A Binuclear Palladium(I) Hydride. Formation, Reactions, and Catalysis†

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(dippp)Pd(Ph)Cl (3) reacts with methanol to yield the novel hydrido Pd(I) dimer {[(dippp)Pd]$_2$(μ-H)(μ-CO)}$^+$Cl$^-$ (1), (dippp)PdCl$_2$ (4), H$_2$, benzene, and formaldehyde. In the presence of NEt$_3$, HNEt$_3^+$Cl$^-$ is formed instead of 4. 1 can also be formed in a reaction of Pd(dippp)$_2$, HCl, and CO. Labeling studies and modeling reactions indicate that the novel transformation of 3 into 1 involves methanolysis of 3 followed by a β-H elimination from a methoxo intermediate to yield formaldehyde, benzene, and the 14e transient (dippp)Pd (7). Formaldehyde decarbonylation, coupling of the palladium carbonyl complex with 7, and protonation lead to 1. Alternatively, 1 can be formed by electrophilic attack of protonated 7, on the carbonyl complex (dippp)Pd(CO). A number of reactivity modes have been identified for 1. Reaction with acetylenes results in bridge-splitting to form (dippp)Pd(η^2-acetylene) and in hydropalladation of the acetylene to form a vinyl complex. The hydropalladation process exhibits high regio- and stereoselectivity, resulting in cis addition and attachment of the Pd atom to the more hindered carbon, indicating electronic control. 1 undergoes exchange of the hydride for deuteride in CD$_3$COCD$_3$, most likely via an enol insertion into Pd-H. In the presence of an olefin, such as cyclooctene or ethyl vinyl ether, catalytic transfer deuteration takes place. α-Deuteration of the latter is preferred, indicating anti-Markovnikov Pd-H addition. The integrity of 1 is maintained during this process. With norbornene, bridge-splitting to form (dippp)Pd(norbornyl) (17) and its CO-insertion product 18 takes place. No H/D exchange catalysis is observed in this case with acetone-d_6. 1 behaves as a Pd(0) complex and exhibits oxidative addition reactivity with chlorobenzene or benzyl chloride, yielding (dippp)Pd(R)Cl. The relevance of this reactivity to Pd-catalyzed reactions is discussed.

Introduction

Hydridopalladium complexes are postulated as intermediates in a variety of catalytic processes, such as hydroformylation of alkenes and alkynes, Heck vinylation of haloarenes, reduction of halocarbons, etc.[1] However, direct proof of such intermediates is generally not available. In general, the chemistry of Pd hydrides is not very well developed, due to their instability, especially under the basic conditions utilized in several of the above-mentioned reactions. A few well characterized palladium hydride complexes, most of them bearing bulky phosphines, were reported. These complexes are usually of the type *trans*-Pd(PR$_3$)$_2$(H)X,[2,3] where X is a monoanionic ligand (halogen, for example), or a neutral ligand (such as a phosphine, resulting in a cationic complex).

During our studies of intermediates in palladium-catalyzed carbonylation reactions, we isolated and characterized a binuclear Pd(I) hydride complex {[(dippp)Pd]$_2$(μ-H)(μ-CO)}$^+$Cl$^-$ (1), which is formed under conditions closely related to those employed in catalytic cycles of methoxycarbonylation and reduction of chloroarenes. The complex exhibits very interesting reactivity patterns that are discussed in this report. While this work was in progress, a very reactive, (Me$_2$NCS$_2$)Pd(PEt$_3$)H complex exhibiting some aspects relevant to complex 1 reactivity was reported.[4] We also discuss here the relevance of the chemistry of 1 to various catalytic processes.

A preliminary report of some aspects of this work has appeared,[5] including the X-ray structure of 1, which will not be repeated here.

Results and Discussion

1. Formation and Characterization of {[(dippp)Pd]$_2$(μ-H)(μ-CO)}$^+$Cl$^-$ (1). During carbonylations of aryl chlorides in basic alcoholic media catalyzed by Pd(dippp)$_2$ (2),[6] an intense red color is observed. ^{31}P{^{1}H} NMR of the reaction mixture exhibits one singlet at 23.0 ppm in addition to a signal of the free dippp ligand. The same complex is obtained when a colorless solution of (dippp)Pd(Ph)Cl (3) in methanol containing a 10-fold excess of NEt$_3$ is heated to 60 °C. Solvent evaporation yields a red solid, which contains HNEt$_3^+$Cl$^-$ and the above Pd complex as a single product.

^{1}H NMR of the compound exhibits a single hydride split into a quintet with J = 41 Hz. The integrations show that there is one hydride per two dippp ligands. IR of the compound exhibits a strong peak at 1789 cm^{-1}, which is retained upon exchanging the hydride for a deuteride (see

† This paper is dedicated to Prof. J. Blum on the occasion of his 60th birthday.

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(2) (a) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371. (b) Munakata, H.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1970**, 881. (c) Munakata, H.; Green, M. L. H. *J. Chem. Soc. A* **1971**, 469 and references therein.

(3) (a) Di Bugno, D.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. (b) Leoni, P.; Sommovigo, M.; Pasquali, M.; Midellini, S.; Braga, D.; Sabatino, P. *Organometallics* **1991**, *10*, 1038. (c) Schunn, R. A. *Inorg. Chem.* **1976**, *15*, 208. (d) Reference 7d. (e) Reference 7c. (f) Reference 7a.

(4) Reger, D. L.; Garza, D. G. *Organometallics* **1993**, *12*, 554.

(5) Portnoy, M.; Frolow, F.; Milstein, D. *Organometallics* **1991**, *10*, 3960.

(6) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742.

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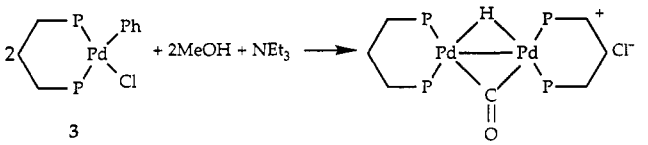
below), indicating that this absorption is due to a bridging carbonyl, which can be directly observed as a very weak quintet signal (δ = 250.9, J = 32 Hz) in $^{13}C\{^1H\}$ NMR. This spectroscopic data combined with elemental analysis and an X-ray diffraction study[5] revealed that the red solid is the Pd(I) complex $\{[dippp)Pd]_2(\mu\text{-}H)(\mu\text{-}CO)\}^+Cl^-$ (1).

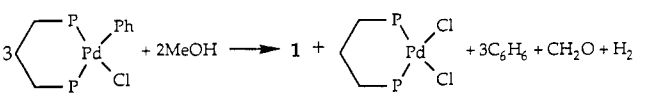
Very few palladium complexes containing bridging hydrides have been observed[7] and the first structural characterization of such a complex was described very recently.[7e] Complexes analogous to 1 were reported for Pd (PPh_3 and dppp ligands)[7a,c,d,f] and for Pt (dppe and dppf ligands).[8] Similarly to these complexes, complex 1 is not rigid. While in the solid state, the two phosphorus atoms coordinated to the same palladium atom are not equivalent, $^{31}P\{^1H\}$ NMR in solution at room temperature exhibits a single signal. The spectral patterns of other nuclei are also averaged, resulting in the hydride and carbonylic carbon being split into quintets by phosphorus. Cooling a solution of complex 1 to −70 °C results in a serious line-broadening in $^{31}P\{^1H\}$ and ^1H NMR, but the limiting spectra are not reached. Complex 1 seems to be more rigid than the analogous PPh_3 complex,[7a] since 1 exhibits broadening of the lines already below −10 °C, while the PPh_3 complex exhibits sharp ^{13}C and ^1H signals at even lower temperatures. The Pt analogs of 1[8] are more rigid, already exhibiting their limiting spectra at −60 to −70 °C.

2. Mechanism of Complex 1 Formation. Additional products of the reaction leading to 1 are benzene, as detected by NMR and GC–MS, and formaldehyde, as detected by the chromotropic acid test.[9] The overall stoichiometry of the transformation is presented in eq 1.



(1)

Complex 1 is formed by reaction of 3 and methanol even in the absence of NEt_3 but, in this case, (dippp)-$PdCl_2$ (4) is also formed in an amount equivalent to 1 (eq 2). This is a result of protonation of 3 to yield 4 and benzene.

