidene could be responsible for the formation of the thermally unstable ylide-stabilized Ni^0 intermediate observed spectroscopically. When the azide reagent is not sufficiently oxidizing to react with the phosphine arm, as in the case of N_3Ad, conversion of the organoazide, likely to a Ni–imido species (**2-NR**), leads to nitrene insertion into the well-positioned C−H bond to generate **8**. Terminal metal–imido species have similarly been proposed in examples of intramolecular C−H amination mediated by iron[15a] and cobalt.[28] The reactivity observed with N_3Ad may also result from Ni-templated extrusion of N_2 to generate a reactive nitrene that is not bound to Ni, a species that can then insert into the Ni-activated arene C−H bond.[25] Alternatively, the putative Ni–imido species could undergo 1,2-addition of the arene C−H bond, reactivity reminiscent of that of early-transition-metal imido complexes,[29] followed by reductive elimination.

To further probe the formation of a Ni–imide intermediate in either ligand oxidation or nitrene insertion (Scheme 3), we attempted an independent synthesis of imide complexes of **2** (Scheme 4). Hillhouse has demonstrated that phosphine-supported Ni^{II} imides (and phosphini-



Scheme 4. Hydrogen atom abstraction from **9** to generate **1-NPh**.

denes) are accessible by either sequential[12,30] or concerted[31] removal of a proton and an electron from a Ni^{I} anilide. Treating **3-Cl** with an equivalent of LiNHAd under a variety of conditions, however, led to reduction of the Ni^{I} complex and conversion to **2**, despite a relatively negative Ni$^{I/0}$ couple for **3-Cl** ($E_{1/2} = -1.39$ V versus ferrocene/ferrocenium).

Salt metathesis of **3-Cl** with either LiNH(dipp) (dipp = 2,6-diisopropylphenyl) or LiNH(C_6H_5) proved possible in ether/toluene mixtures at −35 °C and yielded the Ni^{I} anilides **9-Dipp** and **9-Ph**, respectively, as bright blue solids [**9-Dipp**: λ_{max} (ε): 592 nm (5450 cm^{-1} M^{-1}) in high yields. EPR spectroscopy (toluene glass, 77 K) revealed a nearly axial signal with g values (2.313, 2.095, 2.079) consistent with a metal-centered radical coupled to two phosphorus nuclei, one nitrogen nucleus, and one hydrogen nucleus.[32] The solid-state structures of **9-Dipp** and **9-Ph** (Figure 6) confirmed the installation of an amido moiety, with Ni(1)−N(1) bond lengths of 1.890(2) and 1.889(2) Å and Ni(1)-N(1)-C(31) angles of 141.5(1) and 128.6(2)°, respectively, compared with a Ni–N distance of 1.881(2) Å and Ni-N-C angle of 134.6(2)° in Hillhouse's three-coordinate terminal Ni^{I}–amide, [(dtbpe)NiNH(2,6-diisopropylphenyl)].[12] Notably, the Ni−N bonds are more than 0.1 Å longer than in diazoalkane adduct **2-Ph$_2$CN$_2$**, consistent with multiple-bonding character in that system (see above).

Despite displaying an electrochemically reversible oxidation (−0.80 V versus ferrocene/ferrocenium), the oxidation of **9-Dipp** with ferrocenium triflate led to significant decomposition, with **1** being the only identifiable phosphorus-containing species (full conversion of the oxidant to ferrocene was observed by ^{1}H NMR spectroscopy). Treatment of **9-Dipp** with the stable 2,4,6-tri-*tert*-butylphenoxyl radical led to the same result, with none of the desired reactivity discerned in the extracted equivalents of **1** and 2,4,6-tri-*tert*-butylphenol observed by ^{1}H NMR spectroscopy. Addition of one equivalent of 2,4,6-tri-*tert*-butylphenoxyl radical to a pentane solution of **9-Ph** at −78 °C led to a color change from deep blue to red. Upon warming to room temperature, ^{31}P{^{1}H} and ^{1}H NMR spectroscopic analysis revealed full conversion to the phenol and generation of approximately 60 % of the mono-oxidized Staudinger product, the phosphoranimine **1-NPh**, and approximately 30 % of **2** (Scheme 4).

