Supramolecular *trans*-Coordinating Phosphine Ligands

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We report a new urea-functionalized phosphorus ligand and palladium complexes thereof that self-associate by hydrogen bond formation. The solution studies of a urea-based phosphine ligand {*m*-[EtO-(CO)CH_2NH(CO)NH]$C_6H_4PPh_2$}, **1**, and the palladium complex (**1**)$_2$PdMeCl, **2**, show that intermolecular and intramolecular hydrogen-bonding, respectively, is present between the urea hydrogens and the carbonyl of a second urea moiety. Introduction of NBu_4Cl to **2** results in the disruption of the self-association and the production of {[*trans*-(**1**$_2$Cl)PdMeCl]$^-$[NBu_4]$^+$}, **3**, with an anion-templated, bidentate phosphine ligand system. Although the ligands are hydrogen-bonding to the chloride anion, they remain in a *trans* configuration about the metal center. If another equivalent of **1** is added to **2**, a zwitterionic palladium methyl complex ligated by three phosphine ligands is produced and the chloride anion is abstracted from the metal center into the resulting tris-urea hydrogen-bonding pocket, generating [(**1**$_3$Cl)PdMe], **4**. If at −80 °C ^{13}CO is introduced to **2** instead of **1**, the chloride anion is once again abstracted into the bis-urea pocket and the zwitterionic CO-adduct *trans*-[(**1**$_2$Cl)Pd(^{13}CO)(Me)], **5**, results. However, upon warming to ambient temperature, CO migratory insertion occurs to generate the acetyl species and the chloride anion migrates back to the palladium center, *regenerating* a neutral complex. The analogous CO-adduct of **3** could not be produced since the urea pocket is already blocked with a chloride anion, stressing the subtle control the urea pocket exerts over the reactivity of the palladium center.

Introduction

Ligand modification is the most important tool to control the reactivity and selectivity of homogeneous transition metal catalysts. Bidentate chelating ligands comprise an important class of compounds employed to support these transition metal catalysts.[1] Traditionally bidentate ligands have been produced by conventional synthetic routes, but recent results from our group[2] and others[3,4] have shown that a new class of bidentate ligands can be formed by a self-assembly process of two monodentate species. We have used the zinc(II)porphyrin−pyridyl interaction as an assembly motif to generate bidentate phosphorus-based ligands and have shown that only 14 building blocks were required to generate a library of 48 bidentate phosphorus ligands that was successfully used in hydroformylation and asymmetric allylic alkylation.[2] More recently this approach was extended to asymmetric rhodium-catalyzed hydrogenation of a trisubstituted cyclic enamide, which yielded unprecedented selectivities.[2e] Breit has reported the production of homo- and heterodimeric bidentate, *cis*-coordinated phosphine ligands via hydrogen-bonding interactions, and these ligands performed very well in the rhodium-catalyzed hydroformylation of alkenes.[4bc] The number of hydrogen-bonded bidentate phosphine ligands is still small, and so far only *cis*-coordinated (up to 120° for trigonal bipyramidal) metal complexes have been reported. Even when traditional synthetic routes are employed, there are still relatively few examples of *trans*-spanning bidentate phosphines that do not utilize an additional heteroatom (i.e., are in fact tridentate).[5] These *trans*-spanning ligands allow for the exploration of different coordination geometries about the metal center to provide insight into known catalytic pathways and the development of new catalysts with unique properties. Herein we report the synthesis of a versatile urea-based ligand system that provides the first examples of a hydrogen-bonded *trans*-coordinating bidentate phosphine ligand system (Scheme 1).[6] The bis-urea binding pocket also accommodates chloride anions, which in turn controls the reactivity of the metal center.

Results and Discussion

The urea-based phosphine ligand (*m*-$Ph_2PC_6H_4$NH(CO)NH−CH_2(CO)OEt), **1**, was synthesized by converting *m*-fluoroaniline

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10.1021/om050865r CCC: $33.50
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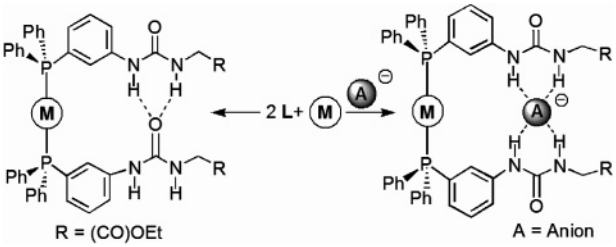
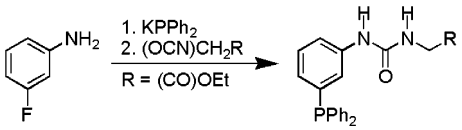
Scheme 1. Formation of a *trans*-Coordinating Phosphine Ligand System via Self-Association, 2 (left), or Anion-Templation, 3 (right)



Scheme 2. Synthesis of Urea-Based Phosphine Ligand 1



into *m*-(diphenylphosphorus)aniline with potassium diphenyl phosphide[7] ($KPPh_2$) and subsequent reaction of *m*-(diphenylphosphorus)aniline with ethyl isocyanatoacetate to generate the urea functionality (Scheme 2). Two equivalents of **1** were added to CODPdMeCl to produce the metal complex $\mathbf{1}_2$PdMeCl, **2**, which was fully characterized by ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR and IR spectroscopy, ESI-MS, and elemental analysis. The singlet observed in the ^{31}P{^{1}H} NMR spectrum at 32.7 ppm indicates that the phosphine ligands are coordinated in a *trans* configuration about the metal center. In addition, a $^3J_{(P-H)}$ value of 6.0 Hz was observed for the Pd−CH_3 resonance, characteristic of palladium complexes with *trans*-coordinated phosphines.[8]

Infrared spectroscopic measurements of **2** in $CDCl_3$ show that, in contrast to **1**, the urea functional groups are involved in hydrogen-bonding even at relatively low concentrations (<14 mM). The hydrogen-bonding is predominantly due to intramolecular interactions, since the ratio between the N−H stretches for free and hydrogen-bonded urea groups, at 3410 and 3340 cm^{-1}, respectively,[9,10] are not concentration dependent between the range of 4 and 42 mM (note that in structure **2** only 50% of the NH groups are involved in hydrogen-bonding). Evidently, the preorganization of the urea groups by coordination to the palladium metal center promotes intramolecular hydrogen-bonding instead of the intermolecular hydrogen-bonding observed with more concentrated solutions of **1** (>20 mM).

Computational studies (DFT, B3LYP) on a model of complex **2** clearly illustrate the intramolecular hydrogen-bonding interaction between the urea NH's and the *n* electrons of the carbonyl group of the urea moiety of the second ligand (Figure 1), and the NH−O distances are 1.95 and 2.17 Å.[11] The palladium complex with the intramolecular hydrogen bonds is energetically more favorable than the non-hydrogen-bonded system by 9 kcal/mol.[12]

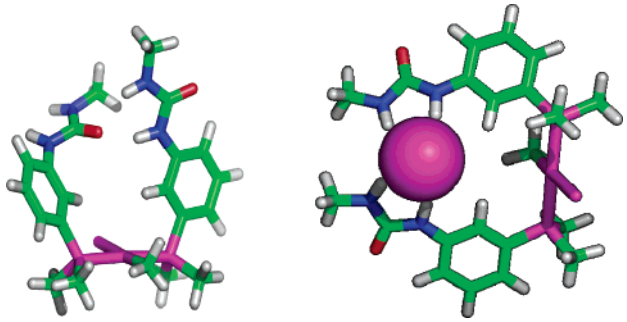


Figure 1. Calculated structure of models of **2** (left) and **3** (right) clearly showing an intramolecular hydrogen bond and the *trans* configuration about Pd and the interactions between Cl and the NH's of the urea's.