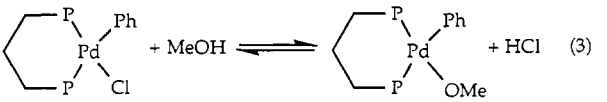


(2)

Interestingly, when CH_3OD is used in these reactions, $\{[(dippp)Pd]_2(\mu\text{-}D)(\mu\text{-}CO)\}^+Cl^-$ (1-d_1) is formed. It exhibits a 1:1:1 triplet in $^{31}P\{^1H\}$ NMR (δ = 22.95, ppm, J_{P-D} = 6 Hz), as well as a quintet with the same coupling constant at −5.2 ppm in D NMR.

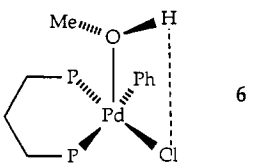
Only traces of unlabeled 1 are detected (probably due to a small amount of CH_3OH in CH_3OD). However, GC–MS analysis of the product benzene is different for the two reactions. While only traces of benzene-d_1 are produced in reaction 1, ca. one-third of the total amount of benzene formed in reaction 2 is monodeuterated benzene. These observations show that (1) the hydride of 1 comes from the OH group of methanol, (2) the proton trapped by Et_3N in reaction 1 and by complex 3 in reaction 2 also comes from the OH (thus C_6H_5D is formed when reaction 2 is performed in CH_3OD), and (3) the benzene formed in reaction 1 and ca. two-thirds of the amount of benzene formed in reaction 2 originates from the phenyl of 3 and from CH_3OH.

A possible source of acid in solution is the metathesis of 3 with methanol to yield the unobserved 5 (eq 3).

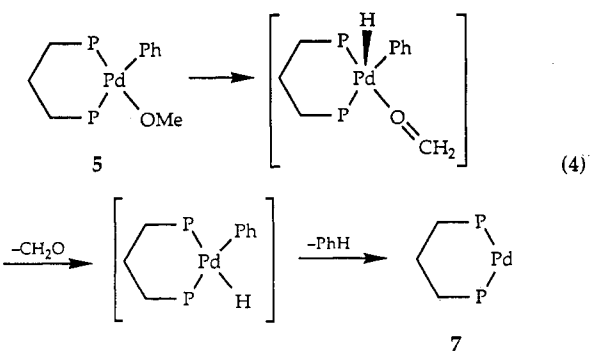


(3)

Methanolysis of 3 may involve methoxide attack at the metal center, but it is more likely (especially since reaction 3 also occurs in neutral medium) that methanol coordination leads to a concerted elimination of HCl promoted by hydrogen bonding (intermediate 6).



β-H elimination of 5 and subsequent reductive elimination would lead to benzene, formaldehyde, and 7 (eq 4).



(4)

Since 5 possesses an empty coordination site, the β-H elimination process can proceed without ligand dissociation. Such nondissociative pathways were shown for several Pd(II) and Pt(II) square planar complexes.[10]

The CO ligand of 1 is probably formed by decarbonylation of formaldehyde, a thermodynamically very fa-

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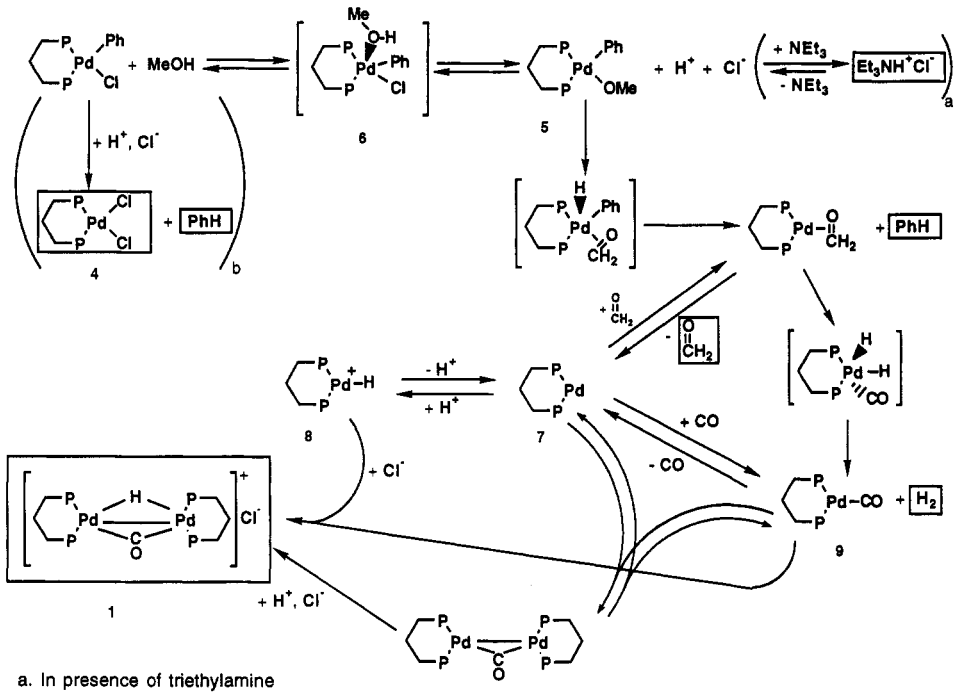
(9) Feigel, F.; Auger, V. *Spot Tests in Organic Analysis*, 7th ed.; Elsevier: New York, 1966; p 434.

(10) (a) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805. (b) Alibrandi, G.; Cusumano, M.; Minniti, D.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 342. (c) Darensbourg, D. J.; Wiegreffe, P.; Riordan, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 5759.

Scheme 1



a. In presence of triethylamine
b. In absence of triethylamine

vorable process. Indeed, when complex **2** is heated with formaldehyde in THF, decomposition of formaldehyde takes place and CO is formed (eq 5).

$$\underset{\mathbf{2}}{Pd(dippp)_2} + (CH_2O)_n \rightarrow Pd(dippp)_x(CO)_{3-x} + H_2 + dippp \quad (5)$$
$$x = 1 \text{ or } 2$$

Aldehyde oxidative addition to Pd(0) metal centers, which is not common, may be driven by the elimination of H_2.

The species most likely to promote the formaldehyde decomposition in reaction 1 is the 14e fragment **7**, which is easily formed from **2** by ligand dissociation, as was proven by an inversion transfer experiment.[11]

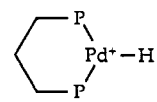
A complex analogous to **1** was reported to be formed by a reaction of a Pd(0) phosphine complex with CO and an acid.[7a,c,d] Having these "ingredients" in the reaction mixture during formation of **1** suggests that the final stage in the formation of **1** is the combination of **7**, CO, and H^+ into the dimer **1**. Indeed, when 0.5 equiv of HCl and of CO (the order of addition is not important) are injected into a sealed vessel containing a stirred THF solution of **2**, an immediate color change from yellow to pink is observed and **1** is formed as a major product (by ^{31}P NMR) (eq 6). The complete mechanism of reactions 1 and 2 is presented in Scheme 1.

$$2 + {}^1/_2HCl + {}^1/_2CO \rightarrow {}^1/_2\mathbf{1} \quad (6)$$

Several possible explanations exist for the combination of **7**, HCl, and CO into **1**. Reaction of **3** with NaOMe in methanol hints at one such explanation. When a methanolic solution of sodium methoxide is added to an equivalent amount of **3**, a dark red solution is immediately formed. Its $^{31}P\{^1H\}$ NMR exhibits a singlet at 22.9 ppm, very close to that of **1** (23.0 ppm), but the ^1H NMR, $^{13}C\{^1H\}$ NMR, and IR spectra of the product are entirely different from those of **1**.

No hydride is observed in ^1H NMR, and the IR pattern exhibits three peaks at 1756, 1799, and 1831 cm^{-1}. While the exact structure of the product is still unclear, a Pd(0) complex with bridging carbonyls (based on IR) seems to be a reasonable hypothesis. Hence, it is possible to suggest that two Pd(0) fragments **7** are bridged by a carbonyl, and the basic Pd(μ-CO)Pd core is protonated by the readily available HCl (or $HNEt_3^+Cl^-$).

Another possibility is that an electrophilic hydride, **8**, formed by protonation of **7** attacks an unsaturated electron-rich (dippp)Pd(CO) fragment **9**, as contrasted by



8

the well-known reaction involving coupling of a nucleophilic hydride with an electron-deficient metal center.[12] In a recently published report,[13] a molybdenum–cobalt dimer bridged by hydride and carbonyl ligands is viewed as a combination of two separate fragments: an electron-poor molybdenum hydride and an electron-rich cobalt carbonyl. A four-center, 4e interaction, similar to the one proposed for the MoCo(μ-H)(μ-CO) core, may be responsible for stabilizing the dimer **1** in our case.