The oxidation of the ligand to generate the phosphoranimine product **1-NPh** upon abstraction of a hydrogen atom from **9-Ph** supports the viability of a putative Ni–imido species (**2-NR**) in facilitating the chemistry observed in reactions of **2** with 1-azidoarenes. The mixture of products (mono- and bis-Staudinger oxidation products **1-NR** and **1-(NR)$_2$**) observed in treating **2** with 1-azido-4-methoxybenzene, for example, may result from a fast reaction between **2** and the azide to generate the mono-oxidized ligand, which loses Ni as a consequence of an unfavorable bite angle, and then is prone to metal-free oxidation by a second equivalent of azide. As the metal-free pathway is unavailable upon in situ hydrogen-atom abstraction, only the mono-Staudinger product is observed (Scheme 4). Alternate reactivity of the imide fragment, possibly through coupling or nitrene dissociation is likely responsible for the regeneration of **2**, although the fate of the remaining nitrene "N−Ph" moiety (that must dissociate to yield **2**) has eluded characterization to date. Attempts to intercept the putative imide fragment with substrates bearing weak C−H bonds (e.g., cyclohexene and 9,10-dihydroanthracene) were unsuccessful.

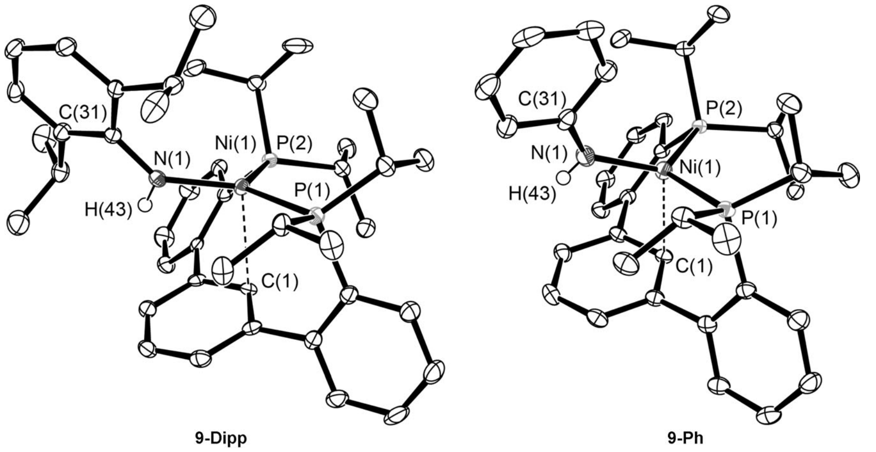
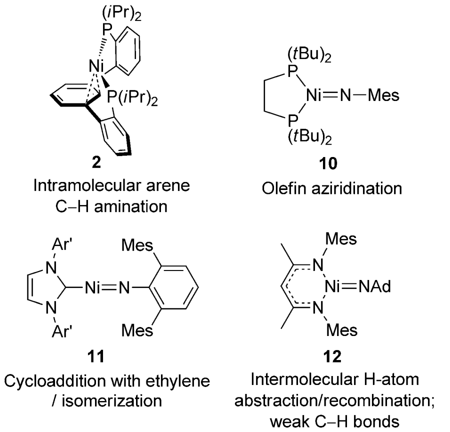


Figure 6. ORTEP of **9-Dipp** and **9-Ph** shown with thermal ellipsoids at 50 % probability levels. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]. **9-Dipp**: C(1)−Ni(1) 2.621(3), Ni(1)−P(1) 2.2312(6), Ni(1)−P(2) 2.2438(5), N(1)−Ni(1) 1.8905(17), N(1)−H(43) 0.78; P(1)-Ni(1)-P(2) 117.40(2), C(31)-N(1)-Ni(1) 141.52(14), N(1)-Ni(1)-P(1) 129.26(5), N(1)-Ni(1)-P(2) 113.24(5). **9-Ph**: C(1)−Ni(1) 2.399(2), Ni(1)−P(1) 2.2397(8), Ni(1)−P(2) 2.2389(7), N(1)−Ni(1) 1.889(2), N(1)−H(43) 0.71; P(1)-Ni(1)-P(2) 120.85(3), C(31)-N(1)-Ni(1) 128.6(2), N(1)-Ni(1)-P(1) 110.50(7), N(1)-Ni(1)-P(2) 124.22(7).