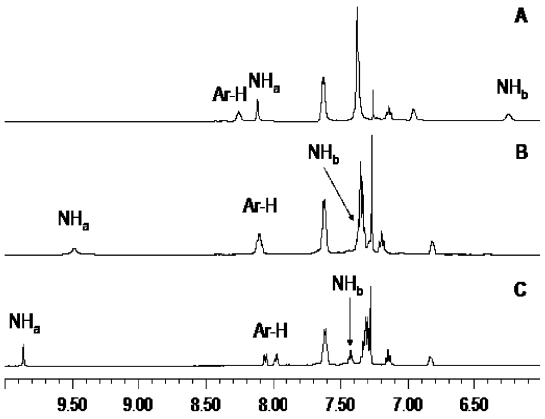


Figure 2. Binding of a chloride anion in the pocket of complex **2** monitored by ^{1}H NMR spectroscopy: (A) solution of **2**; (B) a solution of **2** with 1.0 equiv of *n*Bu_4NCl; and (C) a solution of **2** with 10.0 equiv of *n*Bu_4NCl.

Urea groups are frequently employed to construct receptors for anion recognition,[13] so we anticipated that the bis-urea motif in complex **2** might also bind anions. Addition of various equivalents of tetra-*n*-butylammonium chloride (*n*Bu_4NCl) to a solution of **2** in $CDCl_3$ indeed resulted in significant downfield shifts of the NH resonances of the urea moiety (Figure 2). In the presence of 10 equiv of *n*Bu_4NCl, the NH adjacent to the aryl group shifted to lower field by ~1.7 ppm to 9.84 ppm, whereas the NH next to the CH_2 group shifted ~1.2 ppm downfield. These changes in chemical shifts clearly point to the chloride binding in the bis-urea pocket at the expense of the hydrogen bonds between the urea functionalities,[13] generating a palladium complex supported by an anion-templated bidentate chelating ligand, [($\mathbf{1}_2$Cl)PdMeCl]$^-$[*n*Bu_4N]$^+$, **3** (Scheme 1). The binding constant of the chloride in the pocket of **2**, determined from NMR titrations, is $K = (10 \pm 2) \times 10^2$ M^{-1}, which is much higher than the binding constant associated with the complexation of a single urea ligand **1** to chloride (*n*Bu_4NCl), $K = 55 \pm 5$ M^{-1}.[14] Interestingly, the ligands in **3** are also in a *trans* configuration about the metal center, as evident by the singlet that is present in the ^{31}P{^{1}H} NMR spectrum (at

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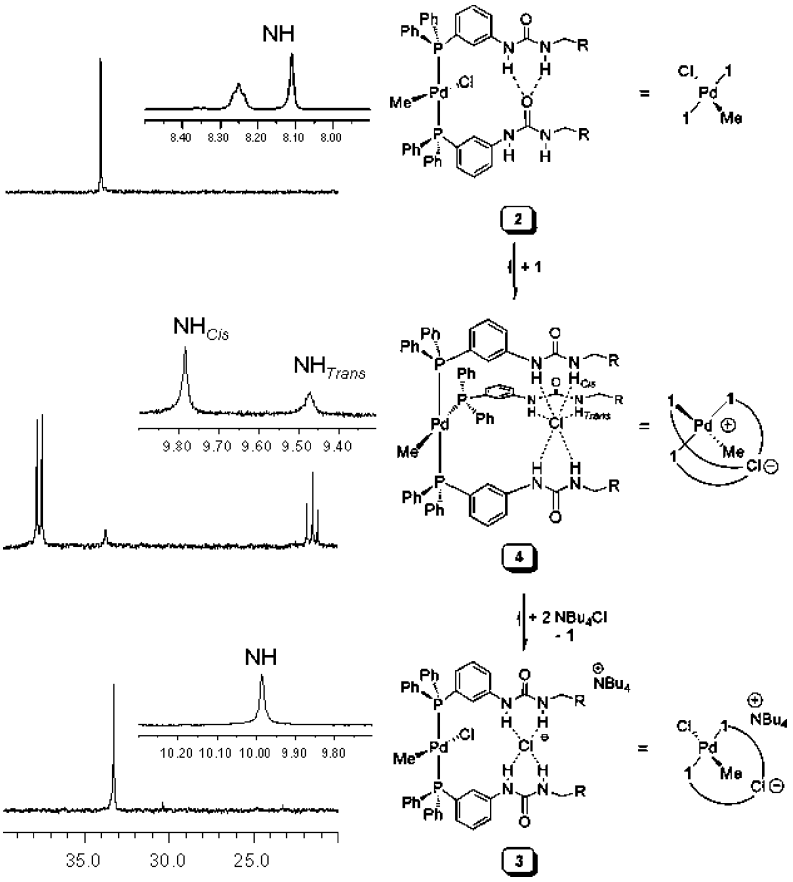
(12) The structures of the complexes were generated using TITAN and were optimized using DFT optimization (B3LYP, 6-31G**).
(13) For select examples: (a) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 5030. (b) Werner, F.; Schneider, H.-J. *Helv. Chim. Acta* **2000**, *83*, 465. (c) Hishizawa, S.; Bühlmann, P.; Iwao, M.; Umezawa, Y. *Tetrahedron Lett.* **1995**, *36*, 6483. (d) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486, and references therein. (e) Scheele, J.; Timmerman, P.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 2613. (f) Tovilla, J. A.; Vilar, R.; White, A. J. P. *Chem. Commun.* **2005**, 4839.
(14) We have analyzed the titration curves with a fitting program developed by Hunter et al.: Bisson, A. P.; Hunter, C. A.; Carlos, J.; Young, K. *Chem. Eur. J.* **1998**, *4*, 845.

Scheme 3. Migration of Chloride Anion to/from the Palladium Center to Generate Zwitterionic and Ionic Complexes and Their Corresponding ^{31}P and ^{1}H NMR Spectra



−80 °C) and the triplet ($^{3}J_{(P-H)}$ = 5.5 Hz) observed for the Pd−CH_3 resonance in the ^{1}H NMR spectrum.[8] Computational studies (DFT, B3LYP) on a model of complex **3** show that the chloride anion fits nicely in the pocket, but that it does not lie perfectly in the plane created by the NH's of the urea groups (Figure 1).[12] This is the first example of a *trans*-coordinating, anion-templated, hydrogen-bonded phosphine ligand system.[5,6,15]

The formation of **3** was also monitored by IR spectroscopy. The two stretching frequencies corresponding to the NH's of **2** disappear upon introduction of 1 equiv of *n*Bu_4NCl, and a new band at a lower wavenumber (3297 cm^{-1}) is observed for the N−H bound to Cl. It is well-known that a larger shift in wavenumbers upon complexation, $\Delta\nu$(N−H), corresponds to a stronger hydrogen-bonding interaction.[16] With $\Delta\nu$(N−H) values of 113 and 70, respectively, the hydrogen bond between the ureas and the chloride anion of **3** is clearly stronger than the self-association of the urea moieties in **2**, likely due to the anionic nature of the chloride. In addition to the increase in strength, the number of hydrogen bonds involved is larger (4 vs 2) in the anion-templated system, enabling the chloride anion to compete with the intramolecular hydrogen-bonded complex.