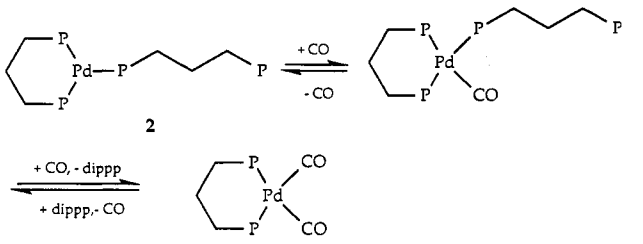
The high stability of the dimer, relative to its components explains why it is readily formed. Complexes **8** and

(11) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665.

(12) (a) Albinati, A.; Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6825. (b) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064. (c) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038. (d) Conroy-Lewis, F. M.; Simpson, S. J.; Brammer, L.; Orpen, A. G. *J. Organomet. Chem.* **1991**, *406*, 197.

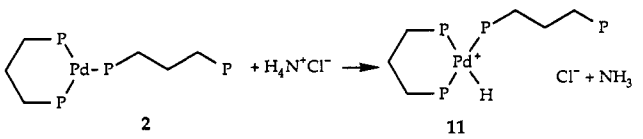
(13) Tsai, J.-C.; Wheeler, R. A.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 1344.

9 are likely to be in equilibrium with the 14e fragment 7, whereas the very stable 1 serves as a thermodynamic sink. The binding of CO to 7 is likely to be reversible, similarly to the reversible binding of CO to 2[14] (eq 7).



(7)

As for the protonated product, 8, or its neutral form 10, it seems to be highly unstable and to exist in a fast equilibrium with 7 and H^+. Numerous attempts to synthesize 10 failed. Apparently, stabilization of the system by the CO ligand is important. The instability of *cis*-hydrido–halide complexes of Pt(II) is well documented.[15] Hydrochlorination of 2 with NH_4Cl resulted in the formation of a colorless complex exhibiting an ABX pattern in $^{31}P\{^1H\}$ NMR. A large coupling constant of 311 Hz (characteristic of P trans to P) between A and B parts of the spectrum, as well as hydride signals [−7.05 (ddd, 147.7 Hz, 13.5 Hz, 4.5 Hz) in ^1H NMR and 2049 cm^{-1} in IR] pointed without doubt to the formation of a cationic product 11 (eq 8).



(8)

A similar product [(dippp)Pd(η^1-dippp)H]$^+OMe^-$ is formed when 2 is heated in methanol. However, in this case, the reaction is reversible and evaporation of the solvent restores the Pd(0) complex 2. Formation of 11 emphasizes the greater basicity (but not necessarily the nucleophilicity) of 2 relative to 7. 11 is much more stable than 8 or 10, the possible products of protonation of 7.

Interestingly, when reaction 1 is performed in the presence of 1 equiv of dippp, a slightly pink solution (rather than red) is formed. The main organometallic product of this reaction is 11 with traces of 1. This is probably because fragment 7, formed by reductive elimination of benzene, is trapped essentially irreversibly by dippp and HCl into 11, before it has a chance to decompose formaldehyde. In the absence of CO, the reaction course is shifted to 11, an alternative thermodynamic sink.

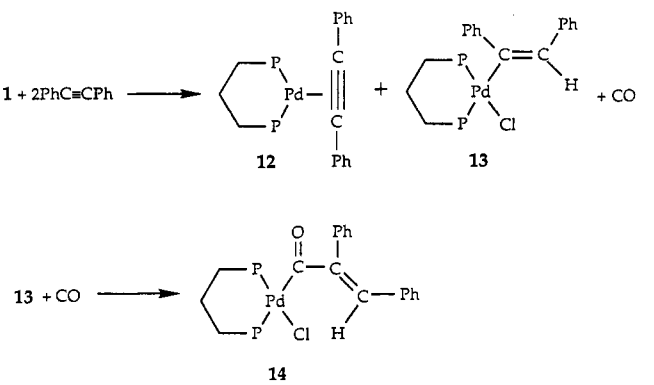
3. Properties of 1. Complex 1 is readily soluble in polar solvents, such as THF, acetone, and methanol, whereas its solubility in aromatic solvents is limited, and it is completely insoluble in saturated hydrocarbons. Crystals suitable for X-ray analysis were obtained upon cooling a saturated toluene solution of 1.[5] Solubility of 1 in aromatic solvents can be attributed to a certain degree of coordination of the chloride to the unsaturated metal center, forming a neutral species. The complex dissolves with decomposition in chlorinated solvents.

1 is fairly air-stable in agreement with its formal oxidation state of +1. Its decomposition when exposed to air takes hours instead of minutes in the case of related Pd(0) complexes, such as 2. On the other hand, Pd(II) complexes of dippp are not air-sensitive.

1 exhibits interesting reactivity patterns toward unsaturated compounds, such as olefins, alkynes, and ketones.

3a. Reactions with Acetylenes. When 1 is heated with 2 equiv of PhC≡CPh in acetone, a white precipitate is formed and the solution turns dark yellow. The precipitate, exhibiting a singlet at 29.7 ppm in $^{31}P\{^1H\}$ NMR and a strong peak at 1832 cm^{-1} in the IR, was identified as (dippp)Pd(η^2-PhC≡CPh) (12) by its ^1H and $^{13}C\{^1H\}$ NMR. The air-sensitive 12 dissolves easily in benzene or THF, but it is only sparingly soluble in acetone. An attempt to dissolve it in chloroform resulted in its decomposition by oxidative addition reactions with the solvent.[16]

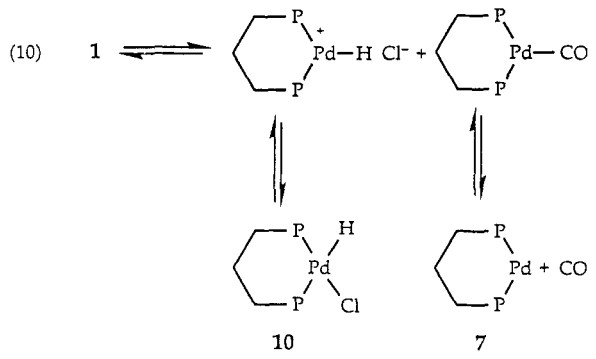
The dark yellow mother liquor from which 12 precipitates contains two principal compounds, each of which exhibits two doublets in $^{31}P\{^1H\}$ NMR: 14.3 and 26.9 ppm (J = 44 Hz), major complex, and 9.9 and 29.4 ppm (J = 64 Hz), minor complex. ^1H NMR of the major compound shows two sets of phenyl signals, as well as a double doublet at 6.56 ppm (J = 13.5 and 2.3 Hz). The minor compound exhibits a number of badly resolved aromatic signals, as well as a singlet at 8.44 ppm. Monitoring of the reaction in a sealed tube revealed that the signal at 8.44 ppm grows slowly at the expense of the signal at 6.56 ppm. It seems reasonable to assign (dippp)Pd(C(Ph)=CHPh)Cl (13) as the major compound and (dippp)Pd(C(O)C(Ph)=CHPh)Cl (14) as the minor one. An IR peak at 1617 cm^{-1}, as well as a J_{P-P} of 64 Hz, fits the acyl complex 14, while the vinylic hydrogen dd at 6.56 ppm fits the vinyl complex 13. The overall stoichiometry is presented in eq 9.



When a solution of 1 in acetone is stirred with 2 equiv of phenylacetylene, at room temperature for 4 h, $^{31}P\{^1H\}$ NMR exhibits formation of two major products, one of which gives two doublets at 29.8 and 12.6 ppm with J = 43 Hz, while the other shows an AB pattern, centered at 31.8 and 32.0 ppm with J = 5.9 Hz. Prolonged stirring results in the gradual disappearance of the second product,

(14) Portnoy, M.; Milstein, D. Unpublished results.
(15) Scrivanti, A.; Botteghi, C.; Toniolo, L.; Berton, A. *J. Organomet. Chem.* **1988**, *344*, 261.
(16) (dippp)Pd($CHCl_2$)Cl is probably formed first, but it is rapidly transformed into 4.

