Articles

Contribution from the Department of Chemistry,
University of California, San Diego, La Jolla, California 92093-0506

Alkyl and Hydrido Phenoxo Complexes of Nickel(II), Palladium(II), and Platinum(II). Hydrido Amido Complexes of Palladium

Allen L. Seligson, Robert L. Cowan, and William C. Trogler*

The compound *trans*-NiHCl(PBz$_3$)$_2$, where Bz = CH$_2$C$_6$H$_5$, has been synthesized in good yield by the reduction of NiCl$_2$(PBz$_3$)$_2$ with Super-Hydride, whereas the Pd and Pt analogues may be prepared by reduction of the corresponding MCl$_2$(PBz$_3$)$_2$ complexes with sodium naphthalide under an ethylene atmosphere, followed by the addition of HCl. Addition of NaOPh to *trans*-NiHCl(P^{i}Pr$_3$)$_2$ or *trans*-NiHCl(PCy$_3$)$_2$, where ^{i}Pr = *i*-C$_3$H$_7$ and Cy = c-C$_6$H$_{11}$, produces the corresponding hydrido phenoxo complexes, while the addition of NaOPh to *trans*-NiHCl(PBz$_3$)$_2$ yields *trans*-NiH(OPh)(PBz$_3$)$_2$·HOPh. Crystals of the latter complex belong to the triclinic space group P$\bar{1}$ with *a* = 10.149 (3) Å, *b* = 14.448 (4) Å, *c* = 16.090 (4) Å, α = 84.29 (2)°, β = 84.64 (2)°, γ = 80.22 (2)°, *V* = 2306 (1) Å^3, and *Z* = 2. Refinement of 148 least-squares parameters for 2358 reflections of *I* > 3σ(*I*) converged to *R* = 0.055. The structure about Ni is square planar with Ni–O = 1.949 (7) Å and Ni–O–C = 123.0 (4)°. The phenol of crystallization is hydrogen-bonded to the oxygen of the coordinated phenoxide, as evidenced by the O···O distance between them of 2.54 (1) Å. The O–H group for the hydrogen-bonded phenol occurs at 3370 cm^{-1} in the solid-state IR spectrum. In CH$_2$Cl$_2$ solution the O–H stretch shifts to 3588 cm^{-1} because of dissociation to form free phenol. When phenol is added to a solution of Pt(C$_2$H$_4$)(PBz$_3$)$_2$, the complex *trans*-PtH(OPh)(PBz$_3$)$_2$ is isolated. Crystals of this complex form as the toluene solvate and belong to the space group P$\bar{1}$ with *a* = 10.105 (5) Å, *b* = 14.762 (4) Å, *c* = 15.964 (6) Å, α = 84.10 (3)°, β = 87.74 (4)°, γ = 69.44 (3)°, *V* = 2231 (2) Å^3, and *Z* = 2. Least-squares refinement of 187 parameters for 5646 observed reflections of *I* > 3σ(*I*) converged to *R* = 0.0511. The structure about Pt conforms to a trans square-planar geometry with Pt–O = 2.130 (6) Å and Pt–O–C = 124.2 (5)°. Addition of phenol to Pd(CH$_3$)$_2$(dmpe), where dmpe = 1,2-bis(dimethylphosphino)ethane, yields Pd(CH$_3$)(OPh)(dmpe), which crystallizes in the orthorhombic space group P*bca* with *a* = 10.667 (3) Å, *b* = 16.460 (6) Å, *c* = 18.449 (5) Å, *V* = 3239 (2) Å^3, and *Z* = 8. The geometry about Pd is square planar with Pd–C = 2.101 (9) Å, Pd–O = 2.098 (6) Å, and Pd–O–C = 124.3 (5)°. The reactivity of these late-transition-metal phenoxides suggests a high nucleophilicity for the metal-bound phenoxide, as evidenced by alkylation at oxygen by methyl iodide or by the insertion of an electrophile such as phenyl isocyanate. Thermally unstable hydrido anilido complexes *trans*-PdH(NHPh)L$_2$, where L = P(^{i}Pr)$_3$ or PCy$_3$, were prepared by addition of NaNHPh to the corresponding hydrido chloro complexes. With the use of Na^{15}NHPh it was possible to definitively characterize the solution structures of these unstable species by NMR spectroscopy. Besides exhibiting alkylation and insertion reactivity similar to the phenoxide complexes, these compounds were extremely susceptible to reductive elimination of aniline on addition of ligands, such as acrylonitrile. Corresponding hydrido anilido complexes of nickel were unstable when generated by similar procedures. A consideration of bond strengths, along with the observed tendencies for reductive elimination, suggests that catalytic animation of olefins by a cycle that requires N–H oxidative addition has thermodynamic limitations for the late transition metals.

Introduction

The possibility of using late-transition-metal amides and alkoxides to transfer these groups to unsaturated organic substrates has been the focus of recent research. Two steps are critical to the development of catalysts for adding amines or alcohols to olefins by the mechanism shown in Scheme I. The first step, oxidative addition of an O–H bond in an alcohol or water has been observed in several late-metal systems.[1-5] By contrast examples of the oxidative addition of N–H bonds are limited to intramolecular examples or to activated N–H bonds as found in amides.[6-10]

Scheme I

X = OH, OR,
NH$_2$, NHR
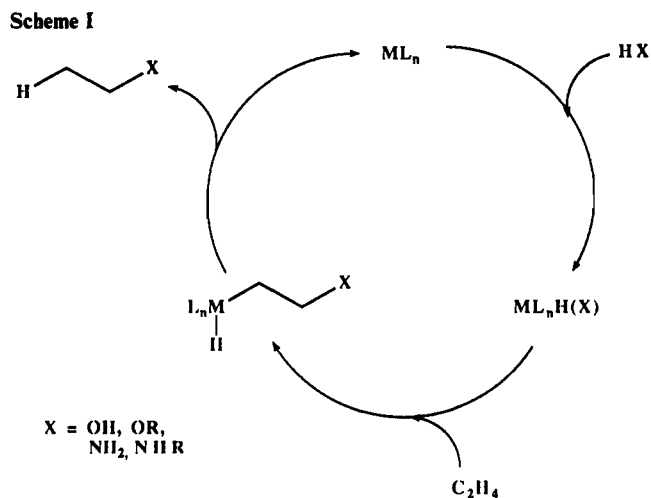
Examples of catalytic hydration and alcoholysis reactions have been limited to activated olefins (e.g., acrylonitrile).[1b,2a,11] We are aware of only one example of a late transition metal catalyzed amination proceeding by the pathway outlined in Scheme I. Aniline can be added to norbornene with IrCl$_2$(C$_2$H$_4$)$_2$(PEt$_3$)$_2$ and

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ZnCl$_2$ as catalysts; however, the reaction generates at most six turnovers after refluxing for 3 days and is limited to norbornene as substrate.[12]

Intramolecular cyclizations of amino olefins can be catalyzed by PdCl$_2$, with benzoquinone added as a sacrificial oxidant,[13] or by organolanthanide complexes.[14] RhCl$_3$ is known to catalyze the addition of secondary amines to ethylene.[15]

In attempting to understand limitations inherent in the mechanism of Scheme I, we have focused our efforts on the synthesis of late-metal hydrido phenoxo and hydrido anilido complexes to study their reactivity with olefinic substrates.[16] Studies of the insertion of acrylonitrile into the platinum–oxygen and platinum–nitrogen bonds in *trans*-PtH(OPh)(PEt$_3$)$_2$ and *trans*-PtH(NHPh)(PEt$_3$)$_2$[16] suggested that further weakening of these bonds might facilitate the insertion of unactivated olefins. To explore this possibility, we sought to prepare nickel or palladium analogues, since this should thermodynamically weaken the metal–oxygen or –nitrogen bond. Whether the change in the metal–oxygen or –nitrogen bond strength facilitates the insertion chemistry rather than an undesirable pathway, such as OH and NH reductive elimination, remained to be tested. Since the chemistry of late-transition-metal hydrido alkoxo and hydrido amido complexes[1–12,16–19] is not well developed, we were also interested in comparing reactivities and stabilities within the Ni–Pt triad.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using modified Schlenk techniques. Liquids were transferred by syringe (or cannula). Materials obtained from commercial sources were used without purification except where noted. Under a nitrogen atmosphere, THF, benzene, toluene, Et$_2$O, and pentane were distilled from potassium benzophenone ketyl, and acetonitrile and methylene chloride were distilled from calcium hydride. Sodium phenoxide was prepared by the reaction between phenol and sodium hydroxide and recrystallized from acetone. Sodium anilide was prepared from NaH and NH$_2$Ph and recrystallized (extremely air- and moisture-sensitive white crystals) from THF/ C$_6$H$_6$/pentane. The complexes *trans*-PdHCl(P^{i}Pr$_3$)$_2$ and *trans*-PdHCl-(PCy$_3$)$_2$[20] were prepared from addition of 1 equiv of HCl[21] to Pd-(C$_2$H$_4$)(P^{i}Pr$_3$)$_2$ and Pd(PCy$_3$)$_2$.[22]

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trans-Chlorohydridobis(tribenzylphosphine)nickel(II), trans-NiH-(Cl)(PBz$_3$)$_2$ (1). To a deep red solution of NiCl$_2$(PBz$_3$)$_2$ (0.502 g, 0.68 mmol) dissolved in THF (20 mL) and cooled to −40 °C was added a slight excess of Super-Hydride (0.70 mL of 1.0 M LiB(C$_2$H$_5$)$_3$H in THF). The reaction solution was stirred at −40 °C for 15 min and warmed to room temperature to yield a red-orange solution. The solvent was removed under vacuum, the resulting residue was redissolved in C$_6$H$_6$ (20 mL), and the solution was stirred over activated charcoal for 10 min. The solution was filtered to yield a yellow-orange solution, which on vacuum removal of solvent gave an oil of the same color. This oil was washed with diethyl ether (3 × 20 mL) while being stirred rapidly to yield a yellow powder, 0.31 g (65%). All attempts at recrystallization resulted in decomposition. Mp: 120–122 °C. ^{1}H NMR (C$_6$D$_6$): δ −23.03 (tr, $^2J_{PH(cis)}$ = 72 Hz, 1 H, Ni–H), 2.98 (s, 12 H, P–CH_2), 7.07–7.23 (m, 30 H, CH$_2$C$_6$H$_5$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 24.33 (s). IR (KBr, cm^{-1}): 1979 (NiH). Anal. Calcd for C$_{42}$H$_{43}$ClP$_2$Ni: C, 71.67; H, 6.16. Found: C, 71.76; H, 5.64.

trans-Hydridophenoxobis(tribenzylphosphine)nickel(II)–Phenol, trans-NiH(OPh)(PBz$_3$)$_2$·HOPh (2). To a solution of 1 (0.320 g, 0.45 mmol) dissolved in THF (5 mL) and C$_6$H$_6$ (5 mL) at 0 °C was added excess NaOPh (0.57 g, 1.35 mmol). The resulting red orange solution was stirred for 30 min and the solvent removed under vacuum to yield an oily product. This residue was washed with diethyl ether (3 × 15 mL) to give a yellow-orange solid. This solid was extracted with toluene (20 mL), and its volume was reduced to ∼5 mL. The toluene solution was layered with pentane (∼20 mL) and cooled to −20 °C in a beaker of MeOH, to yield orange cubes of 2, 0.144 g (42%). Mp: 65 °C. The proton source for lattice phenol may either be from the Ni–H (yield <50%) or from trace protic species during workup. The purposeful addition of 1–2.5 equiv of phenol did not improve the synthesis because of difficulty in crystallizing the crude oil product. ^{1}H NMR (C$_6$D$_6$): δ −26.61 (t, $^2J_{PH(cis)}$ = 76 Hz, 1 H, NiH), 2.72 (s, 12 H, P–CH_2), 6.5–7.5 (mult, 40 H, CH$_2$C$_6$H$_5$ and OC$_6$H$_5$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 22.59 (s). IR (KBr, cm^{-1}): 3370 (OH). Anal. Calcd for C$_{54}$H$_{54}$O$_2$P$_2$Ni: C, 75.80; H, 6.36. Found: C, 76.25; H, 6.57.

trans-Hydridophenoxobis(tricyclohexylphosphine)nickel(II), trans-NiH(OPh)(PCy$_3$)$_2$ (3). To a solution of *trans*-NiH(Cl)(PCy$_3$)$_2$ (0.499 g, 0.76 mmol) in THF (5 mL) and C$_6$H$_6$ (5 mL) at room temperature was added 3 equiv of NaOPh (0.265 g, 2.28 mmol). After the solution was stirred for 1 h, the solvent was removed under vacuum to give an orange solid residue. This solid was extracted with toluene (3 × 8 mL), and the filtrate was concentrated to ∼5 mL and cooled to −20 °C to yield orange crystals of 3, 0.391 g (72%). Anal. Calcd for C$_{42}$H$_{72}$NiOP$_2$: C, 70.68; H, 10.17. Found: C, 70.87; H, 10.22.

