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

Dr. David E. Herbert, Nadia C. Lara, and Prof. Theodor Agapie
Division of Chemistry and Chemical Engineering California Institute of Technology – MC 127-72
1200 E California Boulevard, Pasadena, CA, USA 91125 Fax: 1-626-568-8824
Theodor Agapie: agapie@caltech.edu

Abstract

The meta-terphenyl diphosphine, m-P₂: 1, was utilized to support Ni centers in the oxidation states 0, I and II. A series of complexes bearing different substituents and/or ligands at Ni were prepared to investigate the dependence of metal-arene interactions on oxidation state and substitution at the metal. Compound (m-P₂)Ni (2), shows close Ni(0)-arene interactions between the metal centre and 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 = CH₃CN, CO, Ph₂CN₂), Ni(I)X complexes [3-X: X = Cl, BF₄, N₃, N₃B(C₆F₅)₃] and (m-P₂)Ni(II)Cl₂ (4). Complex 2 reacts with substrates such as diphenyldiazoalkane, sulfur ylides (Ph₂S=CH₂), organoazides (RN₃; R = para-C₆H₅OMe, 1-adamantyl) and N₂O with the locus of observed reactivity dependent on the nature of the substrate, leading to isolation of an η¹-diphenyl diazoalkane adduct (2-Ph₂CN₂), 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 to give the insertion product 8, all derived from the same compound (2). Hydrogen atom abstraction from a nickel(I)-amide (9) and resulting nitrene transfer chemistry supports the viability of nickel-imide intermediates in the reaction of 1 with 1-azido-arenes.

Keywords

Arene compl; amination; C-H activation; group transfer; insertion react

INTRODUCTION

The design of ligands that can support first-row transition metal centers in order to react with molecules such as organoazides, diazoalkanes and nitrous oxide to form terminal, multiply-bound metal imides, carbenes and oxos active in group-transfer reactions has received significant attention recently as atom-efficient routes are sought for the functionalization of unreactive substrates such as olefins and C-H bonds.[1], [2], [3, 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

Correspondence to: Theodor Agapie, agapie@caltech.edu.

EXPERIMENTAL SECTION

Supplementary Information (ESI) available with full experimental details, NMR spectra, crystallographic information for all compounds compounds.

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. ABSTRACT
explored, while terminal copper nitrenes have been proposed as key reactive intermediates in Cu-catalyzed nitrene transfer/C-H amination.\[11\]

Hillhouse and coworkers, notably, have demonstrated that nickel, supported by bulky, donating 1,2-bis(di-tert-butylphosphino)ethane (dtbpe) ligands, can form both three-coordinate imides and carbenes with multiple bonds to main group fragments derived from azides and diazoalkanes and investigated their group transfer reactivity.\[12–14\] Similarly, Warren has examined analogous chemistry at similarly narrow bite-angle beta-diketiminato supported Ni(III) centres.\[9,10\] In these cases, divergent group transfer was observed (e.g., aziridination vs. C-H amination), depending on the coordination number and oxidation state of the metal centre mediating the transformation. Ni-mediated nitrene insertion into a strong aromatic C-H bond, however, was not reported.\[15\]

We have been investigating the chemistry of trans-spanning, multidentate terphenyl diphosphine ligands wherein the central arene ring can act as a multi-hapto binding site and exhibit a range of versatile coordination and non-innocent behaviour.\[16,17\] In this report, we describe the ability of a meta-terphenyl diphosphine (1) to support nickel centers in a variety of oxidation states [Ni(0) L = CH$_3$CN, CO, Pb$_2$CN$_2$, 2-L; Ni(I) X = Cl, BF$_4$, N$_3$, N$_3$-B(C$_6$F$_5$)$_3$; Ni(II) X = Cl$_2$, 3-X] 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 were 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 oxidation state, metal-arene interactions, and the substrate dependence of these reactions are discussed in the context of functionalization of aromatic C-H bonds.

**RESULTS AND DISCUSSION**

Nickel complexes in the oxidation states (0, I, II) were prepared by reaction of 1 with the appropriate nickel precursor (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 supported nickel complex (2) which was isolated as a red-brown solid. Treatment of 1 with NiCl$_2$(DME) (DME = 1,2-dimethoxyethane) provided the Ni(II) diphosphine complex, 4, as purple solid. The orange Ni(I) chloride (3-Cl) was prepared by comproportionation of Ni(II) and Ni(0) precursors via reaction of 1 with 0.5 eq. of Ni(COD)$_2$ followed by addition of 0.5 eq. of Ni(COD)$_2$ followed by addition of 0.5 eq. of (DME)NiCl$_2$.\[17\] Starting with 3-Cl, salt metathesis provided access to structurally related species with anions with 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.

