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Oxidative Addition of N−C and N−H Bonds to Zerovalent Nickel, Palladium, and Platinum

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Reactions of chelating pincer-type PNP ligands based on the bis(*ortho*-phosphinoaryl)amine substructure and containing either an N−H (PN(H)P, **1**) or N−Me (PN(Me)P, **2**) central moiety with group 10 complexes have been explored. Reactions with MCl_2 (MCl_2 = $NiCl_2$, (COD)$PdCl_2$, (COD)$PtCl_2$, COD = 1,5-cyclooctadiene) proceed readily with the loss of either HCl or MeCl and the formation of (PNP)MCl (**7**) where PNP is an anionic, meridional amido-PNP ligand. Alkylation of (PNP)MeCl with MeMgCl gives (PNP)MMe (**9**), and reaction of (PNP)MCl with excess $NaBH_4$ provides (PNP)MH (**8**). (PNP)MH (**8**) compounds react with $CDCl_3$ to regenerate (PNP)MCl (**7**). The transformations **7** → **8** → **7** → **9** are sluggish for M = Pt compared with M = Ni or Pd. Solid-state structures of (PNP)PdH (**8b-Pd**) and (PNP)PdMe (**9b-Pd**) were determined. The environment about Pd in either structure is approximately square planar with a meridional amido-PNP ligand. Reactions of **1** and **2** with L_nM^0 (L_n = $(COD)_2$, $(PPh_3)_4$, $(PBu^t{}_3)_2$) proceed in some cases via N−H or N−C oxidative addition to give either (PNP)MH (**8**) or (PNP)MMe (**9**). The N−H oxidative addition reactions are more facile. Both the N−H and N-Me oxidative addition reactions are kinetically inhibited by liberated phosphines from the L_nM^0 starting material. Thermolysis of (PNP)MMe (**9**, M = Ni, Pd, Pt) in the presence of excess PPh_3 does not lead to N−C reductive elimination, thus indicating irreversibility of the N−C oxidative addition.

Aromatic amination catalyzed by Ni and Pd complexes has evolved into a powerful synthetic tool over the past decade.[1] The process generally involves the M^0/M^{II} redox pair. Formation of C−N bonds via reductive elimination (RE) from a M^{II} center is a crucial step in this process, and it has received substantial attention.[2] While both RE from Pd^{II} and oxidative addition (OA) to Pd^0 have been demonstrated for the carbon−halogen bond,[1,3] only the RE reactions from Pd^{II} have been reported for the C−N bond.[2] RE of C−N is also a crucial step in Pd-catalyzed allylic amination,[4] while OA of C−N may be involved in hydrodenitrogenation of petroleum.[5] OA of N−H bonds is also of interest, as it may be involved in catalytic processes such as amination of alkenes.[6] Several new reports concerning N−H OA appeared recently, but it remains an underexplored reaction.[7] Only a handful of well-defined examples of OA of N−C bonds of neutral substrates to transition metals is known.[8] A study of well-defined OA of C−N and N−H bonds would be beneficial to the understanding of these important elementary steps.

We have recently begun exploring the chemistry of the new PNP pincer ligand **1** (Scheme 1).[9] Utilization of a related group of Fryzuk ligands $[(R_2PCH_2SiMe_2)N]^-$ has allowed for a number of pioneering findings.[10,11] The design of **1** is intended to provide a (potentially) uninegative PNP ligand that is more rigid and robust than the Fryzuk's $[(R_2PCH_2SiMe_2)N]^-$ ligands and with a backbone devoid of *β*-hydrogens and moisture- and oxo-

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(1) (a) Hartwig, J. F. *Synlett* **1997**, 329. (b) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (d) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (e) Hartwig, J. F. In *Modern Amination Methods*; Ricci, A., Ed.; Wiley-VCH: Weinheim, 2000; p 195. (f) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2001**, *219*, 131.

(2) (a) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344. (b) Yamashita, M.; Cuevas Vicario, J. V.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 16347. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2090. (d) Mann, G.; Hartwig, J. F.; Driver, M. S.; Fernandez-Rivas, C. *J. Am. Chem. Soc.* **1998**, *120*, 827. (e) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (f) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (g) Hartwig, J. F.; Richards, S.; Baranano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626. (h) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 3534. (i) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3921.

(3) (a) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944. (b) Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533. (c) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

(4) (a) Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1. (b) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

(5) Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678, and references within.

(6) (a) Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608. (b) Hong, S.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 7886. (c) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.

(7) Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13644, and references therein. See also ref 12c.

(8) (a) Lin, B. L.; Clough, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 2890. (b) Torrent, M.; Musaev, D. G.; Morokuma, K. *Organometallics* **2000**, *19*, 4402. (c) Tayebani, M.; Gambarotta, S.; Yap, G. *Organometallics* **1998**, *17*, 3639. (d) Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132. (e) Chan, Y. W.; Renner, M. W.; Balch, A. L. *Organometallics* **1983**, *2*, 1888. (f) Gandelman, M.; Milstein, D. *Chem. Commun.* **2000**, 1603. (g) C=N bond cleavages are more common, see ref 8d for references. (h) An example of Pd-catalyzed C−N cleavage is the deallylation at N; however for neutral compounds it works only when N bears strongly electron-withdrawing groups. For a review, see: Guibe, F. *Tetrahedron* **1998**, *54*, 2967. (i) N−C oxidative addition of ammonium and iminium salts to low-valent late transition metals has been described: Aresta, M.; Quaranta, E.; Dibenedetto, A.; Giannoccaro, P.; Tommasi, I.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1997**, *16*, 834.

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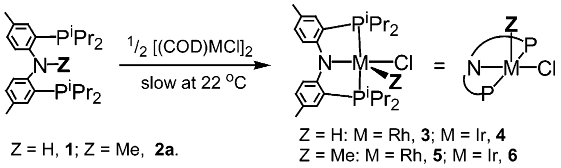
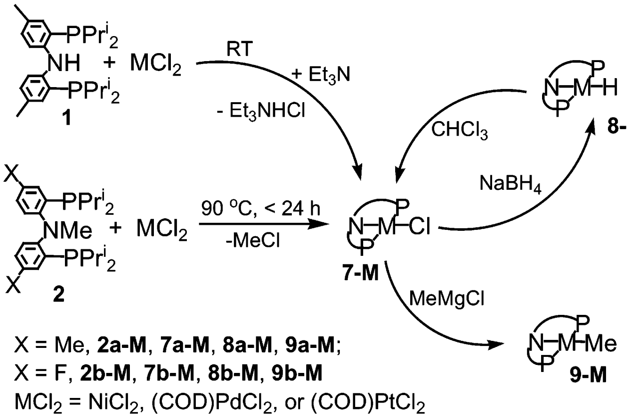
Scheme 1



sensitive functionalities. Two groups have recently reported a PNP ligand similar to **1** and another group: NNN and SNS pincer ligands with a diarylamine backbone.[12,13] We have reported on the chemistry of **1** (or **2**) with Zr, Pd, Rh, and Ir, including the study of the OA of N−C and N−H bonds to Rh^I and Ir^I at ambient temperature (Scheme 1).[9b] The OA reactions in Scheme 1 are topologically similar to the C−H and C−C OA chemistry in the PCP ligand framework.[14] The Pd chemistry reported by us thus far also involved N−H and N−C cleavage reactions, although it is not clear in all instances whether OA steps were involved.[9a,d] Part of the driving force in the N−H and N−C cleavage reactions of **1** and **2** with late transition metals is the preference of the rigid ligand framework for a tridentate, anionic, *mer*-PNP binding mode. We have reasoned that this consideration is also valid for OA of N−H or N−Me of **1** or **2** to zerovalent group 10 metal centers, as the square planar geometry of the products, (PNP)M−H or (PNP)M−Me, matches the preference of the PNP framework. This reasoning has proven to be justified, and we report here our direct observations of oxidative addition of N−H and N−C bonds to zerovalent Ni, Pd, and Pt. To the best of our knowledge, this work is the first example of well-defined OA of N−C bonds in neutral substrates to Pd^0 and Pt^0. It is also worth noting that the C−N OA examples described here involve *unstrained* N−C(sp^3) bonds. OA of N−C bonds to nickel has been described for aziridines,[8a] for N−C(sp^2) bonds in a porphyrin macrocycle,[8e] and for ammonium and iminium salts.[8i]