Although the bis-urea pocket binds chloride anions, it apparently is unable to remove the chloride from the palladium center to form a zwitterionic species. We anticipated, however, that such an intramolecular chloride shift from the metal to the binding site could be promoted by the presence of donors. Indeed, when an "additional" equivalent of **1** was introduced to a solution of **2**, zwitterionic complex **4**, [(**1**$_3$Cl)PdMe], was formed with three phosphine ligands bound to the metal center[17] and the chloride anion in the tris-urea pocket (Scheme 3). Accordingly, the $^{31}P\{^{1}H\}$ NMR spectrum contains a doublet and a triplet that integrate in a ratio of 2:1, with a coupling constant ($^{2}J_{P-Pcis}$ = 37 Hz) that is typical of phosphorus atoms coordinated in a *cis* fashion (Scheme 3, middle).[18,19] Interestingly, the chloride anion is hydrogen-bonding to all three of the urea groups, as there are two signals observed in the ^{1}H NMR spectrum for the NH's adjacent to the aryl ring at 9.79 and 9.47 ppm, which also integrate with respect to one another in a 2:1 ratio. These experiments clearly show that the exchange of these ligands is slow on the NMR time scale. The resonance for the methyl group of this zwitterionic species has shifted downfield to 0.38 ppm from 0.01 ppm for the neutral complex **2**, and it consists of an overlapping set of doublets of triplets instead of the simple triplet observed for **2**.[20] When 2 equiv of *n*Bu_4NCl are added to a solution of **4**, the third phosphine ligand dissociates from the metal to regenerate **3** (Scheme 3, bottom).

(15)) An example of an anion-templated *cis* hydrogen-bonded system was recently reported: Lu, X.-X.; Tang, H.-S.; Ko, C.-C.; Wong, J. K.-Y.; Zhu N.; Yam, V. W.-W. *Chem. Commun.* **2005**, 1572.

(16) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069.

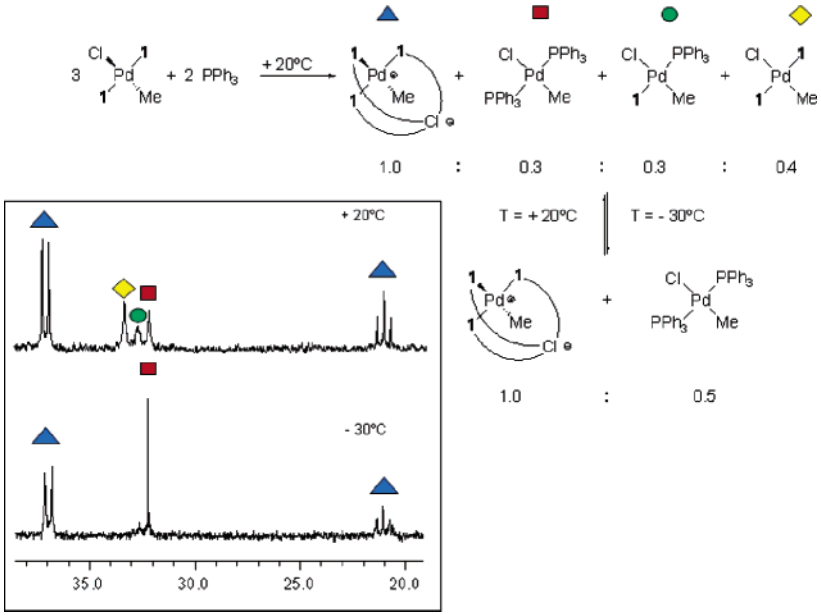
(17) (a) Gretz, E. F.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 6038. (b) Yamashita, R.; Kikukawa, K.; Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1980**, *201*, 463.

(18) (a) Zudin, V. N.; Chinakov, V. D.; Nekipelov, V. M.; Likholobov, V. A.; Yermakov Y. I. *J. Organomet. Chem.* **1985**, *289*, 425. (b) Crumbliss, A. L.; Topping, R. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Germany, 1987; pp 535−547.

(19) A small quantity of **2** and **1** is also observed in the ^{31}P NMR spectrum due to the equilibrium between these three species.

(20) A small amount (5−10%) of an unidentifiable species is sometimes observed in the ^{1}H NMR spectrum, and it is believed to be due to decomposition of **4** that ultimately occurs in solution over several days.

Scheme 4. Thermodynamically Controlled Equilibrium between 4, 2, (1)(PPh$_3$)PdMeCl, and (PPh$_3$)$_2$PdMeCl and Variable-Temperature ^{31}P{^{1}H} Spectra



As expected, the addition of another equivalent of **1** to a solution of **3** (**2** in the presence of 2 equiv of Cl^- to drive the equilibrium to **3**) does not result in the formation of the zwitterionic complex **4**, and only the anion-templated species, **3**, and the free ligand, **1**, are observed in solution. This indicates that the complex formation is under thermodynamic control. A separate experiment using $(Ph_3P)_2PdMeCl$ and 1 equiv of PPh_3 (in CD_2Cl_2) demonstrates that the urea pocket is necessary to generate the zwitterionic palladium species with three phosphine ligands, since only two singlets were observed (even at low temperatures) in the ^{31}P{^{1}H} NMR spectrum for $(Ph_3P)_2PdMeCl$ and free PPh_3.

We were interested in probing the importance of the third urea−chloride interaction in complex **4** and if this interaction was required to facilitate the phosphine−chloride substitution reaction of complex **2**. Therefore an additional experiment was conducted in which PPh_3 (2/3 equiv) was added to a solution of complex **2** instead of ligand **1**. If the third urea is not important, we expected to see a similar substitution of the chloride by PPh_3. However, if the third urea−chloride interaction is crucial for the substitution process, a mixture of complex **2** and free PPh_3 should be observed, or a rearrangement of the ligands takes place resulting in a mixture of complexes. The typical doublet and triplet in the ^{31}P NMR spectrum and the two singlets for the NH's hydrogen-bonded to the chloride anion near 10 ppm (in a 2:1 ratio) were observed, with the corresponding methyl resonance at 0.39 ppm in the ^{1}H NMR spectrum, indicating the formation of **4** at ambient temperature. Signals at 33.0, 32.3, and 31.8 ppm due to **2**, (**1**)(PPh$_3$)PdMeCl,[21] and $(PPh_3)_2PdMeCl$, respectively, are also apparent at 20 °C, and the four metal complexes are present in a 1.0:0.4:0.3:0.3 ratio (Scheme 4). This clearly indicates that the third urea significantly stabilizes the binding of the chloride. Interestingly, if the sample is cooled to −30 °C, the equilibrium shifts in favor of **4**, and the remaining 1/3 of Pd metal is ligated by the "residual" PPh_3 in solution to generate $(PPh_3)_2PdMeCl$. At this temperature, these two complexes are present in a 2:1 ratio, but if the solution is warmed back up to ambient temperature, all four of the palladium complexes are observed in solution again and in the same ratio as before. (Free phosphine, **1**, and/or PPh_3 are also present in solution, but the amount of free phosphine decreases significantly upon cooling to −30 °C and returns after the solution is rewarmed to room temperature.) This temperature dependence indicates a low barrier for the exchange process between the different species. The formation of the most stable palladium complex at −30 °C, **4**, is enthalpy driven. If the reverse experiment is performed, such that $(Ph_3P)_2$-PdMeCl is mixed with 2 equiv of **1**, comparable resonances are observed in the ^{31}P and ^{1}H NMR spectra, except that due to the rapid exchange between **2**, (**1**)(PPh$_3$)PdMeCl, and $(PPh_3)_2$-PdMeCl on the NMR time scale, only a broad resonance (instead of 3 singlets) is present at 32.5 ppm.