In comparison to the intramolecular arene C−H amination observed here, Hillhouse's dtbpe-supported Ni–imido species (**10**, Figure 7), with a more acute *cis* arrangement of phosphorus ligands (P-Ni-P: 91.12(5)°)[13] reacted with ethylene to give aziridination products (instead of insertion into



2 Intramolecular arene C–H amination

10 Olefin aziridination

11 Cycloaddition with ethylene / isomerization

12 Intermolecular H-atom abstraction/recombination; weak C–H bonds

Figure 7. Divergent reactivity for reported Ni imides.

a C–H bond).[3a] DFT studies supported a mechanism wherein dissociation of a phosphine arm allows for C–N bond-forming reductive elimination from a three-coordinate T-shaped azametallacyclobutane intermediate.[33] The two-coordinate Ni–imido species, [(IPr*)NiN(2,6-$Mes_2C_6H_3$)] (**11**, IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene, Mes = 2,4,6-$Me_3C_6H_2$), moreover, reacts with ethylene to give a similar azametallacyclobutane intermediate. However, the steric encumbrance of the large carbene ligand prevents the optimal geometry for C–N reductive elimination and instead N–H reductive elimination leads to a vinylamine product via a 1,2-hydride shift or β-hydride elimination followed by N–H reductive elimination.[4] Warren's β-diketiminato Ni^{III} imide, [Ni=NAd] [N-Ni-N: 94.43(9)°; **12**], in turn, reacts with weak C–H bonds via hydrogen-atom abstraction to give [Ni]–NHAd, and [Ni]–NRAd or [Ni]–NRHAd upon radical recombination.[10] Thus, the amination of **2** by N_3Ad represents a divergent C–H functionalization by a Ni–phosphine complex with a wide bite angle and a unique example of formal nitrene insertion into a strong arene C–H bond upon reaction with an azide reagent.

Conclusion

The use of *meta*-terphenyl diphosphine **1** as a ligand for engendering labile metal–arene interactions was demonstrated for Ni in various oxidation states and coordination environments. The extent of the interaction between the metal and the central arene depends largely on the oxidation state and the binding strength of additional ligands, and evidence of these interactions can be observed both in solution and the solid state. The Ni^0 complex **2** has been shown to bind diphenyldiazomethane in a terminal fashion, displaying a Ni–N distance suggestive of multiple bonding. Complex **2** reacts with 1-azido-arenes or 1-azido-adamantane with either oxidation of a phosphine arm or insertion of a nitrene fragment into an aryl C–H bond. A rare example of a phospha-Stevens-type rearrangement upon reaction of **2** with an alkylidene transfer agent was also recorded. These results suggest that modification of the ligand at the central C–H position, as well as the substituents at phosphorus, to prevent such intramolecular pathways may be useful in diverting reactivity towards productive intermolecular group transfer and C–H functionalization.

Acknowledgements

The authors thank Larry M. Henling for invaluable crystallographic assistance, the late Dr. Michael W. Day for solving the crystal structure of **4**, and Caltech for generous funding and support. The Bruker KAPPA APEXII X-Ray diffractometer was purchased via an NSF CRIF:MU award to Caltech (CHE-0639094). The Gordon and Betty Moore Foundation, the Beckman Institute and the Sanofi-Aventis BRP are thanked for their support of the Molecular Observatory at Caltech and the SSRL beamline, operated for the DOE and supported by its Office of Biological and Environmental Research and by the NIH and NIGMS (P41 M103393) and the NCRR (P41RR001209).

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Received: July 2, 2013