(Ethene)bis(tribenzylphosphine)nickel(0), Ni(CH$_2$═CH$_2$)(PBz$_3$)$_2$. To a suspension of NiCl$_2$(PBz$_3$)$_2$ (0.200 g, 0.27 mmol) and NaBH$_4$ (0.031 g, 0.55 mmol) in THF (5 mL) under CH$_2$═CH$_2$ purge was added MeOH (0.5 mL). Evolution of gas was observed, and after 3 min of rapid stirring, the solution turned yellow. Solvent was evaporated under ethylene purge and the residue redissolved in C$_6$D$_6$ for identification of product. ^{1}H NMR (C$_6$D$_6$): δ 2.83 (s br, PCH_2), 5.24 (s br, CH_2), 7.09 (s br, C$_6$H$_5$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 13.96 (s).

Reaction of Ni(CH$_2$═CH$_2$)(PBz$_3$)$_2$ with HCl. To a solution of Ni-(CH$_2$═CH$_2$)(PBz$_3$)$_2$ in C$_6$D$_6$ (generated as discussed above) was added a dioxane solution of HCl (5 μL of 4.0 M). The ^{1}H and ^{31}P{^{1}H} NMR spectra confirmed the production of 1.

Reaction of Ni(CH$_2$═CH$_2$)(PBz$_3$)$_2$ with Phenol. To a solution of Ni(CH$_2$═CH$_2$)(PBz$_3$)$_2$ in C$_6$D$_6$ was added a solution of phenol in C$_6$D$_6$. The ^{1}H and ^{31}P{^{1}H} NMR spectra confirmed the production of 2.

trans-Hydridophenoxobis(triisopropylphosphine)nickel(II), trans-NiH(OPh)(P^{i}Pr$_3$)$_2$ (4). To a solution of *trans*-NiHCl(P^{i}Pr$_3$)$_2$ (0.638 g, 1.53 mmol) in THF (8 mL) and C$_6$H$_6$ (8 mL) at room temperature was added 3 equiv of NaOPh (0.535 g, 4.61 mmol). The initial red-orange solution turned orange immediately, and the solution was stirred for 1 h. The solvent was removed under vacuum to leave an orange residue.

(22) These were prepared by a procedure similar to that for known platinum analogues; see: Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 101. Head, R. A. *Ibid.* **1989**, *24*, 313. Preparations are similar to that for compounds 5 and 6.

This was extracted with C_6H_6 (2 × 8 mL) and filtered. Solvent was removed from the filtrate under vacuum to yield an orange oil. All attempts to solidify or crystallize this oil failed. ^{1}H NMR (C_6D_6): δ −27.92 (t, $^2J_{PH(cis)}$ = 76 Hz, 1 H, Ni-*H*), 1.17 (d br, 36 H, CH−C*H$_3$*), 1.81 (m br, 6 H, P−C*H*), 6.70 (t br, 1 H, OC$_6$*H$_5$*), 7.22 (d br, 2 H, OC$_6$*H$_5$*), 7.35 (tr br, 2H, OC$_6$*H$_5$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 42.93 (s). IR (neat, cm^{-1}): 1950 (NiH).

trans-Chlorohydridobis(tribenzylphosphine)palladium(II), *trans*-PdHCl(PBz$_3$)$_2$ (5). To a yellow solution of PdCl$_2$(PBz$_3$)$_2$ (0.400 g, 0.51 mmol) in THF (15 mL) under an ethylene purge was added dropwise 2 equiv of sodium naphthalide solution in THF (4.28 mL, 0.25 M) until the green color of naphthalide persisted (∼5.2 mL added). A dioxane solution of HCl (0.13 mL, 4.0 M) was then added dropwise with rapid stirring. The resulting solution was concentrated to yield an oil, which was redissolved in C_6H_6 (5 mL). The solution was stirred over activated charcoal for 15 min. The solution was then filtered and concentrated to ∼1 mL. To this was added Et$_2$O (10 mL), and the solution was stirred for 20 min as a gray solid precipitated. This was washed with Et$_2$O (2 × 10 mL). The solid was filtered out and redissolved in C_6H_6 (2 mL), and the solution layered with pentane in an attempt to crystallize 5, yielding an impure gray solid, 0.214 g (56%). Mp: 100–101 °C dec. ^{1}H NMR (C_6H_6): δ −13.99 (tr, $^2J_{PH(cis)}$ = 11 Hz, 1 H, Ni-*H*), 3.17 (s, 12 H, P−C*H$_2$*), 7.05 (m, 18 H, C*H$_2$*C$_6$H$_5$) 7.19 (m, 12 H, CH$_2$C$_6$*H$_5$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 28.53 (s). IR (KBr, cm^{-1}): 2018 (PdH).

(Ethene)bis(tribenzylphosphine)palladium(0), Pd(CH$_2$=CH$_2$)(PBz$_3$)$_2$. To a pale yellow solution of PdCl$_2$(PBz$_3$)$_2$ (0.209 g, 0.27 mmol) in THF (3 mL) under an ethylene purge was added dropwise 2 equiv of sodium naphthalide solution in THF (0.21 mL, 0.25 M) until the green color of sodium naphthalide persisted. Solvent was evaporated under ethylene purge and the residue redissolved in C_6D_6 for identification of product. ^{1}H NMR (C_6D_6): δ 3.13 (s, 12 H, P−C*H$_2$*), 4.42 (s br, 4 H, C*H$_2$*), 7.33–7.50 (m, 30 H, CH$_2$C$_6$*H$_5$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 9.66 (s).

Reaction of Pd(CH$_2$=CH$_2$)(PBz$_3$)$_2$ with Phenol. To a solution of Pd(CH$_2$=CH$_2$)(PBz$_3$)$_2$ in C_6D_6 was added a solution of phenol in C_6D_6. ^{31}P{^{1}H} NMR spectroscopy revealed Pd(P(CH$_2$C$_6$H$_5$)$_3$)$_3$[29] as the only identifiable product.

cis-(Bis(dimethylphosphino)ethane)methylphenoxopalladium(II), Pd-(Me)(OPh)(dmpe) (12). This compound, previously reported by Yamamoto et al.,[18] has been prepared by a similar procedure. A solution of phenol (0.065 g, 0.70 mmol) in Et$_2$O (5 mL) was added to an Et$_2$O (5 mL) solution of Pd(CH$_3$)$_2$(dmpe) (0.200 g, 0.70 mmol). The initial colorless solution, after 5 min, turns cloudy, and a white precipitate results. After 1 h, the solvent is filtered off and the remaining white solid redissolved in CH$_2$Cl$_2$ (5 mL). The mixture is filtered. The filtrate is concentrated to ∼2 mL and layered with Et$_2$O (12 mL), resulting in colorless crystals of 12, 0.227 g (89%). Spectral data for 12 agree with that previously reported.

(Ethene)bis(tribenzylphosphine)platinum(0), Pt(CH$_2$=CH$_2$)(PBz$_3$)$_2$. To a pale yellow solution of PtCl$_2$(PBz$_3$)$_2$ (0.210 g, 0.24 mmol) in THF (4 mL) under an CH$_2$=CH$_2$ purge was added dropwise 2 equiv of sodium naphthalide solution in THF (1.92 mL, 0.25 M) until the green color of sodium naphthalide persisted. The solvent was removed under vacuum and the residue redissolved in C_6H_6 (5 mL). The solution was again put under CH$_2$=CH$_2$ purge. The solution was stirred over activated charcoal for 15 min and filtered to give a pale yellow solution. The solvent was again removed under vacuum and the residue dissolved in C_6D_6 for product identification. ^{1}H NMR (C_6D_6): δ 2.96 (t, $^2J_{PH}$ = 2.5 Hz, $^3J_{PH}$ = 25 Hz, 12 H, PC*H$_2$*), 2.13 (s, $^2J_{PtH}$ = 59 Hz, 4 H, C*H$_2$*), 7.09–7.31 (m, 30 H, C$_6$*H$_5$*). ^{31}P{^{1}H} NMR (C_6H_6): δ 15.66 (s, $^1J_{PtP}$ = 3643 Hz).

trans-Chlorohydridobis(tribenzylphosphine)platinum(II), PtHCl-(PBz$_3$)$_2$ (6). To a yellow solution of PtCl$_2$(PBz$_3$)$_2$ (0.502 g, 0.58 mmol) in THF (15 mL) under an ethylene purge was added dropwise 2 equiv of sodium naphthalide solution in THF (4.60 mL, 0.25 M) until the green color of the sodium naphthalide persisted. The solvent was removed in vacuo, the residue was redissolved in C_6H_6 (15 mL), and the solution was stirred over activated charcoal under an ethylene purge for 20 min. The solution was filtered, yielding a pale yellow filtrate to which a dioxane solution of HCl (0.14 mL, 4.0 M) was added with rapid stirring. The resulting pale yellow solution was concentrated under vacuum to yield a yellow oil. This oil was washed with diethyl ether (3 × 20 mL) to precipitate a light yellow solid. This solid was redissolved in C_6H_6 (10 mL), and the solution was stirred over activated charcoal for 20 min. The solution was filtered, and the resultant pale yellow filtrate was concentrated to ∼4 mL and layered with pentane (20 mL). This yielded colorless crystals of 6, contaminated with PtEtCl(PBz$_3$)$_2$ (these were inseparable by the techniques attempted), 0.206 g (42%). ^{1}H NMR (C_6D_6): δ −17.03 (t, $^1J_{PtH}$ = 1264 Hz, $^2J_{PH(cis)}$ = 12 Hz, 1 H, Pt-*H*), 3.25 (s, $^3J_{Pt-H}$ = 28 Hz, 12 H, P−C*H$_2$*), 6.82–7.43 (m, 30 H, CH$_2$C$_6$*H$_5$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 23.77 (s, $^1J_{Pt-P}$ = 2960 Hz).

trans-Hydridophenoxobis(tribenzylphosphine)platinum(II)−0.5-Toluene, *trans*-PtH(OPh)(PBz$_3$)$_2$·0.5C$_7$H$_8$ (7). To a pale yellow solution of PtCl$_2$(PBz$_3$)$_2$ (0.507 g, 0.58 mmol) in THF (15 mL) under an ethylene purge was added dropwise 2 equiv of sodium naphthalide solution in THF (4.60 mL, 0.25 M) until the green color of sodium naphthalide persisted. The solvent was removed under vacuum and the residue redissolved in C_6H_6 (15 mL). This solution was stirred over activated charcoal under an ethylene purge for 15 min and filtered to give a pale yellow solution. To this solution, while it was being stirred rapidly, was added a solution of phenol (0.054 g, 0.58 mmol) in diethyl ether (5 mL). After 30 min the solvent was removed under vacuum, to give a yellow oil. This oil was washed with pentane (3 × 15 mL) to precipitate a yellow solid. The solid was redissolved in toluene (5 mL), and the solution was stirred over activated charcoal for 20 min. The solution was concentrated to 1.5 mL and layered with pentane (15 mL) to yield colorless crystals of 7, 0.263 g (51%). Mp: 127–130 °C. ^{1}H NMR (C_6D_6): δ −21.05 (t, $^1J_{PtH}$ = 1080 Hz, $^2J_{PH}$ = 14 Hz, 1 H, Pt-*H*), 3.05 (s, $^3J_{PtH}$ = 30 Hz, 12 H, P−C*H$_2$*): 6.85–7.32 (m, 39 H, OC$_6$*H$_5$*, CH$_2$C$_6$*H$_5$* and 0.5 C$_6$H$_5$C*H$_3$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 26.57 (s, $^1J_{PtP}$ = 3094 Hz). IR (KBr, cm^{-1}) 2267 (PtH). Anal. Calcd for C$_{51.5}$H$_{50.5}$OP$_2$Pt: C, 65.63; H, 5.40. Found: C, 64.72; H, 5.93.

