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Synthesis and Characterization of Palladium Complexes Supported by an NPN-Phosphido Ancillary Ligand

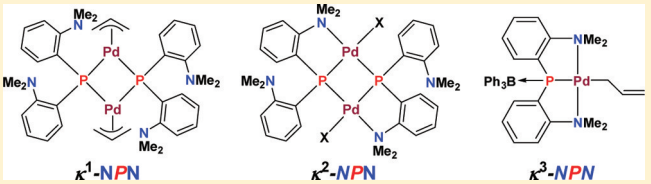
Morgan C. MacInnis,[†] Robert McDonald,[‡] and Laura Turculet*[,†]

[†]Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

[‡]X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Supporting Information

ABSTRACT: The Pd^{II} coordination chemistry of the phosphido ligand $[(2\text{-}Me_2NC_6H_4)_2P]^-$ (NPN) is reported, along with the results of studies documenting the utility of such complexes as catalyst precursors for the Heck arylation of olefins. Examples of κ^1-, κ^2-, and κ^3-NPN coordination to Pd are described. The secondary phosphine (NPN)H (**1**) was reacted with 0.5 equiv of $[(C_3H_5)PdCl]_2$ to afford the dimeric species $[(\kappa^2\text{-}NPN)PdCl]_2$ (**2**) in 96% yield. Similarly, the reaction of **1** with 0.33 equiv of $[Pd(OAc)_2]_3$ led to the formation of dimeric $[(\kappa^2\text{-}NPN)PdOAc]_2$ (**3**) in 98% yield. Complexes **2** and **3** were both crystallographically characterized to reveal dipalladium species that feature bridging phosphido groups, as well as terminal chloride and acetate ligands, respectively. Treatment of **3** with Me_3SiOTf resulted in the formation of the analogous triflate complex $[(\kappa^2\text{-}NPN)PdOTf]_2$ (**4**; 78% yield). Treatment of **2** with $(C_3H_5)MgCl$ afforded the thermally sensitive, phosphido-bridged complex $[(\kappa^1\text{-}NPN)Pd(\eta^3\text{-}C_3H_5)]_2$ (**5**) in 87% yield. The solid-state structure of **5** was confirmed by X-ray crystallography. Precoordination of BPh_3 to the NPN phosphido group was attempted in order to discourage the formation of phosphido-bridged (NPN)Pd species. Thus, the reaction of **1** with 1 equiv each of KCH_2Ph and BPh_3 led to the formation of $[N(P{\cdot}BPh_3)N]K$ (**6**), which was isolated in 88% yield. The related complex $[N(P{\cdot}BH_3)N]H$ (**7**) was prepared by treatment of **1** with $BH_3{\cdot}THF$, and crystallographic characterization confirmed the preferential coordination of the NPN ligand phosphorus to BH_3. The reaction of **6** with 0.5 equiv of $[Pd(C_3H_5)Cl]_2$ led to the formation of $[\kappa^3\text{-}N(P{\cdot}BPh_3)N]Pd(\eta^1\text{-}C_3H_5)$, which was isolated in 45% yield. Complexes **2**–**4** were established as precatalysts for the Heck coupling of ethyl acrylate and haloarenes.



INTRODUCTION

Monoanionic tridentate ligands comprised of a central anionic X-type donor fragment flanked by two neutral L-type donors (i.e., κ^3-LXL, where X is typically C or N) have proven to be particularly useful in supporting platinum-group-metal complexes that exhibit unique reactivity and structural features.[1,2] Given this progress, it is surprising that the exploration of such ligand architectures featuring alternative central donor atoms including silicon[3] and phosphorus[4,5] has received relatively little attention; indeed, despite the remarkable advancements that have been achieved by use of tridentate bis(phosphino)amido (PNP) ligands in platinum-group-metal chemistry,[1,2e−l] the synthesis and characterization of related complexes supported by phosphido-based (i.e., R_2P^-) pincer ancillary ligands is limited to the work of Mazzeo, Peters, and co-workers,[4b,j] as well as van der Vlugt and co-workers.[4k] In these reports complexes of the type $(\kappa^3$-PPP)MX (M = Pd, Pt) are reported, including, in the case of the Pd analogues, their use in the allylation of aldehydes.[4b] Given that the incorporation of phosphido fragments into pincer ligand frameworks is likely to promote the formation of late-metal complexes that may exhibit new and unusual reactivity, it is evident that the further development of platinum-group-metal complexes supported by phosphido-based multidentate ligands is warranted.

We have recently reported on the synthesis and reactivity of coordinatively unsaturated late-metal complexes supported by new bis(phosphino)silyl pincer ligands of the type $[\kappa^3\text{-}(2\text{-}R_2PC_6H_4)_2SiMe]^-$ (R = Ph, Cy; κ^3-PSiP),[3a−e] including examples of Ir species that can undergo facile intermolecular C−H and N−H bond activation chemistry,[3a] as well as palladium and nickel complexes that participate in unusual Si−C bond cleavage reactions.[3b] To complement these investigations, and encouraged by the rich and diverse chemistry exhibited by platinum-group-metal complexes featuring bis(phosphino)amido ligation,[1,2e−l] we have initiated a synthetic and reactivity study of platinum-group-metal complexes featuring phosphido-based NPN ligands, including $[(2\text{-}Me_2NC_6H_4)_2P]^-$ (NPN). We report herein on the ability of $[(2\text{-}Me_2NC_6H_4)_2P]^-$ and the BPh_3 adduct $[(2\text{-}Me_2NC_6H_4)_2P{\cdot}BPh_3]^-$ to support monodentate, bidentate, and tridentate coordination complexes of Pd^{II} and the application of dimeric, phosphido-bridged $[(\kappa^2\text{-}NPN)PdX]_2$ (X = Cl, OAc, OTf) species of this type as precatalysts for the Heck arylation of ethyl acrylate.