Catalytic applications of (PNP)MX compounds such as Heck coupling should likely involve (PNP)MR intermediates (M = Ni, Pd, Pt; R = H, hydrocarbyl).[9a,14b,15,16] It has been proposed that the activity of the PCP complexes of Pd^{II} in Heck coupling may stem from the formation of finely divided metallic Pd^0, possibly via some RE reaction from a (PCP)Pd^{II}R complex.[17] Part of our interest in exploring the presently reported chemistry was to examine the likelihood of N−R reductive elimination in (PNP)MR as a potential catalyst deactivation pathway.

Scheme 2



Results and Discussion

Independent Preparation of 7, 8, and 9. Our strategy was to conduct thermal reactions of **1** or **2** with soluble M^0 precursors. We anticipated that the isolation of **8-M** and **9-M**, the anticipated OA products, from such reactions may prove difficult. Therefore we sought to prepare and fully characterize **8-M** and **9-M** by independent means in order to be able to unambiguously identify them spectroscopically in the OA reactions. This was accomplished as outlined in Scheme 2. The transformations **1** → **7**, **2** → **7**, **7** → **8**, and **8** → **7** have been previously reported for M = Pd.[9a,d] Fortuitously, the Ni and Pt analogues behaved similarly and the alkylation (**7** → **9**) proceeded smoothly in all cases. MCl$_2$ precursors reacted with **1** at 22 °C to give **7-M**. For Ni and Pt, **7-M** was observed even before addition of base (closed vessel). The unusually high basicity of the parent Fe and Ru amides has been demonstrated and attributed to the enhancement of basicity at N via $d_\pi - p_\pi$ repulsion.[18] In this light, it is rather remarkable (even taking into account the lower basicity of *diaryl*amide) that the late metal amides **7-M** are not (fully) protonated by HCl. The behavior of **7-M** is also in contrast with that of complexes ((Ph$_2$PCH$_2$SiMe$_2$)$_2$NH)MCl$_2$ (M = Ni, Pd, Pt), which do not spontaneously lose HCl.[10e] We believe that this reflects the strong preference of **1** to bind to the metal as an anionic (upon loss of proton), meridional

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(9) (a) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326. (b) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792. (c) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700. (d) Fan, L.; Yang, L.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4778.

(10) (a) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839−2845. (b) Fryzuk, M. D.; Berg, D. J.; Haddad, T. S. *Coord. Chem. Rev.* **1990**, *99*, 137. (c) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (d) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 6993. (e) Fryzuk, M. D.; Macneil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918−930.

(11) (a) For Re chemistry with the Fryzuk ligand see: Ozerov, O. V.; Huffman, J. C.; Watson, L. A.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 6363, and references within. (b) Ozerov, O. V.; Gerard, H. F.; Watson, L. A.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **2002**, *41*, 5615.

(12) (a) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007. (b) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813. (c) Winter, A. M.; Eichele, K.; Mack, H.-G.; Potuznik, S.; Mayer, H. A.; Kaska, W. C. *J. Organomet. Chem.* **2003**, *682*, 149.

(13) (a) Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 2885. (b) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753. (c) Peters, J. C.; Harkins, S. B.; Brown, S. D.; Day, M. W. *Inorg. Chem.* **2001**, *40*, 5083.

(14) (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406. (d) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774. (e) Sundermann, A.; Uzan, O.; Milstein, D.; Martin, J. M. L. *J. Am. Chem. Soc.* **2000**, *122*, 7095.

(15) (a) Kraatz, H.-B.; Van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Isr. J. Chem.* **2001**, *41*, 163. (b) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619. (b) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (d) Shaw, B. L. *New. J. Chem.* **1998**, *22*, 77. (e) Shaw, B. L.; Perera, S. D.; Staley, E. A. *Chem. Commun.* **1998**, 1361.

(16) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*, Benchtop Edition; Academic Press: London, 1990. (c) Crisp, G. T. *Chem. Soc. Rev.* **1998**, *27*, 427. (d) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(17) Eberhard, M. R. *Org. Lett.* **2004**, *6*, 2125.

(18) (a) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44. (b) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799. (c) Fox, D. J.; Bergman, R. G. *Organometallics* **2004**, *23*, 1656.

Table 1. Selected NMR Data for 7-M, 8-M, and 9-M in C_6D_6, δ ppm

^{31}P NMR	M = Ni	M = Pd	M = Pt
7a-M	34.2	48.2	41.3 (J_{P-Pt} = 2666 Hz)
7b-M	33.6	47.4	40.7 (J_{P-Pt} = 2669 Hz)
8a-M	56.2	59.8	59.3 (J_{P-Pt} = 2781 Hz)
8b-M	56.0	59.2	58.8 (J_{P-Pt} = 2792 Hz)
9a-M	35.4	41.1	41.0 (J_{P-Pt} = 2840 Hz)
9b-M	35.4	40.8	40.9 (J_{P-Pt} = 2855 Hz)

^{19}F NMR	M = Ni	M = Pd	M = Pt
7b-M	−130.4	−130.3	−130.1
8b-M	−132.8	−132.9	−132.5
9b-M	−132.7	−132.9	−132.6

^1H NMR	M = Ni	M = Pd	M = Pt
8a-M, M−*H*	−18.43 (J_{H-P} = 64 Hz)	−10.33 (J_{H-P} = 6 Hz)	−12.16 (J_{H-P} = 14, J_{H-Pt} = 1017 Hz)
8b-M, M−*H*	−18.67 (J_{H-P} = 64 Hz)	−10.59 (J_{H-P} = 6 Hz)	−12.43 (J_{H-P} = 14, J_{H-Pt} = 1021 Hz)
9a-M, M−C*H₃*	−0.32 (J_{H-P} = 9 Hz)	0.64 (J_{H-P} = 6 Hz)	1.17 (J_{H-P} = 6 Hz)
9b-M, M−C*H₃*	−0.42 (J_{H-P} = 9 Hz)	0.55 (J_{H-P} = 6 Hz)	1.06 (J_{H-P} = 6 Hz)

^{13}C NMR	M = Ni	M = Pd	M = Pt
9a-M, M−CH_3	−25.9 (J_{C-P} = 24 Hz)	−21.0 (J_{C-P} = 7 Hz)	−31.7 (J_{C-P} = 7 Hz, J_{C-Pt} = 588 Hz)
9b-M, M−CH_3	−26.1 (J_{C-P} = 25 Hz)	−21.0 (J_{C-P} = 7 Hz)	−31.9 (J_{C-P} = 7 Hz, J_{C-Pt} = 576 Hz)

PNP ligand because of the prearranged and rigid geometry of the ligand backbone.

The rates of the reactions between **2** and MCl_2 precursors (M = Ni, Pt) in C_6D_6 were generally faster for the more basic **2a** (although they were probably influenced by the solubility of MCl_2). This is similar to our previous observations for Pd.[9d] The mechanistic possibilities for N−C cleavage in the transformation of **2** to **7** for Ni and Pt are the same as those we have previously outlined for Pd.[9d] The details are outside the scope of this report and will be investigated separately.