Scheme 2



while a number of secondary products are formed. When the reaction is performed at 60 °C, only the first primary product and the secondary products are detected. White crystals precipitate from the resulting yellow-orange solution after standing for 2 days. The crystals are readily soluble in acetonitrile and are identified as (dippp)Pd(C(Ph)=CH_2)Cl (**15**), according to their $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR. Determination of the stereochemistry of the vinyl ligand is based on the mutual coupling constant of the vinylic hydrogens, which appears as two ddd patterns: 6.25 (25.6 Hz, 6.3 Hz, 0.7 Hz) and 5.61 (11.5 Hz, 1.4 Hz, 0.7 Hz). The small coupling constant of 0.7 Hz is characteristic of geminal coupling and, therefore, the two hydrogens are located on the vinylic carbon β to palladium (the phenyl is bound to the α-carbon). The largest splitting of each set is due to coupling with the phosphorus trans to the vinyl ligand, while the medium splitting is due to coupling with the phosphorus cis to it. Since the splitting of vinyl hydrogens trans to the metal center by phosphorus is associated with larger coupling constants than those of hydrogens cis to the metal center, the signal at 6.25 ppm is assigned to H located trans to Pd, while the signal at 5.61 ppm is H cis to Pd. The vinyl hydrogen cis to Pd is shifted upfield by ca. 0.6 ppm relative to the hydrogen trans to palladium, a typical feature of such systems.[17] Comparison of the coupling constants of the vinylic hydrogen of **13** (13.5 and 2.3 Hz) to those of **15** reveals that they are more similar to the constants of H cis to Pd. Hence, the cis stereochemistry is assigned to the vinyl group of **13**. This stereochemistry is retained for **14**, assuming that CO insertion does not alter the geometry of the double bond.

The second primary product (AB pattern with 6 Hz coupling constant) is assigned to (dippp)Pd(η^2-PhC≡CH) (**16**), which could be obtained by an alternative route.[18] The interesting reactivity of this complex will be reported elsewhere.

The reaction of **1** with acetylenes results in splitting the complex into two components: a Pd(II) hydride that inserts one molecule of acetylene into the Pd–H bond, and a Pd(0) fragment **7** that is stabilized by π-bonding of the second molecule of acetylene. The CO released during this *splitting* process subsequently reacts to some extent with the product of insertion into Pd–H. It is possible that spontaneous splitting of **1** through the equilibrium in Scheme 2 is shifted to the right by trapping **10** and **7** with acetylenes. The stability of solutions of **1** in the absence of a substrate, however, makes this possibility unlikely. Occurrence of equilibrium 10 in the absence of a substrate should cause decomposition of **1** through CO leaking and through reversible dissociation of HCl from **10**, followed by its reaction with another molecule of **10** to form dichloride complex **4** and H_2.

A route likely to be responsible for the reaction of **1** with alkynes is *substrate induced splitting* of the dimer. Alkyne coordination to the unsaturated **1**, followed by hydride migration probably promotes the dimer splitting, demonstrating again the importance of the hydride for dimer stability.

The stereo- and regioselectivity of the insertion is remarkable. Complete regioselectivity is demonstrated by insertion of phenylacetylene, leading exclusively to the product in which the Pd atom is attached to the more hindered phenyl substituted carbon atom.

While the recently reported hydropalladation of alkynes by (Me_2NCS_2)Pd(PEt_3)H[4] does not seem to be very selective, the reaction with 1-pentyne shows a clear tendency to form the product with Pd attached to the more sterically hindered carbon. The absence of steric control was attributed to the "very low steric hindrance around the palladium center". The Pd center of complex **1** is, however, very sterically hindered because of the bulky dippp ligand. This steric hindrance is expressed in $^{13}C\{^1H\}$ and ^1H NMR spectra of the insertion product **15**, where the sterically demanding 1-Ph–vinyl group restricts some rotational freedom of the P^iPr_2 moiety cis to it, thus causing broadening of this group carbon and hydrogen signals. Despite this steric hindrance, formation of other possible isomers, in which Pd is bound to the less-hindered carbon of the double bond, is not observed. Thus, we suggest that in hydropalladation of alkynes, electronic directing effects (even minor, such as in the case of phenylacetylene or 1-pentyne) are significantly more important than steric effects.

Also noteworthy is the stereoselectivity of the insertion of diphenylacetylene with **1**, leading exclusively to the cis-insertion product **13**. Cis hydrometalation of alkynes is attributed to a concerted, four-center transition state, while trans addition, observed in reactions of alkynes with electron-withdrawing substituents, involves an electron-transfer mechanism.[17b] In recent studies, a "partial electron-transfer component" of the mechanism was responsible for a trans-insertion product even in the reaction with 1-pentyne.[4] Absence of any trans-insertion product in the reaction of **1** with diphenylacetylene excludes the possibility of an electron-transfer mechanism in this reaction.

Formation of the acyl product using the reaction of **1** with diphenylacetylene shows that **13** and probably **15** can be easily carbonylated under a CO atmosphere (only a stoichiometric amount of CO is present during the reaction). In contrast, the vinylic complex (Me_2NCS_2)Pd(PEt_3)[C(CO_2Me)=$CHCO_2Me$] does not insert CO, in accordance with the lower nucleophilicity of its vinyl group.[4]

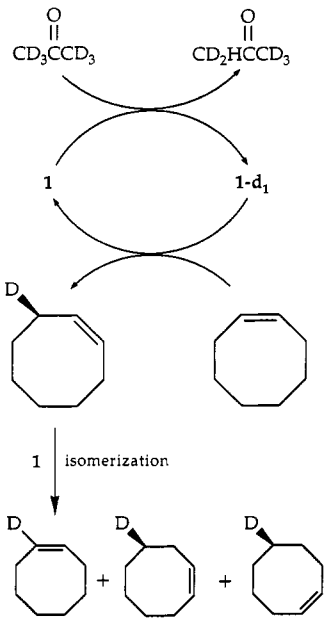
3b. Reactions with Olefins and Ketones (Enols). Although heating a solution of complex **1** with olefins generally does not bring about any obvious changes, subsequent experiments revealed that olefins are not completely inert toward **1**.

I. Reaction of 1 with Acetone-d_6 and with Olefins. When **1** is heated to 60 °C for a couple of hours in acetone-

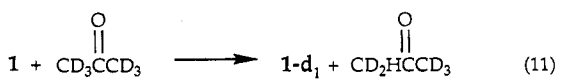
(17) (a) Reference 4. (b) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961.

(18) Weisman, A.; Milstein, D. Unpublished results.

Scheme 3



d_6, complete exchange to generate **1**-d_1 is observed. A parallel increase in the amount of acetone-d_5 was observed in ^{1}H NMR (eq 11).

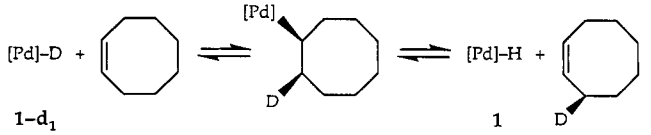


(11)

When **1** is heated in acetone-d_6 in the presence of an olefin (except norbornene) catalytic transfer of D atoms from the solvent to the olefin is observed. Thus, when a large excess of cyclooctene is heated with **1** in an acetone-d_6 solution for a couple of days, D NMR reveals three broad signals at 5.58, 2.10, and 1.45 ppm, appropriate for the vinylic, allylic, and aliphatic signals of cyclooctene, respectively. Although the allylic signal is partially obscured by the signal of the solvent, the minimal estimation of the number of equivalents of D atoms transferred to cyclooctene is 39 times that of the number of equivalents of **1**. The estimation, based on an internal standard of benzene-d_6, proves that *catalytic* transfer deuteration of cyclooctene by **1** has taken place with an overall turnover number of at least 39. ^{31}P{^{1}H} NMR of the reaction mixture exhibits mostly **1** and only a small amount of **1**-d_1.

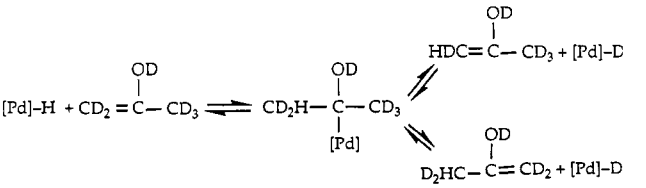
The general scheme for this catalytic transformation is presented in Scheme 3.

While the mechanism of the reaction of **1**-d_1 with the olefin is straightforward, proceeding through insertion of the double bond into Pd–H, followed by β-H elimination (eq 12), the deuteration of **1** by acetone-d_6 is less clear.



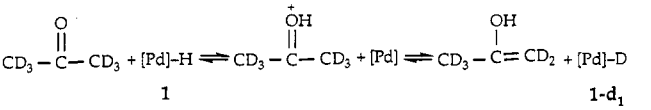
(12)

Although direct C–D activation of acetone-d_6 by **1** is not ruled out completely, it is unlikely because no D–H scrambling with other solvents, such as methanol or acetonitrile is observed. We favor a mechanism proceeding through the enolic form of acetone (eq 13).

