Synthesis, Characterization, and Reactivity of [((^{i}Pr)$_2$P(CH$_2$)$_3$P(^{i}Pr)$_2$)(PCy$_3$)PdH][OR]

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The preparation of (DIPPP)Pd(PR$_3$) and [(DIPPP)(PR$_3$)PdH][OR′] (DIPPP = bis(1,3-diisopropylphosphino)propane; R = Cy, Et; R′ = Ar, CF$_3$SO$_2$) is reported. (DIPPP)Pd(PCy$_3$) and [(DIPPP)(PCy$_3$)PdH][CF$_3$SO$_3$] have been structurally characterized. (DIPPP)Pd(PR$_3$) complexes catalyze the reaction of ethylene with carbon monoxide and phenols to give aryl propionates. In situ ^{31}P NMR experiments have shown that the resting state of the catalyst in these transformations is the binuclear species [{(DIPPP)Pd}$_2$(μ-H)(μ-CO)][OPh].

Introduction

Protonation of a transition-metal center to produce a transition-metal hydride is widely recognized as being a crucial step in the functionalization of olefins.[1] A large number of cationic palladium hydrides have been reported in the literature,[2] but their role in catalytic transformations involving olefins still remains unclear. Among all the metals described in the literature, palladium catalyzes a wide variety of reactions, including the hydroformylation and carbonylation of olefins and the carbonylation of acetylenes to methyl methacrylate.[3] Despite the fact that we can find a selection of well-characterized palladium hydrides such as *trans*-Pd(PCy$_3$)$_2$(H)(OPh),[4a] [(PEt$_3$)$_3$Pd(H)][BPh$_4$],[4b] and [(PPh$_3$)$_2$Pd(H)(CO)Pd(PPh$_3$)$_2$][CF$_3$CO$_2$],[4c] their behavior under conditions relevant to catalysis is still poorly understood.[4d]

In this contribution, we will describe a set of isostructural cationic complexes capable of catalyzing the transformation of ethylene into aryl propionate by reaction of the alkene, CO, and the appropriate phenol. Our strategy was to prepare a nucleophilic palladium center by attaching electron-rich phosphines such as DIPPP (bis(l,3-diisopropylphosphino)propane) and auxiliary ligands such as PCy$_3$ and PEt$_3$. By making the Pd center more nucleophilic, we in effect protonated the metal with a moderately weak acid such as phenol or even an aliphatic alcohol. These cationic Pd hydride complexes would then be able to catalyze the synthesis of, for example, aryl propionates from ethylene, carbon monoxide, and phenol. There is some precedent in the literature for the protonation of Pd(0) complexes with alcohols and phenols. Milstein observed the formation of [(DIPPP)PdH(η^1-DIPPP)][OMe][5] when heating (DIPPP)$_2$Pd with MeOH, and Leoni reported *trans*-[Pd(PCy$_3$)$_2$(H)(OPh)]·PhOH,[4a] which was obtained by reaction of Pd(PCy$_3$)$_2$ with phenol. However, their reactivities under catalytic conditions have not been reported.

Experimental Section

General Comments. All manipulations and preparations were carried out inside a nitrogen-filled drybox. Dry solvents were purchased from Aldrich and degassed before use. Pd(PCy$_3$)$_2$,[6] Pd(PEt$_3$)$_3$,[4b] and DIPPP[7] were prepared as described in the literature. The alcohols and phenols were purchased from Aldrich and used without further purification. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on GE 300 and Omega 500 MHz spectrometers. Chemical shift values are reported in ppm relative to TMS for ^{1}H and 85% H$_3$PO$_4$ for ^{31}P. In situ, high-pressure NMR experiments were performed in a 10 mm sapphire tube.