Compounds **7-M** were converted to the hydrides **8-M** by action of excess $NaBH_4$ in an ^iPrOH/THF mixture. **8-M** reacted with $CDCl_3$ to regenerate **7-M**. **7-M** was alkylated with MeMgCl in THF to give **9-M**. The reactions for M = Ni and Pt were performed in a **1** (or **2**) → **7** → **8** → **7** → **9** sequence on an 80 μmol scale without purification of intermediates, which were nonetheless sufficiently pure for unambiguous NMR analyses. The purity of the crude **9-M** thus synthesized was >95% by NMR. Isolated yields of 40−70% (based on 4 steps from **1** or **2** on an 80 μmol scale) of analytically pure **9-M** were obtained by recrystallization. For all the reactions in the sequence **7** → **8** → **7** → **9** the rates followed the order Pd > Ni ≫ Pt. The sluggishness of the metathetic reactions of **7-Pt** is reminiscent of the early work by Fryzuk et al. where (κ^3-*P*,*N*,*P*-($Ph_2PCH_2SiMe_2)_2N$)MCl underwent alkylation for M = Ni and Pd, but not for M = Pt.[10e]

All compounds **7**−**9** were characterized by ^1H, ^{31}P, ^{13}C, and ^{19}F (where applicable) NMR (Tables 1−5). All compounds displayed C_{2v} symmetry on the NMR time scale, consistent with the approximately square planar geometry about the metal centers. Selected NMR data are presented in Table 1. The ^1H and ^{13}C NMR data unambiguously establish the presence of the M−H functionality in **8** and of the M−CH_3 functionality in **9**. The ^{19}F NMR chemical shifts depend only marginally on the metal, but do show notable dependence on the nature of the ligand *trans* to the amido N. The ^{19}F NMR resonance of **7b-M** is downfield of the resonances of **8b-M** and **9b-M**. The H and Me ligands in **8b-M** and **9b-M** are strong *trans*-influence ligands, while Cl in **7b-M** is not. Consequently, the lone pairs of the N−M σ-bonds are more N-based in **8b-M** and **9b-M** and the amido donor should bear a higher partial negative charge. This makes the diarylamido system more electron rich and is reflected in the increased shielding of the F nuclei.

Table 2. ^1H NMR Data for 7a-M, 8a-M, and 9a-M (only the PNP ligand resonances shown)

no.	CH_{Ar}	CH_{Ar}	CH_{Ar}	CH_{iPr}	Me_{Ar}	Me_{iPr}	Me_{iPr}
7a-Ni	7.50(d, 8)	6.89	6.70(d, 8)	2.21(m)	2.11	1.51(q, 8)	1.25(q, 7)
7a-Pd	7.66(d, 8)	6.82	6.75(d, 8)	2.29(m)	2.12	1.43(q, 7)	1.12(q, 7)
7a-Pt	7.73(d, 8)	6.88	6.74(d, 8)	2.50(m)	2.14	1.42(q, 8)	1.12(q, 8)
8a-Ni	7.82(d, 8)	6.97	6.90(d, 8)	2.05(m)	2.22	1.23(q, 7)	1.04(q, 7)
8a-Pd	7.91(d, 8)	6.92	6.92(d, 8)	2.03(m)	2.22	1.21(q, 7)	0.98(q, 7)
8a-Pt	7.94(d, 8)	6.92	6.91(d, 8)	2.11(m)	2.22	1.18(q, 7)	0.98(q, 7)
9a-Ni	7.71(d, 8)	6.99	6.82(d, 8)	2.05(m)	2.13	1.27(q, 8)	1.15(q, 7)
9a-Pd	7.84(d, 8)	6.92	6.86(d, 8)	2.17(m)	2.20	1.21(q, 8)	0.9(q, 7)
9a-Pt	7.89(d, 8)	6.95	6.86(d, 8)	2.35(m)	2.21	1.23(q, 8)	1.08(q, 7)

Table 3. ^1H NMR Data for 7b-M, 8b-M, and 9b-M (only the PNP ligand resonances shown)

no.	CH_{Ar}	CH_{Ar}	CH_{Ar}	CH_{iPr}	Me_{iPr}	Me_{iPr}
7b-Ni	7.12(m)	6.75(m)	6.57(m)	2.04(m)	1.41(q, 8)	1.09(q, 7)
7b-Pd	7.25(m)	6.67(m)	6.60(m)	2.09(m)	1.29(q, 8)	0.97(q, 8)
7b-Pt	7.36(m)	6.73(m)	6.63(m)	2.31(m)	1.31(q, 8)	0.97(q, 7)
8b-Ni	7.46(m)	6.84(m)	6.76(m)	1.85(m)	1.11(q, 7)	0.89(q, 7)
8b-Pd	7.55(m)	6.81(m)	6.78(m)	1.82(m)	1.09(q, 8)	0.83(q, 8)
8b-Pt	7.58(m)	6.80(m)	6.78(m)	1.91(m)	1.10(q, 8)	0.85(q, 8)
9b-Ni	7.36(m)	6.86(m)	6.69(m)	1.95(m)	1.16(q, 7)	1.00(q, 7)
9b-Pd	7.49(m)	6.80(m)	6.74(m)	1.96(m)	1.10(q, 8)	0.93(q, 8)
9b-Pt	7.54(m)	6.81(m)	6.75(m)	2.14(m)	1.11(q, 8)	0.94(q, 8)

The $^1J_{P-Pt}$ values for **7**,**8**,**9-Pt** are typical of the square planar Pt^{II} complexes with *trans*-phosphines. The $^1J_{H-Pt}$ values in **8-Pt** fit well with the values for other known Pt^{II} hydrides if the *trans*-influence arguments are considered.[19] *trans*-$(Cy_3P)_2PtHX$ compounds represent a useful comparison.[20a] Higher $^1J_{H-Pt}$ values are observed when H is *trans* to a weak *trans*-influence ligand such as a chloride ($^1J_{H-Pt}$ = 1300 Hz) or triflate ($^1J_{H-Pt}$ = 1585 Hz), while lower values correspond to a stronger *trans*-influence X, such as H ($^1J_{H-Pt}$ = 796 Hz) or Ph ($^1J_{H-Pt}$ = 595 Hz).[20] The intermediate $^1J_{H-Pt}$ values in **8-Pt** attest to the amido of the PNP ligand being a donor of *trans*-influence that is intermediate between that of halides and hydrocarbyls (or hydride). The $^1J_{H-Pt}$ value in **8-Pt** is similar to that (1080 Hz) found in *trans*-$((PhCH_2)_3P)_2PtH(OPh)$.[21] The ^1H NMR chemical shift of M−H in **8-M** is sensitive to the nature of M and the order of increasing shielding Pd < Pt < Ni in **8-M** is the same as in the series of *trans*-$(Cy_3P)_2MHCl$ compounds.[20a,22] The origin of the comparatively high J_{HP} and J_{CP} values for **8-Ni** and **9-Ni** is not clear. However, this phenomenon has precedence in the square-planar complexes of group 10 metals. The *cis*-$^2J_{H-P}$ values in

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(19) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; p 6. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 242

(20) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422. (b) $^1J_{H-Pt}$ = 741 Hz in a (PCP)PtH complex where PCP = *o*-$C_6H_3(CH_2PBu^t_2)_2$: Kimmich, B. F. M.; Bullock, R. M. *Organometallics* **2002**, *21*, 1504.

(21) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371.