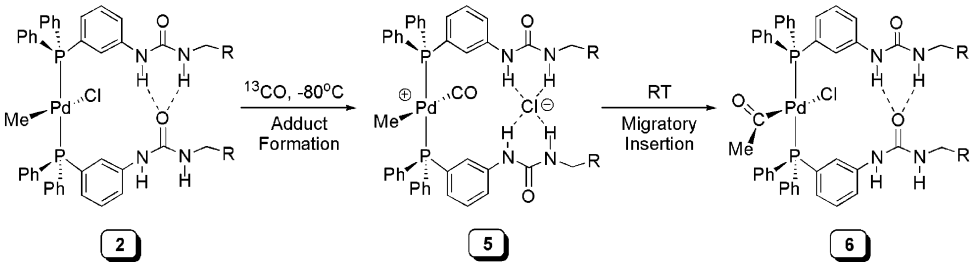
Since in complex **2** the chloride can be readily substituted by a ligand to generate a zwitterionic complex, the reactivity of **2** was examined in the presence of ^{13}CO. At −78 °C, ^{13}CO was bubbled through an NMR tube solution of **2** in CD_2Cl_2 (or the NMR tube was pressurized with 5 bar of CO), and at this temperature, resonances corresponding to the four-coordinate CO-adduct, **5**,[22,23] were observed at 30.8 ppm and at 179.6 ppm in the ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra, respectively (Scheme 5). In the ^{1}H NMR spectrum, the resonance for the N−H adjacent to the aryl ring shifted downfield by 2.05 ppm to 10.20 ppm, indicating a similar substitution of the chloride anion as observed in the presence of additional ligand. Upon warming to room temperature, migratory insertion occurred to produce the acetyl species, $(\mathbf{1})_2Pd(C(O)CH_3)Cl$, **6**, and singlets at 21.0 ppm in the ^{31}P{^{1}H} spectrum and 233.5 ppm in the ^{13}C{^{1}H} NMR spectra showed that the ligands are still bound to the metal in a *trans* configuration. After the formation of the acetyl species, the chemical shift of the NH's indicated that the chloride is no longer present in the pocket, but has migrated back to the

(21) (**1**)$(Ph_3P)_2PdMeCl$ was identified by comparison with a separate NMR tube experiment.

(22) Shultz, C. S.; Ledford, J.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6351.

(23) The major species present in solution (between −80 and −40 °C) is the four-coordinate CO-adduct, which was followed by variable-temperature NMR spectroscopy, and it formed the acetyl complex. Below −70 °C, an unidentifiable minor species is observed in solution, and this complex is a potential intermediate that ultimately results in the formation of the acetyl product.

Scheme 5. Reactivity of 2 with ^{13}CO



palladium center, *regenerating* a neutral species. In comparison, when ^{13}CO was introduced to a CD_2Cl_2 solution of $(Ph_3P)_2$-PdMeCl at −78 °C, a four-coordinate ^{13}CO-adduct was not observed in the $^{13}C\{^1H\}$ NMR spectra, showing that the bis-urea pocket is necessary to generate a cationic palladium center with a free site available for ^{13}CO coordination. When the analogous experiment is performed with **3** (i.e., the pocket of **2** is blocked by an external chloride anion), the four-coordinate ^{13}CO-adduct was also not observed in the $^{13}C\{^1H\}$ NMR spectrum between −80 and 20 °C. On the other hand, at room temperature and presumably via an unobserved five-coordinate CO-adduct,[24] an acetyl species, $[(\mathbf{1}_2Cl)Pd((CO)CH_3)Cl]^-[n Bu_4N]^+$, **7**, was produced, as evident by the new resonances in the $^{31}P\{^1H\}$ and the $^{13}C\{^1H\}$ NMR spectra at 21.8 and 230.2 ppm, respectively.[25] On the basis of the ^1H NMR spectrum, the *trans*-coordinating, chloride-templated, phosphine ligand system also remains intact after the formation of the acetyl complex. The inability to observe the four-coordinate CO-adduct of **3** emphasizes the subtle control of the bis-urea pocket on the reactivity of the metal center.[13e]

Conclusion

In summary, a new urea-based phosphine ligand has been synthesized and the urea functional groups of the palladium complex **2** self-associate to produce the first example of a *trans*-coordinating hydrogen-bonded ligand system. The addition of chloride anions to **2** converts it into the chloride-templated, *trans*-coordinating bidentate phosphine metal species **3**. The presence of additional ligand **1** (or PPh_3) leads to the formation of a zwitterionic complex, $[(\mathbf{1}_3Cl)PdMe]$, with three phosphine ligands bound to the metal center and the chloride anion in a tris-urea pocket. The formation of this complex is reversible, as the chloride moves back to the palladium upon addition of $n Bu_4NCl$. These experiments clearly show that the complex responds to external stimuli as a consequence of the supramolecular interactions. The palladium metal center also shows special reactivity toward CO as a result of the presence of the bis-urea pocket. Substitution of the chloride by CO is observed, resulting in the formation of zwitterionic complexes with the chloride being transferred from the metal center to the bis-urea binding site. Interestingly, after CO migratory insertion occurs to form the palladium-acetyl species, the chloride migrates back to the palladium center. In view of future developments of self-assembled bidentate ligands based on hydrogen bonds the current results are important, since it suggests that reactions that produce salts as side-products might change the ligation around the metal center. Currently, investigations are underway to study this and to extend this approach, such as the use of a large variety of anions, including chiral templating anions, to induce unique reactivities and selectivities at the metal center.

Experimental Section

General Conditions. All manipulations were performed under argon using standard Schlenk techniques. Toluene was distilled from sodium, and CH_2Cl_2, pentane, $CDCl_3$, and CD_2Cl_2 were distilled from CaH_2. The metal complex CODPdMeCl was synthesized according to a literature procedure.[26] The palladium complex $(Ph_3P)_2PdMeCl$[27] was synthesized in an analogous manner to compound **2**. The ^{13}CO was purchased from Praxair. All other reagents were purchased from Aldrich or Acros and used as received. The NMR spectra were recorded on a Varian Inova 500 and a Bruker DRX 300 NMR spectrometer in $CDCl_3$ unless otherwise specified. The IR spectra were measured on a BIO-RAD FTS-7 in a NaCl solution cell in $CDCl_3$. Electrospray-ionization mass spectra (in MeOH) were recorded on a Shimadzu LCMS-2010A via direct injection. Elemental analysis was performed by H. Kolbe Mikroanalytisches Laboratorium.