cis-(Bis(dimethylphosphino)ethane)ethylchloroplatinum(II)−Dichloromethane, Pt(Et)Cl(dmpe)·CH$_2$Cl$_2$ (8). To a solution of Pt(Et)-Cl(COD) (where COD = 1,5-cyclooctadiene) (0.34 g, 0.94 mmol) in C_6H_6 (10 mL) was added dropwise a solution of dmpe (0.16 mL, 0.94 mmol), resulting in a white precipitate. The reaction mixture was stirred for $^1/_2$ h and the solvent removed by vacuum. The resulting white solid was washed with hexanes (2 × 20 mL) and redissolved in CH$_2$Cl$_2$ (5 mL). This solution was stirred over a activated charcoal for 15 min and filtered, to yield a colorless filtrate. The filtrate was concentrated to ∼2 mL and then layered with Et$_2$O (15 mL) to yield 0.335 g (87%). Mp: 140 °C. ^{1}H NMR (CDCl$_3$): δ 1.22 (m), 1.53 (d), 1.62 (d), 1.72 (m) (the complex splitting patterns of this compound presented difficulty in assignment of these resonances), 5.35 (s, 2 H, C*H$_2$*Cl$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 19.62, 34.19 ($^2J_{PtP}$ = 4234, 1525 Hz). Anal. Calcd for C$_8$H$_{21}$ClP$_2$Pt·CH$_2$Cl$_2$: C, 23.71; H, 4.58. Found: C, 24.22; H, 5.14.

cis-(Bis(dimethylphosphino)ethane)ethylphenoxoplatinum(II), Pt-(Et)(OPh)(dmpe) (9). To a solution of 8 (0.101 g, 0.25 mmol) in THF (20 mL) was added 3 equiv of NaOPh (0.086 g, 0.75 mmol). The solution was stirred for 24 h whereupon a fine white precipitate formed. The solvent was removed under vacuum and the residue dissolved in C_6H_6 (25 mL). The solution was stirred over activated charcoal for 15 min and was filtered, and the colorless filtrate was vacuum evaporated to give a white solid. The white solid was redissolved in CH$_3$CN (∼2 mL) and concentrated slightly. The solution was then layered with Et$_2$O (15 mL), and colorless crystals of 9 formed after several days, 0.078 g (68%). Mp: 146–152 °C dec. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.12 (m), 1.24 (d, P−C*H$_3$*), 1.60 (d, P−C*H$_3$*), 1.50 (m), 1.70 (m), 6.40 (t, J = 7 Hz, 1 H, C$_6$*H$_5$*), 6.70 (d, J = 8 Hz, 2 H, C$_6$*H$_5$*), 6.98 (t, J = 8 Hz, 2 H, C$_6$*H$_5$*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 10.0, 32.5 ($^2J_{Pt-P}$ = 3831, 1573 Hz, $^2J_{PP}$ = 6 Hz). Anal. Calcd for C$_{14}$H$_{26}$OP$_2$Pt: C, 35.98; H, 5.61. Found: C, 36.64; H, 5.74.

cis-(Bis(dimethylphosphino)ethane)(ethene)platinum(0), *cis*-Pt-(CH$_2$=CH$_2$)(dmpe). This was synthesized by an analogous procedure to that of Pt(CH$_2$=CH$_2$)(PBz$_3$)$_2$. ^{1}H NMR (C_6D_6): δ 2.25 (s, $^2J_{PtH}$ = 60 Hz, C*H$_2$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 23.86 (s, J_{PtP} = 3110 Hz).

Reactions of 2–4 with Methyl Iodide. Approximately 15 mg of metal complex was loaded into an NMR tube and dissolved in 0.45 mL of C_6D_6. Methyl iodide was then added by a microliter syringe (10 μL). After 2 h at room temperature, the ^{1}H and ^{31}P NMR spectra showed conversion to the corresponding NiHIL$_2$ species along with production of anisole.

Reactions of 2–4 with Phenyl Isocyanate. Approximately 15 mg of metal complex was loaded into an NMR tube and dissolved in 0.45 mL of C_6D_6. Excess phenyl isocyanate was then added by a microliter syringe (10 μL). After a 3-h reaction time at room temperature, the ^{1}H and ^{31}P NMR spectra were recorded. Reaction products will be discussed in the main text.

Generation of *trans*-hydrido(phenylamido)bis(triisopropylphosphine)-palladium(II), *trans*-PdH(NHPh)(P^{i}Pr$_3$)$_2$ (10). A 5-mm NMR tube was charged with *trans*-PdHCl(P^{i}Pr$_3$)$_2$ and NaNHPh and then sealed under a nitrogen atmosphere. The palladium complex was then dissolved in C_6D_6, and the contents were stirred for 10 min to pulverize the anilide sufficiently to initiate reaction. After 20 min, the reaction contained only traces of the starting hydrido chloro complex. The presence of excess NaNHPh seems to stabilize the product, since decanting of the solution initiated decomposition. Solutions of 10 in benzene are stable for 2 h with little decomposition; however, after this period of time the decomposition rate appears to increase exponentially. ^{1}H NMR (C_6D_6): δ 7.25 (t, J = 8 Hz, *m*-C$_6$*H$_5$*), 6.72 (d, J = 8 Hz, *o*-C$_6$*H$_5$*), 6.47 (t, J = 7 Hz, *p*-C$_6$*H$_5$*), 1.96 (m, P−C*H*), 1.77 (s, N−*H*), 1.12 (q, P−CH−C*H$_3$*), −14.06

Table I. Crystallographic Data and Summary of Data Collection and Refinement for Compounds **2**, **7**, and **12**

	2	**7**	**12**
formula	$C_{54}H_{54}O_2P_2Ni$	$C_{51.5}H_{50.5}OP_2Pt$	$C_{13}H_{24}OP_2Pd$
fw	855.69	942.51	364.68
cryst system	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Pbca$
a, Å	10.149 (3)	10.165 (5)	10.667 (3)
b, Å	14.448 (4)	14.762 (4)	16.460 (6)
c, Å	16.090 (4)	15.964 (6)	18.449 (5)
α, deg	84.29 (2)	84.10 (3)	90.0
β, deg	84.64 (2)	87.74 (4)	90.0
γ, deg	80.22 (2)	69.44 (3)	90.0
V, Å^3	2306.3 (11)	2231.2 (16)	3239.3 (16)
d_{calc}, g cm^{-3}	1.232	1.403	1.495
μ, mm^{-1}	0.528	3.28	1.311
scan type	ω	$\omega-2\theta$	$\omega-2\theta$
scan speed, deg/min	variable, 5–29	variable, 5–29	variable, 2–15
no. of unique data	8061	7891	2137
no. of reflcns used ($I > 3\sigma(I)$)	2358	5646	1402
no. of params	148	187	112
Z	2	2	8
scan range, deg	$3.0 < 2\theta < 50.0$	$3.0 < 2\theta < 50.0$	$3.0 < 2\theta < 55.0$
largest resid peak, e/Å^3	0.45	1.40	0.57
R	0.0550	0.0511	0.0458
R_w	0.0620	0.0667	0.0723
GOF	1.78	1.16	0.66

(s, Pd–H). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.0 (s).

Synthesis of *trans*-Hydrido(phenylamido)bis(tricyclohexylphosphine)palladium(II), *trans*-PdH(NHPh)(PCy₃)₂ (11). To a vigorously stirred benzene solution of *trans*-PdHCl(PCy₃)₂ (0.271 g, 0.385 mmol) was added excess NaNHPh (0.081 g, 0.704 mmol) dissolved in THF (2 mL). This caused the initially colorless solution to immediately turn bright yellow and slightly cloudy. The solvent was removed in vacuo and the solid residue extracted twice with cyclohexane (10 mL, 2 mL). The filtrate was concentrated slightly, diluted with pentane (10 mL), and then cooled (~10 °C) overnight to yield small yellow crystals of the product. Yield: 0.15 g (51%). The recrystallization step must be performed at room temperature or below with scrupulously dried and deoxygenated solvents, since the palladium complex is susceptible to reductive elimination of aniline and will yield Pd(PCy₃)₂ upon workup. Complex **11** is thermally unstable but can be stored for several weeks if kept at –10 °C. ^{1}H NMR (C_6D_6): δ 7.25 (t, $J = 8$ Hz, m-C_6H_5), 6.74 (d, $J = 8$ Hz, o-C_6H_5), 6.45 (t, $J = 7$ Hz, p-C_6H_5), –13.89 (s, Pd–H). ^{31}P{^{1}H} NMR (C_6H_6): δ 40.6 (s).

Generation of *trans*-PdH(^{15}NHPh)(P^{i}Pr₃)₂ (10-n) and *trans*-PdH-(^{15}NHPh)(PCy₃)₂ (11-n). The procedure outlined for **10** was followed where the solid reactants were mixed in a 5-mm NMR tube and C_6D_6 subsequently injected. Reaction times of 30 min were required to yield the products with only traces of the starting hydrido chloro complex detected. ^{1}H NMR (C_6D_6) for **10-n**: δ 1.77 (d, $^1J_{^{15}NH} = 67$ Hz, N–H), –14.06 (d, $^2J_{^{15}NH} = 24$ Hz, Pd–H). ^{15}N{^{1}H} NMR (C_6D_6): δ 4.8 (t, $^2J_{^{15}NP} = 3$ Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.0 (s). ^{1}H NMR (C_6D_6) for **11-n**: δ –13.89 (d, $^2J_{^{15}NH} = 24$ Hz, Pd–H). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.6 (s).

Reaction between 11 and Water To Yield Bis(tricyclohexylphosphine)palladium(0). A benzene-d_6 solution of **11** contained in a 5-mm NMR tube was injected with water (10 μL). The addition caused an instantaneous loss of the original yellow color to yield a colorless solution. Analysis by ^{31}P{^{1}H} NMR spectroscopy determined the reaction product to be Pd(PCy₃)₂ by comparison of the spectral parameters to those of an authentic sample. ^{31}P{^{1}H} NMR (C_6D_6): δ 39.5 (s).

Reaction between 11 and Acetylene To Yield *trans*-Hydrido(acetylido)bis(tricyclohexylphosphine)palladium(II), *trans*-PdH(C≡CH)-(PCy₃)₂. A C_6D_6 solution of **11** was saturated with acetylene by purging the solution for 30 min. The reaction reached completion within 1 h at room temperature to yield the hydrido acetylide product. ^{1}H NMR (C_6D_6): δ 2.58 (s, C≡C–H), –9.01 (s, Pd–H). ^{31}P{^{1}H} NMR (C_6D_6): δ 47.3 (s).

Reaction between 11 and Ethylene To Yield (Ethene)bis(tricyclohexylphosphine)palladium(0), Pd(C₂H₄)(PCy₃)₂. A 5-mm NMR tube containing **11** dissolved in C_6D_6 was bubbled with ethylene for 30 min. Within 1 h the sample had reacted to yield the olefin complex as identified by ^{1}H and ^{31}P NMR spectroscopies. An authentic sample prepared from the reaction between Pd(PCy₃)₂ and ethylene in C_6D_6 was used in the comparison. ^{31}P{^{1}H} NMR (C_6D_6): δ 38.1 (s).