RESULTS AND DISCUSSION

Treatment of 2-lithio-*N*,*N*-dimethylaniline with 0.5 equiv of PCl_3 followed by reduction with $LiAlH_4$ afforded the desired secondary phosphine $[(2\text{-}Me_2NC_6H_4)_2P]H$ (**1**, (NPN)H) in 79% isolated yield. The ^1H NMR spectrum of **1** exhibits a characteristic doublet at 5.52 ppm ($^1J_{PH}$ = 221 Hz)

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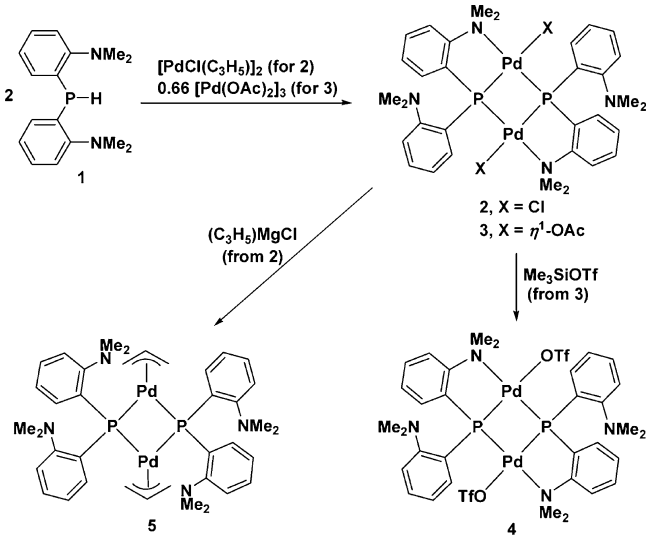
corresponding to the P–*H* resonance, while the ^{31}P NMR spectrum of **1** features a doublet at −59.3 ppm ($^{1}J_{PH}$ = 220 Hz).

The reaction of **1** directly with Pd^{II} starting materials led to the isolation of phosphido-bridged dimeric complexes of the type $[(\kappa^2\text{-}NPN)PdX]_2$ (**2**, X = Cl; **3**, X = η^1-OAc). Treatment of **1** with $^1/_2$ equiv of $[PdCl(C_3H_5)]_2$ in benzene at 65 °C led to the precipitation of red crystalline **2**, which was isolated in 96% yield (Scheme 1). The X-ray crystal structure of **2**

Scheme 1. Synthesis of the Palladium Complexes 2–5



confirms the formation of a phosphido-bridged dimeric Pd complex in which the NPN ligand is coordinated to the metal center in a κ^2-*NPN* fashion (Figure 1); solution and refinement

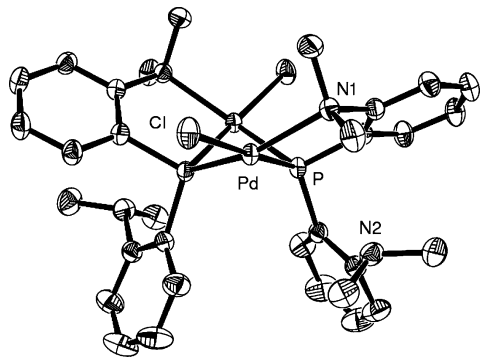


Figure 1. ORTEP diagram for **2** shown with 50% displacement ellipsoids. Only one of the two crystallographically independent half-molecules of **2** is shown (with the full structure generated via application of crystallographically imposed 2-fold rotational symmetry), and hydrogen atoms have been removed for clarity. The crystallographically unique atoms are labeled. Selected interatomic distances (Å) and angles (deg): Pd–P, 2.2213(5); Pd–P′, 2.2462(5); Pd′–P, 2.2166(5); Pd′–P′, 2.2495(5); Cl–Pd–P, 175.65(2); Cl–Pd–P′, 101.18(2); Cl–Pd–N, 95.15(4); P–Pd–P′, 76.00(2); P–Pd–N, 86.34(4); P′–Pd–N, 153.53(5).

data for all crystallographically characterized compounds featured herein are collected in Table 1. Each Pd center in **2** also features a terminal chloride ligand, resulting in approximate square-planar coordination geometry at the metal center. The dimer features a slightly unsymmetrical puckered Pd_2P_2 core, such that the dihedral angle between the two square planes defined by the coordination sphere of each Pd center in the dimeric structure is 83.78(4)°. The Pd···Pd distance of 3.196 Å in **2** is long,[6] suggesting that Pd–Pd bonding does not play a significant role in the observed structure.[7] The Pd–P distances in **2** (2.2166(5)–2.2495(5) Å) are comparable to the Pd–phosphido distance of 2.2533(9) Å found in the monomeric phosphido complex $[\kappa^3\text{-}(2\text{-}^i Pr_2PC_6H_4)_2P]PdCl$.[4b] By comparison with the latter monomeric κ^3-PPP complex, the dinuclear bridged structure adopted by **2** establishes that phosphido bridging within a dinuclear species is preferred over a monomeric κ^3-NPN motif, owing to the comparatively poor donor ability of the dimethylamino fragments within the NPN ligand.

The room-temperature ^{1}H NMR spectrum of **2** (methylene chloride-d_2) features a single resonance corresponding to the ligand dimethylamino protons at 2.76 ppm, as well as one set of aromatic proton resonances. The observed spectrum suggests two possible scenarios: (a) compound **2** is monomeric in solution and features effective C_2V symmetry or (b) compound **2** is dimeric in solution as well as in the solid state and is fluxional, giving rise to an averaged ^{1}H NMR spectrum at room temperature. Variable-temperature ^{1}H NMR spectroscopy of **2** (Figure 2, methylene chloride-d_2) revealed substantial line-shape changes. In particular, three decoalescence events were observed at low temperature for the resonance corresponding to the dimethylamino protons, consistent with rapid exchange of free and bound NMe_2 groups in a dimeric complex, as well as slowed C_{aryl}–N bond rotation and inversion at both free and bound NMe_2 nitrogen donors. When the solution was cooled to −55 °C, the resonance corresponding to the dimethylamino protons decoalesced into two broad resonances centered at 3.25 and 2.10 ppm (ca. 1:1 ratio), respectively, consistent with the slowed exchange of free and bound NMe_2 groups. The $\Delta G^{\ddagger}$ value was estimated as ∼10 kcal mol^{-1} for this process.[8] At −70 °C decoalescence of the resonance centered at 3.25 ppm was observed, giving rise to two singlets at 3.35 and 3.11 ppm (ca. 1:1 ratio, Figure 2), respectively. Finally, at −80 °C decoalescence of the resonance centered at 2.10 ppm was observed, giving rise to two broad peaks centered at 2.58 and 1.45 ppm (ca. 1:1 ratio, Figure 2), respectively. The latter processes are consistent with slowed C_{aryl}–N bond rotation and inversion at both the free and bound NMe_2 nitrogen donors. Thus, at the low-temperature limit the ^{1}H NMR spectrum of **2** is in agreement with the C_2-symmetric structure observed in the solid state, suggesting that **2** is likely dimeric and fluxional in solution, resulting in an averaged spectrum at elevated temperatures. Further support for this structural assignment was provided by variable-temperature ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **2** (methylene chloride-d_2) features a single resonance at −54.0 ppm, and no line-shape changes were observed when the spectrum was acquired at low temperature; these data are consistent with an absence of monomer–dimer equilibrium for **2**, suggesting that the line-shape changes that are observed in the variable-temperature ^{1}H NMR spectra of this compound are indeed due to fluxional processes within the dipalladium complex.