Synthesis of *m*-(Diphenylphosphorus)aniline. A THF solution of potassium diphenylphosphide (4.04 g, 1.80×10^{-2} mol) and *m*-fluoroaniline (2.01 g, 1.81×10^{-2} mol) were combined in a Schenk flask and refluxed for 3 days. The THF was removed in vacuo, and the yellow solid was washed with degassed H_2O (4×20 mL). The *m*-(diphenylphosphorus)aniline was purified by column chromatography (eluent: 100% $CHCl_3$). Yield: 3.692 g, 74.0%. ^1H NMR: δ 7.90−7.15 (m, 10H, C_6H_5), 7.20 (m, 1H, C_6H_4), 6.67 (m, 3H, C_6H_4), and 3.62 (br s, 2H, N*H*). $^{13}C\{^1H\}$: δ 146.2 (br s, N*C*-aryl), 138.1 (m, PC_{ipso}), 137.2 (m, PC_{ipso}), 133.8 (d, *o*-PC_6H_5, $^2J_{P-C} = 19.5$ Hz), 129.4 (d, *m*-PC_6H_4N, $^3J_{P-C} = 7.3$ Hz), 128.5 (d, *m*-PC_6H_5, $^3J_{P-C} = 12.2$ Hz), 128.3 (s, *p*-C_6H_5P), 124.2 (d, *o*-PC^6H_4N, $^2J_{P-C} = 19.5$ Hz), 120.0 (d, *o*-PC_6H_4N, $^2J_{P-C} = 19.5$ Hz), 115.6 (s, *p*-PC_6H_4N). $^{31}P\{^1H\}$: δ −4.49 ppm.

Synthesis of 1. A Schenk flask was charged with *m*-(diphenylphosphorus)aniline (1.414 g, 5.10×10^{-3} mol), which was dissolved in CH_2Cl_2 (10 mL). Ethyl isocyanatoacetate (0.656 g, 5.08×10^{-3} mol) was added via syringe to the reaction mixture, and it was stirred at room temperature for 4 h. The solvent was removed in vacuo, and toluene (15 mL) was added to the white sticky solid. Initially the white solid dissolved in the toluene, but after approximately 20 min of stirring a white, thick opaque powder precipitated out of the toluene solution. The solvent was removed by filtration, and the precipitate was washed with toluene (∼5 mL) twice more. The white solid was dried under reduced pressure. Yield: 1.765 g, 85.2%. ^1H NMR: δ 7.51 (d, 1H, C_6H_4, $^3J_{H-H} = 8.7$ Hz), 7.44−7.20 (m, 11H, C_6H_4 and C_6H_5), 7.02 (t, 2H, C_6H_4, $^3J_{H-H} = 7.5$ Hz), 6.49 (s, 1H, N*H*), 5.22 (m, 1H, N*H*CH_2), 4.21 (q,

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(25) Since the CO and methyl groups should be arranged *cis* with respect to one another for facile migratory insertion to occur and these palladium complexes were never observed in this coordination mode, the carbonylation must occur immediately upon rearrangement to the *cis* species, which is followed by a successive rearrangement to the thermodynamic *trans*-acetyl product.

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2H, CH_2CH$_3$, $^3J_{H-H}$ = 7.2 Hz), 4.00 (d, 2H, NHCH_2, $^3J_{H-H}$ = 5.1 Hz), 1.27 (t, 3H, CH$_2$CH_3, $^3J_{H-H}$ = 7.2 Hz). ^{13}C{^{1}H}: δ 171.2 (*C*═O), 155.6 (*C*═O), 138.8 (d, N*C*-aryl, $^3J_{P-C}$ = 8.5 Hz), 137.9 (m, PC_{ipso}), 136.7 (m, PC_{ipso}), 133.8 (d, PC*C*H, $^2J_{P-C}$ = 19.5 Hz), 129.3 (d, *m*-PC_6H_4N , $^3J_{P-C}$ = 7.3 Hz), 128.8 (s, *p*-PC_6H_5), 128.5 (d, *m*-PC_6H_5, $^3J_{P-C}$ = 7.3 Hz), 125.2 (m, PC_6H_4N), 124.9 (s, PC_6H_4N), 120.8 (s, *p*-PC_6H_4N), 61.5 (s, OCH_2CH$_3$), 41.9 (s, HNCH_2), and 14.0 (s, CH$_2$$CH_3$). ^{31}P{^{1}H}: δ −4.19 ppm. IR (ν_{max}): 3434 (NH$_{free}$), 3317 (NH$_{Assoc}$), 1744 (C═O$_{Ester}$), 1696 (C═O$_{Amide\ I}$), 1532 (C−N$_{Amide\ II}$), and 1204 (C−O) cm^{-1}. Anal. Calcd for $C_{23}H_{23}N_2O_3P$: C, 67.98; H, 5.70; N, 6.89. Found: C, 68.08; H, 5.79; N, 6.80.

Synthesis of *trans*-(1)$_2$PdMeCl (2). 1,5-Palladium methylchlorocyclooctadiene (CODPdMeCl) (0.095 g, 3.58 × 10^{-4} mol) was combined with 2 equiv of **1** (0.291 g, 7.16 × 10^{-4} mol), and CH$_2$Cl$_2$ (10 mL) was syringed into the Schlenk, yielding a clear, pale yellow solution. The reaction mixture was stirred overnight, and the solution becomes a deep yellow color. The solution was concentrated to approximately 3 mL, and pentane (5 mL) was added to the reaction mixture, generating a yellow sticky precipitate. The solvent was removed by filtration, and the purification of the solid was repeated twice more. Last, CH$_2$Cl$_2$ (5 mL) and pentane (5 mL) were syringed onto the solid, and it was stirred at room temperature for 30 min. The volatiles were removed in vacuo. Yield: 0.315 g, 90.7%. ^{1}H NMR: δ 8.29 (br m, 2H, C-*H* aryl), 8.15 (s, 2H, N-*H*), 7.66 (m, 8H, C$_6H_5$), 7.40 (br s, 14H, C$_6H_5$), 7.16 (br t, 2H, C-*H* aryl, $^3J_{H-H}$ = 8.5 Hz), 6.98 (br s, 2H, C-*H* aryl), 6.26 (br s, 2H, CH$_2$N*H*), 4.11 (q, 4H, CH_2CH$_3$, $^3J_{H-H}$ = 7.0 Hz), 3.72 (d, 4H, CH_2-NH, $^3J_{H-H}$ = 5.0 Hz), 1.23 (t, 6H, CH$_2$CH_3, $^3J_{H-H}$ = 7.0 Hz) and 0.01 (t, PdCH_3, $^3J_{P-H}$ = 6.0 Hz). ^{13}C{^{1}H}: δ 171.3 (*C*═O), 156.2 (*C*═O), 139.1 (t, NC_{ipso}, J_{P-C} = 7.7 Hz), 134.9 (t, *C* aryl, J_{P-C} = 6.2 Hz), 131.2 (t, PC_{ipso}, J_{P-C} = 22.9 Hz), 131.0 (t, PC_{ipso}, J_{P-C} = 21.4 Hz), 128.9 (br m, *C* aryl), 128.7 (s, *C* aryl), 128.1 (m, *C* aryl), 127.0 (*C*$_6$H$_4$), 122.5 (*C*$_6$H$_4$), 61.0 (OCH_2CH$_3$), 41.6 (HNCH_2), 14.1 (CH$_2$$CH_3$), and 6.4 (Pd$CH_3$). ^{31}P{^{1}H}: δ 32.7 ppm. IR (ν_{max}): 3411 (NH$_{free}$), 3329 (NH$_{Assoc}$), 1738 (C═O$_{Ester}$), 1695 (C═O$_{Amide\ I}$), 1553 (C−N$_{Amide\ II}$), and 1209 (C−O) cm^{-1}. Anal. Calcd for $C_{47}H_{49}N_4O_6P_2$-ClPd: C, 58.25; H, 5.09; N, 5.78. Found: C, 58.35; H, 5.15; N, 5.66.