The compounds described have all been characterized by single crystal X-ray diffraction. The central arene is bound $\eta^2$ to the metal centre 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 nickel [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 $\sigma$-donor ligand such as CH$_3$CN to the Ni(0) centre 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]. Binding of more $\pi$-acidic ligands has a similar effect. For example, in the CO adduct 2-CO, the Ni(1)-C(1) distance is increased to 2.254(1) 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 becomes

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more acute in the lower oxidation state complexes, with closer 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_{6}D_{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 13C{1H} NMR spectrum of 2 contains a triplet at 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 solution. Both the 1H and 13C{1H} NMR spectra of 2 are consistent with an average C₅-symmetric structure in solution at room temperature, indicating fast exchange with the nickel center shuttling between the two sides of the pseudo-mirror plane relating the two phosphine moieties on the time scale of the NMR experiments.

In comparison with the solid-state structure of 2, all the yellow or orange Ni(I) complexes 3-X [X = Cl, BF₄, N₃, N₃B(C₆F₅)₃] show longer metal-arene distances [Ni(1)-C(1): 3-Cl 2.562(1), 3-BF₄ 2.4976(15); 3-N₃ 2.6182(8); 3-N₃B(C₆F₅)₃ 2.3958(4) Å]. Comparing 3-BF₄ to 3-Cl and 3-N₃, 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 of the Ni-bound azide by addition of B(C₆F₅)₃ to a solution of 3-N₃ renders the azido moiety a weaker donor, resulting in a shorter Ni(1)-C(1) contact in 3-N₃B(C₆F₅)₃ compared with 3-N₃ (Figure 2). Thus, the arene binds more strongly to the electron-rich Ni(0) in 2 by virtue of stronger metal-to-ligand back-bonding compared with 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 nickel complexes, the reactivity with group transfer reagents was investigated.

Addition of a stoichiometric amount of diphenyldiazooalkane to a solution of 2 in hexanes, resulted in the isolation of a 1:1 adduct (2-Ph₂CN₂; Scheme 2). 1H NMR spectroscopic analysis of 2-Ph₂CN₂ revealed that the diagnostic central arene C-H resonances were found at much lower field (1H: 8.29 ppm, 13C{1H}: 108 ppm; C₆D₆, assigned by HSQC), suggesting weaker metal-arene interactions. Indeed, the solid-state structure of 2-Ph₂CN₂ confirmed this change in bonding (Figure 3). The nickel-carbon distance in 2-Ph₂CN₂ is considerably elongated compared with 2 [Ni(1)-C(1) 2.511(2) Å]. The diazoalkane moiety binds in almost linear fashion [Ni(1)-N(1)-N(2) angle = 160.5(2)°]. Interestingly, the Ni-N distance is significantly shorter at 1.75(2) Å compared with the terminal acetonitrile adduct 2-CH₃CN [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-Ph₂CN₂ is only slightly longer than for the 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 observed by 1H NMR spectroscopy (cf. 2 vs. 4-Cl₂).

With the diazoalkane adduct 2-Ph₂CN₂ in hand, thermal extrusion of dinitrogen was attempted in order to access a nickel carbene.[14] Extensive heating of solutions of 2-Ph₂CN₂ in benzene or toluene (80–110 °C), however, slowly regenerated 2 after days with no observable intermediates. The diazoalkane fragment was converted under these conditions to three detectable products: tetraphenylethylene, 1,2-bis(diphenylmethene)hydrazine and N-(diphenylmethylene)-1,1-diphenylmethanamine, in a 50:40:10 ratio (GC). Control reactions heating solutions of diphenyldiazomethane at equivalent concentrations for the same period of time yielded the hydrazine exclusively in