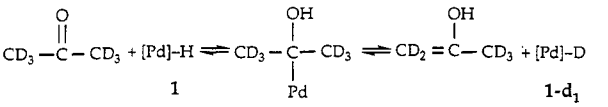


(13)

Another enol-involving mechanism may proceed via protonation of the ketone by **1** (eq 14). This is a type of acid-catalyzed enolization. Another possibility is carbonyl insertion into the Pd–H bond, followed by β-elimination (eq 15).



(14)



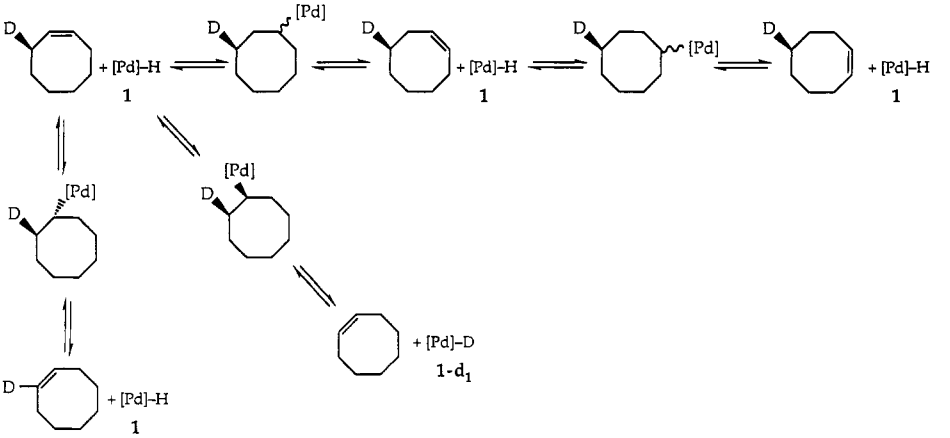
(15)

The mechanism of enol insertion seems to be the most likely in analogy with the reactivity of a simple olefin (cyclooctene).

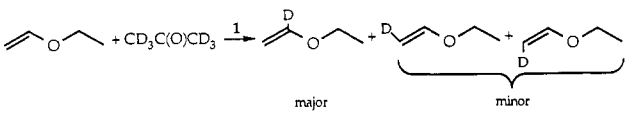
Assuming that both the olefin insertion into Pd–D and β-H elimination from the insertion product occur in a cis mode, cyclooctene monodeuterated in the allylic position should be obtained as the primary product. Indeed, the allylic peak in D NMR is the biggest. However, the rate of hydrogen exchange between **1** (or **1**-d_1) and the olefin is significantly higher than that between **1** and acetone-d_6, although the concentration of the olefin is only ca. 1/15th that of acetone-d_6 (most of complex **1** in solution is not deuterated). Thus, cyclooctene, after being deuterated, undergoes a number of isomerizing "encounters" with **1**, each of which consists of insertion into Pd–H, followed by β-H elimination, leading to cyclooctene deuteration in all positions (Scheme 4). Most of the cyclooctene obtained is di- or trideuterated since the number of equivalent of D atoms transferred is more than twice that of the cyclooctene in solution. Isotope effects can play a significant role in these reactions.

Heating ethyl vinyl ether with a catalytic amount of **1** in acetone-d_6 leads, after a couple of days, to a new signal in D NMR at 6.44 ppm (dd, 2.2 Hz, 0.1 Hz), which is at the same chemical shift as that of the vinylic hydrogen α to oxygen. The vicinal D–H coupling constants are in excellent agreement with the vicinal H–H coupling constants in nondeuterated vinyl ethyl ether (14.5 Hz, trans, and 6.8 Hz, cis). Significantly smaller signals are also observed at chemical shifts of the two vinylic hydrogens β to oxygen (3.91 and 4.12 ppm). It is difficult to measure precisely the ratio of integration between the D signals at the vinylic positions because of unreliable integrations of the small signals at the β-position. However, these signals are only a few percent of the signal at the α-position. Heating the solution for an additional 4 days results in an increase of the three deuterium signals of ethyl vinyl ether, accompanied by the change in ratio between the β and α deuterations. The ratio of integration in positions α/(β trans to O)/(β cis to O) is 5:1:1. The overall amount of deuterated olefin reveals that a catalytic reaction has taken

Scheme 4



place with ca. 20 turnovers (eq 16). Prolonged heating of the mixture caused decomposition of ethyl vinyl ether and slow disappearance of **1** through multiple reactions with the decomposition products.



(16)

$^{31}P\{^1H\}$ NMR of the mixture (before decomposition) shows that ca. 25% of the complexes are **1** and 75% are **1**-d_1. This observation, as well as the lower number of turnovers achieved in the catalysis during a longer period of heating, as compared to that of cyclooctene, hints that the rate of insertion of the ether into the Pd–H bond is lower than that of cyclooctene.

Another interesting point is the preference for deuteration at the α-position of vinyl ether, revealing *anti-Markovnikov* addition of the Pd–H moiety to the olefin. Both steric and electronic effects can direct the addition toward this mode,[19] and it is not clear which one is responsible in this case.

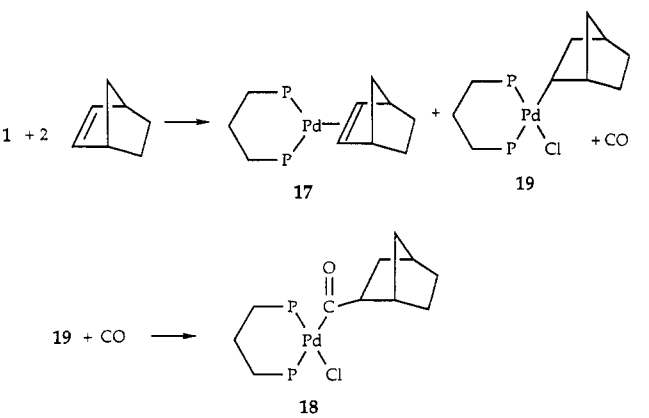
Not only olefins can be deuterated catalytically by **1** using acetone-d_6 as D donor. The ^1H NMR spectrum of a diethyl ketone/acetone-d_6 mixture, which was heated with a catalytic amount of **1**, exhibits mainly signals of diethyl ketone. However, four additional peaks appear near the triplet of diethyl ketone in an apparent double doublet pattern with J = 7.4 Hz and J = 1.1 Hz. Since this pattern is partially hidden by the much larger triplet, it is logical to assume that the four signals are part of a double 1:1:1 triplet pattern that represents a methyl signal of $-CDH-CH_3$ (the second coupling constant is ca. one-seventh of the first, as expected in this case). This assumption is further supported by D NMR where, in addition to the very strong signal of acetone-d_6, a small double quartet is observed at 2.41 ppm with J_q = 1.1 Hz and J_d = 2.6 Hz. The chemical shift and coupling constants are appropriate for the D atom of $C_2H_5C(O)CHDCH_3$. $^2J_{H-D}$ = 2.6 Hz gives an H–H geminal constant of 17.5 Hz, within the expected range. The estimated amount of the monodeuterated product shows that a catalytic, although slow, transfer deuteration with five turnovers has taken place.

(19) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F.; *J. Organomet. Chem.* **1992**, *430*, 357.

The mechanism of HD exchange between **1** and acetone-d_6 also drives the D–H exchange between **1**-d_1 and diethyl ketone, completing the catalytic cycle of Scheme 5.

The exclusive deuteration at the α-position fits mechanisms involving enols, but does not rule out a C–H activation process, since the activity of the α-position is much larger than that of the β-position.

II. Reaction with Norbornene. When **1** is heated in a sealed tube with a large excess of norbornene in acetone, $^{31}P\{^1H\}$ NMR monitoring exhibits slow growth of a singlet at 30.2 ppm, and a pair of doublets at 8.5 and 30.4 ppm with J = 71.7 Hz. The singlet is assigned to a Pd(0) complex (dippp)Pd(η^1-norbornene) (**17**), which was synthesized by two alternative paths.[14] The doublets are assigned to **18**, according to their shifts and the characteristic coupling constant.[20] Sometimes traces of complex **19**, which we have prepared separately, are also observed. Thus, reaction 17, similar to reaction 9, takes place.