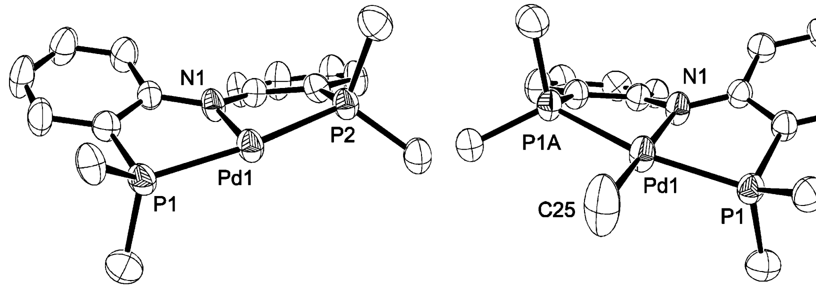


Figure 1. ORTEP drawing (30% probability ellipsoids) of **8b-Pd** (left) and **9b-Pd** (right) showing selected atom labeling.[24] Omitted for clarity: H and F atoms, methyls of the ^{i}Pr groups. Selected bond distances (Å) and angles (deg) follow. **8b-Pd**: Pd1−P1, 2.2619(15); Pd1−P2, 2.2658(15). **9b-Pd**: Pd1−P1, 2.2914(3); Pd1−C25, 2.061(2); N1−Pd1−C25, 179.994.

Table 4. $^{13}C\{^1H\}$ NMR Data for 7a-M, 8a-M, and 9a-M (only the PNP ligand resonances shown)

no.	CN_{Ar}	C_{Ar}	C_{Ar}	C_{Ar}	C_{Ar}	C_{Ar}	CH_{iPr}	Me_{Ar}	Me_{iPr}	Me_{iPr}
7a-Ni	162.3(13)	132.3	131.9	126.1(4)	120.4(18)	116.6	23.9(12)	20.4	18.6	17.7
7a-Pd	162.5(11)	132.9	132.7	126.1(4)	119.7(18)	116.6(4)	25.2(11)	20.5	18.8	18.2
7a-Pt	162.3(10)	132.6	132.3	126.2(4)	119.6(22)	116.2(5)	25.2(15)	20.3	18.2	17.9
8a-Ni	161.8(12)	132.6	132.5	123.5(3)	122.6(17)	114.8(5)	23.7(13)	20.6	19.5(3)	18.4
8a-Pd	161.3(11)	133.4	132.6	123.6(3)	121.8(18)	115.3(6)	24.3(12)	20.5	19.8(4)	18.5
8a-Pt	162.2(10)	133.6	132.5	124.3(4)	122.1(22)	115.6(5)	25.2(16)	20.4	19.7(3)	18.4
9a-Ni	161.9(13)	132.1	131.9	123.4(3)	121.4(18)	115.3(5)	23.8(11)	20.6	18.9	18.0
9a-Pd	161.2(10)	132.7	132.3	123.5(3)	120.8(18)	115.6(5)	24.8(11)	20.6	19.0(2)	18.3
9a-Pt	162.1(10)	132.9	132.2	124.2(3)	121.1(23)	116.0(5)	25.2(15)	20.5	18.6	18.2

Table 5. $^{13}C\{^1H\}$ NMR Data for 7b-M, 8b-M, and 9b-M (only the PNP ligand resonances shown)

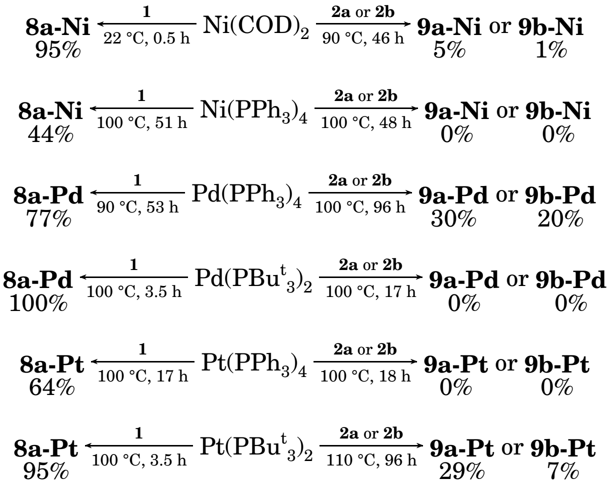
no.	CN_{Ar}	CF_{Ar}	C_{Ar}	C_{Ar}	C_{Ar}	C_{Ar}	CH_{iPr}	Me_{iPr}	Me_{iPr}
7b-Ni	160.4(13)	154.4(5,238)	121.8(18,5)	118.3(0,24)	117.5(0,22)	116.3(6,6)	23.9(12)	18.3	17.4
7b-Pd	160.4(10)	154.6(5,238)	120.6(18,5)	118.5(0,23)	118.1(0,21)	116.0(7,7)	24.9(11)	18.4	17.7
7b-Pt	160.5(10)	155.1(5, 37)	120.8(22,5)	118.1(0,23)	118.0(0,22)	115.7(6,6)	25.1(15)	18.0	17.6
8b-Ni	160.0(13)	153.9(4,237)	123.9(16,4)	118.1(0,21)	118.1(0,21)	114.2(6,6)	23.6(13)	19.2(3)	18.1
8b-Pd	159.5(10)	153.9(4,236)	122.9(17,4)	118.8(0,21)	118.3(0,22)	114.7(6,6)	24.2(13)	19.5(4)	18.2
8b-Pt	160.5(10)	154.3(4,237)	123.2(18,5)	118.9(0,21)	118.1(0,22)	114.8(6,6)	24.9(16)	19.4(2)	18.2
9b-Ni	160.1(12)	153.8(5,236)	122.6(16,5)	117.9(0,22)	117.4(0,21)	114.8(6,6)	23.7(11)	18.7	17.6
9b-Pd	159.5(10)	153.9(4,235)	121.8(18,4)	118.2(0,22)	118.1(0,22)	114.9(6,6)	24.7(11)	18.8	18.0
9b-Pt	160.4(9)	154.3(5,236)	122.1(22,5)	118.3(0,21)	118.0(0,22)	115.2(6,6)	25.1(15)	18.3	17.9

trans-$(Cy_3P)_2MHCl$ are 74 Hz for M = Ni,[22a] 12 Hz for M = Pd,[22b] and 12 Hz for M = Pt.[20a] The *cis*-$^2J_{C(aryl)-P}$ values in (PCP)M−OH compounds (PCP = *o*-$C_6H_3(CH_2PPr^i{}_2)_2$) are 17 Hz for M = Ni and ca. 0 Hz for M = Pd.[23]

X-ray Structural Studies. The solid-state structures of **8b-Pd** and **9b-Pd** were elucidated by X-ray diffraction studies (Figure 1). The hydride ligand in **8b-Pd** could not be reliably located and refined, but its presence is unequivocally established by the solution NMR data. The coordination environment about Pd is approximately square planar in both structures. The deviation from the idealized square planar geometry is primarily caused by the chelate PNP constraint with the P−Pd−P angles of 168.38(5)° in **8b-Pd** and 163.21(2)° in **9b-Pd**. The Pd−N distances in **8b-Pd** (2.086(4) Å) and **9b-Pd** (2.0938(15) Å) are similar to each other and are longer than those in **7a-Pd** (2.0258(19) Å) and in (PNP)Pd−OAc (PNP = deprotonated **1**; 2.015(5) Å). The difference in the Pd−N distances is consistent with the *trans*-influence argument presented above to rationalize the ^{19}F NMR chemical shifts. The molecule of **9b-Pd** lies on a crystallographic C_2 axis.

Oxidative Addition to M^0. We selected several commercially available M^0 compounds for our OA study. $M(PPh_3)_4$ complexes are commercially available for all three group 10 metals. $M(PBu^t{}_3)_2$ for M = Pd, Pt, and $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) were also commercially available and provide a set of ligands that should be displaced more easily than PPh_3. Oxidative addition of N−H in the reaction of **1** with $Pd_2(dba)_3$ has been communicated.[9a] The summary of our results is given in Scheme 3. All reactions were conducted in C_6D_6.