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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 tetra-substituted olefin to 60% of the observed products. Mechanisms involving dissociated and metal-bound diphenylazomethane 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, as reported by Milstein and coworkers who demonstrated this method’s utility in preparing a range of late metal carbenes such as Grubbs’ catalyst.$^{[19]}$ Deprotonation of diphenylmethyldisulfonium 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{$^1$H} NMR spectrum collected immediately upon warming exhibited two doublets (δ$_P$ = 48.4, 39.0 ppm; J$_{PP}$ = 9 Hz) indicating inequivalent magnetic environments for the phosphines of the ligand coupling weakly to one another, while the $^1$H 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 (δ$_H$ = 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 stronger coupling (δ$_P$ = 58.4, 35.8 ppm; J$_{PP}$ = 86 Hz). These were accompanied by two multiplets in the $^1$H NMR spectrum assigned to benzylic protons [δ$_H$ = 3.00 ppm (1H, dd, 2J$_{HH}$ = 13.2, 2J$_{HP}$ = 5.7 Hz), 2.85 ppm (1H, dd, 2J$_{HH}$ = 13.2, 2,3J$_{HP}$ = 9.9, 3.5 Hz)] coupling both to one another and to the phosphorus nuclei of the ligand. These data suggest rearrangement of mono-ylide 5 to a benzylphosphine (6). This rearrangement is reminiscent of the phosphorus-analog 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 nickel(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 nickel. This suggests that nickel is involved in the methylene transfer reaction, although the intermediacy of a nickel-methylidene may not be required. The observed attack of phosphine on the methylene carbon suggests that the putative nickel-methylidene (or nickel-methylidene/diphenylsulfide adduct) is electrophilic.$^{[23]}$

This unusual rearrangement to generate 6 suggests that although initial binding may occur at nickel, the final locus of reactivity in 2 can be the phosphate arms, which may or may not dissociate in the process. Indeed, when treated with an oxygen-atom transfer reagent such as N$_2$O, oxidation of a phosphine arm and loss of metal was observed. Similarly, 2 reacted with arylazides [1-azido-4-methoxybenzene, 1-azido-4-(trifluoromethyl)benzene] to give Staudinger oxidation products (oxidation of phosphate arms to phosphoranimines) and loss of metal (Scheme 3). A mixture of bis-oxidized and mono-oxidized products was observed with one equivalent of arylazide, even when carried out at low temperature (−35 °C). Different modes of reactivity have been described stemming from organic azides activated by a metal center, including formal fragment insertion into metal-phosphine bonds.$^{[24],[25, 26]}$

As the oxidation of 1 by 1-azidoarenes proceeds in the absence of nickel to yield a bis(phosphorane), less reactive 1-azidoadamantine (N$_3$Ad) 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. Treatment of 2 with 1-azido-adamantane at −35 °C led to only a slight shift of the $^{31}$P{$^1$H} resonance of 2 from 40.8 to 40.4 ppm, consistent with the phosphines.
remaining bound to a Ni(0) center. $^1$H 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 terphenyl backbone. The solid-state structure of the product (8) revealed that an azide-derived adamantylnitrene had inserted into the central C-H of 2 (Figure 5). The aminated Ni(0) product 8 retains close metal-arene contacts [Ni(1)-C(1) 2.053(6); Ni(2)-C(2) 2.198(7) Å].

No reaction was observed between N$_3$Ad and 3-Cl or 3-BF$_4$, indicating that the Ni(I) centre is not reactive enough either due to steric constraints or for not being sufficiently reducing. Neither was any reaction observed between 1-azido-adamantane and the benzyl phosphine Ni(0) complex 6, likely as a consequence of the increased steric crowding wrought on the metal centre in 6 compared with in 2 as the benzylphosphine arm allows the metal centre to form a tighter interaction with the central arene and form a more acute P-Ni-P angle [129.073(12)$^\circ$; cf. 2: 139.06(2)$^\circ$].

Assembling these observations together, we propose that, as observed for the diazoalkane adduct 2-Ph$_2$CN$_2$, azide reagents may initially bind above the central arene, on the far side of the metal from the activated C-H bond (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, N$_2$O). Dissociation of a phosphine arm may be involved in the conversion of 2 to 6. In this case, attack of a phosphine arm on the proposed nickel-methyldiene could be responsible for the formation of the thermally unstable ylide-stabilized Ni(0) intermediate observed by spectroscopy. When the azide reagent is not sufficiently oxidizing to react with the phosphine arm, as in the case of N$_3$Ad, conversion of the organoazide, likely to a nickel-imido (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$^{[28]}$ and cobalt$^{[29]}$. The reactivity observed with N$_3$Ad may also result from Ni-templated extrusion of N$_2$ to generate a reactive nitrene that is not bound to Ni, which then can insert into the Ni-activated arene C-H bond$^{[25]}$. Alternatively, the putative nickel-imido could undergo 1,2-addition of the arene C-H bond reminiscent of early metal imido reactivity$^{[30]}$, followed by reductive elimination.