Reaction between 11 and Acrylonitrile To Yield Acrylonitrilebis(tricyclohexylphosphine)palladium(0), Pd[CH₂=CH(CN)](PCy₃)₂. A 5-mm NMR tube containing **11** dissolved in C_6D_6 was treated with excess

acrylonitrile. Within 30 min, aniline and the π-olefin complex of Pd-(PCy₃)₂ were produced. The identity of the palladium(0) complex was verified by comparison of the NMR spectra with those of an authentic sample prepared from treating Pd(PCy₃)₂ with acrylonitrile. ^{31}P{^{1}H} NMR (C_6D_6): δ 38.0 (d, $^2J_{PP} = 11$ Hz), 33.7 (d, $^2J_{PP} = $ Hz).

Reaction between 11 and Phenyl Isocyanate To Yield *trans*-Hydrido-(N,N'-diphenylureato-N)bis(tricyclohexylphosphine)palladium(II), *trans*-PdH[NPhC(O)NHPh](PCy₃)₂. A benzene solution of **11** prepared from *trans*-PdHCl(PCy₃)₂ (0.265 g, 0.376 mmol) and NaNHPh (0.073 g, 0.634 mmol) was treated with PhNCO (0.10 mL, 0.11 g, 0.92 mmol). The addition caused an immediate color change from bright yellow to pale brown. The solvent was removed in vacuo to yield a viscous oil. Evacuation for 4 h yielded a solid residue that would not redissolve in benzene. Spectroscopic analysis of the product by ^{31}P NMR spectroscopy showed it to be Pd(PCy₃)₂. The intermediate insertion product could be generated in solution and observed by ^{31}P{^{1}H} and ^{1}H NMR spectroscopies but was not stable to workup and isolation. ^{1}H NMR (C_6D_6): δ –14.55 (t, $^2J_{PH} = 11$ Hz, Pd–H). ^{31}P{^{1}H} NMR (C_6D_6): δ 39.7 (s).

X-ray Structure Determinations. X-ray crystallographic analyses were performed with the use of a Nicolet R3m/V automated diffractometer equipped with a graphite crystal monochromator and a Mo X-ray tube. Orientation matrix and unit cell parameters were determined by the least-squares fitting of 20 machine-centered reflections ($15° < 2\theta < 30°$) and confirmed by examination of axial photographs. Intensities of three check reflections were monitored every 197 reflections, throughout data collection. Structure solutions and data workup were performed on a DEC Microvax II computer with SHELXTL PLUS version 3.4 software. Details on crystal and intensity data are given in Table I. Positional and thermal parameters and bond distances and angles are listed in Tables II–IV.

An orange cube-shaped crystal of **2** of approximate dimensions 0.34 × 0.23 × 0.22 mm was used for the room-temperature crystal and intensity data collection. The unit cell parameters and lack of systematic absences suggested $P1$ or $P\bar{1}$ as the space group. The structure was solved by direct methods and refined well in $P\bar{1}$. An absorption correction was applied from ψ-scan data (minimum/maximum transmission 0.90/0.95). All non-hydrogen and non-carbon atoms were refined anisotropically. All phenyl groups were treated as isotropic rigid groups. All hydrogen atoms were generated in idealized positions for the structure factor calculations.

A colorless cube-shaped crystal of **7** of approximate dimensions 0.39 × 0.31 × 0.21 mm was used for the room-temperature crystal and intensity data collection. The unit cell parameters and the lack of systematic absences suggested $P1$ or $P\bar{1}$ as the space group. The structure was solved by direct methods in $P\bar{1}$. An absorption correction was applied from ψ-scan data (minimum/maximum transmission 0.68/0.97). All non-hydrogen and non-carbon atoms were refined anisotropically including C(100), C(101), C(102), and C(103) of the inversion-disordered toluene of crystallization. All phenyl groups were treated as isotropic rigid groups. All hydrogen atoms were generated in idealized positions for the structure factor calculations. The largest peak (e/Å^3) in the final difference Fourier map was located 0.99 Å from Pt in the position expected for the hydride ligand.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for **2**, **7**, and **12**

	x	y	z	V(eq)[a]		x	y	z	V(eq)[a]
					2				
Ni	4450 (1)	7605 (1)	2608 (1)	45 (1)	C(31)	5221	6189	26	45 (3)
P(1)	5513 (3)	7139 (2)	1456 (2)	43 (1)	C(40)	2404 (9)	9176 (6)	3806 (5)	54
P(2)	4000 (3)	8346 (2)	3735 (2)	43 (1)	C(42)	1956 (7)	9950 (4)	2365 (4)	62 (3)
O	2908 (6)	6947 (4)	2766 (4)	54 (3)	C(43)	1860	10735	1780	86 (4)
C(2)	4156 (5)	5545 (5)	3413 (4)	53 (3)	C(44)	2150	11586	1993	82 (4)
C(3)	4168	4646	3822	71 (3)	C(45)	2538	11654	2792	81 (4)
C(4)	2984	4266	3963	79 (4)	C(46)	2634	10869	3376	66 (3)
C(5)	1788	4784	3694	73 (3)	C(41)	2344	10018	3163	49 (3)
C(6)	1776	5683	3285	60 (3)	C(50)	3796 (9)	7497 (6)	4665 (5)	49
C(1)	2960	6063	3144	46 (3)	C(52)	3977 (5)	8105 (5)	6052 (4)	60 (3)
C(10)	5513 (9)	8078 (6)	587 (5)	48	C(53)	3389	8502	6781	76 (3)
C(12)	7415 (6)	8977 (4)	673 (4)	62 (3)	C(54)	1996	8681	6924	78 (3)
C(13)	7887	9788	836	72 (3)	C(55)	1191	8461	6339	83 (4)
C(14)	6991	10556	1120	67 (3)	C(56)	1778	8064	5611	66 (3)
C(15)	5623	10512	1242	60 (3)	C(51)	3171	7885	5468	49 (3)
C(16)	5151	9700	1079	57 (3)	C(60)	5181 (9)	9084 (6)	4008 (6)	51
C(11)	6048	8933	795	43 (2)	C(62)	7289 (7)	8090 (4)	4541 (3)	59 (3)
C(20)	7308 (9)	6708 (6)	1548 (5)	48	C(63)	8645	7710	4429	73 (3)
C(22)	7801 (7)	4973 (5)	2035 (3)	80 (4)	C(64)	9377	7911	3673	72 (3)
C(23)	8038	4251	2673	98 (4)	C(65)	8752	8492	3031	70 (3)
C(24)	8062	4469	3496	86 (4)	C(66)	7396	8872	3143	57 (3)
C(25)	7849	5408	3682	81 (4)	C(61)	6664	8671	3898	47 (3)
C(26)	7613	6129	3044	57 (3)	O(9)	1589 (7)	7884 (4)	1603 (4)	73 (3)
C(21)	7589	5912	2221	48 (3)	C(92)	957 (7)	6536 (4)	1084 (3)	63 (3)
C(30)	4927 (9)	6200 (6)	962 (5)	45	C(93)	527	6136	425	71 (3)
C(32)	6489 (6)	5809 (4)	−317 (4)	61 (3)	C(94)	307	6670	−335	82 (4)
C(33)	6762	5845	−1184	70 (3)	C(95)	517	7606	−436	77 (3)
C(34)	5767	6261	−1710	68 (3)	C(96)	947	8007	223	66 (3)
C(35)	4500	6640	−1367	73 (3)	C(91)	1167	7472	983	55 (3)
C(36)	4227	6604	−500	59 (3)					
					7				
Pt	2555 (1)	2324 (1)	2465 (1)	46 (1)	C(65)	7099	1795	1452	101 (4)
P(1)	2975 (2)	3136 (2)	3487 (1)	46 (1)	C(66)	6227	1244	1470	82 (3)
P(2)	2562 (3)	1533 (2)	1317 (2)	55 (1)	C(61)	5317	1368	802	75 (3)
O(1)	330 (6)	2716 (4)	2528 (4)	57 (3)	C(10)	3983 (10)	3890 (7)	3059 (6)	59 (2)
C(2)	−161 (6)	4318 (5)	1820 (4)	65 (3)	C(12)	2430 (8)	5515 (5)	2405 (4)	78 (3)
C(3)	−1167	5196	1512	89 (3)	C(13)	1781	6134	1705	106 (4)
C(4)	−2594	5341	1618	106 (4)	C(14)	2033	5808	904	99 (4)
C(5)	−3014	4607	2031	109 (4)	C(15)	2933	4863	804	92 (4)
C(6)	−2007	3729	2339	84 (3)	C(16)	3581	4244	1505	71 (3)
C(1)	−581	3584	2233	57 (3)	C(11)	3330	4570	2305	59 (2)
C(40)	1705 (11)	628 (7)	1501 (6)	67 (3)	C(20)	4033 (9)	2409 (7)	4383 (6)	55 (2)
C(42)	3247 (9)	−1050 (6)	2075 (5)	101 (4)	C(22)	5521 (6)	710 (5)	4064 (4)	75 (3)
C(43)	3861	−1727	2751	142 (6)	C(23)	6805	15	3869	84 (3)
C(44)	3555	−1478	3575	123 (5)	C(24)	8001	272	3757	96 (4)
C(45)	2636	−553	3722	106 (4)	C(25)	7913	1223	3839	86 (3)
C(46)	2023	124	3046	87 (3)	C(26)	6628	1918	4034	69 (3)
C(41)	2328	−125	2222	70 (3)	C(21)	5433	1661	4146	54 (2)
C(50)	1571 (11)	2379 (7)	444 (6)	64 (2)	C(30)	1443 (10)	3976 (7)	4014 (6)	58 (2)
C(52)	347 (7)	1508 (6)	−341 (4)	81 (3)	C(32)	1043 (7)	3673 (5)	5560 (4)	73 (3)
C(53)	168	1089	−1053	105 (4)	C(33)	548	3204	6236	83 (3)
C(54)	1008	1102	−1763	112 (5)	C(34)	−110	2550	6090	83 (3)
C(55)	2028	1534	−1761	109 (4)	C(35)	−272	2365	5269	80 (3)
C(56)	2208	1953	−1049	92 (4)	C(36)	223	2834	4593	66 (3)
C(51)	1367	1940	−339	65 (3)	C(31)	881	3488	4739	56 (2)
C(60)	4263 (11)	854 (8)	866 (7)	74 (3)	C(100)	5981 (19)	4224 (14)	5313 (19)	148 (12)
C(62)	5280 (8)	2041 (6)	115 (4)	95 (4)	C(101)	6318 (25)	4683 (19)	4638 (18)	154 (16)
C(63)	6153	2591	96	108 (4)	C(102)	5321 (33)	5519 (18)	4289 (16)	141 (14)
C(64)	7062	2468	764	116 (5)	C(103)	5775 (53)	5814 (30)	3685 (25)	150 (27)
					12				
Pd(1)	2158 (1)	2101 (1)	242 (1)	32 (1)	C(7)	1012 (16)	3407 (6)	−1161 (6)	89 (6)
C(1)	2319 (12)	999 (5)	808 (6)	63 (5)	O(1)	2903 (6)	1547 (4)	−687 (3)	45 (3)
P(1)	1644 (3)	2717 (1)	1253 (1)	35 (1)	C(12)	2902 (6)	652 (3)	−1673 (3)	42 (2)
C(2)	171 (12)	2450 (6)	1667 (5)	49 (5)	C(13)	2268	162	−2169	44 (2)
C(3)	2770 (13)	2660 (7)	1975 (6)	63 (6)	C(14)	962	117	−2152	57 (3)
C(4)	1523 (11)	3820 (5)	1074 (5)	45 (4)	C(15)	290	562	−1639	62 (3)
C(5)	980 (12)	3962 (5)	326 (5)	49 (5)	C(16)	924	1052	−1142	51 (2)
P(2)	1862 (3)	3347 (1)	−313 (1)	40 (1)	C(11)	2230	1097	−1159	38 (2)
C(6)	3262 (14)	3952 (6)	−455 (6)	63 (5)					