Generation of {[*trans*-(1$_2$Cl)PdMeCl]$^-$[NBu$_4$]$^+$ } (3). The anion-templated complex was produced in situ in an NMR tube. The reagents **2** (0.010 g, 1.03 × 10^{-5}) and *n*Bu$_4$NCl (0.003 g, 1.1 × 10^{-5} mol) were combined and dissolved in CDCl$_3$ (0.5 mL). On the basis of NMR spectroscopy, the reaction proceeds to completion. ^{1}H NMR: δ 9.49 (s, 2H, N-*H*), 8.12 (br m, 4H, C-*H* aryl), 7.63 (m, 8H, C$_6H_5$), 7.36 (m, 12, C$_6H_5$), 7.29 (br s, 2H, CH$_2$N*H*), 7.20 (br t, 2H, C-*H* aryl, $^3J_{H-H}$ = 7.5 Hz), 6.83 (br s, 2H, C-*H* aryl), 4.15 (q, 4H, CH_2CH$_3$, $^3J_{H-H}$ = 7.5 Hz), 3.99 (d, 4H, CH_2NH, $^3J_{H-H}$ = 5.5 Hz), 3.10 (m, 8H, NBu), 1.49 (m, 8H, NBu), 1.29−1.22 (m, 14H, NBu and CH$_2$CH_3), 0.86 (t, 12H, NBu, $^3J_{H-H}$ = 7.0 Hz), and 0.03 (t, 3H, PdCH_3, $^3J_{P-H}$ = 6.0 Hz). ^{13}C{^{1}H}: δ 171.0 (*C*═O), 156.5 (*C*═O), 140.6 (t, NC_{ipso}, $^3J_{P-C}$ = 7.7 Hz), 134.9 (t, *o*-PC_6H_5, $^2J_{P-C}$ = 6.0 Hz), 131.8 (t, PC_{ipso}, $^1J_{P-C}$ = 21.4 Hz), 130.8 (t, PC_6H_5, J_{P-C} = 22.1 Hz), 129.7 (s, *p*-PC_6H_5), 128.5 (m, PC_6H_4N), 127.8 (t, *m*-PC_6H_5, $^3J_{P-C}$ = 4.5 Hz), 127.0 (m, PC_6H_4N), 126.0 (PC_6H_4N), 60.6 (OCH_2CH$_3$), 58.8 (s, *n*Bu), 41.7 (HNCH_2), 23.9 (s, *n*Bu), 19.6 (s, *n*Bu), 14.2 (CH$_2$$CH_3$) 13.6 (s, *n*Bu), and 6.6 (PdCH_3). ^{31}P{^{1}H}: δ 32.0 ppm. IR (ν_{max}): 3398 (NH$_{Assoc}$), 1749 (C═O$_{ester}$), 1692 (C═O$_{Amide\ I}$), 1556 (C−N$_{Amide\ II}$), and 1201 (C−O) cm^{-1}.

Formation of [(1$_3$Cl)PdMe], 4, in Situ. Both the palladium complex **2** (0.010 g, 1.03 × 10^{-5}mol) and **1** (0.004 g, 9.84 × 10^{-6} mol) were weighed into separate vials, dissolved into CD$_2$Cl$_2$ (0.3 mL each), and combined in an NMR tube. On the basis of NMR spectroscopy, the reaction proceeded to completion. ^{1}H NMR (CD$_2$Cl$_2$): δ 9.79 (s, 2H, N-H_{2a}), 9.47 (s, 2H, N-H_{2b}), 8.01 (d, 2H, Ar-H, $^3J_{H-H}$ = 8.1 Hz) 7.83 (d, 1H, Ar-H, $^3J_{H-H}$ = 7.2 Hz), 7.74 (br t, 2H, Ar-H, $^3J_{H-H}$ = 7.5 Hz), 7.62−6.85 (m, 36H, Ar-H, N-$H_{1a,}$ N-H_{1b}), 6.70 (m, 1H, Ar-H), 6.39 (m, 2H, Ar-H), 6.01 (t, 1H, Ar-H), 4.19 (q, 6H, CH_2CH$_3$, $^3J_{H-H}$ = 7.2 Hz), 4.08 (d, 2H, CH_2NH, $^3J_{H-H}$ = 5.7 Hz), 4.02 (d, 4H, CH_2NH, $^3J_{H-H}$ = 5.7 Hz), 1.28 (t, 9H, CH$_2$CH_3, $^3J_{H-H}$ = 7.2 Hz), and 0.38 (br d × t, 3H, PdCH_3). ^{13}C{^{1}H}: δ 171.0 (*C*═O), 156.3 (*C*═O), 140.84, 140.77, 140.0, 139.8, 135.1, 134.8, 134.7, 132.12, 132.08, 132.0, 131.8, 130.9, 130.4, 130.1, 129.9, 129.5, 128.5, 128.2, 128.1, 124.8, 124.6, 124.4, 121.3 and 121.0 (Ar-*C*), 61.0 (OCH_2CH$_3$), 60.9 (OCH_2CH$_3$), 42.0 (HNCH_2), 41.7 (HNCH_2), 14.2 (CH$_2$$CH_3$), 14.1 (CH$_2$$CH_3$), and 6.6 (Pd$CH_3$). ^{31}P{^{1}H}: δ 37.8 (d, 2P, P$_{(cis\ to\ Me)}$, $^2J_{P-Pcis}$ = 37 Hz) and 22.3 (t, 1P, P$_{(trans\ to\ Me)}$, $^2J_{P-Pcis}$ = 37 Hz).

Competition Studies between 4 and *n*Bu4NCl and between 3 and 1. Stock solutions of **1** (0.013 g, 0.041 M), **2** (0.024 g, 0.021 M), and *n*Bu$_4$NCl (0.009 g, 0.041 M) were prepared in CD$_2$Cl$_2$. Complex **4** was generated in situ by combining **2** (0.4 mL, 8.3 × 10^{-6} mol) and **1** (0.20 mL, 8.3 × 10^{-6} mol); afterward, *n*Bu$_4$NCl was added in 3 portions (1.5, 1.5, and 1.0 mL) and monitored by ^{1}H and ^{31}P NMR spectroscopy to determine the number of equivalents of chloride anion necessary to generate **3** as well as **1** bound to a chloride anion. Summing the volumes of the three portions, 2.0 equiv of *n*Bu$_4$NCl were required.