To further probe the formation of a nickel 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 diphosphine-supported Ni(II) imides (and phosphinidenes) are accessible by either sequential$^{[12, 31]}$ or concerted$^{[32]}$ 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$^{II}$/I couple for 3-CI of $E_{1/2} = −1.39$ V vs. ferrocene/ferrocenium.

Salt metathesis with either LiNH(dipp) (dipp = 2,6-di-iso-propylphenyl) or LiNH(C$_6$H$_5$)$_2$ proved possible in ether/toluene mixtures at −35 °C and yielded the Ni(I) anilides 9-Ph and 9-Dipp as bright blue solids [e.g., 9-Dipp: $\lambda_{\text{max}} (\varepsilon)$: 592 nm (5450 cm$^{-1}$M$^{-1}$)] in high yields. EPR spectroscopy (toluene glass, 77K) revealed a nearly axial signal with g-values (2.313, 2.095, 2.079) consistent with a metal-centered radical showing coupling to two phosphorus, one nitrogen and one hydrogen nucleus$^{[33]}$. The solid-state structure of 9-Ph and 9-Dipp (Figure 6) confirmed the installation of an amido moiety, with a Ni-N bond distance of Ni(1)-N(1): 1.889(2) Å and a Ni(1)-N(1)-C(31)$_{\text{anilide}}$ angle of 141.6(2)$^\circ$, compared with values of 188.1(2)$^\circ$ and 134.6(2)$^\circ$ in Hillhouse’s three-coordinate terminal nickel(I)-amide,
(drbpe)NiNH(2,6-di-iso-propylphenyl).\(^{[12]}\) Notably, the Ni-N distances are more than 0.1 Å larger than in diazoalkane adduct 2-Ph\(_2\)CN\(_2\), consistent with multiple bonding character in that system (vide supra).

Despite displaying an electrochemically reversible oxidation (−0.80 V vs ferrocene/ferrocenium), oxidation of 9-Dipp with ferrocenium triflate led to significant decomposition, with unaffected ligand 1 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 radical, 2,4,6-tri-tert-butylphenoxyl radical, led to the same result, with no 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 in pentane to a solution of 9-Ph in the same 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 spectroscopic analysis revealed full conversion to the phenol and generation of ~60% of mono-Staudinger phosphoranimine of 1 and ~30% of 2 (Scheme 4).

The oxidation of the ligand to generate the phosphoranimine product upon abstraction of an H-atom from 9-Ph supports the viability of the putative Ni-imido species (2-NR) in facilitating the chemistry observed in reactions of 2 with 1-azidoarenes. The mix of products [mono-, bis-Staudinger oxidation products 1-NR and 1-(NR)\(_2\)] observed in treating 2 with 1-azido-4-methoxybenzene, for example, may result from fast reactivity of 2 with the azide to generate the mono-oxidized ligand, which loses Ni as a consequence of an unfavourable bite angle, and then is prone to metal-free oxidation. As the metal-free pathway is unavailable upon in situ H-atom abstraction, only the mono-Staudinger product is observed (Scheme 4). Alternate reactivity of the imide fragment, possibly through coupling or nitrene dissociation likely is 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, 9,10-dihydroanthracene) were unsuccessful.

In comparison to the intramolecular arene C-H amination observed here, Hillhouse’s dtbpe-supported Ni-imido (10, Figure 7), with a more acute cis arrangement of P-ligands [P-Ni-P: 91.12(5)°\(^{[13]}\)] reacted with ethylene to give aziridination products (instead of insertion into a C-H bond).\(^{[34]}\) DFT studies supported a mechanism wherein dissociation of a phosphine arm allows for C-N bond-forming reductive elimination (RE) from a three-coordinate, T-shaped azamatallacyclobutane intermediate.\(^{[35]}\) The rigorously two-coordinate nickel-imido, (IPr*)Ni=N(2,6-dimesitylphenyl) \(^{[11]}\), IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene, moreover, reacts with ethylene to give a similar azamatallacyclobutane intermediate, however the steric encumberance of the large carbene ligand prevents the optimal geometry for C-N reductive elimination and N-H RE leads to a vinylamine product via a 1,2-hydride shift or \(\beta\)-hydride elimination followed by N-H RE.\(^{[4]}\) Warren’s \(\beta\)-diketiminato supported 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\(_3\)Ad 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 ability of a meta-terphenyl bis(phosphine) (1) to provide labile metal-arene interactions was demonstrated for 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 diphenylrazomethane in a terminal fashion, displaying a Ni-N distance suggestive of multiple bonding. Compound 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.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