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

A colorless cube-shaped crystal of **12** of approximate dimensions 0.36 × 0.31 × 0.28 mm was used for the room-temperature crystal and intensity data collection. The unit cell parameters and systematic absences

$0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), $hk0$ ($h = 2n + 1$), $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) uniquely indicated *Pbca* as the space group. The structure was solved by direct methods. No ab-

Table III. Selected Bond Distances (Å) and Angles (deg) for **2** and **7** [M = Ni (**2**) and Pt (**7**)]

	2	7
M–P(1)	2.163 (3)	2.257 (3)
M–P(2)	2.171 (3)	2.271 (3)
M–O(1)	1.949 (7)	2.130 (6)
P(1)–C(10)	1.849 (8)	1.829 (12)
P(1)–C(20)	1.837 (9)	1.830 (9)
P(1)–C(30)	1.845 (10)	1.851 (9)
P(2)–C(40)	1.846 (9)	1.829 (13)
P(2)–C(50)	1.857 (8)	1.841 (9)
P(2)–C(60)	1.840 (10)	1.830 (10)
O(1)–C(1)	1.354 (8)	1.341 (8)
O(9)–C(91)	1.348 (10)	
O(1)–O(9)	2.544 (10)	
P(1)–M–P(2)	159.0 (1)	167.8 (1)
P(1)–M–O(1)	104.6 (2)	102.1 (2)
P(2)–M–O(1)	96.4 (2)	88.9 (2)
C(1)–O(1)–M	123.0 (4)	124.2 (5)
C(10)–P(1)–M	114.0 (3)	110.0 (3)
C(20)–P(1)–M	113.6 (3)	117.2 (3)
C(30)–P(1)–M	118.3 (3)	117.8 (4)
C(40)–P(2)–M	116.5 (3)	113.4 (3)
C(50)–P(2)–M	110.2 (3)	111.2 (4)
C(60)–P(2)–M	119.2 (3)	117.9 (4)
O(1)–C(1)–C(2)	121.4 (4)	123.0 (4)
O(1)–C(1)–C(6)	118.5 (3)	116.9 (4)
O(9)–C(91)–C(92)	121.8 (4)	
O(9)–C(91)–C(96)	118.2 (9)	

Table IV. Selected Bond Distances (Å) and Angles (deg) for **12**

Pd(1)–C(1)	2.101 (9)	Pd(1)–O(1)	2.098 (6)
Pd(1)–P(1)	2.192 (2)	O(1)–C(11)	1.351 (8)
Pd(1)–P(2)	2.313 (2)		

C(1)–Pd(1)–P(1)	89.8 (3)	P(2)–Pd(1)–O(1)	94.3
P(1)–Pd(1)–P(2)	86.2 (1)	Pd(1)–O(1)–C(11)	124.3 (5)
C(1)–Pd(1)–O(1)	90.0 (3)		

sorption correction was applied. The phenyl group of the OPh ligand was treated as an isotropic rigid group. All other atoms were refined anisotropically except hydrogen atoms, which were generated in idealized positions for the structure factor calculations and were not refined.

Results

Preparation of MHClL₂ (M = Ni (1), Pd (5), Pt (6); L = PBz₃). An attempt to synthesize NiHCl(PBz₃)₂ by a method analogous to that used by Green[23] for L = PCy₃ or PⁱPr₃ (reduction of NiCl₂(PBz₃)₂ with NaBH₄) was unsuccessful. This reaction resulted in decomposition of the NiCl₂(PBz₃)₂ starting material. The need for a weaker reducing agent was apparent. Several were surveyed,[24] but Super-Hydride [LiB(C₂H₅)₃H] gave the highest yield and produced the least difficulties in product isolation. This reaction still must be carried out at –40 °C in THF to obtain a reasonable yield of product. The complex was characterized by the upfield hydride triplet resonance at –23.03 ppm ($^2J_{P-H}$ = 72.0 Hz) in the ¹H NMR spectrum and by a singlet resonance at 24.33 ppm in the ³¹P{¹H} NMR spectrum, which resembles the spectra of bis(phosphine) square-planar hydrido chloro complexes reported previously.[23] The solid-state IR spectrum revealed an absorption at 1979 cm⁻¹ for the Ni–H stretching vibration. Compound **1** may be stored indefinitely at room temperature under an inert atmosphere.

An alternative methodology was necessary for the synthesis of the analogous palladium and platinum species. Here we chose to oxidatively add HCl to the corresponding metal ethylene complexes:

$$
\begin{array}{c}
\text{Bz}_3\text{P} \\ \diagdown \\ \diagup \\ \text{Bz}_3\text{P}
\end{array}
\text{M}\!-\!\|\; + \text{HCl} \longrightarrow
\left[
\begin{array}{c}
\text{Bz}_3\text{P} \quad \text{H} \\ \diagdown\;\diagup \\ \quad\text{M} \\ \diagup\;\diagdown \\ \text{Bz}_3\text{P} \quad \text{Cl}
\end{array}
\right]
\longrightarrow
\begin{array}{c}
\text{PBz}_3 \\ | \\ \text{H}\!-\!\text{M}\!-\!\text{Cl} \\ | \\ \text{PBz}_3
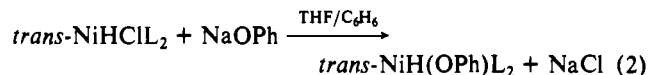\end{array}
\quad (1)
$$
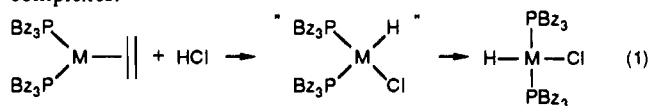
(23) Green, M. L. H.; Saito, T.; Tanfield, P. J. *J. Chem. Soc. A* **1971**, 152. (b) Green, M. L. H.; Munakata, H.; Saito, T. *J. Chem. Soc. A* **1971**, 469.

(24) Na[BH₃CN] gave no product, and Na[HB(OMe)₃] gave impure product in low yield.

These ethylene complexes can be generated in situ by the reduction of the dichloride species with 2 equiv of sodium naphthalide under an ethylene purge, as described in the Experimental Section. The ethylene compounds were not isolated but characterized spectroscopically, and further reactions of the solutions were carried out shortly after generation. The dropwise addition of a dioxane/HCl[21] solution to rapidly stirred solutions of the ethylene complexes produced MHCl(PBz₃)₂. On workup these compounds could be isolated in fair yield and crystallized by layering a C₆H₆ solution of the compound with pentane. These compounds exhibit spectroscopic characteristics similar to those of the nickel complex above and are also believed to possess a trans-phosphine square-planar geometry. Similar reactivity of Ni(CH₂= CH₂)(PBz₃)₂ with HCl was observed by ¹H NMR spectroscopy, but this reaction was not pursued further.

Preparation and Characterization of NiH(OPh)L₂ (L = PⁱPr₃ (4), PCy₃ (3), PBz₃ (2)). Addition of an excess of sodium phenoxide to a C₆H₆/THF solution of NiHClL₂ at room temperature resulted in the formation of *trans*-NiH(OPh)L₂ (eq 2).

$$\textit{trans}\text{-NiHClL}_2 + \text{NaOPh} \xrightarrow{\text{THF/C}_6\text{H}_6}$$
$$\textit{trans}\text{-NiH(OPh)L}_2 + \text{NaCl} \quad (2)$$

These compounds can be isolated in reasonable yield and must be handled under an inert atmosphere. Compounds **2–4** were identified by ¹H NMR spectroscopy, with the hydride resonance shifted upfield from the corresponding hydrido chloro species. Confirmation of the nickel-bound phenoxide was established by the change in chemical shift of the phenyl protons, in comparison to those of free phenol. The appearance of the upfield triplet hydride resonance and a singlet resonance in the ³¹P{¹H} NMR spectra suggested a square-planar trans-phosphine geometry for these complexes. We were unable to obtain crystals of **3** or **4** suitable for X-ray diffraction studies, but with the tribenzylphosphine derivative crystals of **2** were easily obtained. Its X-ray structure confirmed the trans square-planar geometry around nickel and showed a molecule of phenol in the crystal lattice hydrogen-bonded to the coordinated phenoxide. A broad OH stretching frequency was observed at 3370 cm⁻¹ in the solid-state IR spectrum for the lattice phenol. In CH₂Cl₂ the OH stretching frequency shifted to 3588 cm⁻¹. There was no appearance of an OH stretch in the IR spectrum for compounds **3** and **4**, which is consistent with their formulation as phenol-free compounds.

We also observed the formation of **2** by ³¹P and ¹H NMR spectroscopy when phenol was added to a C₆D₆ solution of Ni(CH₂=CH₂)(PBz₃)₂. The latter complex was generated as described in the Experimental Section.

Preparation and Characterization of PtR(OPh)L₂ [R = H (L = PBz₃) (7), R = C₂H₅ (L₂ = dmpe) (9)]. Because of the success with oxidative addition of HCl to Pt(CH₂=CH₂)(PBz₃)₂, we attempted a similar reaction with phenol as an acid. When a Et₂O solution of 1 equiv of phenol is added to a C₆H₆ solution of Pt(CH₂=CH₂)(PBz₃)₂, the resulting solution contains the desired hydrido phenoxo product, **7**, and it can be isolated in fair yield. As for the nickel phenoxides, compound **7** can be characterized easily by ¹H NMR spectroscopy. An upfield triplet resonance at –21.05 ppm, flanked by platinum satellites ($^1J_{PtH}$ = 1080 Hz), identifies the platinum hydride trans to the bound phenoxide. This geometry and connectivity is further confirmed by a single-crystal X-ray structure analysis of **7**. Unlike the case for the nickel complex, a free molecule of phenol was not found in the crystal lattice.

In an attempt to prepare a cis hydrido phenoxo complex, Pt(CH₂=CH₂)(dmpe) was generated in solution. When a diethyl ether solution of 1 equiv of phenol was added to the platinum ethylene complex (under an ethylene purge), a colorless solution results. Attempts to isolate crystalline product from this reaction resulted only in a colorless oil. The ³¹P{¹H} NMR spectrum revealed two doublets flanked by platinum satellites. The ¹H NMR spectrum displayed no observable hydride resonance and an extremely complicated alkyl region from platinum satellites and from coupling to the inequivalent phosphorus of the dmpe
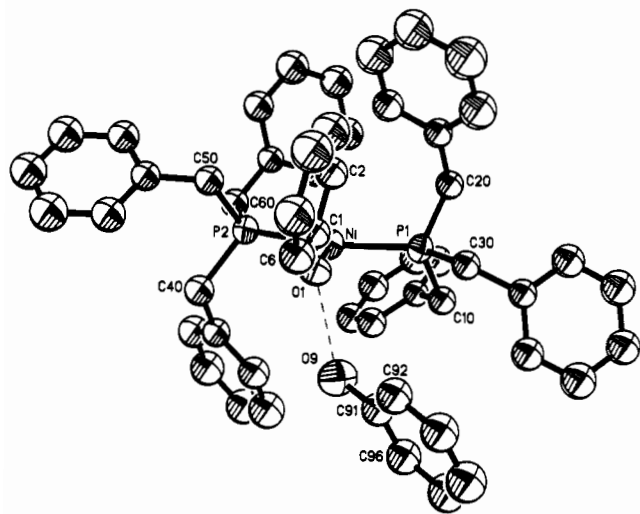
Figure 1. Thermal ellipsoid plot (50%) and atom-numbering scheme for **2**.
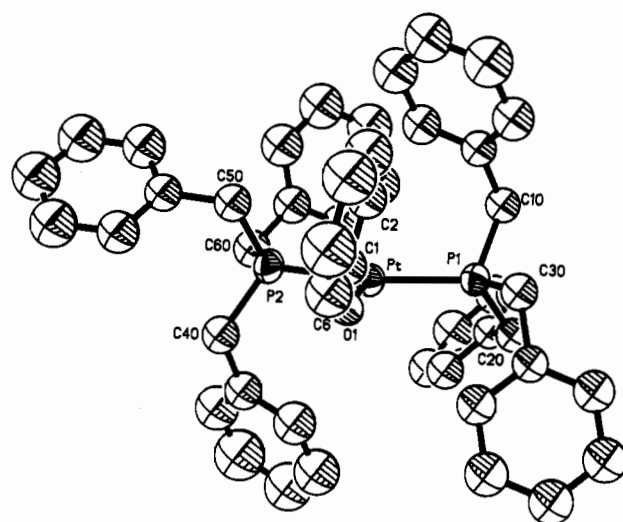

Figure 2. Thermal ellipsoid plot (50%) and atom-numbering scheme for **7**.