Scheme 3



The reaction mixtures were thermolyzed until either complete conversion to the product or until no further increase in product concentration over time was detected by NMR.The N−H OA was found to be more facile than the N−C OA. The N−H OA was particularly facile in the case of the reaction of **1** with $Ni(COD)_2$. The reactions of **2a** or **2b** with $Ni(PPh_3)_4$ and $Pd(PBu^t{}_3)_2$

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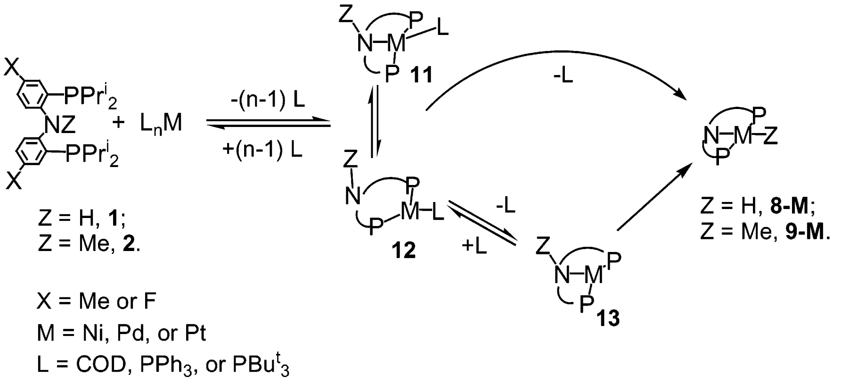
(22) (a) Green, M. L. H.; Saito, T.; Tanfield, P. J. *J. Chem. Soc. A* **1971**, 152. (b) Munakata, H.; Green, M. L. H. *J. Chem. Soc. D: Chem. Commun.* **1970**, 881.

(23) Campora, J.; Palma, P.; Del Rio, D.; Alvarez, E. *Organometallics* **2004**, *23*, 1652.

Scheme 4



led to mixtures of unidentified compounds that contained only traces of **9-Ni** and no **9-Pd**, respectively. Thermolysis of **2a** or **2b** with Pt(PPh$_3$)$_4$ did *not* lead to any NMR-detectable change. In the reaction of **1** with Pt(PPh$_3$)$_4$, an intermediate was observed and tentatively identified as [(**1**)Pd(PPh$_3$)] (**10a-Pd**). Similar intermediates were *not* observed in the reactions involving **2a** or **2b** or the reactions involving M(PBu$^t_3$)$_2$ (M = Pd, Pt). We favor an explanation based on the steric effects; that is, only the smallest combination (i.e., **1** and PPh$_3$, but not **1**/PBu$^t_3$, **2**/PPh$_3$, or **2**/PBu$^t_3$) may bind to the same metal center. This restriction is applicable regardless of whether **1** and **2** bind in the κ^3-*P*,*N*,*P* or the κ^2-*P*,*P* fashion.

The reactions of **2a** and **2b** with Pd(PPh$_3$)$_4$ and Pt(PBu$^t_3$)$_2$ led only to partial conversion to **9-M**. The reaction mixture contained only the reactants and the products (**9-M** and free PR$_3$). Further heating did not affect the composition of the solution. A similar situation was observed in the reactions of **1** with M(PPh$_3$)$_4$ (M = Ni, Pd, Pt), except for the presence of **10**. The incomplete conversion could be observed because either (a) of the establishment of an equilibrium between the reactants and products or (b) the free PPh$_3$ or PBu$^t_3$ released in the reaction shut down the kinetically necessary PR$_3$ dissociation. To test this, we performed thermolyses (18 h, 110 °C) of authentic samples of **9b-Ni**, **9b-Pd**, and **9b-Pt** in the presence of 10 equiv of PPh$_3$ in C$_6$D$_6$. The **9-M** compounds remained intact (within NMR detection limits), ruling out hypothesis (a).

Mechanistic Considerations. The well-supported mechanistic determinations are difficult in this system. In most cases we observed no intermediates and the reactions require rather harsh conditions. Scheme 4 presents the proposed possible mechanistic pathways for OA of N−H and N−C bonds described in this report. The first step is the coordination of **1** or **2** to the metal center with concomitant loss of all but one L. The PNP ligand may be bound to the metal in either the κ^3-*P*,*N*,*P* (**11**) or the κ^2-*P*,*P* (**12**) fashion. The group 10 metal centers in the oxidation state zero are a poor match for the weak and hard diarylamine donor, so **12** is a distinct possibility. It does not seem probable that more than one L can remain bound to M together with PNP. The observation of (**1**)Pd(PPh$_3$) (**10**) supports this assumption. Whether **11** or **12** is the more thermodynamically stable form, the coordination of N is probably a necessary step prior to N−H or N−C oxidative addition. The OA can occur in concert with loss of the last L to give directly **8** or **9**. The other possibility is the loss of L prior to N−H or N−C bond rupture to give the intermediate **13**. While we have not observed **13**, it seems likely that in the case of L = COD and especially L = PBu$^t_3$ loss of L from **11** or **12** will be more facile than for L = PPh$_3$. In fact, it is even hard to imagine that PBu$^t_3$ can be bound to the metal simultaneously with η^2- or η^3-PNP (as in **11** or **12**). In accord with this assertion, higher conversions to **8-M** and to **9-Pt** were achieved when using M(PBu$^t_3$)$_2$ (M = Pd, Pt) as compared with using M(PPh$_3$)$_4$. It may be argued that the higher conversions with the M(PBu$^t_3$)$_2$ precursors are a reflection of the greater donicity of PBu$^t_3$ compared to PPh$_3$. However, this would be a factor only if PBu$^t_3$ is bound to the metal during the N−C OA step. For steric reasons, it seems unrealistic.

The inhibition of the OA by the released phosphine is easily understood. The OA step must be preceded by a preequilibrium formation of **11**(**12**) and/or **13**. Free phosphine will suppress the formation of **11** or **12** and also suppress the dissociation of L from **11** or **12**. Since **13** was not observed in any of the reactions, excess phosphine should inhibit the reaction whatever the rate-limiting step.

Conclusion

We have synthesized a series of (PNP)MR (M = Ni, Pd, Pt; R = H, Me) compounds starting with MCl$_2$ precursors and established that the same compounds can be formed via oxidative addition of N−H and N−C bonds of the neutral PNP ligands **1** and **2** to zerovalent metal centers. The zerovalent reagents utilized in this study are commonly used in catalysis. Our results demonstrate that oxidative addition of N−H and unstrained N−C bonds to Ni^0, Pd^0, and Pt^0 centers is possible and, in the presented cases, irreversible. This augurs that the potential catalytic intermediates (PNP)MR (M = Ni, Pd, Pt; R = H, hydrocarbyl) will not decompose by irreversible M−R reductive elimination. The strong directing effect of the prearranged geometry of the PNP chelate ligand and the somewhat smaller bond strengths of the diarylamine N−H and N−CH$_3$ bonds[25] favorably influence the thermodynamics of the

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(24) ORTEP plots were created using Ortep-3 for Windows. Farugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(25) (a) Lucarini, M.; Pedrielli, P.; Pedulli, G. F.; Valgimigli, L.; Gigmes, D.; Tordo, P. *J. Am. Chem. Soc.* **1999**, *121*, 11546. (b) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *J. Org. Chem.* **1997**, *62*, 3413. (c) Budyka, M. F. *J. Mol. Struct.* **2003**, *629*, 127.

oxidative addition reactions presented here. In the absence of these factors the N−H and N−C oxidative addition reactions may be thermodynamically unfavorable but not high enough in energy to be kinetically inaccessible processes. This is especially relevant to the use of M^0 catalysts in conjunction with polyfunctional substrates and ligands where some degree of the directing influence is present. For such cases, the demonstration of the feasibility of the N−H and N−C oxidative addition to M^0 may spur the design of novel catalytic schemes or point to potential M^0 catalyst deactivation.