The reaction of **1** with $^1/_3$ equiv of $[Pd(OAc)_2]_3$ in benzene at room temperature resulted in the formation of **3** in 98% isolated yield (Scheme 1) with the apparent loss of acetic acid. The X-ray crystal structure of **3**·C_6H_6 (Figure 3) indicates the formation of a phosphido-bridged dimeric Pd complex that is analogous to **2** (Pd1···Pd2 = 3.1897(4) Å). As in the case of **2**, the ^{1}H NMR spectrum of **3** (benzene-d_6) is consistent with an

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Table 1. Crystallographic Data for 2, 3·C_6H_6, 5, and 7

	2	3·C_6H_6	5	7
empirical formula	$C_{32}H_{40}Cl_2N_4P_2Pd_2$	$C_{42}H_{52}N_4O_4P_2Pd_2$	$C_{38}H_{50}N_4P_2Pd_2$	$C_{16}H_{24}N_2PB$
formula wt	826.32	951.62	837.56	286.15
cryst dimens	0.31 × 0.26 × 0.22	0.38 × 0.24 × 0.21	0.32 × 0.16 × 0.08	0.54 × 0.09 × 0.08
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2/n$	$P\bar{1}$	$P2_1/n$	$Pbca$
a (Å)	19.7889(14)	11.7857(15)	9.8192(4)	13.8992(16)
b (Å)	9.4338(7)	11.8320(15)	18.1484(7)	14.8869(17)
c (Å)	20.2742(15)	15.682(2)	20.4887(8)	16.4172(19)
α (deg)	90	91.9195(18)	90	90
β (deg)	114.9868(10)	96.8964(18)	92.9071(4)	90
γ (deg)	90	95.3691(17)	90	90
V (Å^3)	3430.6(4)	2159.3(5)	3646.4(2)	3397.0 (7)
Z	4	2	4	8
ρ_{calcd} (g cm^{-3})	1.600	1.464	1.526	1.119
μ (mm^{-1})	1.325	0.951	1.106	0.154
transmissn range	0.7592–0.6841	0.8253–0.7140	0.9177–0.7198	0.9878–0.9214
2θ limit (deg)	54.96	52.84	54.90	51.00
index ranges	$-25 \le h \le 25$	$-14 \le h \le 14$	$-12 \le h \le 12$	$-16 \le h \le 16$
	$-12 \le k \le 12$	$-14 \le k \le 14$	$-23 \le k \le 23$	$-18 \le k \le 18$
	$-26 \le l \le 26$	$-19 \le l \le 19$	$-26 \le l \le 26$	$-19 \le l \le 19$
total no. of data collected	28 274	14 929	31 701	23 216
no. of indep rflns	7861	8723	8325	3154
R_{int}	0.0257	0.0271	0.0304	0.0915
no. of obsd rflns	6906	6448	7184	2074
no. of data/restraints/params	7861/0/379	8723/0/435	8325/3/443	3154/8/209
goodness of fit	1.055	0.946	1.034	1.012
R1 ($F_o^2 \ge 2\sigma(F_o^2)$)	0.0220	0.0314	0.0227	0.0574
wR2 ($F_o^2 \ge -3\sigma(F_o^2)$)	0.0592	0.0759	0.0567	0.1550
largest peak, hole (e Å^{-3})	0.558, −0.249	0.516, −0.280	0.738, −0.493	0.308, −0.211

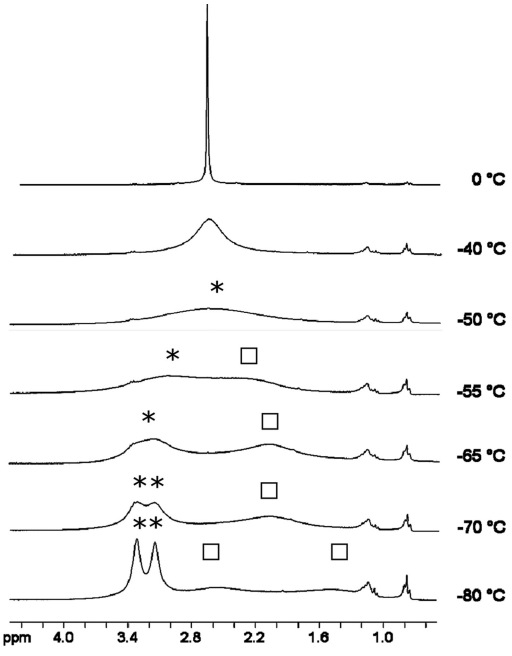

Figure 2. Variable-temperature ^{1}H NMR spectra of **2** (methylene chloride-d_2) showing line-shape changes in the dimethylamino proton region of the spectrum (* and □ correspond to unique NMe resonances observed at low temperature).

averaged structure at room temperature, as indicated by the presence of only one NMe_2 resonance at 2.60 ppm, as well as only one set of aromatic proton resonances. The reaction of **3** with Me_3SiOTf in benzene solution resulted in precipitation of the presumptive triflate analogue **4**, which was isolated in 78% yield.

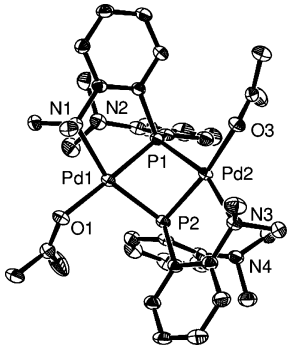

Figure 3. ORTEP diagram for 3·C_6H_6 shown with 50% displacement ellipsoids. Hydrogen atoms have been removed for clarity. Selected interatomic distances (Å) and angles (deg): Pd1–P1, 2.2091(8); Pd1–P2, 2.2670(8); Pd2–P1, 2.2488(8); Pd2–P2, 2.2163(8); P1–Pd1–P2, 75.26(3); Pd1–P1–Pd2, 91.37(3); P1–Pd1–O1, 172.77(6); P2–Pd1–N1, 155.71(6); P1–Pd2–P2, 75.48(3); Pd1–P2–Pd2, 90.70(3); P2–Pd2–O3, 167.16(7); P1–Pd2–N3, 158.96(7).