Complex **3** was generated in situ by combining **2** (0.4 mL, 8.3 × 10^{-6} mol) and *n*Bu$_4$NCl (0.20 mL, 8.3 × 10^{-6} mol) and verified by ^{1}H and ^{31}P NMR spectroscopy. The ligand **1** (0.20 mL, 8.3 × 10^{-6} mol) was added to the solution, and it was determined by NMR spectroscopy that only 1 equiv of *n*Bu$_4$NCl to form **3** was not sufficient to prevent the formation of a mixture of **4** and complex **3** with free ligand **1**.

In a separate experiment, complex **3** was generated in situ, but a larger excess of *n*Bu$_4$NCl (0.005 g, 1.8 × 10^{-5} mol) was utilized with **2** (0.008 g, 8.3 × 10^{-6} mol). Upon addition of **1** (0.003 g, 7.4 × 10^{-6}), only **3** and free **1** were observed in the ^{1}H and ^{31}P NMR spectra (vide supra).

Formation of *trans*-[(1$_2$Cl)Pd(^{13}CO)(Me)] (5) by Bubbling ^{13}CO. The palladium complex **2** (0.0135 g, 1.39 × 10^{-5} mol) was dissolved in CD$_2$Cl$_2$ (0.7 mL), and the NMR tube was cooled to −78 °C. At this temperature, the ^{13}CO-adducts were generated by bubbling ^{13}CO through the yellow solution for 7 min. ^{13}C NMR (*T* = −80 °C): δ (CD$_2$Cl$_2$) 179.7 and 177.7 ppm (C═O of CO-adducts). ^{31}P NMR (*T* = −80 °C): δ (CD$_2$Cl$_2$) 33.6 and 30.8 ppm (CO-adducts). At −30 °C, only one CO-adduct that corresponds to **5** is visible in the spectra. ^{13}C NMR (*T* = −30 °C): δ (CD$_2$Cl$_2$) 179.7 ppm (C═O). ^{31}P NMR (*T* = −30 °C): δ (CD$_2$Cl$_2$) 33.6 (CO-adduct). The CO migratory insertion was followed by NMR spectroscopy, and on the basis of the NMR data, the reaction proceeds to completion (100%). The NMR data are the same as for **4** (vide supra).

Formation of *trans*-(1)$_2$Pd(C(O)Me)Cl by High Pressure via a CO-Adduct. The palladium complex **2** (14.741 mg, 1.53 × 10^{-5} mol) was weighed out into a Schlenk flask and dissolved in CD$_2$Cl$_2$ (2.0 mL). The yellow solution was transferred to the high-pressure NMR tube and cooled to −78 °C for 1 h. CO gas (5.0 bar) was pressurized into the tube, and the progress of the reaction was monitored by variable, low-temperature NMR spectroscopy. The formation of the four-coordinate CO-adduct (**5**) with the chloride anion displaced into the urea hydrogen-bonding pocket was apparent from the ^{1}H NMR spectrum. ^{1}H NMR (*T* = −80 °C): δ (CD$_2$Cl$_2$) 10.20 (br s, 2H N*H*-Ar), 8.32 (br s, 2H, Ar-*H*), 7.95−6.80 (br m, 26H, Ar-*H* and CH$_2$N*H*), 6.60 (br s, 2H, Ar-*H*), 4.40−2.95 (br m, 8H, CH_2CH$_3$ and CH_2NH), 1.15 (br s, 6H, CH$_2$CH_3), and 0.42 (br s, 3H, PdCH_3). ^{31}P{^{1}H} NMR (*T* = −80 °C): δ (CD$_2$Cl$_2$) 30.8 ppm (s). If the NMR tube is left in the NMR spectrometer for 185 min at −30 °C, the reaction progresses to the production of the acetyl compound. NMR data for **6** are listed below.

Formation of *trans*-(1)$_2$Pd(C(O)Me)Cl (6) in Situ. The palladium species **2** (0.0084 g, 8.66 × 10^{-6} mol) was dissolved in

$CDCl_3$ (0.7 mL), and the acetyl species was generated by bubbling CO gas through the yellow solution for 10 min at room temperature in an NMR tube. On the basis of NMR data, the reaction proceeds to completion (100%). ^{1}H NMR: δ 8.58 (br m, 2H, PCC*H*N of C_6H_4), 7.97 (s, 2H, N-*H*), 7.90−7.20 (br m, 12H, C_6H_5 and C_6H_4), 7.10 (br s, 2H, C_6H_4), 7.00, (br s, 2H, C_6H_4), 6.13 (br s, 2H, CH_2NH), 4.11, (q, 4H, CH_2CH_3, $^3J_{H-H}$ = 7.0 Hz), 3.64 (br s, 4H, CH_2NH), 1.40 (br s, PdCH_3), and 1.22 (t, 6H, CH_2CH_3, $^3J_{H-H}$ = 7.0 Hz). ^{13}C{^{1}H}: δ 184. 2 (Pd(*C*=O)CH_3), 171.7 (*C*=O), 155.8 (*C*=O), 139.4 (m, NC_{ipso}), 134.6 (br m, C_6H_5), 131.4 (br m, *C* aryl), 130.5 (s, *C* aryl), 129.2 (PC*C*N of C_6H_4), 128.4 (br m, C_6H_5), 127.1 (s, C_6H_4), 122.9 (s, C_6H_4), 61.1 (OCH_2CH_3), 41.6 ($HNCH_2$), 39.4 (Pd(CO)*C*H_3), and 14.1 (CH_2CH_3). ^{31}P{^{1}H}: δ 20.2 ppm. IR (ν_{max}): 3414 (NH_{free}), 3341 (NH_{Assoc}), 1746 (C=O_{ester}), 1692 (C=OMe), 1553 (C−$N_{Amide\ II}$), and 1205 (C−O) cm^{-1}.

Synthesis of $(Ph_3P)_2$PdMeCl.[27] Both CODPdMeCl (0.097 g, 3.66 × 10^{-4} mol) and triphenylphosphine (0.191 g, 7.28 × 10^{-4} mol) were combined in a Schlenk flask, and CH_2Cl_2 (10 mL) was added to the contents. The reaction mixture never fully dissolved in the solvent, but after about 10 min, considerably more white precipitate was present in the flask. The reaction was stirred at room temperature for 24 h. Pentane (5 mL) was syringed into the reaction mixture, and the solvent was removed by cannula filtration. The white solid was washed twice more with pentane (2 × 2 mL), and the residual solvent was removed under reduced pressure. Yield: 0.241 g, 96.6%. ^{1}H NMR: δ 7.73 (m,12H, C_6H_5), 7.42 (m, 18H, C_6H_5), and −0.01 (t, 3H, PdCH_3, $^3J_{P-H}$ = 6.0 Hz). ^{31}P NMR: δ 30.7 ppm.