Experimental Section

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, pentane, Et_2O, C_6D_6, THF, and isooctane were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred, and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene, 1,4-dioxane, $CDCl_3$, and CH_2Cl_2 were dried with and then distilled or vacuum transferred from CaH_2. Compounds (COD)-$PtCl_2$,[26] **1**,[9a] **2a**,[9b] **2b**,[9d] **7a-Pd**,[9a] **8a-Pd**,[9a] and **7b-Pd**[9d] were prepared according to published procedures. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^1H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced externally to 1.0 M CF_3CO_2H in $CDCl_3$ at δ −78.5 ppm.

NMR Data for 7-M, 8-M, and 9-M. The NMR data are presented in Tables 1−5. In Tables 2 and 3, the chemical shift value is followed in parentheses by multiplicity of the signal and by value(s) of the apparent coupling constant in Hz. The ^1H NMR resonances of the Me hydrogens of the isopropyl groups (Me^iPr in Tables 2 and 3) are doublets of virtual triplets where $J_{H-H} \approx J_{H-P}$, thus resulting in an apparent quartet. In $^1H\{^{31}P\}$ spectra, the CH_{iPr} resonance is a septet and the Me_{iPr} resonance is a doublet. In Tables 4 and 5, the chemical shift value is followed in parentheses by J_{C-P} and J_{C-F} in that order. If $J_{C-F} = 0$, it is omitted. If both $J_{C-P} = 0$ and $J_{C-F} = 0$, they are omitted. C−P coupling results in a virtual triplet substructure. C−F coupling results in a doublet substructure. A combination of C−P and C−F coupling results in either a virtual triplet of doublets or a doublet of virtual triplets.

7a-Ni, 8a-Ni, and 9a-Ni. Method A. **1** (17.1 mg, 40 μmol) and anhydrous $NiCl_2$ (5.2 mg, 40 μmol) were loaded into a J. Young NMR tube along with 0.6 mL of C_6D_6 and vigorously shaken. Emerald-green color of **7a-Ni** began to appear. This suspension was heated at 90 °C for 18 h. NMR analysis showed essentially only **7a-Ni** (some solids were also visible). Two drops of Et_3N was added (fumes of presumably Et_3NHCl were observed before contact). The mixture was heated at 90 °C for 2 h. Method B. **2a** (17.7 mg, 40 μmol) and anhydrous $NiCl_2$ (5.2 mg, 40 μmol) were loaded into a J. Young NMR tube along with 0.6 mL of C_6D_6 and vigorously shaken. This mixture was heated at 90 °C. After 45 min a 1.25:1 ratio of **7a-Ni** to **2a** was observed by NMR. After 18 h, only **7a-Ni** was detected by ^{31}P NMR. 1,5-COD and MeCl were also observed (by ^1H NMR). This solution was combined with that from method A, diluted with Et_2O, and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of **7a-Ni** (>98% purity). This solution was transferred into a Schlenk flask, the NMR tube was rinsed out with several portions of THF (ca. 5 mL), and the rinsate was added to the flask. To this solution was added 0.20 g (5.3 mmol) of $NaBH_4$, followed by 5 mL of EtOH. This was stirred for 2 h, during which time the mixture turned yellow-brown. The volatiles were removed, and the residue was extracted with Et_2O and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of the **8a-Ni** product (>98% purity). This solution was treated with 0.020 mL of CH_2Cl_2 and was allowed to stand for 2 h at ambient temperature. NMR analysis showed a 5:1 mixture of **8a-Ni** to **7a-Ni** along with production of MeCl. A 0.020 mL portion of $CDCl_3$ was added. After 15 min the ratio of **8a-Ni** to **7a-Ni** was 1:20. After 18 h, only **7a-Ni** was observed by NMR.

Table 6. Elemental Analysis Data for 9-M

compound	formula	C, found (calcd)	H, found (calcd)
9a-Ni	$C_{27}H_{43}NNiP_2$	64.54 (64.56)	8.91 (8.63)
9a-Pd	$C_{27}H_{43}NP_2Pd$	58.85 (58.96)	7.98 (7.88)
9a-Pt	$C_{27}H_{43}NP_2Pt$	50.79 (50.78)	6.95 (6.79)
9b-Ni	$C_{25}H_{37}F_2NNiP_2$	58.90 (58.85)	7.57 (7.31)
9b-Pd	$C_{25}H_{37}F_2NP_2Pd$	53.66 (53.82)	6.78 (6.68)
9b-Pt	$C_{25}H_{37}F_2NP_2Pt$	46.64 (46.44)	5.80 (5.77)

The volatiles were removed in vacuo, the residue was dissolved in isooctane, and then the volatiles were removed in vacuo in order to remove residual $CDCl_3$. The residue was dissolved in 5 mL of Et_2O/1 mL of dioxane. MeMgCl was added (40 μL of 3.0 M in THF, 120 μmol). The reaction mixture was stirred at ambient temperature. After 1 h NMR analysis of an aliquot showed ca. 2:1 mixture of **9a-Ni** to **7a-Ni**. An additional 50 μL of MeMgCl (3.0 M in THF, 150 μmol) was added, and the mixture was stirred for 18 h. The volatiles were removed in vacuo; the residue was treated with a few drops of MeOH, extracted with Et_2O, and filtered through plugs of silica gel and Celite. The volatiles were removed in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of the **9a-Ni** product (>95% purity). The volatiles were removed in vacuo, and the residue was recrystallized from 1 mL of pentane at −35 °C to produce 27 mg of analytically pure (Table 6) **9a-Ni** (67%).

7b-Ni, 8b-Ni, and 9b-Ni. 2b (36.0 mg, 80 μmol) and anhydrous $NiCl_2$ (15.6 mg, 120 μmol) were loaded into a J. Young NMR tube along with 0.6 mL of C_6D_6. The NMR tube was heated at 90 °C for 4 days, while being monitored periodically by NMR. After 4 days, >98% conversion to green **7b-Ni** was observed. MeCl was also observed. This solution was transferred into a Schlenk flask, the NMR tube rinsed out with several portions of THF (ca. 5 mL), and the rinsate was added to the flask. To this solution was added 0.20 g (5.3 mmol) of $NaBH_4$, followed by 5 mL of ^iPrOH. This was stirred for 6 h at 40 °C, during which time the mixture turned yellow-brown. The volatiles were removed in vacuo, and the residue was extracted with Et_2O and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of the **8b-Ni** product (>98% purity). This solution was treated with 0.5 mL of $CDCl_3$ and 3 mL of Et_2O and was allowed to stand for 18 h at ambient temperature. The color of the solution changed to green (**7b-Ni**) in <5 min. After 18 h, the volatiles were removed in vacuo, the residue was dissolved in isooctane, and then the volatiles were removed in vacuo in order to remove residual $CDCl_3$. The residue was dissolved in 6 mL of 1:1 Et_2O/THF mixture. A 0.2 mL sample of dioxane was added to it, followed by MeMgCl (60 μL of 3.0 M in THF, 180 μmol). The reaction mixture was stirred for 5 h at ambient temperature, during which time it turned orange. The volatiles were removed in vacuo, and the residue was treated with a few drops of MeOH, extracted with Et_2O, and filtered through plugs of silica gel and Celite. The volatiles were removed in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of the **9b-Ni** product (>95%

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(26) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346.

purity). The volatiles were removed in vacuo, and the residue was recrystallized from 1 mL of pentane at −35 °C to produce 29 mg of analytically pure (Table 6) **9b-Ni** (72%).