Attempts to generate a Pd–H complex by the reaction of **2** with $LiEt_3BH$ were not successful and led to the formation of intractable reaction mixtures. However, **2** reacted cleanly with $(C_3H_5)MgCl$ to form the new thermally sensitive allyl–Pd complex **5** (Scheme 1). The X-ray crystal structure of **5** confirms the formation of a phosphido-bridged dimeric η^3-allyl Pd complex that features κ^1-*N*PN coordination (Figure 4). As

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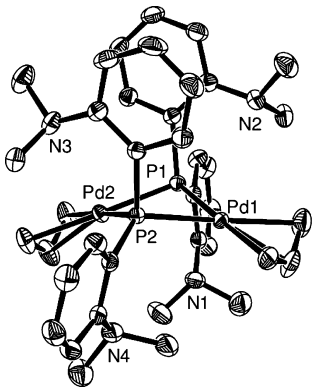

Figure 4. ORTEP diagram for **5** shown with 50% displacement ellipsoids. Hydrogen atoms have been removed for clarity, and only the major component of the disordered allyl fragment is shown. Selected interatomic distances (Å) and angles (deg): Pd1−P1, 2.3418(5); Pd2−P1, 2.3192(5); Pd1−P2, 2.3440(5); Pd2−P2, 2.3181(5); Pd1−C1, 2.205(2); Pd1−C2, 2.154(2); Pd1−C3, 2.177(2); Pd1−P1−Pd2, 96.197(19); P1−Pd2−P2, 78.798(18); Pd1−P2−Pd2, 96.165(19); P1−Pd1−P2, 77.827(18); P1−Pd1−C3, 176.83(6); P2−Pd1−C1, 170.26(8).

in the case of **2** and **3**, the dimer features a puckered Pd_2P_2 core (Pd1···Pd2 = 3.47 Å). However, unlike the former complexes, η^3-allyl coordination in **5** results in a κ^1-*NPN* bonding motif in which both N-donor fragments remain uncoordinated to Pd.

The room-temperature ^{1}H NMR spectrum of **5** (toluene-d_8) features broad resonances that are consistent with fluxional character. A single broad resonance corresponding to the ligand dimethylamino protons is observed at 2.52 ppm, and a broad resonance corresponding to the terminal allylic protons is observed at 3.09 ppm. When the solution was cooled to −50 °C, the resonance corresponding to the dimethylamino protons decoalesced into two resonances at 2.71 and 2.30 ppm (ca. 1:1 ratio). Line-shape changes were also observed for the allylic protons upon cooling; however, these resonances remained quite broad down to −80 °C and exhibited substantial overlap with each other as well as with the resonances corresponding to the dimethylamino protons, and as such we are unable to comment definitively on the nature of the dynamic properties of **5**. Complex **5** decomposed in room-temperature benzene solution over the course of several hours to form a mixture of unidentified products (^{1}H, ^{31}P NMR).

The utility of (PCP)Pd^{II} pincer complexes as catalysts in C−C coupling reactions is well-established,[2a,b,9] and amido-centered monomeric (PNP)Pd^{II} complexes have also recently been shown to act as effective precatalysts for the Heck arylation of olefins.[10,11] In a preliminary effort to assess the catalytic efficacy of dimeric (κ^2-*NPN*)Pd^{II} phosphido species such as **2**−**4**, the utility of these complexes as precatalysts in the Heck coupling of aryl halides and ethyl acrylate was probed (eq 1). Catalytic runs were carried out at Pd loadings of 0.5 mol % (0.25 mol % of precatalyst) between 110 and 140 °C and for reaction times ranging from 2 to 20 h. As a control, no degradation was observed (^{31}P NMR) after heating **2** at 140 °C for over 14 h under the catalytic reaction conditions. Selected catalytic results are given in Table 2.

The coupling of ethyl acrylate and substituted iodo-, bromo-, and chloroarenes was investigated in the course of these studies. With 4-iodonitrobenzene, conversions of >98% were achieved after 5 h at 140 °C using **2**, **3**, or **4** as the precatalyst, and the

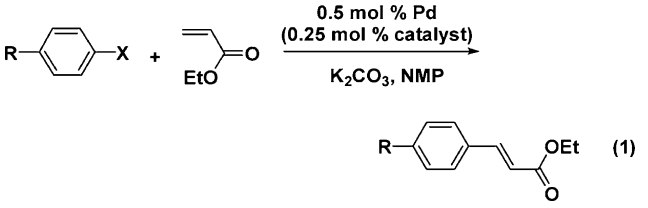

Table 2. Catalytic Performance of 2−4 in the Heck Arylation of Ethyl Acrylate

entry	cat.[a]	X	R	temp (°C)	time (h)	yield (%)[b]
1	**2**	I	NO_2	110	10	>98
2	**2**	I	NO_2	140	5	>98
3	**2**	I	NO_2	140	2	62
4	**2**	I	Me	110	20	>98
5	**2**	I	Me	140	10	>98
6	**2**	Br	NO_2	110	20	>98
7	**2**	Br	NO_2	110	10	91
8	**2**	Br	Me	110	20	20
9	**2**	Br	Me	140	10	>98
10	**2**	Cl	NO_2	140	10	87
11	**2**	Cl	Me	140	20	0
12	**3**	I	NO_2	140	5	>98
13	**4**	I	NO_2	140	5	>98

[a]0.5 mol % Pd (0.25 mol % catalyst). [b]Determined on the basis of ^{1}H NMR data; no conversion was observed in the absence of catalyst.

desired Heck coupling product was the only arene-containing product formed on the basis of ^{1}H NMR spectroscopic analysis of the crude reaction mixtures. Similarly high conversions were observed when using 4-iodotoluene after either 20 h at 110 °C or 10 h at 140 °C, using **2** as the precatalyst. With 4-bromonitrobenzene, >90% conversions to the desired Heck product were observed under similar reaction conditions. By comparison, the coupling of 4-bromotoluene and ethyl acrylate required heating to 140 °C in order to attain high conversions. For the significantly less reactive 4-chloronitrobenzene, 87% conversion was obtained after 10 h at 140 °C, while the relatively deactivated substrate 4-chlorotoluene gave no conversion even after heating for 20 h at 140 °C. Attempts to couple ethyl acrylate and bromobenzene under these reaction conditions using **2** as the catalyst resulted in nearly exclusive formation of biphenyl (^{1}H NMR), presumably arising from homocoupling of bromobenzene. In addition, attempts to reduce the catalyst loading to 0.1 and 0.05 mol % of Pd in the coupling of ethyl acrylate and 4-iodonitrobenzene resulted in the formation of nitrobenzene (^{1}H NMR; > 98% conversion to nitrobenzene after 20 h at 140 °C using **2** as the catalyst at a loading of 0.05 mol % Pd). Overall, the performance of [(κ^2-*NPN*)PdX]$_2$ complexes as precatalysts for the Heck arylation of olefins was comparable to that previously determined for related monomeric (κ^3-PNP)PdX complexes, as reported by Ozerov and co-workers.[10a] While compounds **2**−**4** are clearly dinuclear species in the solid state (as evidenced by the crystal structures of **2** and **3**), it is not currently known whether mononuclear variants of these compounds play a role in the generation of catalytically active Pd species in situ.