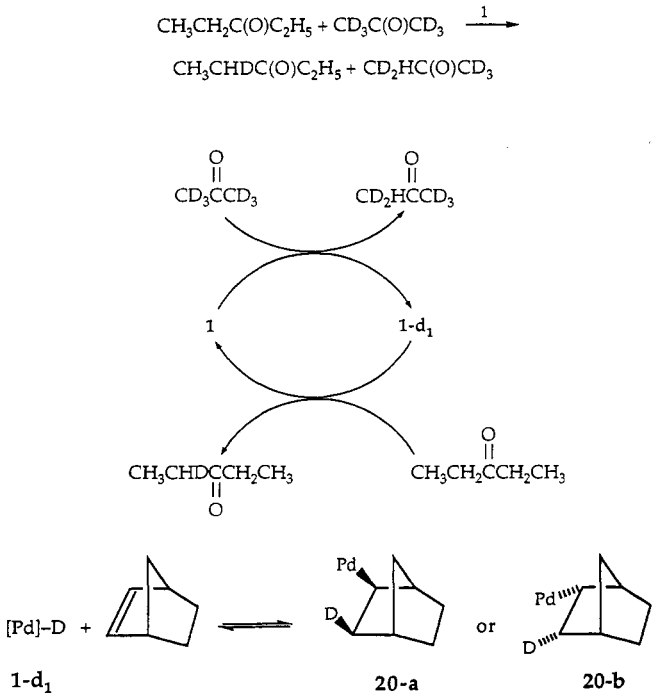


(17)

When the same experiment is performed in acetone-d_6, no deuteration of norborene is observed.

At this stage, we would like to discuss the differences in reactivity of alkynes, simple olefins, and norbornene toward **1**. The reason for the absence of deuterium incorporation into norbornene is directly deduced from the mechanism of this process. As was discussed before, olefin insertion into the Pd–D bond proceeds in the cis mode. Assuming this for a norbornene molecule (eq 18), we obtain the intermediate **20-a** (exo addition) or **20-b** (endo addition). The process of β-hydrogen elimination demands an H or D atom *cis* to Pd. Such a process with **20-a** will be redundant. Although a bridgehead hydrogen is placed cis to Pd in **20-b**, its elimination is impossible,

Scheme 5

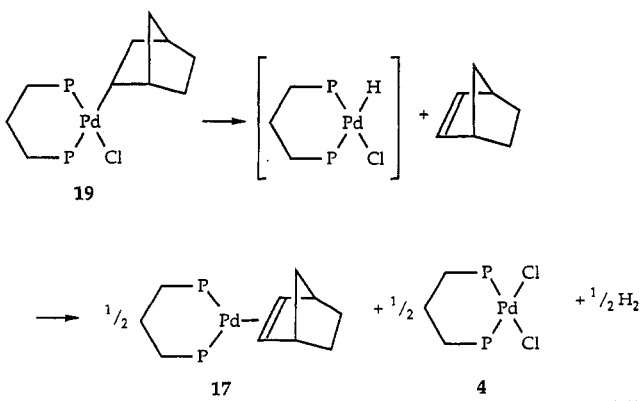


(18)

since double bonds are not formed at bridgeheads. Therefore, also in **20-b**, the only atom available for β elimination is D. Thus, β-hydrogen elimination leads back to 1-d_1, and norbornene remains nondeuterated.

Another important factor in the reactivity of norbornene and acetylenes toward 1 versus that of other olefins is the stability of the hydropalladation products. Complexes **13** and **15** resulting from such insertion of alkynes are stable at 60 °C, β-H elimination from the alkenyl ligand being highly unlikely. β-H elimination from the products of insertion of cyclooctene or other simple olefins into Pd–H bond is rapid and these complexes are unobservable although they are undoubtedly intermediates in the catalytic reactions (Scheme 3 and reaction 16).

Complex **19**—the product of norbornene insertion into the intermediate (dippp)Pd(H)Cl—is sufficiently stable to be observed in solution[14] and even isolated by an alternative route. Above 0 °C, it decomposes to form **17**, **4**, and H_2 (eq 19). The lifetime of **19** is sufficient for CO

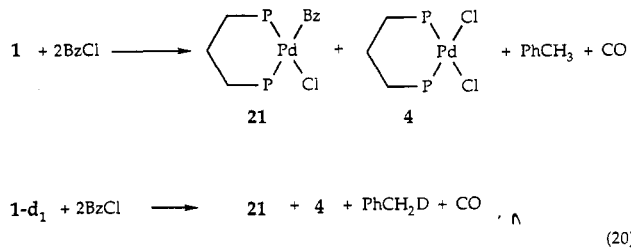


(19)

insertion to take place (reaction 17). The greater stability of **19**, as compared to analogous products of "simple" olefin insertion is caused by an increase in steric strain that accompanies transformation of norbornyl into norbornene during β-H elimination.[21]

Thus, the rate of β-H elimination from products of hydropalladation of the unsaturated bonds determines the mode of the reaction between 1 and unsaturated substrates. Whenever the β-H elimination is completely restricted (acetylenes), fast formation of the insertion products is observed followed by a slower carbonylation. When the β-H elimination is fast (cyclooctene, for example) no change in the reaction mixture composition is observed, except for hydrogen atom exchange between 1 and the substrate. In the borderline case (norbornene), when the rate of β-H elimination is slower and comparable to that of carbonylation, the carbonylated product forms slowly, while the preceding product of H migration appears as an intermediate of low concentration.

3c. Reactions of 1 with Chlorinated Hydrocarbons. When 1 is heated with 2 equiv of benzyl chloride in acetone-d_6, a white precipitate of (dippp)$PdCl_2$ (**4**) is formed and the solution turns from red to yellow. The major complex in the mother liquor exhibits two doublets in $^{31}P\{^1H\}$ NMR at 14.9 and 33.4 ppm (J = 47.9 Hz). The ^1H NMR spectrum of the solution exhibits a set of aromatic signals, a set of dippp hydrogens, and a double doublet pattern in the benzylic region: 3.08 ppm (10.1 Hz, 4.0 Hz). The IR spectrum of the residue after solvent evaporation lacks any significant carbonyl absorption. According to this, the major organometallic compound in solution is (dippp)-Pd(CH_2Ph)Cl (**21**). An additional product exhibits a complicated aromatic pattern and two signals in the benzylic region: a singlet at 2.30 ppm and a 1:1:1 triplet with J = 2.2 Hz at 2.28 ppm. These signals are assigned to a mixture of $PhCH_3$ and $PhCH_2D$. Equation 20 describes the overall reaction.



(20)

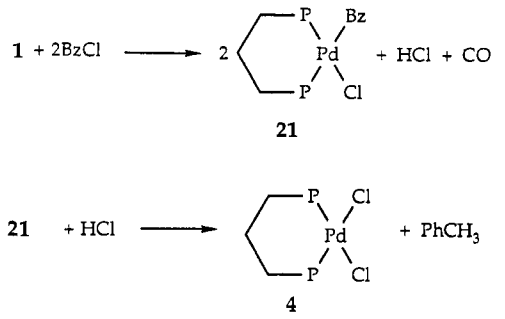
Formation of **4** and an equivalent amount of toluene seems to be the result of protonation of the oxidative product **21** (eq 21). Formation of **4** by decomposition of **10** can be excluded since it should lead to generation of H_2 and not to toluene (see eq 19).

Prolonged standing of the reaction mixture in a sealed tube results in the appearance of a small amount of new compound, which exhibits in $^{31}P\{^1H\}$ NMR two doublets [8.5 (67.7 Hz), 30.9 ppm (67.7 Hz)]. The chemical shifts and the coupling constant are pertinent to (dippp)Pd-(C(O)Bz)Cl.[20]

The fact that 1 first reacts with benzyl chloride as a Pd(0) compound, and the oxidative addition product is protonated or carbonylated only afterwards, sheds light on the role of 1 in the catalytic carbonylations of aryl chlorides.[6] It seems that under the basic conditions utilized in such reactions, 1 acts as a Pd(0) synthone. The HCl formed is trapped by the base and is prevented from

(20) In our work with Pd(II) complexes of dippp, coupling constants of 63–73 Hz were found, characteristic of acyl complexes.

(21) Reference 1, p 287.



(21)

attacking (dippp)Pd(Ar)Cl, the product of oxidative addition of ArCl to Pd(0). This hypothesis is supported by the following experiment:

When 1 is heated overnight in a closed vessel with a large excess of chlorobenzene and triethylamine, a yellow solution is formed. $^{31}P\{^1H\}$ NMR revealed almost quantitative formation of **3**.[22] Approximately 10% of (dippp)Pd(C(O)Ph)Cl (**22**)[22] is detected. Although traces of the dichloride complex **4** are also formed, we believe that under CO atmosphere this would be completely prevented. Fast trapping of **3** by CO would form **22**, which is less susceptible to protonation. Thus, **1** is part of the carbonylation catalytic cycle or acts as a stock of protected, but readily available, Pd(0).