9a-Pd. 7a-Pd (45.5 mg, 80 μmol) was dissolved in 5 mL of Et_2O, and MeMgCl (40 μL of 3.0 M in THF, 120 μmol) was added to it. Within 1 min, the color changed to light yellow. The mixture was stirred for 1 h, then 100 μL of MeOH was added, and the mixture was stripped to dryness. The residue was treated with silica gel, extracted with Et_2O, and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization. The volatiles were removed in vacuo from this C_6D_6 solution, and the residue was recrystallized from a minimum amount of Et_2O to give 30 mg (66%) of analytically pure (Table 6) **9a-Pd**.

8b-Pd. 8b-Pd was synthesized (from **7b-Pd** and $NaBH_4$) analogously to the previously reported synthesis of **8a-Pd**.[9a]

9b-Pd. 7b-Pd (46.2 mg, 80 μmol) was dissolved in 5 mL of Et_2O, and MeMgCl (40 μL of 3.0 M in THF, 120 μmol) was added to it. Within 1 min, the color changed to light yellow. The mixture was stirred for 1 h, then 6 drops of MeOH and 3 mL of pentane was added. The resultant suspension was treated with silica gel and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization. The volatiles were removed in vacuo from this C_6D_6 solution, and the residue was recrystallized from a minimum amount of Et_2O to give 32 mg (72%) of analytically pure (Table 6) **9b-Pd**.

7a-Pt, 8a-Pt, and 9a-Pt. Method A. **1** (17.1 mg, 40 μmol) and (COD)$PtCl_2$ (15.0 mg, 40 μmol) were loaded into a J. Young NMR tube along with 0.6 mL of C_6D_6 and vigorously shaken. After 1 h at 22 °C, NMR analysis showed essentially only **7a-Pt** (some solids were also visible). Two drops of Et_3N was added (fumes of presumably Et_3NHCl were observed before contact). The mixture was heated at 90 °C for 2 h. Method B. **2a** (17.7 mg, 40 μmol) and (COD)$PtCl_2$ (15.0 mg, 40 μmol) were loaded into a J. Young NMR tube along with 0.6 mL of C_6D_6 and vigorously shaken. A thick suspension formed within 1 min. This mixture was heated at 90 °C. After 45 min, the solution was clear and a 95:5 ratio of **7a-Pt** to **2a** was observed by NMR. After 18 h, this ratio was 98:2. 1,5-COD and MeCl were also observed. This solution was combined with that from method A, diluted with Et_2O, and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of **7a-Pt** (>98% purity). The C_6D_6 solution of **7a-Pt** was diluted with 5 mL of THF and 5 mL of ^{i}PrOH, and $NaBH_4$ (0.20 g, 5.3 mmol) was added to it. The resulting mixture was stirred for 2 h at 40 °C. This solution was diluted with Et_2O and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization. An 89:11 mixture of **8a-Pt** to **7a-Pt** was observed. This was sufficient to unambiguously characterize **8a-Pt** by ^1H, ^{31}P, and ^{13}C NMR. This 0.6 mL C_6D_6 solution was treated with 0.5 mL of $CDCl_3$ and heated at 90 °C. After 10 h, a 1:5 ratio of **8a-Pt** to **7a-Pt** was observed. After 96 h, this ratio became 2:98. This solution was transferred into a Schlenk flask, the NMR tube was rinsed out with several portions of Et_2O (ca. 5 mL), and the rinsate was added to the flask. The volatiles were removed in vacuo, the residue was treated with 1 mL of isooctane, and the volatiles were removed in vacuo again. The residue was dissolved in Et_2O, and to this solution was added MeMgCl (0.100 mL of 3.0 M in THF, 300 μmol). After stirring for 24 h the solution was treated with a few drops MeOH, and then the volatiles were removed in vacuo. The residue was extracted with Et_2O and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization of **9a-Pt** (>95% purity). The volatiles were removed from this solution, and the residue was recrystallized from ether/pentane at −35 °C to produce 20 mg of analytically pure (Table 6) **9a-Pt** (39%).

7b-Pt, 8b-Pt, and 9b-Pt. 2b (36.0 mg, 80 μmol) and (COD)-$PtCl_2$ (30.0 mg, 80 μmol) were loaded into a J. Young NMR tube along with 0.6 mL of C_6D_6 and vigorously shaken. NMR analysis after 1 h showed ca. 25% conversion to **7b-Pt**. Heating of this NMR tube at 90 °C for 18 h resulted in near quantitative conversion to **7b-Pt**. Free 1,5-COD and MeCl were also observed by ^1H NMR. This solution was transferred into a Schlenk flask, the NMR tube was rinsed out with several portions of THF (ca. 5 mL), and the rinsate was added to the flask. To this solution was added 0.20 g (5.3 mmol) of $NaBH_4$, followed by 5 mL of ^{i}PrOH. This was stirred for 24 h. NMR analysis of an aliquot indicated >98% conversion to **8b-Pt**. The volatiles were removed, and the residue was extracted with Et_2O and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization (>95% purity). The volatiles were removed in vacuo, and the residue was dissolved in $CDCl_3$ in a J. Young tube and placed into a 90 °C oil bath. After 13 h, the ratio of **8b-Pt** to **7b-Pt** was ca. 1:2. After 72 h, it became ca. 2:98, with only traces (<2%) of other impurities. This solution was transferred into a Schlenk flask, the NMR tube was rinsed out with several portions of Et_2O (ca. 5 mL), and the rinsate was added to the flask. The volatiles were removed in vacuo, the residue was treated with 1 mL of isooctane, and the volatiles were removed in vacuo again. The residue was dissolved in Et_2O, and to this solution was added MeMgCl (0.100 mL of 3.0 M in THF, 300 μmol). After stirring for 18 h, NMR analysis of an aliquot showed >98% conversion to **9b-Pt**. The solution was treated with a few drops MeOH, and then the volatiles were removed in vacuo. The residue was extracted with Et_2O and filtered through plugs of silica gel and Celite. The volatiles were removed from the filtrate in vacuo, and the residue was dissolved in C_6D_6 for NMR characterization (>95% purity). The volatiles were removed from this solution, and the residue was recrystallized from ether/pentane at −35 °C to produce 19 mg of analytically pure (Table 6) **9b-Pt** (37%).

General Notes on Oxidative Addition Reactions. For each reaction, first the ligand (**1** or **2a** or **2b**) was dissolved in 0.6 mL of C_6D_6 in a J. Young NMR tube and a drop of an internal standard was added to the solution. For **1** and **2a** the integration standard was 1,4-dioxane and the integration of the ^1H NMR spectra was used for the quantitative analysis; for **2b**, fluorobenzene was used as the integration standard and the integration of the ^{19}F NMR spectra was used for the quantitative analysis. Before the addition of the metal-containing reagent a spectrum (^1H or ^{19}F NMR) was collected and the ratio between the ligand and the standard was determined by integration. The conversion to **8-M** or **9-M** was quantitatively analyzed by integration versus the standard.

Ni(COD)$_2$ and 1. Ni(COD)$_2$ (11.1 mg, 40 μmol) was added to the solution of **1** (17.1 mg, 40 μmol). NMR analysis after 1 h at 22 °C showed 95% conversion to **8a-Ni**.

Ni(COD)$_2$ and 2a or 2b. Ni(COD)$_2$ (11.1 mg, 40 μmol) was added to the solution of 40 μmol of **2a** (17.7 mg) or **2b** (18.0 mg). The NMR tube was heated at 90 °C. NMR analysis after 1 h at 22 °C showed a mixture of unidentified compounds and ca. 5% **9a-Ni** or 1% **9b-Ni**. The amount of **9a-Ni** or **9b-Ni** did not increase after 46 h at 90 °C.