In an effort to further explore the coordination chemistry of NPN-type ligation, we considered that the precoordination of a Lewis acid to the phosphido donor might encourage the formation of monomeric (κ^3-NPN)Pd complexes. In this regard, treatment of **1** with KCH_2Ph followed by BPh_3 led to

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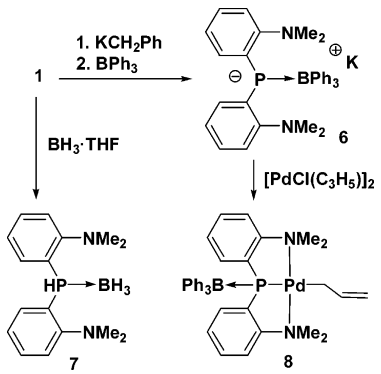
the formation of the BPh_3 adduct **6** (Scheme 2). The ^1H NMR spectrum of **6** (benzene-d_6) is consistent with the formation of

Scheme 2. Synthesis of Compounds 6−8



a phosphido species, as indicated by the disappearance of the P−*H* resonance in **1**, and is consistent with the formation of a 1:1 (NPN)·BPh_3 adduct. The observation of a single ^1H NMR resonance corresponding to the NMe_2 protons in **6** (2.25 ppm) supports a formulation where BPh_3 is coordinated to the phosphido P atom, rather than to an NMe_2 group. The $^{31}P\{^1H\}$ NMR spectrum of **6** features a resonance at −36.4 ppm, while the $^{11}B\{^1H\}$ NMR spectrum features a slightly broad resonance at −6.0 ppm (cf. free BPh_3 at 68.0 ppm).[12] On the basis of these NMR data we tentatively formulate **6** as an adduct of the type $[N(P{\cdot}BPh_3)N]K$ that features coordination of the phosphido group to boron. Although we were unable to obtain X-ray-quality crystals of **6**, we were able to crystallographically characterize the related complex $[N(P{\cdot}BH_3)N]H$ (**7**), which was prepared by treatment of **1** with $BH_3{\cdot}THF$ (Scheme 2). The solid-state structure of **7** (Figure 5) confirmed

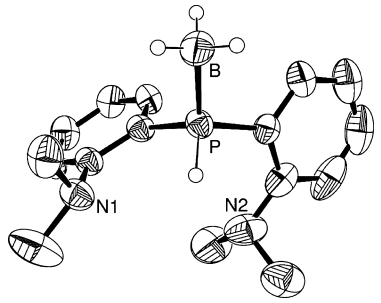


Figure 5. ORTEP diagram for **7** shown with 50% displacement ellipsoids. Selected hydrogen atoms have been removed for clarity.

the preferential coordination of the NPN ligand phosphorus to BH_3.

Treatment of **6** with $^1/_2$ equiv of $[PdCl(C_3H_5)]_2$ led to the formation of the new Pd allyl complex **8** (Scheme 2). Complex **8** is formulated as $[\kappa^3\text{-}N(P{\cdot}BPh_3)N]Pd(\eta^1\text{-}C_3H_5)$ on the basis of solution NMR characterization. The ^1H NMR spectrum of **8** (benzene-d_6) is consistent with a 1:1 (NPN)·BPh_3 adduct. The $^{11}B\{^1H\}$ NMR spectrum of **8** features a broadened resonance at 16.5 ppm, which is consistent with coordinated BPh_3 (vide supra). The η^1 coordination of the allyl ligand is supported by the observation of the allyl ^{13}C NMR resonances (benzene-d_6) at 132.6, 118.3 (d, J_{CP} = 12 Hz), and 32.8 ppm (d, J_{CP} = 17 Hz).[13] Such η^1-allyl coordination is consistent with the formation of a $[\kappa^3\text{-}N(P{\cdot}BPh_3)N]Pd$ species, as alternative formulations, including $[\kappa^2\text{-}N(P{\cdot}BPh_3)N]Pd(C_3H_5)$ and the dinuclear, phosphido-bridged complex $\{[\kappa^1\text{-}(N{\cdot}BPh_3)PN]Pd(C_3H_5)\}_2$, require η^3-allyl coordination in order to achieve a 16-electron configuration. The coordination of the allyl fragment to Pd rather than B is supported by the observation of C−P coupling, which is consistent with coordination of both the NPN ligand and the allyl ligand to Pd. The isolation of **8** establishes the coordination of a Lewis acid to the phosphido donor of the NPN ligand as a viable strategy for encouraging the formation of mononuclear complexes of such multidentate phosphido ligands.

SUMMARY AND CONCLUSIONS

The facile synthesis of a phosphine precursor to an NPN diaminophosphido ligand has been accomplished, and preliminary coordination chemistry studies with Pd have been conducted. In the course of these studies $[(2\text{-}Me_2NC_6H_4)_2P]^-$ ligation has been shown to support monodentate and bidentate coordination complexes of Pd^{II}. Complexes of the type $[(\kappa^2\text{-}NPN)PdX]_2$ (X = Cl, OAc, OTf) serve as precatalysts for the Heck arylation of ethyl acrylate and exhibit catalytic performance that is comparable (on a per-Pd basis) to that of related monomeric $(\kappa^3\text{-}PNP)PdX$ species. In solution these dinuclear complexes exhibit dynamic behavior, likely resulting from exchange of free and bound NMe_2 ligand arms. The complex $[(\kappa^2\text{-}NPN)PdCl]_2$ serves as a precursor for the η^3-allyl species $[(\kappa^1\text{-}NPN)Pd(\eta^3\text{-}C_3H_5)]_2$, in which η^3-allyl coordination has displaced an NMe_2 donor from the Pd coordination sphere. This phenomenon is in contrast to the κ^2-*NPN* binding mode observed for the acetate complex **3**, which features monodentate acetate ligands, and likely reflects the more favorable interaction between the electron-rich Pd center and the η^3-allyl ligand relative to the hard acetate ligands. In an effort to discourage the formation of phosphido-bridged dinuclear complexes, precoordination of BPh_3 to NPN was pursued. Upon reaction of $[N(P{\cdot}BPh_3)N]K$ with $[PdCl(C_3H_5)]_2$, the η^1-allyl complex $[\kappa^3\text{-}N(P{\cdot}BPh_3)N]Pd(\eta^1\text{-}C_3H_5)$ (**8**) was isolated, which establishes the coordination of a Lewis acid to the phosphido donor of the NPN ligand as a viable strategy for encouraging the formation of mononuclear κ^3-*NPN* complexes. These studies establish the versatility of NPN^- ligation, which has proven capable of adopting κ^1-, κ^2-, and pincer-like κ^3-NPN binding motifs.