Figure 3. Thermal ellipsoid plot (50%) and atom-numbering scheme for **12**.

ligand. We determined that this complex was PtEt(OPh)(dmpe) (**9**) by its independent synthesis (and crystallization with analytical purity) from the metathesis reaction between PtEtCl(dmpe) (**8**) and NaOPh. Comparison of the ^{31}P and ^{1}H NMR spectra showed that these were identical compounds.

The acidity of phenol not only lends itself to oxidative addition chemistry but also allows protonolysis of metal–alkyl bonds. When PdMe$_2$(dmpe) is combined with 1 equiv of phenol, methane is evolved and **12** forms. This provides another synthetic route to *cis*-bis(phosphine) platinum group metal alkyl phenoxides. While our work was in progress, Yamamoto et al. also reported this reaction.[18] Here we report the X-ray crystal structure of **12**, for comparison with the analogous trans complexes.

Crystal Structure Determination of 2, 7, and 12. Slow cooling of a toluene solution of **2** layered with pentane yielded crystals of **2** suitable for analysis by X-ray diffraction. Complex **2** exhibits a trans square-planar geometry (Figure 1) with the hydride coordinated trans to the phenoxide ligand. The angles about the nickel atom are distorted from an ideal square-planar geometry. Steric crowding between the tribenzylphosphine and phenoxide ligands causes the phosphines to tilt toward the small hydride group with an angle P(1)–Ni–P(2) of 159.0 (1)°. This deviation is also seen in *trans*-PtH(OPh)(PEt$_3$)$_2$[16a] but to a lesser extent. The nickel–oxygen distance of 1.949 (7) Å in **2** is shorter than the platinum–oxygen bond length in *trans*-PtH(OPh)(PEt$_3$)$_2$[16a] by approximately 0.1 Å. The Ni–O–C(1) angle of 123.0 (4)° suggests sp^2 hybridization for the phenoxide ligand. In addition to the coordinated phenoxide ligand, molecules of free phenol crystallized in the lattice. The oxygen–oxygen distance of 2.544 Å between coordinated phenoxide and free phenol is in a range where hydrogen bonding occurs, as seen in other late-transition-metal phenoxide complexes.[5,18,19] Though we were unable to locate the hydrogen between O and O(9), its presence was established in the IR spectrum, as noted above.

The structure of **7** also exhibits a trans square-planar geometry (Figure 2) around the metal center (with similar angular deviations as observed above). No free phenol crystallized in the lattice along with **7**, even when free phenol was purposely introduced on recrystallization. The structure of **7** resembles that of *trans*-PtH-(OPh)(PEt$_3$)$_2$[16a] with the small differences attributed to the more sterically demanding tribenzylphosphine ligand.

Layering a methylene chloride solution of **12** with Et$_2$O produces single crystals suitable for X-ray diffraction studies. As expected compound **12** exhibits a nearly ideal cis square-planar geometry, as shown in Figure 3. The Pd–O bond distance of 2.098 (6) Å falls in the same range as in *trans*-PdH(OPh)(PCy$_3$)$_2$[5] and *trans*-Pd(Me)(OPh)(PMe$_3$)$_2$[18] (2.135 (2) and 2.106 (3) Å, respectively). There is a small change in the metal–oxygen bond distance when the ligand trans to the coordinated phenoxide is changed from H$^-$ or CH$_3^-$ to P(CH$_3$)$_2$R. The Pd(1)–O(1)–C(11)
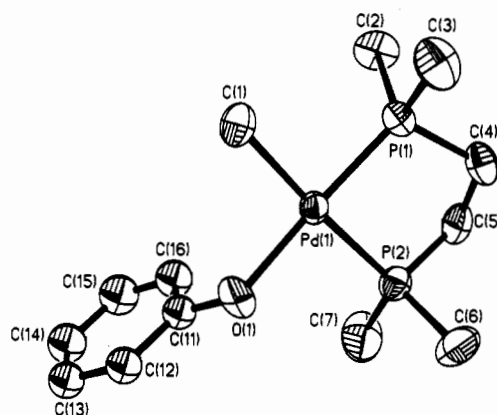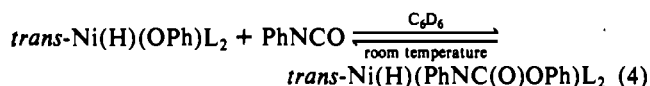
angle of 124.3 (5)° resembles that in other palladium phenoxides reported,[5,18] as well as in the nickel and platinum examples discussed above.

Reactivity of MH(OPh)L$_2$. When C$_6$D$_6$ solutions containing 20 mg of **2**, **3**, or **4** in a NMR tube are combined with an excess amount of CH$_3$I at room temperature, new resonances were observed in the ^{1}H and ^{31}P NMR spectra after several hours. The organic ether anisole was identified (^{1}H NMR) by the addition of authentic sample to the reaction tube. The metal complexes were identified as the corresponding NiHIL$_2$ complexes (eq 3).

$$trans\text{-NiH(OPh)L}_2 + CH_3I \xrightarrow[\text{room temperature}]{C_6D_6} trans\text{-NiHIL}_2 + CH_3OPh \quad (3)$$
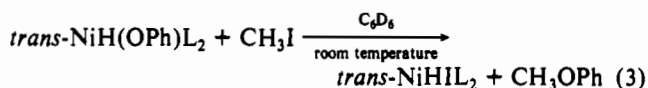
For L = PCy$_3$ and P^{i}Pr$_3$ the iodo compounds have been previously reported[23] and exhibit ^{1}H and ^{31}P NMR spectra identical with those of the products we observe. The complex NiHI(PBz$_3$)$_2$ has not been previously reported. The downfield shift of the hydride to −18.66 ppm and shift of the ^{31}P NMR resonance to 27.77 ppm, similar to L = PCy$_3$ and P^{i}Pr$_3$, suggests this compound is also a hydrido iodo species.

When phenyl isocyanate is added to a C$_6$D$_6$ solution of **2**, **3**, or **4**, we are able to observe by ^{1}H NMR spectroscopy a total conversion of the hydrido phenoxo species into a new hydride species. The hydride resonances for L = PBz$_3$, PCy$_3$, and P^{i}Pr$_3$ appear at −23.01, −24.95, and −24.93 ppm, respectively, about 3 ppm downfield from the corresponding hydrido phenoxo resonance. We assign this new hydride species to the hydrido–phenyl *N*-phenylcarbamato insertion product (eq 4). Similar reactivity has been observed previously with *trans*-PtH(OPh)(PEt$_3$)$_2$, where the insertion product *trans*-PtH(PhNC(O)OPh)(PEt$_3$)$_2$ was iso-

$$trans\text{-Ni(H)(OPh)L}_2 + \text{PhNCO} \xrightarrow[\text{room temperature}]{C_6D_6}$$

$$trans\text{-Ni(H)(PhNC(O)OPh)L}_2 \quad (4)$$

lated and characterized.[16a] This compound also exhibits a 3 ppm downfield shift of the hydride resonance compared to the hydrido phenoxo complex. Attempts to isolate the reaction product of **3** with phenyl isocyanate (observed by ¹H NMR) resulted only in recovery of starting material. This suggests a reversible insertion reaction occurs and is consistent with a higher kinetic lability for nickel(II).[25]

Synthesis and Characterization of Palladium Anilide Complexes. Hydrido amido complexes of palladium are unknown.[17b] The hydrido anilido complexes of palladium(II) *trans*-PdH-(NHPh)(PᶦPr₃)₂ (**10**) and *trans*-PdH(NHPh)(PCy₃)₂ (**11**) were prepared by metathesis of the corresponding hydrido chloro complexes with a slight excess of sodium anilide (eq 5). Palla-

$$\text{PdHClL}_2 + \text{NaNHPh} \xrightarrow[L = P^iPr_3, PCy_3]{C_6H_6}$$

$$\text{NaCl(s)} + \text{PdH(NHPh)L}_2 \quad (5)$$

dium(II) prefers the amide ligand over chloride, and the metathesis reaction goes to completion even with near stoichiometric amounts of anilide. This contrasts with the platinum analogues, which require removal of chloride before the metathesis reaction with anilide will proceed to completion.[16]
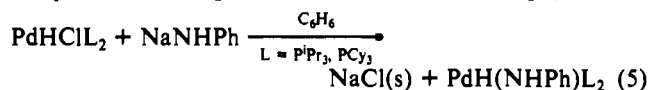
Complex **10** is thermally unstable and could not be isolated as a solid; however, it is stable in benzene solution for several hours. The PCy₃ complex is stable enough to be isolated as fine pale yellow needles by cooling a saturated solution of the complex in cyclohexane/pentane (yield 51%). Complex **11** is thermally sensitive and will decompose at room temperature within days; however, it can be stored for several weeks if kept at low temperature (−10 °C). The products of thermal decomposition of **11** are aniline and Pd(PCy₃)₂, which have been identified by comparison of their ¹H and ³¹P{¹H} NMR spectra to those of authentic samples.[22] The decomposition is insidious, since decomposition can occur during recrystallization to yield crystals of Pd(PCy₃)₂, which visibly resemble **11**. A definitive test for decomposition is by NMR analysis of the sample.

The ¹H NMR spectrum of **10** in C₆D₆ shows the resonances expected for the aromatic protons in the anilide ring: δ 7.25 (t, J = 8 Hz, m-C₆H₅), 6.72 (d, J = 8 Hz, o-C₆H₅), 6.47 (t, J = 7 Hz, p-C₆H₅). The phosphine resonances at δ 1.96 and 1.12 are assigned to the secondary and methyl protons, respectively. The N–H proton occurs as a singlet at δ 1.77, while the Pd–H resonance appears as a singlet with a chemical shift of −14.06 ppm.[26] The hydride resonance does not show coupling to the cis-phosphorus atoms; however, the ³¹P{¹H} NMR spectrum exhibits a singlet at 53.0 ppm, which is consistent with a trans structure for the complex.

Complex **11** exhibits ¹H NMR resonances similar to those for complex **10**. For example, the aromatic and hydride resonances are δ 7.24 (t, J = 8 Hz, m-C₆H₅), 6.74 (d, J = 8 Hz, O-C₆H₅), 6.45 (t, J = 7 Hz, o-C₆H₅), and −13.89 (s, Pd–H). The N–H resonance is obscured by the broad resonances from the cyclohexyl protons between 2.2 and 1.1 ppm. The ³¹P{¹H} NMR spectrum exhibits a singlet at 40.6 ppm, which again suggests a trans geometry.

Definitive evidence for the structures of **10** and **11** was obtained by preparing ¹⁵N-labeled complexes and examining their NMR spectra for coupling to the newly incorporated spin-active nucleus. Both complexes exhibit identical ¹⁵N couplings with the metal hydride ($^2J_{^{15}NH}$ = 24 Hz) as observed by ¹H NMR spectroscopy, and complex **11** also shows a $^1J_{^{15}NH}$ coupling of 67 Hz, which closely resembles that of 71 Hz in *trans*-PtH(¹⁵NHPh)(PEt₃)₂.[16] The ³¹P{¹H} NMR spectrum of **11**, recorded in C₆D₆ solvent, is a singlet and does not show coupling with the cis ¹⁵N nucleus, as was also observed for *trans*-PtH(¹⁵NHPh)(PEt₃)₂;[16] however, the

¹⁵N{¹H} NMR spectrum for complex **10** shows a triplet (4.8 ppm downfield of ¹⁵NH₂Ph, $^2J_{P-^{15}N}$ = 3 Hz) from weak coupling with equivalent cis ³¹P nuclei. These data provide substantial evidence that the anilide ligand is bound to palladium and provide the first examples of hydrido amido complexes of palladium.