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**References**


27. While mixtures of iPr₃P and N₃Ad (Ad = 1-adamantyl) have been reported to reversibly form kinetically stable phosphazide adducts, no N₃Ad/1 adduct was observed at room temperature. See: Fortman GC, Captain B, Hoff CD. Inorg Chem. 2009; 48:1808–1810. [PubMed: 19235943]
Figure 1.
ORTEPs of 2, 2-CH$_3$CN, 2-CO and 4 with thermal ellipsoids shown at 50% probability levels. 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) 2.177(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) 130.617(12), C(31)-N(1)-Ni(1) 164.70(9). 2-CO: Ni(1)-P(1) 2.2123(6), Ni(1)-P(2) 2.1954(5), C(31)-Ni(1) 1.7567(12), C(31)-O(1) 1.1517(15), C(1)-Ni(1) 2.2545(14), P(1)-Ni(1)-P(2) 125.937(17), O(1)-C(31)-Ni(1) 177.94(11). 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).
Figure 2.
ORTEPs of 3-BF₄, 3-N₃ and 3-BN₃(C₆F₅)₃ with thermal ellipsoids shown at 50% probability levels. Selected bond lengths (Å) and angles (°) for 3-BF₄: 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) 155.11(1), B(1)-F(1)-Ni(1) 128.78(10).
3-N₃: 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), N(1)-N(1)-N(2) 140.29(8), N(1)-N(2)-N(3) 177.13(11).
3-BN₃(C₆F₅)₃: Ni(1)-P(1) 2.2620(9), Ni(1)-P(2) 2.2674(8), Ni(1)-N(1) 1.973(3), N(1)-N(2) 1.156(4), N(2)-N(3) 1.194(4), C(1)-Ni(1) 2.399(3), N(3)-B(1) 1.590(4); P(1)-Ni(1)-P(2) 153.26(3), Ni(1)-N(1)-N(2) 153.4(3), Ni(1)-N(2)-N(3) 173.4(3), N(2)-N(3)-B(1) 124.6(2).
Figure 3.
ORTEP of 2-Ph₂CN₂ with thermal ellipsoids shown at 50% probability levels. 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).
Figure 4. ORTEP of 6 with thermal ellipsoids shown at 50% probability levels. Selected bond lengths (Å) and angles (°): C(1)-Ni(1) 1.9614(9), C(6)-Ni(1) 2.0614(9), 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).
Figure 5.
ORTEP of 8 with thermal ellipsoids shown at 50% probability levels. 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).
**Figure 6.**
ORTEP of 9-Dipp and 9-Ph shown with thermal ellipsoids at 50% probability levels. Selected bond lengths (Å) and angles (°): **9-Dipp:** C(1)-Ni(1) 2.621(3), Ni(1)-P(1) 2.2303(8), Ni(1)-P(2) 2.2413(7), N(1)-Ni(1) 1.889(2), N(1)-H(43) 0.77; P(1)-Ni(1)-P(2) 117.40(3), C(31)-N(1)-Ni(1) 141.6(2), N(1)-Ni(1)-P(1) 129.46(8), N(1)-Ni(1)-P(2) 113.04(8). **9-Ph:** C(1)-Ni(1) 2.399(2), Ni(1)-P(1) 2.2396(8), Ni(1)-P(2) 2.2390(7), N(1)-Ni(1) 1.891(2), N(1)-H(43) 0.88; P(1)-Ni(1)-P(2) 120.85(3), C(31)-N(1)-Ni(1) 128.38(17), N(1)-Ni(1)-P(1) 110.44(7), N(1)-Ni(1)-P(2) 124.33(7).
Figure 7.
Divergent reactivity for reported nickel imides.
Scheme 1.
Synthesis of Ni complexes 2, 3-X and 4.
Scheme 2.
Reactivity of 2 towards diphenyl diazoalkane and methyldiene transfer reagents.
Scheme 3.
Reactivity of 2 towards organoazides.
Scheme 4.
H-atom abstraction from 9 to generate 1-NPh.