EXPERIMENTAL SECTION

General Considerations. All experiments were conducted under nitrogen in an MBraun glovebox or using standard Schlenk techniques. Dry, oxygen-free solvents were used unless otherwise indicated. All nondeuterated solvents were deoxygenated and dried by sparging with nitrogen and subsequent passage through a double-column solvent purification system provided by MBraun Inc. Tetrahydrofuran and diethyl ether were purified over two activated alumina columns, while benzene and pentane were purified over one activated alumina column and one column packed with activated Q-5. All purified solvents were stored over 4 Å molecular sieves. Benzene-d_6, toluene-d_8, and methylene chloride-d_2 were degassed via three freeze−pump−thaw cycles and stored over 4 Å molecular sieves. The compounds $[(C_3H_5)PdCl]_2$ and $[Pd(OAc)_2]_3$ were purchased from Strem and used as received. 2-Lithio-*N*,*N*-dimethylaniline[14a] and KCH_2Ph[14b] were prepared according to previously published procedures. $LiAlH_4$ was purified by extraction into Et_2O, followed by filtration to remove insoluble components. Distilled water was deoxygenated by sparging with nitrogen for ca. 40 min. All other reagents were purchased from Aldrich and used without further purification. Unless otherwise stated,

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^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 202.5, and 160.5 MHz (respectively), with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H and ^{13}C), 85% H_3PO_4 in D_2O (for ^{31}P), or $BF_3{\cdot}OEt_2$ (for ^{11}B). Variable-temperature NMR data were collected on a Bruker AC-250 spectrometer. ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{13}C-DEPT, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC NMR experiments. In some cases, fewer than expected unique ^{13}C NMR resonances were observed, despite prolonged acquisition times. Elemental analyses were performed by Desert Analytics, Inc. of Tucson, AZ, and Canadian Microanalytical Service Ltd. of Delta, British Columbia, Canada.

(NPN)H (1). A solution of 2-lithio-*N*,*N*-dimethylaniline (4.13 g, 32.5 mmol) in ca. 50 mL of Et_2O was added dropwise via cannula to a precooled (−78 °C), stirred solution of PCl_3 (1.42 mL, 2.23 g, 16.3 mmol) in ca. 50 mL of Et_2O. The resulting reaction mixture was warmed to room temperature over the course of 3 h. An off-white precipitate formed during this time. The reaction mixture was cooled once again to −78 °C, and a solution of $LiAlH_4$ (0.65 g, 17.0 mmol) in ca. 30 mL of Et_2O was added via cannula. The reaction mixture was warmed to room temperature and stirred for an additional 4 h. The mixture was then cooled to 0 °C, and the reaction was quenched by dropwise addition of 40 mL of degassed water. The organic fraction was cannula transferred away from the aqueous layer, which was extracted with diethyl ether (2 × 100 mL). All organic fractions were combined and dried over anhydrous $MgSO_4$ under a nitrogen atmosphere. Following filtration, the volatile components were removed in vacuo, affording the target compound (3.50 g, 79%) as a colorless oil that solidified upon standing at −35 °C. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.34 (m, 2 H, H_{arom}), 7.11 (m, 2 H, H_{arom}), 6.94 (m, 2 H, H_{arom}), 6.85 (t, 2 H, H_{arom}, J = 7 Hz), 5.52 (d, 1 H, PH, $^{1}J_{PH}$ = 221 Hz), 2.56 (s, 12 H, NMe_2). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 158.1 (d, C_{arom}, J_{CP} = 14 Hz), 136.4 (d, CH_{arom}, J_{CP} = 4 Hz), 133.2 (d, C_{arom}, J_{CP} = 13 Hz), 129.9 (CH_{arom}), 124.6 (CH_{arom}), 120.4 (CH_{arom}), 45.6 (NMe_2). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ −59.3. Anal. Calcd for $C_{16}H_{21}N_2P$: C, 70.57; H, 7.77; N, 10.29. Found: C, 70.85; H, 7.72; N, 10.51.

[(κ^2-*NPN*)PdCl]$_2$ (2). A room-temperature solution of **1** (0.20 g, 0.74 mmol) in ca. 5 mL of benzene was added to a room-temperature solution of $[(C_3H_5)PdCl]_2$ (0.13 g, 0.37 mmol) in ca. 2 mL of benzene. The resulting orange solution was transferred to a 250 mL thick-walled resealable Schlenk tube adapted with a Teflon stopcock, and the reaction mixture was heated at 65 °C for 2.5 h. The formation of a red crystalline precipitate was observed. The reaction mixture was cooled to room temperature, and in the glovebox, the supernatant solution was removed by pipet. The remaining crystalline residue was washed with pentane (3 × 5 mL) and subsequently dried in vacuo to give **2** as a microcrystalline red-orange solid (0.29 g, 96%). ^{1}H NMR (500 MHz, methylene chloride-d_2): δ 8.02 (m, 2 H, H_{arom}), 7.35−7.29 (4 H, H_{arom}), 7.00 (t, 2 H, H_{arom}, J = 7 Hz), 2.76 (s, 12 H, NMe_2). ^{13}C{^{1}H} NMR (125.8 MHz, methylene chloride-d_2): δ 158.3 (C_{arom}), 139.7 (m, CH_{arom}), 132.6 (CH_{arom}), 132.4 (apparent t, C_{arom}, J_{CP} = 18 Hz), 126.7 (CH_{arom}), 122.9 (CH_{arom}), 49.2 (NMe_2). ^{31}P{^{1}H} NMR (202.5 MHz, methylene chloride-d_2): δ −54.0. Anal. Calcd for $C_{32}H_{40}Cl_2N_4P_2Pd_2$: C, 46.51; H, 4.88; N, 6.78. Found: C, 46.49; H, 4.75; N, 6.58. A single crystal of **2** suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

[(κ^2-*NPN*)PdOAc]$_2$ (3). A room-temperature solution of **1** (0.15 g, 0.55 mmol) in ca. 5 mL of benzene was added to a room-temperature solution of $[Pd(OAc)_2]_3$ (0.12 g, 0.18 mmol) in ca. 2 mL of benzene. The resulting bright orange solution was allowed to stand at room temperature for 20 min. The volatile components were removed in vacuo, and the remaining residue was washed with pentane (3 × 5 mL) and dried in vacuo to afford **3** as a bright yellow-orange solid (0.23 g, 98%). ^{1}H NMR (500 MHz, benzene-d_6): δ 8.38 (br s, 2 H, H_{arom}), 6.88 (t, 2 H, H_{arom}, J = 7 Hz), 6.80 (t, 2 H, H_{arom}, J = 7 Hz), 6.74 (d, 2 H, H_{arom}, J = 8 Hz), 2.60 (s, 12 H, NMe_2), 2.13 (s, 3 H, CH_3CO_2). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 175.8 (CH_3CO_2), 158.2 (C_{arom}), 139.7 (CH_{arom}), 132.8 (m, C_{arom}), 131.5 (CH_{arom}), 126.9 (CH_{arom}), 123.3 (CH_{arom}), 48.8 (NMe_2), 23.5 (CH_3CO_2). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ −52.0. Anal. Calcd for $C_{36}H_{46}N_4O_4P_2Pd_2$: C, 49.50; H, 5.31; N, 6.41. Found: C, 50.03; H, 5.56; N, 5.66. A single crystal of **3**·C_6H_6 suitable for X-ray diffraction analysis was grown from benzene solution at room temperature.