Reactions of PdH(NHPh)(PCy₃)₂ (11). The reactivity of complex **11** has been investigated by using ¹H and ³¹P{¹H} NMR spectroscopy. Reactions were performed in 5-mm NMR tubes sealed under nitrogen with the appropriate reactant added. Complex **11** reacts quickly with compounds containing protic hydrogens to give aniline and a new palladium hydride complex of the deprotonated substrate. The reaction with water was expected to yield aniline and *trans*-PdH(OH)(PCy₃)₂; however, the hydroxo species for palladium has never been observed and the only palladium-containing product identified by ³¹P{¹H} NMR spectroscopy is Pd(PCy₃)₂. This complex may arise from reductive elimination of water from an intermediate hydrido hydroxo complex. This is consistent with the report of Yoshida et al.[27] that Pd(PCy₃)₂ is inert to methanol and water. This suggests that, unlike the PtL₂ analogues,[2] oxidative addition of water or methanol to Pd(0) is unfavorable.

The addition of acetylene to **11** yields *trans*-PdH(C≡CH)-(PCy₃)₂, as seen in the ¹H NMR spectrum (−9.01 ppm, Pd–H). Analysis of the reaction mixture by ³¹P{¹H} NMR spectroscopy shows clean transformation of the starting material to a new phosphorus-containing species at 47.3 ppm. The identity of the hydrido acetylide product has been verified by preparing the complex from *trans*-PdH(NO₃)(PCy₃)₂[20,28] and LiC≡CH·N-H₂CH₂CH₂NH₂ and comparing their NMR spectra. It is noteworthy that the reaction of **11** with acetylene gas is a clean synthetic procedure, while the metathesis reaction produces several byproducts, as evidenced by ³¹P{¹H} NMR spectroscopy.

The reaction between **11** and PhNCO proceeds instantly to yield a new complex with a single peak at 39.7 ppm in the ³¹P{¹H} spectrum. The new hydride resonance (¹H NMR) occurs as a triplet at −14.55 ppm with $^2J_{P-H}$ = 11 Hz. These chemical shifts and peak multiplicities clearly indicate the product possesses a trans geometry and a slightly weaker trans influence ligand than anilide. For these reasons, and by analogy to our previous work with platinum hydrido anilides,[16] we formulate the complex as *trans*-PdH[PhNC(O)NHPh](PCy₃)₂. Attempts at workup led to the isolation of Pd(PCy₃)₂.

Reductive elimination of aniline from the metal center dominates the reaction chemistry of **11** with ethylene and acrylonitrile. These two olefins add to yield aniline and the corresponding olefin complexes of Pd(PCy₃)₂. The identity of these olefin complexes was established by their direct synthesis from Pd(PCy₃)₂ and the olefin. The reaction with acrylonitrile is noteworthy, since the platinum complex *trans*-PtH(NHPh)(PEt₃)₂ cleanly inserts the olefin into the metal–nitrogen bond[16] while palladium does not. For palladium it appears that these olefins coordinate and induce reductive elimination.

Discussion

Synthesis and Reactivity of Hydridophenoxonickel and -platinum Complexes. The first hydrido phenoxo complex of nickel, **3**, was reported by Jonas and Wilke[4a] and more recently characterized by Darensbourg, Ludwig, and Riordan.[4b] This compound was prepared by oxidative addition of phenol to Ni(PCy₃)₂. This synthetic strategy is limited, since few isolable bis(phosphine)-nickel(0) complexes are known. Treatment of the hydrido chloro complexes of nickel(II) with NaOPh (eq 2) allows the synthesis of **2–4**.

The oxidative addition of phenol to Pd(PCy₃)₂ has also been reported to yield *trans*-PdH(OPh)(PCy₃)₂·HOPh.[5] Because of the success of this reaction, we attempted to prepare other palladium hydrido phenoxide species by the metathesis technique. When PdHClL₂ (L = PᶦPr₃, PBz₃) and sodium phenoxide are

(25) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishing Co.: Monterey, CA, 1985.
(26) These can be compared to the compound *trans*-PtH(NHPh)(PEt₃)₂.[16]

(27) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.
(28) The complex *trans*-PdH(NO₃)(PCy₃)₂ was prepared from the reaction between *trans*-PdHCl(PCy₃)₂ and TlNO₃ in C₆H₆/MeOH solvent. This complex has been prepared previously by a different method.[20]
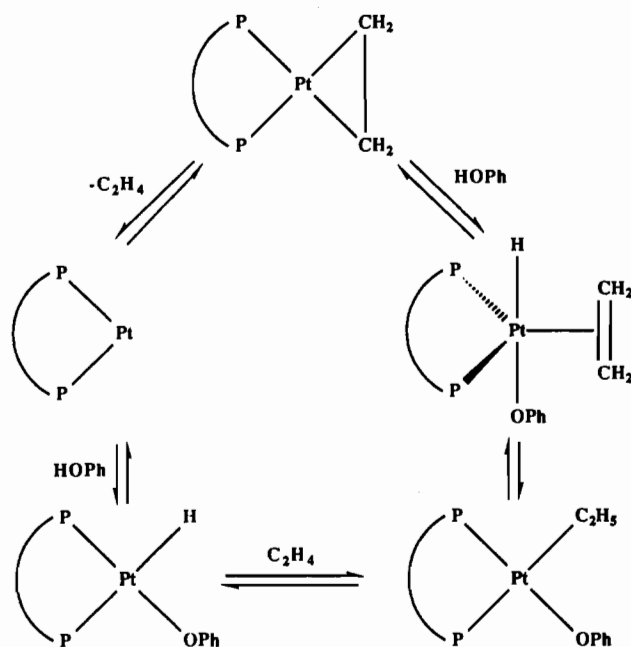
Scheme II

Scheme III
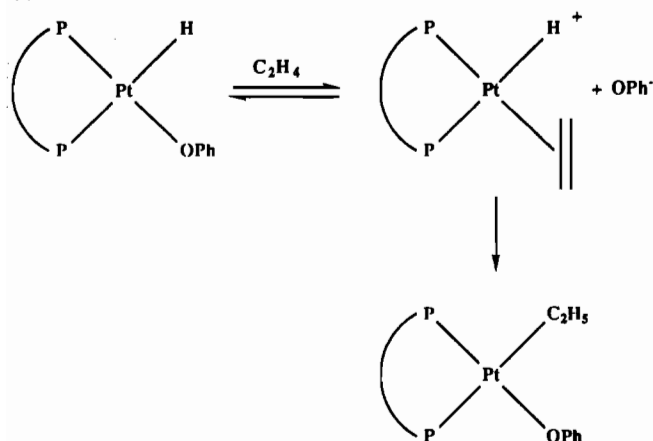
combined, they yield only PdL$_n$[29] compounds and free phenol, in contrast to the nickel analogues. When Pd(CH$_2$=CH$_2$)L$_2$ was combined with phenol, we again observe only PdL$_n$[29] species present. This suggests that palladium hydrido phenoxide species are unstable toward reductive elimination of phenol at room temperature when a weak ligand, such as ethylene, is present. With the coordinatively unsaturated Pd(PCy$_3$)$_2$ species oxidative addition may occur.[5]

Similar oxidative-addition reactions were attempted with M(CH$_2$=CH$_2$)(PBz$_3$)$_2$ (M = Ni, Pt). In contrast to the results obtained with palladium, the reaction between the nickel complex and phenol yielded **2**, as identified by its ^{1}H and ^{31}P NMR spectra. For M = platinum, **7** was isolated in reasonable yield. This procedure eliminates several steps in comparison to the procedure used in the synthesis of PtH(OPh)(PEt$_3$)$_2$. These results imply that the M = Pt and Ni compounds have a more favorable thermodynamics for oxidative addition of phenol than for M = Pd. The tendency for Pt(0) to have more favorable energetics for oxidative addition than Pd(0) is well-known for the H–H and C–H oxidative-addition reactions. Low and Goddard[30] attribute this to the lower d^{10} → d^{9}s^1 promotion energy for Pt(0) of 11.0 kcal/mol in comparison to the 21.9 kcal/mol necessary for the corresponding promotion in Pd(0). This consideration arises because only the d^{9}s^1 configuration can form the two additional σ bonds required by oxidative addition. Since Ni(0) has the d^{9}s^1 configuration as the lowest singlet state for the free atom,[30] promotion energy considerations should favor oxidative addition even more. While we recognize that differing metal–ligand bond strengths will also affect the thermodynamics of oxidative addition, the relative promotion energies helps one rationalize the anomalous reactivity of Pd(0).

The success of oxidative addition of phenol to the platinum ethylene complex prompted us to attempt to synthesize a cis phosphine hydrido phenoxo species that contained the chelating bis(phosphine) dmpe. Oxidative addition of phenol to Pt-(CH$_2$=CH$_2$)(dmpe) yielded a colorless oil, which exhibited ^{31}P NMR resonances consistent with a platinum complex that contained two inequivalent cis-phosphorus nuclei. Neither ^{1}H NMR nor IR spectroscopy showed the presence of a hydride ligand. The complexity of the alkyl region in the ^{1}H NMR spectra from the phosphorus and platinum coupling made an assignment difficult. We noted that a *cis*-phosphinealkylmethoxoplatinum complex, prepared previously by Brynzda,[31] exhibited phosphorus resonances with similar $^1J_{PtP}$ coupling constants. This led us to conclude that an alkyl phenoxo complex had formed. This reactivity has precedent; Pd(cyclohexyne)(dppe) is easily protonated by the weak acid *p*-cresol to yield a cyclohexenyl cresolate complex.[32] To test

this hypothesis, PtEtOPh(dmpe) was synthesized by an alternative pathway, and it exhibited a ^{31}P NMR spectrum identical with that obtained in the preceding reaction.

One possible mechanism for this transformation is shown in Scheme II. This resembles the mechanism proposed by Whitesides and co-workers[33] for the reaction between Pt-(C$_2$H$_4$)(PPh$_3$)$_2$ and strong protonic acids. Although phenol is not a strong acid, the chelating dmpe ligand is a much stronger donor than PPh$_3$. Cationic hydrido olefin complexes similar to the intermediate species in Scheme II have been spectroscopically identified and isolated.[34] On warming, these compounds were shown to insert ethylene into the platinum–hydride bond to produce a alkylplatinum moiety.[35]

An alternative pathway would involve direct oxidative addition of phenol to the metal center. This resembles the microscopic reverse of the mechanism proposed by Bryndza et al.[36] for the thermal decomposition of bis(phosphine)alkylalkoxoplatinum complexes. In this scheme either ethylene will remain bound to the metal center to yield a five-coordinate platinum intermediate or prior dissociation of ethylene will result in the formation of a cis hydrido phenoxo intermediate. Either step must be followed by ethylene insertion into the hydride to yield the observed product **9**, as shown in Scheme III. We have observed that the addition of phenol to the ethylene complex in the absence of excess ethylene results in precipitation of platinum metal. Excess ethylene must be needed to drive the equilibrium toward one of the ethylene species mentioned above. Similar reactivity for the oxidative addition of phenol to Pt(CH$_2$=CH$_2$)(PBz$_3$)$_2$ was not observed. However, when HCl was added to the analogous ethylene complex, besides the production of the desired product **6**, Pt(C$_2$H$_5$)(Cl)-(PBz$_3$)$_2$ forms. These data do not permit us to favor either scheme over the other at present.