Ni(PPh$_3$)$_4$ and 1. Ni(PPh$_3$)$_4$ (33.2 mg, 30 μmol) was added to the solution of **1** (12.7 mg, 30 μmol). After 20 h at ambient temperature, a mixture of 40% **8a-Ni**, 41% **1**, PPh_3, and a few unidentified compounds was produced. The fraction of **8a-Ni** increased only slightly after heating at 100 °C for 51 h (44% **8a-Ni**, 17% **1**).

Ni(PPh$_3$)$_4$ and 2a or 2b. Ni(PPh$_3$)$_4$ (33.2 mg, 30 μmol) was added to the solution of 30 μmol of **2a** (13.3 mg) or **2b** (13.5 mg). NMR analysis after 1 h at 22 °C showed a mixture of unidentified compounds and no **9a-Ni** or **9b-Ni**. The NMR tube was heated at 90 °C, but no **9a-Ni** or **9b-Ni** was observed after 24 h.

Pd(PPh$_3$)$_4$ and 1. Pd(PPh$_3$)$_4$ (46.0 mg, 40 μmol) was added to the solution of **1** (17.1 mg, 40 μmol). A homogeneous solution formed. NMR analysis indicated a mixture of PPh$_3$, Pd(PPh$_3$)$_4$, **1**, and (**1**)Pd(PPh$_3$). The latter was tentatively identified on the basis of the observed ^{31}P NMR (δ 21.6 (t, 96 Hz, 1P), 13.6 (d, 96 Hz, 2P)) and partial ^{1}H NMR (δ 11.55, br t, NH) spectra. After 24 h at 22 °C, ca. 5% **8a-Pd** was observed. The NMR tube was heated at 90 °C. The conversion to **8a-Pd** was 54% after 1.5 h, 72% after 6 h, and 77% after 53 h.

Pd(PPh$_3$)$_4$ and 2a or 2b. Pd(PPh$_3$)$_4$ (46.0 mg, 40 μmol) was added to the solution of 40 μmol of **2a** (17.7 mg) or **2b** (18.0 mg). A homogeneous solution formed in each case. NMR analysis after 15 min at 22 °C showed only the starting materials present. The NMR tube was heated at 100 °C. After 2 h, 12% **9a-Pd** or 10% **9b-Pd** was observed. After 20 h, 30% **9a-Pd** or 20% **9b-Pd** was observed, and the conversion did not change after another 3 days at 100 °C.

Pd(PBu^t$_3$)$_2$ and 1. Pd(PBu^t$_3$)$_2$ (20.4 mg, 40 μmol) was added to the solution of **1** (17.1 mg, 40 μmol). A homogeneous solution formed. After 2 h at 22 °C, NMR analysis indicated a mixture of PBu^t$_3$, Pd(PBu^t$_3$)$_2$, **1**, and **8a-Pd** (8%). The NMR tube was heated at 100 °C. The conversion to **8a-Pd** was 92% after 70 min and 100% after 3.5 h.

Pd(PBu^t$_3$)$_2$ and 2a or 2b. Pd(PBu^t$_3$)$_2$ (20.4 mg, 40 μmol) was added to the solution of 40 μmol of **2a** (17.7 mg) or **2b** (18.0 mg). A homogeneous solution formed in each case. NMR analysis after 30 min at 22 °C showed only the starting materials present. The NMR tube was heated at 100 °C. After 17 h a mixture of unidentified products formed, and no **9a-Pd** or **9b-Pd** was observed.

Pt(PPh$_3$)$_4$ and 1. Pt(PPh$_3$)$_4$ (31.1 mg, 25 μmol) was added to the solution of **1** (12.0 mg, 27 μmol). A homogeneous solution formed. The NMR tube was heated at 100 °C. The conversion to **8a-Pt** was 58% after 0.5 h, 64% after 17 h, and 65% after 96 h (at this point also 25% **1** was observed).

Pt(PPh$_3$)$_4$ and 2a or 2b. Pt(PPh$_3$)$_4$ (31.1 mg, 25 μmol) was added to the solution of 25 μmol of **2a** (11.1 mg) or **2b** (11.3 mg). A homogeneous solution formed in each case. NMR analysis after 15 min at 22 °C showed only the starting materials present. The NMR tube was heated at 100 °C. After 24 h no **9a-Pt** or **9b-Pt** was observed and the mixture consisted essentially of only the starting materials (>90%).

Pt(PBu^t$_3$)$_2$ and 1. Pd(PBu^t$_3$)$_2$ (24.0 mg, 40 μmol) was added to the solution of **1** (17.1 mg, 40 μmol). A homogeneous solution formed. After 2 h at 22 °C, NMR analysis indicated that only the starting materials were present. The NMR tube was heated at 100 °C. The conversion to **8a-Pt** was 78% after 70 min and 95% after 3.5 h.

Pd(PBu^t$_3$)$_2$ and 2a or 2b. Pt(PBu^t$_3$)$_2$ (24.0 mg, 40 μmol) was added to the solution of 40 μmol of **2a** (17.7 mg) or **2b** (18.0 mg). A homogeneous solution formed in each case. NMR analysis after 30 min at 22 °C showed only the starting materials present. The NMR tube was heated at 100 °C. After 48 h, 25% **9a-Pt** or 7% **9b-Pt** was observed. After 96 h, 29% **9a-Pt** or 7% **9b-Pt** was observed.

Thermolyses of 9b-M with PPh$_3$. Three J. Young NMR tubes were charged each with PPh$_3$ (19.0 mg, 72 μmol). Into three tubes were added respectively 7.2 μmol of **9b-Ni** (3.7 mg), **9b-Pd** (4.0 mg), and **9b-Pt** (4.6 mg). C$_6$D$_6$ (0.6 mL) was added to each NMR tube, and they were heated at 100 °C. No change was detected by ^{19}F, ^{31}P, or ^{1}H NMR.

X-ray Structure Determination. Single crystals of **8b-Pd** and **9b-Pd** suitable for X-ray diffraction measurements were obtained by recrystallization from ether/pentane mixtures at −35 °C. Crystals were mounted in glass capillaries. Data collection was carried out at room temperature (low-temperature apparatus was not available) on a CAD-4 Turbo diffractometer equipped with Mo Kα radiation.[27] For **8b-Pd** and **9b-Pd**, data were collected to $2\theta_{\max} = 23.7°$ and 30.4°, respectively, the lower 2θ value corresponding to poorer crystal quality for **8b-Pd**. The structures were solved by direct methods (SIR92).[28] Full-matrix least squares refinement was carried out using the Oxford University *Crystals for Windows* system.[29] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and updated after each least squares cycle. On the final electron density difference map for **8b-Pd**, a peak of height 0.8 e$^-$ was observed at a distance of 1.2 Å from the Pd atom, in the square plane, and approximately bisecting the P−Pd−P angle. However, it was not possible to refine this putative hydride peak; the final refinement does not include contributions from that atom. A PLATON analysis of void volume for compound **8b-Pd** revealed a void volume of 47.9 Å^3 per asymmetric unit. Missing solvent could not be located on electron density difference maps, nor could the voids be successfully modeled using the PLATON SQUEEZE[30,31] technique.

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Supporting Information Available: Full reports on the structures of **8b-Pd** and **9b-Pd** in the form of CIF files. This material is available via the Internet free of charge at http://pubs.acs.org.

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[27] Straver, L. H. *CAD4-EXPRESS*; Enraf-Nonius: Delft, The Netherlands, 1992.

[28] Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[29] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

[30] van der Sluis, P.; Spek, A. *Acta Crystallogr., Sect. A* **1990**, *A46*, 194.

[31] (a) Spek, A. L. *Acta Crystallogr*., *Sect. A* **1990**, *A46*, C34. (b) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 1998.