[(κ^2-*NPN*)PdOTf]$_2$ (4). Neat Me_3SiOTf (0.083 mL, 0.10 g, 0.46 mmol) was added via syringe to a room-temperature solution of **3** (0.20 g, 0.23 mmol) in ca. 5 mL of benzene. A yellow precipitate formed immediately upon addition. The resulting reaction mixture was stirred at room temperature for 30 min. The volatile components were then removed in vacuo, and the remaining residue was washed with benzene (5 mL), followed by pentane (3 × 7 mL), and dried in vacuo to afford **4** as a yellow solid (0.19 g, 78%). ^{1}H NMR (250 MHz, methylene chloride-d_2): δ 8.00 (m, 2 H, H_{arom}), 7.45 − 7.35 (4 H, H_{arom}), 7.01 (m, 2 H, H_{arom}), 2.75 (s, 12 H, NMe_2). ^{13}C{^{1}H} NMR (125.8 MHz, methylene chloride-d_2): δ 158.0 (C_{arom}), 138.9 (CH_{arom}), 133.9 (m, CH_{arom}), 129.8 (C_{arom}), 127.6 (m, CH_{arom}), 123.3 (m, CH_{arom}), 49.0 (NMe_2). ^{31}P{^{1}H} NMR (101.3 MHz, methylene chloride-d_2): δ −31.3. ^{19}F{^{1}H} NMR (235.4 MHz, methylene chloride-d_2): δ −77.2. Anal. Calcd for $C_{34}H_{40}F_6N_4O_6P_2Pd_2S_2$: C, 38.76; H, 3.83; N, 5.32. Found: C, 38.77; H, 3.73; N, 5.12.

[(κ^1-*NPN*)Pd(η^3-C_3H_5)]$_2$ (5). A precooled (−30 °C) solution of **2** (0.14 g, 0.17 mmol) in ca. 5 mL of THF was treated with $(C_3H_5)MgCl$ (2.0 M in THF, 0.17 mL, 0.34 mmol). The resulting reaction mixture was warmed to room temperature over the course of 25 min. The volatile components were removed in vacuo, and the remaining residue was extracted into benzene (ca. 10 mL). The benzene extract was filtered through Celite and evaporated to dryness to afford a yellow solid that was recrystallized from ca. 10 mL of Et_2O at −30 °C to afford **5** (0.12 g, 87%) as a yellow microcrystalline solid. ^{1}H NMR (500 MHz, toluene-d_8): δ 7.68 (br s, 2 H, H_{arom}), 6.95 (m, 2 H, H_{arom}), 6.80 (m, 2 H, H_{arom}), 6.63 (m, 2 H, H_{arom}), 5.13 (quin, 1 H, η^3-C_3H_5, J = 10 Hz), 3.09 (br s, 4 H, η^3-C_3H_5), 2.52 (br s, 12 H, NMe_2). ^{13}C{^{1}H} NMR (125.8 MHz, toluene-d_8): δ 128.4 (CH_{arom}), 122.8 (CH_{arom}), 120.1 (CH_{arom}), 117.0 (t, η^3-C_3H_5, J = 5 Hz), 46.2 (NMe_2). ^{31}P{^{1}H} NMR (202.5 MHz, methylene chloride-d_2): δ −103.1. Repeated attempts to obtain satisfactory elemental analysis for **5** were not successful, likely due to the thermally sensitive nature of this compound. A single crystal of **5** suitable for X-ray diffraction analysis was grown from Et_2O solution at −30 °C.

[N(P·BPh$_3$)N]K (6). A precooled (−30 °C) solution of **1** (0.20 g, 0.74 mmol) in ca. 7 mL of THF was treated with a precooled (−30 °C) solution of KCH_2Ph (0.096 g, 0.74 mmol) in ca. 3 mL of THF. The resulting red-orange solution was warmed to room temperature over the course of 20 min. The reaction mixture was cooled to −30 °C, and a solution of BPh_3 (0.18 g, 0.74 mmol) in ca. 3 mL of THF was added, resulting in a color change to bright yellow. The reaction mixture was warmed to room temperature over the course of 20 min. The volatile components of the reaction mixture were removed in vacuo to afford a yellow solid that was washed with pentane (5 × 5 mL) to give **6** (0.36 g, 88%) as a bright yellow powder. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.70 (d, 6 H, BPh_{ortho}), 7.32 (m, 2 H, H_{arom}), 7.06 (t, 6 H, BPh_{meta}, J = 7 Hz), 6.91 − 6.80 (7 H, BPh_{para} + H_{arom}), 6.59 (t, 2 H, H_{arom}, J = 7 Hz), 2.25 (s, 12 H, NMe_2). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 158.1 (d, C_{arom}, J = 16 Hz), 141.5 (d, C_{arom}, J = 20 Hz), 139.0 (CH_{arom}), 136.1 (d, BPh_{ortho}, J = 9 Hz), 127.9 (BPh_{ipso}), 127.5 (BPh_{meta} + CH_{arom}), 123.9 (BPh_{para}), 123.7 (CH_{arom}), 119.7 (CH_{arom}), 46.0 (NMe_2). ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6): δ −36.4. ^{11}B{^{1}H} NMR (160.5 MHz, benzene-d_6): δ −6.0 (br s). Anal. Calcd for $C_{34}H_{35}BKN_2P$: C, 73.91; H, 6.38; N 5.07. Found: C, 73.59; H, 6.58; N, 4.77.