Structural Data for Hydridophenoxonickel and -platinum Complexes. Over the past few years there have been several crystal structures of late-transition-metal phenoxo compounds reported.[5,16a,18,19] In this manuscript we report the first X-ray structure

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Table V. Oxygen–Oxygen Distances of Late-Metal Hydrogen-Bonded Phenoxo Compounds

	O···O, Å
trans-NiH(OPh)(PBz₃)₂·HOPh	2.544[a]
trans-NiMe(OPh)(PMe₃)₂·HOPh	2.602[b]
trans-PdMe(OPh)(PMe₃)₂·HOPh	2.593[b,c]
trans-PdMe(OPh)(PMe₃)₂·HOCH(CF₃)Ph	2.601[b]
cis-PtMe[OCH(CF₃)₂](PMe₃)₂·HOCH(CF₃)₂	2.63[b]
trans-PdH(OPh)(PCy₃)₂·HOPh	2.63[d]
trans-PdH(OC₆F₅)(PCy₃)₂·HOC₆F₅	2.57[d]
Rh(OC₆H₄CH₃)(PMe₃)₃·HOC₆H₄CH₃	2.62[e]

[a] Reported in this work. [b] See ref 18. [c] $\Delta H = -5.6$ kcal/mol (CD₂-Cl₂), measured by variable-temperature ¹H NMR spectroscopy. [d] See ref 5. [e] See ref 19. $\Delta H = -14.0 \pm 0.4$ kcal/mol (cyclohexane) and -11.4 ± 0.5 kcal/mol (C₆H₆), measured by calorimetric determination.

determination of a hydridophenoxonickel complex. The structure of **2** differs from its platinum analogue **7** by the inclusion of a hydrogen-bonded phenol in the lattice. This has also been observed for *trans*-NiCH₃(OPh)(PMe₃)₂·HOPh.[18] The nickel–oxygen bond distances are within experimental error of each other, which is consistent with the small difference in the trans effect between hydride and methyl ligands. The O–O distance of 2.544 Å between the coordinated phenoxide and free phenol is ~0.05 Å shorter in **2** than in the alkylnickel compound.

The OH stretching frequency of the hydrogen-bonded phenol shifts from 3370 cm⁻¹ in the solid-state IR spectrum of **2** to 3588 cm⁻¹ in solution. This shift to higher frequency in the solution IR spectrum results from dissociation to form free phenol. The only other report of the O–H stretching frequency in a hydrogen-bonded late-metal phenoxide is that of 3180 cm⁻¹ observed[5] for PdH(OPh)(PCy₃)₂·HOR with R = C₆H₅ or C₆F₅. The insensitivity of this vibration to R and the possible interference from C–H stretching vibrations leads us to be cautious about making comparisons. Hydrogen bonding to anionic ligands is evident in some other transition-metal systems[37] but seems to be common in late-transition-metal alkoxides and phenoxides.

We were unable to measure the association constant for hydrogen bonding because of the low stability of **2** in solution; however, its strength can be estimated by comparison of the hydrogen-bonded O···O distance. The shortest reported distances for two oxygen atoms bridged by a proton fall in a range 2.29–2.34 Å,[38] for strong or very strong hydrogen bonds. An O···O distance of 2.544 Å falls in the range of moderately strong hydrogen bonds. Similar O···O distances are reported for HCOOH (2.58 Å), KHC₂O₄ (2.518 Å), and KH₃(SeO₃)₂ (2.566 (1) Å).[39] Table V lists the O···O bond distances for several late-transition-metal complexes that contain hydrogen-bonded phenoxide ligands. Compound **2** has an O···O distance ~0.03 Å shorter than any of the others reported to date. This suggests that **2** may have the strongest hydrogen bond in the solid state.

Reactivity Comparisons of MH(OPh)L₂. Our expectation that altering the metal center of the hydrido phenoxo compound from platinum to nickel would increase reactivity appears to be correct. Unfortunately, the increased reactivity lowered the energy pathway for reductive elimination instead of that for olefin insertion. The reactions of **2**, **3**, or **4** with olefins (activated or unactivated) result in reductive elimination of phenol in contrast to the insertion chemistry found for PtH(OPh)(PEt₃)₂.[16a]

Compounds **2–4** did exhibit insertion chemistry similar to that for PtH(OPh)(PEt₃)₂[16a] with phenyl isocyanate. The reaction of

these compounds with phenyl isocyanate results in the formation of new *trans*-hydrido(phenyl *N*-phenylcarbamato-*N*)metal complexes. Although these compounds could not be isolated, they are spectroscopically similar to the insertion product isolated from the reaction with PtH(OPh)(PEt₃)₂.[16a] The recovery of starting material from workup of the reaction of **3** with excess phenyl isocyanate suggests that the insertion is readily reversed.

The nucleophilicity of the phenoxide ligand is also retained when it is bound to a d⁸-metal center. Thus, the reaction between **2–4** and excess methyl iodide in nonionizing benzene solvent results in the formation of anisole, by nucleophilic attack of the phenoxo ligand on CH₃I.

The reactivity of **7** parallels that of PtH(OPh)(PEt₃)₂[16a] closely, so it will not be discussed in depth. The only difference is that many reactions of **7** require heating, whereas the less hindered PtH(OPh)(PEt₃)₂[16a] species reacts at room temperature. Compound **7** is stable to reductive elimination at 70 °C for several hours in C₆D₆. This increased stability apparently results from the larger cone angle of tribenzylphosphine as compared to triethylphosphine.[40] The bulky phosphine favors the trans conformation and hinders the hydride and phenoxo ligands from becoming cis to one another, which would facilitate reductive elimination.

Reactivity of Hydridoanilidopalladium Complexes. The first example of hydrido amido complexes of palladium were synthesized and characterized by spectroscopic techniques. The reactivity of the palladium complexes, while anticipated to be similar to platinum analogues, was dominated by N–H reductive elimination of aniline. The only example of insertion was obtained by the reaction between phenyl isocyanate and **11** to yield *trans*-PdH(PhNC(O)NHPh)(PCy₃)₂. Acrylonitrile, which inserted cleanly into the Pt–N bond of *trans*-PtH(NHPh)(PEt₃)₂,[16] only served to induce reductive elimination of aniline from **11** with no evidence for insertion. Although palladium–amide complexes show the expected enhancement of reactivity, the ease with which reductive elimination occurs precludes the use of palladium as a catalyst for reactions involving insertions into the metal–amide bond or in activation of the N–H bond by Pd(0) complexes. Attempts to generate analogous hydridoanilidonickel(II) complexes by metathesis reactions at −70 °C were unsuccessful because of immediate decomposition.

Conclusions

The present studies, together with our earlier work,[16] suggest nearly balanced thermodynamics for the equilibrium of eq 6 and

$$ \text{(6)} $$

$$ \text{(7)} $$
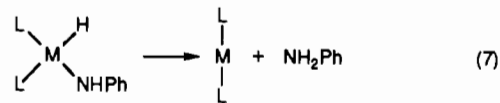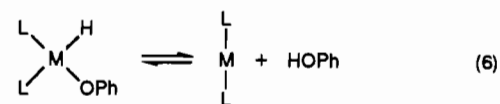
an equilibrium that lies to the right for eq 7 for M = Ni, Pd, and Pt and L = phosphine ligand. Thus, while some hydrido phenoxo complexes can be prepared by oxidative addition of phenol[4–6] to zerovalent complexes, the hydrido anilido complexes can only be prepared by metathesis reactions of *trans*-metal(II) hydride species. The *trans*-hydridoanilidometal complexes are metastable and decompose according to eq 7 when nucleophiles are present to allow trans to cis conversion. The relative instability of the anilidometal complexes is consistent with Bryndza and Bercaw's observation that M–NR₂ bonds are weaker than M–OR bonds for the late transition metals.[41] A discouraging observation on realizing insertion chemistry with these complexes is the ease with which substrates that can ligate (e.g., acrylonitrile or CO) promote the reductive elimination reactions shown in eqs 6 and 7. When

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one considers the order of bond strengths[41] M–C > M–O > M–N together with the order N–H > O–H > C–H, we conclude that catalytic amination of olefins by the mechanism of Scheme I will be difficult to achieve unless the N–H bond is activated (e.g., in NH$_2$COR).[7,42] Heterolytic activation paths that take advantage of the inherent acidity of N–H bonds are being explored in our

laboratories as an alternative mechanism for catalytic amination.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates and figures showing complete atom-numbering schemes for **2** and **7** (9 pages); tables of observed and calculated structure factors (66 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403,
Department of Chemistry, University of California, Davis, California 95616, and
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Effects of HgCl$_2$ and W(CO)$_5$ Coordination on the Structure of a 1,2-Dihydrophosphete (Phosphacyclobutene)

Kenneth M. Doxsee,*,† Erin M. Hanawalt,† Gregory S. Shen,† Timothy J. R. Weakley,† Håkon Hope,‡ and Carolyn B. Knobler§

The synthesis and structural characterization of 1,3,4-triphenyl-1,2-dihydrophosphete and its complexes with mercuric chloride and tungsten pentacarbonyl are reported. Changes in bond lengths and angles upon metal coordination are consistent with an increased bonding contribution from the phosphorus s orbital. This rehybridization is supported by ^{1}H, ^{13}C, and ^{31}P NMR spectral studies. Metal coordination does not lead to any significant skewing of the geometry of the phosphacyclobutene ring toward the corresponding ring-opened 1-phosphabutadiene form, and in fact may have the reverse effect.

Introduction

Small-ring carbocyclic and heterocyclic compounds continue to be of considerable interest. Questions about ring strain in these materials make them fertile ground for physical study, while the rich reaction chemistry of such compounds, frequently driven by relief of this ring strain, makes them key targets for synthetic study. Preliminary accounts suggest that phosphacyclobutenes (1,2-dihydrophosphetes) may provide convenient synthetic entry into unusual new classes of phosphorus heterocycles.[1–8] However, work in this area has been hampered by the lack of a simple, general route to the phosphacyclobutene ring system. Until recently, only a single representative, bearing a *P*-amino substituent, had been prepared in its uncomplexed form,[5] while several other phosphacyclobutenes had been isolated in the form of their tungsten pentacarbonyl complexes or their *P*-oxides.[2] We have developed[9,10] a simple and efficient synthesis of a variety of uncomplexed, trivalent, non-heteroatom-substituted phosphacyclobutenes and have taken advantage of this unique opportunity to embark on an examination of the structure and reactivity of these simple phosphorus heterocycles.

Reactivity of tungsten-coordinated phosphacyclobutenes consistent with electrocyclic ring opening to 1-phosphabutadienes, followed by [4 + 2] cycloaddition with added dienophiles, has been reported.[3] Indeed, on the basis of results of an X-ray diffraction analysis of one of these tungsten complexes, some distortion of the ground-state structure of the phosphacyclobutene toward the corresponding ring-opened form has been inferred.[2,11] Although similar propensity toward ring opening has been documented in other small-ring heterocycles,[12–15] our initial studies[16] of the reactivity of a simple, uncomplexed representative of this class of compounds, phosphacyclobutene **1**, appeared to be inconsistent with this proposal. In light of the differences between the reactivity of uncomplexed phosphacyclobutene **1** and that of one of the reported tungsten complexes, we felt it was critical to study the effects of metal coordination on both the structure and reactivity of **1**. For this comparison, we chose to examine two quite different metal complexes—the mercuric chloride complex (**2**), to permit

an assessment of the importance of metal electrophilicity on complex structure and reactivity, and the tungsten pentacarbonyl complex (**3**), to facilitate comparison with literature reports. Herein, we report the synthesis and structural characterization of uncomplexed phosphacyclobutene **1** and its metal complexes, **2** and **3**.
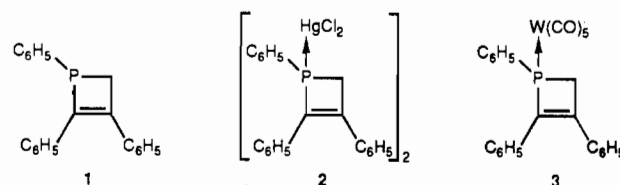
Results

Addition of 1 equiv of phenyldichlorophosphine to a solution of 2,3-diphenyl-1-titanacyclobut-2-ene[17] in benzene results in

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†University of Oregon.
‡University of California—Davis.
§University of California—Los Angeles.