Conclusions

The structure and mode of formation of **1** are interesting and can shed light on the role of hydride and carbonyl ligands in stabilizing metal–metal bonds in dimers and clusters. Especially intriguing is the mechanism of "self-assembly" of **1** from (dippp)Pd fragments, HCl, and CO.

It is important to consider the formation of complexes of the type **1** in reactions involving organopalladium(II) intermediates in alcoholic media, and the possibility that binuclear complexes are involved in catalysis in such systems should not be overlooked.

Complex **1** can be viewed as a stabilized palladium hydride (with (CO)Pd(dippp) as a protective group) with two mutually cis phosphines on Pd. This is a synthone of complex **10**, which is unfortunately too unstable to be studied directly. Palladium complexes with a readily available coordination site cis to a hydride ligand are rare[23] and bear considerable potential for design and study of various hydride-involving catalytic cycles. Actually, part of this potential was demonstrated here—the easy migration of the hydride to unsaturated bonds followed by CO insertion can be part of various catalytic cycles, such as hydroformylation and methoxycarbonylation of alkynes, olefins, and aryl halides. When proper reagents are chosen, such cycles can be accomplished with **1** or other complexes of this type. Considering the high regio- and stereoselectivity of insertion reactions of **1** makes potential catalytic processes even more interesting.

The catalytic transfer deuteration demonstrated in our work is performed under mild conditions and can be used for labeling various unsaturated substrates. The degree of selectivity depends on the unsaturated compound. Further research may lead to development of this catalytic cycle, as well as to the elaboration of other catalytic reactions based on **1**.

Experimental Section

1. General Considerations. All procedures with air- and water-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres, equipped with an MO-40 purification system) or on a high vacuum line using Schlenk techniques. All solvents were reagent grade or better. Methanol (Biolab) was distilled over magnesium. Acetone (Merck) was dried over molecular sieves (4 Å). Aromatic solvents (Frutarom) were distilled over sodium/benzophenone ketyl. All solvents were degassed and stored under highly pure nitrogen after distillation. All deuterated solvents were purchased from Aldrich and dried over 3-Å molecular sieves. The purest available KOH pellets, diphenylacetylene, norbornene, phenylacetylene, ethyl vinyl ether, and benzyl chloride were purchased from Merck or Aldrich and were used as received. Pd(dippp)$_2$ and (dippp)Pd(Ph)Cl, were synthesized according to reported procedures.[24] ^1H, ^{31}P, ^{13}C, and D NMR measurements, were recorded at 400, 162, 100, and 61 MHz, respectively, using a Bruker AMX400 spectrometer. ^1H, D, and ^{13}C chemical shifts are reported in ppm downfield from $SiMe_4$ and referenced to the residual solvent-h_1, residual solvent-d_1, and all -d solvent peaks, respectively. ^{31}P chemical shifts are reported in ppm downfield from phosphoric acid and were referenced to external 85% H_3PO_4.

2. Synthesis. Synthesis of [(dippp)Pd]$_2$(μ-CO)(μ-H)$^+$Cl$^-$ (1). In a typical experiment, a 10-mL pressure bottle was charged with 170 mg of (dippp)Pd(Ph)Cl (**3**), 3 mL of methanol, and 694 mg (20 equiv) of NEt_3. The bottle was capped and heated at 60 °C overnight. The color changed to deep red. Evaporation of the volatiles and several extraction–evaportion cycles with acetone produced 102 mg (71.6% yield) of a red solid. IR: ν(C=O) 1789 cm^{-1}. $^{31}P\{^1H\}$ NMR (methanol-d_4): δ 23.0 (s). ^1H NMR (methanol-d_4): δ 1.15 (bm, 48H, CH_3), 1.87 (bm, 8H, P—CH_2), 2.11 (bm, 4H, CH_2), 2.29 (d heptet, $^2J_{P-H}$ = 13.6, $^3J_{H-H}$ = 6.8 Hz, 8H, CH), −5.17 (quintet, $^2J_{P-H}$ = 41.1 Hz, 1H, Pd—H—Pd). $^{13}C\{^1H\}$ NMR (methanol-d_4): δ 18.4 (bs, CH_3), 20.7 (bs, CH_3), 26.5 (bm, CH), 19.2 (bm, P—CH_2), 24.2 (bs, CH_2), 250.9 (quintet, $^2J_{P-C}$ = 32 Hz, CO). Anal. Calcd: C, 44.86; H, 8.32; Cl, 4.3. Found: C, 44.45; H, 8.25; Cl, 4.5.

Synthesis of [(dippp)Pd]$_2$(μ-CO)(μ-D)$^+$Cl$^-$ (1-d_1) (Route A). A pressure bottle charged with a solution of **1** in acetone-d_6 was heated at 60 °C overnight. Evaporation of the solvent yielded 1-d_1 quantitatively.

Synthesis of 1-d_1 (Route B). The procedure was the same as for **1** using CH_3OD instead of CH_3OH. $^{31}P\{^1H\}$ NMR: δ 22.95 (D – triplet (1:1:1), $^2J_{P-D}$ = 6 Hz). D$\{^1H\}$ NMR (methanol): δ −5.17 (quintet, $^2J_{P-D}$ = 6 Hz). IR: ν(C=O) 1789 cm^{-1}.

Reaction of Pd(dippp)$_2$ (2) with HCl and CO. CO was bubbled for 1 min through a solution of 58 mg of **2** in 4 mL of THF, placed in a two-necked, 50-mL flask. The flask was then washed with argon, and 0.9 mL (0.5 equiv) of HCl gas was injected into the flask. The color of the solution turned reddish-pink. $^{31}P\{^1H\}$ NMR indicated **1** as a major compound of the mixture. The same results were obtained when the order of addition of CO and HCl was reversed.

Reaction of 2 with Paraformaldehyde. A solution of 51 mg of **2** in 2 mL of THF was mixed with 57 mg (ca. 25 equiv) of $(CH_2O)_n$. The slurry was heated at 100 °C for several hours. The resulting solution (almost colorless after cooling) was found identical to a solution of Pd(dippp)$_2$ under an atmosphere of CO.

Reaction of 1 with Benzyl Chloride. Characterization of (dippp)Pd(Bz)Cl. A solution containing 10 mg of benzyl chloride (ca. 2.2 equiv) in 1 mL of acetone was added to 30 mg of **1** in a pressure bottle. After heating overnight at 60 °C the red color disappeared and a yellowish solution with a white precipitate was formed. The precipitate was filtered off, dried, and identified as (dippp)$PdCl_2$.[5] Evaporation of the solution

(22) Characterized in ref 6.

(23) A Pd–hydride complex in ref 4, as well as complexes with bridging hydrides[7] are probably the only cases.

(24) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655.

and extraction of the residue with acetone-d_6 yielded pure (dippp)-Pd(Bz)Cl. IR: ν(C=C) 1593 cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 14.9 (d, J = 47.9 Hz), 33.4 (d, J = 47.9 Hz); ^1H NMR (acetone-d_6): δ 7.64 (bd, J = 7.8 Hz, 2H, H_{ortho}), 7.00 (t, J = 7.2 Hz, 2H, H_{meta}), 6.86 (t, J = 7.1 Hz, 1H, H_{para}), 3.08 (dd, J_{P-H} = 10.1 Hz, J_{P-H} = 4.0 Hz, 2H, Pd—CH_2), 2.47 (d heptet, J_{P-H} = 7.5 Hz, J_{H-H} = 7.1 Hz, 2H, CH), 2.43 (d heptet, J_{P-H} = 9.9 Hz, J_{H-H} = 7.1 Hz, 2H, CH), 1. 90 (m, 2H, CH_2), 1.64 (m, 2H, P—CH_2), 1.53 (m, 2H, P—CH_2), 1.30 (dd, J_{P-H} = 16.2 Hz, J_{H-H} = 7.2 Hz, 6H, CH), 1.22 (dd, J_{P-H} = 13.1 Hz, J_{H-H} = 6.9 Hz, 6H, CH_3), 1.11 (dd, J_{P-H} = 12.7 Hz, J_{H-H} = 7.0 Hz, 6H, CH_3), 1.07 (dd, J_{P-H} = 17.1 Hz, J_{H-H} = 7.3 Hz, 6H, CH_3). Anal. Calcd: C, 51.88; H, 8.11. Found: C, 52.18; H, 8.35.