[N(P·BH$_3$)N]H (7). A solution of **1** (0.10 g, 0.37 mmol) in ca. 5 mL of THF was treated with $BH_3{\cdot}THF$ (1.0 M in THF, 0.37 mL, 0.37 mmol). The reaction mixture was allowed to stand at room temperature for 1 h. The volatile components of the reaction mixture were subsequently removed in vacuo to afford **7** (0.10 g, 98%) as a white solid. ^{1}H NMR (500 MHz, benzene-d_8): δ 7.79 (m, 2 H, H_{arom}), 7.06 (d of quart, 1 H, PH, $^{1}J_{PH}$ = 410 Hz, $^{3}J_{HH}$ = 7 Hz), 7.04 (t, 2 H, H_{arom}, J = 8 Hz), 6.84 − 6.81 (4 H, H_{arom}), 2.21 (s, 12 H, NMe_2), 2.07 (br m, 3 H, BH_3). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6): δ 157.6

(C_{arom}), 135.2 (d, CH_{arom}, J = 13 Hz), 132,5 (CH_{arom}). 127.6 (C_{arom}), 125.5 (d, CH_{arom}, J = 12 Hz), 122.2 (d, CH_{arom}, J = 5 Hz), 45.7 (NMe_2). $^{31}P\{^1H\}$ NMR (202.5 MHz, benzene-d_6): δ −23.2 (d, $^1J_{PB}$ = 56 Hz). $^{11}B\{^1H\}$ NMR (160.5 MHz, benzene-d_6): δ −37.8. Anal. Calcd for $C_{16}H_{24}BN_2P$: C, 67.16; H, 8.45; N 9.79. Found: C, 67.35; H, 8.37; N, 9.70. A single crystal of **7** suitable for X-ray diffraction analysis was grown from Et_2O solution at −30 °C.

[κ^3-*N*(*P*·BPh_3)*N*]Pd(η^1-C_3H_5) (8). A solution of **6** (0.10 g, 0.18 mmol) in ca. 5 mL of benzene was treated with a solution of $[Pd(C_3H_5)Cl]_2$ (0.033 g, 0.090 mmol) in ca. 2 mL of benzene. The resulting dark red reaction mixture was allowed to stand at room temperature for 5 min. The reaction mixture was filtered through Celite, and the volatile components were removed in vacuo. The remaining residue was extracted into Et_2O (ca. 10 mL), and the Et_2O extracts were filtered through Celite to afford a dark red solution that was concentrated in vacuo to ca. 5 mL and refrigerated at −30 °C to give **8** (0.054 g, 45%) as a dark red microcrystalline solid. ^1H NMR (500 MHz, benzene-d_8): δ 7.57 (m, 6 H, BPh_{ortho}), 7.26−7.19 (9 H, BPh_{meta} + BPh_{para}), 6.99 (m, 2 H, H_{arom}), 6.88 (m, 2 H, H_{arom}), 6.75 (m, 4 H, H_{arom}), 5.62 (m, 1 H, η^1-C_3H_5), 4.55 (m, 1 H, η^1-C_3H_5), 4.45 (m, 1 H, η^1-C_3H_5), 2.58 (m, 2 H, η^1-C_3H_5), 1.98 (s, 12 H, NMe_2). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 157.5 (d, C_{arom}, J = 13 Hz), 142.2 (BPh_{ipso}), 137.0 (d, C_{arom}, J = 38 Hz), 132.6 (η^1-C_3H_5), 132.0 (BPh_{ortho}), 131.8 (CH_{arom}), 130.6 (CH_{arom}), 127.9 (BPh_{meta}), 126.7 (d, CH_{arom}, J = 5 Hz), 126.1 (BPh_{para}), 123.4 (CH_{arom}), 118.3 (d, η^1-C_3H_5, J_{CP} = 12 Hz), 47.5 (NMe_2), 32.8 (d, η^1-C_3H_5, J_{CP} = 17 Hz). $^{31}P\{^1H\}$ NMR (202.5 MHz, benzene-d_6): δ −0.8. $^{11}B\{^1H\}$ NMR (160.5 MHz, benzene-d_6): δ 16.5 (br s). Anal. Calcd for $C_{37}H_{40}BN_2PPd$: C, 67.24; H, 6.10; N 4.24. Found: C, 66.95; H, 5.74; N, 4.38.

Crystallographic Solution and Refinement Details. Crystallographic data for **2**, **3**·C_6H_6, **5**, and **7** were obtained at 193(±2) K on either a Bruker PLATFORM/SMART 1000 CCD diffractometer or a Bruker D8/APEX II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction (including SAINT) were supplied by Bruker. Gaussian integration (face-indexed) was employed as the absorption correction method for **3**·C_6H_6 and **5**, while for **2** and **7** SADABS (Bruker) was employed as the absorption correction method. For both **2** and **3**·C_6H_6, the structure was solved by use of the Patterson search/structure expansion, whereas direct methods were employed for **5** and **7**. All structures were refined by use of full-matrix least-squares procedures (on F^2) with R1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. During the structure solution process for **2**, two crystallographically independent half-molecules of the target complex were located in the asymmetric unit and refined in a satisfactory manner; for simplicity, discussion of metrical parameters is limited to one of the crystallographically independent half-molecules. During the structure solution process for **3**·C_6H_6, attempts to refine peaks of residual electron density as solvent benzene carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure[15] as implemented in PLATON.[16] A total solvent-accessible void volume of 374.8 Å^3 with a total electron count of 99 (consistent with two molecules of solvent benzene or one molecule per formula unit of **3**) was found in the unit cell. During the structure solution process for **5**, one of the allyl fragments was found to exhibit a conformational disorder that was modeled in a satisfactory manner by using a 55:45 split occupancy. Distances within the two conformers of the disordered allyl group in **5** were constrained to be equal (within 0.01 Å) during refinement: d(C4A−C5A) = d(C4B−C5B); d(C5A−C6A) = d(C5B−C6B); d(C4A···C6A) = d(C4B···C6B). Disorder within the dimethylamino fragments in **7** were modeled in a satisfactory manner by using a 65:35 split occupancy; the N1−C17A, N1−C18A, N1−C17B, N1−C18B, N2−C27A, N2−C28A, N2−C27B, and N2−C28B bond lengths were constrained to be equal (within 0.05 Å) during refinement.

Representative Procedure for the Catalytic Heck Arylation of Ethyl Acrylate. All catalytic runs were conducted under a nitrogen atmosphere in 100 mL resealable Schlenk tubes adapted with a Teflon stopcock. The Pd catalyst **2** (2.1 mg, 0.005 mmol), K_2CO_3 (0.21 g, 1.5 mmol), haloarene (1.00 mmol), and ethyl acrylate (0.14 mL, 1.3 mmol) were dissolved in 3 mL of *N*-methylpyrrolidone in a reaction tube containing a magnetic stir bar. The reaction vessel was placed in a temperature-controlled oil bath set at the desired temperature. Conversions were determined on the basis of ^1H NMR spectroscopic data (average of at least two runs).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving single-crystal X-ray diffraction data for **2**, **3**·C_6H_6, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: laura.turculet@dal.ca. Fax: 1-902-494-1310. Tel: 1-902-494-7190.

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