Attempted Formation of the ^{13}CO-Adduct of $(Ph_3P)_2$PdMeCl and Production of $(Ph_3P)_2$Pd(^{13}C(O)Me)Cl in Situ. The palladium complex (0.010 g, 1.47 × 10^{-5} mol) was weighed into a Schenk flask and dissolved in CD_2Cl_2 (1.4 mL). The solution was transferred to an NMR tube and cooled at −78 °C for 20 min. For 7 min, the ^{13}CO was bubbled through the solution at this temperature. The sample was placed in the NMR spectrometer at −78 °C, and the progress of the reaction was monitored. At −78 °C, only free ^{13}CO (i.e., no CO-adduct) was observed in the ^{13}C-{^{1}H} NMR spectrum, and only one sharp singlet was present in the ^{31}P{^{1}H} NMR spectrum. ^{1}H NMR (T = −80 °C): δ (CD_2Cl_2) 7.62 (m, 12H, C_6H_5), 7.43 (m, 18H, C_6H_5), and −0.17 (br t, 3H, PdCH_3). ^{13}C NMR (T = −80 °C): δ (CD_2Cl_2) 184.1 ppm (free ^{13}CO). ^{31}P NMR (T = −80 °C): δ (CD_2Cl_2) 32.7 ppm. Upon warming the sample to 20 °C, the palladium acetyl complex was formed on the basis of NMR spectroscopy. ^{1}H NMR (T = 20 °C): δ (CD_2Cl_2) 7.75 (m, 12H, C_6H_5), 7.44 (m, 18H, C_6H_5), and 1.38 (br s, 3H, Pd(CO)CH_3). ^{13}C NMR (T = 20 °C): δ (CD_2Cl_2) 235.4 ppm (Pd(*C*O)Me). ^{31}P NMR (T = 20 °C): δ (CD_2Cl_2) 20.3 ppm.

Formation of {[*trans*-(1_2Cl)Pd(C(O)Me)Cl]$^-$[NBu_4]$^+$ } (7). The complex **2** (0.019 g, 1.96 × 10^{-5} mol) was weighed into a vial and dissolved in $CDCl_3$ (0.6 mL). The *n*Bu_4NCl (0.2 mL) from a 0.100 M stock solution in $CDCl_3$ was syringed into an NMR tube containing the palladium species. Carbon monoxide (CO) was bubbled through the reaction mixture for 15 min at room temperature to generate the acetyl complex **7**. The reaction proceeds to completion on the basis of NMR spectroscopy. ^{1}H NMR: δ 9.80 (s, 2H, N-*H*), 8.45 (br m, 2H, C_6H_4), 8.20 (br m, 2H, C_6H_4), 8.02 (br s, 2H, CH_2NH), 7.65−7.06 (m, 20H, C_6H_5) 7.19 (t, 2H, C_6H_4, $^3J_{H-H}$ = 7.5 Hz), 6.77 (m, 2H, C_6H_4), 4.18 (q, 4H, CH_2CH_3, $^3J_{H-H}$ = 7.5 Hz), 4.03 (br s, 4H, CH_2NH), 2.92 (m, 8H, NBu), 1.48 (br s, 3H, PdCH_3), 1.38 (m, 8H, NBu), 1.28 (t, 6H, CH_2CH_3, $^3J_{H-H}$ = 7.5 Hz), 1.14 (m, 8H, NBu), and 0.79 (t, 12H, NBu, $^3J_{H-H}$ = 7.5 Hz). ^{13}C{^{1}H}: δ 184.2 (Pd*C*OCH_3), 171.2 (*C*=O), 156.5 (*C*=O), 140.7 (s, PC_6H_4N), 135.7 (m, C_6H_5), 133.4 (m, C_6H_5), 132.0 (m, C_6H_5), 130.2 (m, C_6H_5), 128. 8 (m, PC_6H_4N), 128.1 (s, C_6H_5), 127.9 (m, PC_6H_4N), 125.9 (s, PC_6H_4N), 120.9 (s, PC_6H_4N), 60.7 (OCH_2CH_3), 58.6 (*n*Bu), 41.8 ($HNCH_2$), 39.2 (PdCO*C*H_3), 23.8 (*n*Bu), 19.5 (*n*Bu), 14.2 (CH_2CH_3), and 13.6 (NBu). ^{31}P{^{1}H}: δ 20.9 ppm. IR: 3298 (NH_{Assoc}), 1748 (C=O_{ester}), 1688 (Pd(C=O)Me), 1556 (C−$N_{Amide\ II}$), and 1200 (C−O) cm^{-1}.

Attempted Formation of the ^{13}CO-Adduct of 3. The in situ formation of {[*trans*-($\mathbf{1}_2$Cl)Pd(^{13}CO)(Me)Cl]$^-$[NBu_4]$^+$} was attempted by the same procedure as for *trans*-($\mathbf{1}$)$_2$Pd(^{13}CO)(Me)Cl except that **2** (0.0084 g, 8.66 × 10^{-6} mol) was combined with 15 equiv of *n*Bu_4NCl (0.030 g, 1.08 × 10^{-4} mol) and dissolved in CD_2Cl_2 (0.7 mL) before bubbling ^{13}CO through the solution at −78 °C for 7 min. No ^{13}CO-adduct was observed at −80 °C (only free ^{13}CO at 184.2 ppm; however, upon warming the NMR tube, CO migratory insertion occurred and the reaction proceeded to completion (100%)). The NMR data are the same as for **5** (vide supra).

Competition Studies between 2 and Ph_3P and between $(Ph_3P)_2$PdMeCl and 1. The palladium complex **2** (10.006 mg, 1.03 × 10^{-5} mol) and 2/3 equiv of PPh_3 (1.877 mg, 7.15 × 10^{-6} mol) were weighed together and dissolved in CD_2Cl_2 (0.8 mL). ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 20, 0, −20, −30, and −40 °C. ^{31}P{^{1}H}: (T = 20 °C) δ 36.6 and 21.1 (**4**, 1.0 equiv), 33.0 (**1**, 0.4 equiv), 32.3 ((**1**)(PPh_3)PdMeCl, 0.3 equiv), 31.8 (($Ph_3P)_2$-PdMeCl, 0.3 equiv), and −4.4 (br s of **1** and/or PPh_3, 0.4 equiv) ppm; (T = −30 °C) δ 36.6 and 21.1 (**4**, 1 equiv), 31.8 (($Ph_3P)_2$-PdMeCl, 0.5 equiv), and −4.4 (br s of **1** and/or PPh_3, 0.05 equiv) ppm.

The palladium species $(Ph_3P)_2$PdMeCl (0.007 g, 1.0 × 10^{-5} mol) and 2 equiv of **1** (0.008 g, 2.0 × 10^{-5} mol) were weighed together and dissolved in CD_2Cl_2 (0.8 mL). ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded only at ambient temperature. ^{31}P{^{1}H}: (T = 20 °C) δ 36.6 and 21.1 (**4**, 1.0 equiv), 32.5 (**1**, (**1**)(PPh_3)PdMeCl and $(Ph_3P)_2$PdMeCl 0.9 equiv), and −4.4 (br s of **1** and/or PPh_3, 1.0 equiv) ppm.

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Supporting Information Available: NMR titrations, IR studies, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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