Reaction of 1 with C_6H_5Cl under Basic Conditions. 1 (17 mg) dissolved in 1 mL of dioxane was added to a solution of 92 mg (40 equiv) of PhCl and 82 mg (40 equiv) of triethylamine. The red solution was heated at 95 °C overnight. The resulting crude yellow solution was analyzed by $^{31}P\{^1H\}$ NMR (see text).

Reaction of 1 with PhC≡CPh. Characterization of (dippp)Pd(PhC≡CPh), (dippp)Pd(*cis*-C(Ph))=CHPh)Cl, and (dippp)Pd(C(O)C(Ph)=CH(Ph)). A solution of 14 mg of diphenylacetylene (2 equiv) in 2 mL of acetone was added to 32 mg of 1. The solution was heated in a pressure bottle at 60 °C overnight, upon which the color turned dark yellow and a white precipitate formed. The precipitate was separated out, washed with cold acetone, and dried to yield 14 mg (67% yield) of (dippp)-Pd(PhC≡CPh). IR: ν(C=C) 1832 cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 29.7 (s). ^1H NMR (C_6D_6): δ 7.69 (broad dd, $^3J_{H-H}$ = 7.4 Hz, $^5J_{H-H}$ = 0.8 Hz, 4H, H_{ortho}), 7.21 (t, J = 7.7 Hz, 4H, H_{meta}), 7.01 (tm, $^3J_{H-H}$ = 7.4 Hz, $^5J_{H-H}$ = 0.8 Hz, 2H, H_{para}), 1.83 (apparent octet, J_{P-H} = J_{H-H} = 7.0 Hz, 4H, CH), 1.66 (m, 2H, CH_2), 1.14 (m, 4H, P—CH_2), 1.10 (dd, J_{P-H} = 16.0 Hz, J_{H-H} = 7.1 Hz, 12H, CH_3), 0.94 (dd, J_{P-H} = 14.2 Hz, J_{H-H} = 6.9 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.0 (t, J = 12.2 Hz, C_{ipso}), 128.5 (t, J = 1.7 Hz, C_{ortho}), 127.9 (s, C_{meta}), 124.9 (s, C_{para}), 123.9 (dd, $J_{P-C(trans)}$ = 66.4 Hz, $J_{P-C(cis)}$ = 3.7 Hz, -C≡), 27.2 (apparent dd, J = 6.7 Hz, J = 3.4 Hz, CH), 23.8 (t, J = 6.2 Hz, CH_2), 21.0 (apparent dd, J = 8.2 Hz, J = 4.8 Hz, P—CH_2), 20.0 (apparent quintet, J = 5.2 Hz, CH_3), 18.1 (S, CH_3). Anal. Calcd: C, 62.09; H, 7.91. Found: C, 61.88; H, 7.82.

Two major components were characterized in the mother liquor: (1) (dippp)Pd(*cis*-C(Ph))=CHPh)Cl: $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 14.3 (d, J = 44.3 Hz), 26.9 (d, J = 44.3 Hz); ^1H NMR (acetone-d_6) δ 7.58 (dd, ^3J = 8.0 Hz, ^5J = 1.2 Hz, 2H, H_{ortho} close to Pd), 7.40 (m, 2H, H_{ortho} distant from Pd), 7.08 (t, J = 7.6 Hz, 2H H_{meta} close to Pd), 6.98 (t, J = 7.7 Hz, H_{meta} distant from Pd), 6.90 (m, 2 H, H_{para} distant and close to Pd), 6.56 (dd, $J_{P(trans)-H}$ = 13.5 Hz, $J_{P(cis)-H}$ = 2.3 Hz, 1H, =CH–), 2.56 (bm, 2H, CH), 2.44 (bm, 2H, CH), 2.20 (bm, 2H, CH_2), 1.71 (m, 2H, P—CH_2), 1.58 (m, 2H, P—CH_2), 1.44 (dd, J_{P-H} = 17.9 Hz, J_{H-H} = 7.2 Hz, 6H, CH_3), 1.42 (bm, 6H, CH_3), 1.25 (dd, J_{P-H} = 14.6 Hz, J_{H-H} = 6.9 Hz, 6H, CH_3), 1.22 (bm, 6H, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 164.6 (d, J = 127.1 Hz, Pd—C(Ph)=), 140.4 (dd, $J_{P(trans)-C}$ = 13.0 Hz, $J_{P(cis)-C}$ = 1.8 Hz, 1H, =CH–), 149.0 (d, J = 2.3 Hz, C_{ipso} close to Pd), 151.0 (s, C_{ipso} distant from Pd), other signals are obscured by overlap. (2) (dippp)Pd(C(O)C(Ph)=CH(Ph)): IR ν(CO) 1617 cm^{-1}; $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 9.90 (d, J = 64.2 Hz), 29.4 (d, J = 64.2 Hz); ^1H NMR (acetone-d_6) δ 7.05–7.40 (m, 10H, aromatic protons), 8.44 (s, =CH–), other signals are obscured.

Reaction of 1 with PhC≡CH. Characterization of (dippp)Pd(C(Ph)=CH_2)Cl. A solution of 10 mg of phenylacetylene (2 equiv) in 2 mL of acetone was added to 39 mg of 1. The solution was heated in a pressure bottle overnight at 60 °C. The resulting yellow-orange solution was analyzed by ^{31}P, ^{13}C, and ^1H NMR and by IR. After standing at room temperature for 2 days, a white precipitate was formed. The precipitate was separated out, washed with a little cold acetone, and identified as (dippp)Pd(C(Ph)=CH_2)Cl. IR: 1460, 1593 cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 11.6 (d, J = 43.3 Hz), 28.0 (d, J = 43.3 Hz); ^1H NMR (C_6D_6): δ 8.26 (dm, J = 7.1 Hz, 2H, H_{ortho}), 7.39 (tm, J = 7.7 Hz, 2H, H_{meta}), 7.22 (tm, J = 7.3 Hz, 1H, H_{para}), 6.25 (ddd, $J_{P(trans)-H}$ = 25.6 Hz, $J_{P(cis)-H}$ = 6.3 Hz, $^2J_{H-H}$ = 0.7 Hz, 1H, =CH—H trans to Pd), 5.61 (ddd, $J_{P(trans)-H}$ = 11.5 Hz, $J_{P(cis)-H}$ = 1.4 Hz, $^2J_{H-H}$ = 0.7 Hz, 1H, =CH—H cis to Pd), 2.63 (bm 2H, CH), 2.12 (bm, 2H, CH_2), 1.89 (bm, 2H, CH), 1.57 (dd, J_{P-H} = 16.3 Hz, J_{H-H} = 7.3 Hz, 6H, CH_3), 1.42 (m, 6H, CH_3), 1.10 (m, 2H, P—CH_2), 1.04 (dd, J_{P-H} = 12.7 Hz, J_{H-H} = 7.0 Hz, 6H, CH_3), 0.88 (bm, 8H, P—CH_2 and CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 167.1 (d, J = 122.8 Hz, Pd—C(Ph)=), 149.4 (dd, $J_{P(trans)-C}$ = 5.0 Hz, $J_{P(cis)-C}$ = 2.2 Hz, C_{ipso}), 128.5 (d, J = 3.1 Hz, C_{ortho}), 127.4 (s, C_{meta}), 125.2 (s, C_{para}), 117.9 (d, J = 3.2 Hz, =CH_2), 2.65 (bs, CH), 25.2 (bs, CH), 24.3 (bs, CH), 22.0 (d, J = 6.9 Hz, CH_2), 21.5 (bs, CH_3), 20.7 (d, J = 5.2 Hz, CH_3), 18.3 (bs, CH_3), 17.8 (dd, J = 22.8 Hz, J = 12.0 Hz, P—CH_2), 16.7 (dd, J = 9.7 Hz, J = 2.0 Hz, P—CH_2). Anal. Calcd: C, 52.98; H, 7.93. Found: C, 53.20; H, 8.09.

Reaction of 1 with Norbornene. A solution of 70 mg of norbornene (20 equiv) in 2 mL of acetone was added to 31 mg of 1, and the resulting solution was heated at 60 °C for 7 days in a pressure bottle, while the reaction was monitored by $^{31}P\{^1H\}$ NMR.

D Transfer from Acetone-d_6 to other Substrates Catalyzed by 1-d_1. In a typical experiment, ca. 20 equiv of a substrate was added to a solution of 25 mg of 1 or 1-d_1 in 0.5 mL of acetone-d_6. The solution as heated in a pressure bottle at 60 °C for a number of days, while the reaction was monitored by $^{31}P\{^1H\}$, D, and ^1H NMR.

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