Synthesis of (DIPPP)Pd(PR$_3$) (1a, R = Cy; 1b, R = Et). One molar equivalent of DIPPP (1.1 g, 4 mmol) was added to a colorless solution of Pd(PCy$_3$)$_2$ (2.64 g, 4 mmol) in 60 mL of THF. After 3 h of stirring, the resulting yellow solution was evaporated and the orange, oily residue was extracted with toluene (20 mL). The toluene solution was mixed with acetonitrile, and the mixture was cooled at −35 °C overnight. Orange-yellow crystals of complex **1a**, along with a small amount of PCy$_3$, were collected upon filtration. The impurity

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Table 1. $^{31}P\{^1H\}$ and ^1H NMR Data for Complexes 5a−e and 6a−e[a]

	R	R′	δ_A	δ_M	δ_X	$^2J_{AX}$	$^2J_{AM}$	$^2J_{MX}$	δ(Pd−H)	$^2J_{H-P_{trans}}$	$^2J_{H-P_{cis}}$
5a	Cy	*p*-CNC_6H_4	41.9	35.6	13.8	309	23	41	−7.70	172	17; 7
5b	Cy	C_6H_5	40.9	36.5	13.6	308	24	40	−7.79	171	17; 7
5c	Cy	CF_3CH_2	41.6	35.7	13.9	310	24	40	−7.81	172	18; 7
5d	Cy	FCH_2CH_2	41.8	35.8	14.0	309	23	40	−7.60 (br)	nr	nr
5e	Cy	CH_3	42.7	36.8	15.1	308	24	42	−7.65 (br)	nr	nr
6a	Et	*p*-CNC_6H_4	12.5	12.0	32.2	321	27	42	−7.13	173	16; 3
6b	Et	C_6H_5	12.3	11.9	32.5	320	28	41	−7.10	177	15; 2.5
6c	Et	CF_3CH_2	12.3	12.0	32.3	320	28	41	−7.03	178	15; nr
6d	Et	FCH_2CH_2	12.6	12.2	32.6	321	27	42	−6.9 (br)	nr	nr
6e	Et	CH_3	12.6	12.3	32.8	321	27	41	−6.8 (br)	nr	nr

[a] δ values are given in ppm and *J* values in Hz.

was removed by sublimation, under dynamic vacuum at 90 °C. The overall process afforded the complex (DIPPP)Pd(PCy_3) in 80% yield. Anal. Calcd for $C_{33}H_{67}P_3Pd$: C, 59.7; H, 10.2. Found C, 59.7; H, 10.2.

The triethylphosphine derivative **1b** was prepared by direct reaction of Pd(PEt_3)$_3$ with 1 molar equiv of DIPPP in toluene. Yellow crystals of (DIPPP)Pd(PEt_3) were obtained upon crystallization from an acetonitrile solution in 85% yield. Anal. Calcd for $C_{21}H_{49}P_3Pd$: C, 50.4; H, 9.8. Found C, 50.7; H, 10.1.

1a: $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) AX_2 spin system, δ_A 47.5 (PCy_3), δ_X 19.8 ($^iPr_2P(CH_2)_3P^iPr_2$), $^2J_{AX}$ = 81 Hz; $^1H\{^{31}P\}$ NMR (toluene-d_8, 499.9 MHz) δ 1.08 (d, *J* = 7 Hz, 12H), 1.24 (d, *J* = 7 Hz, 12H), 1.30 (m), 1.38 (m), 1.58 (m), 1.70 (m), 1.82 (m), 2.13 (m); $^{13}C\{^1H,^{31}P\}$ NMR (toluene-d_8, 125.7 MHz) δ 25 (CH_2), 31.6 (CH_2), 20.3 (CH_3), 18.3 (CH_3), 28 (CH), 36.9 (CH), 31.7 (CH_2), 28.4 (CH_2), 27.3 (CH_2). **1b**: $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) AX_2 spin system, δ_A 19.0 (PEt_3), δ_X 24.0 ($^iPr_2P(CH_2)_3P^iPr_2$), $^2J_{AX}$ = 92 Hz; $^1H\{^{31}P\}$ NMR (toluene-d_8, 499.9 MHz) δ 1.04 (d, *J* = 7 Hz, 12H), 1.14 (d, *J* = 7 Hz, 12H), 1.60 (b, 9H), 1.36 (m, 4H), 1.50 (b, 6H), 1.69 (d, *J* = 7 Hz, 4H), 1.82 (m, 2H); $^{13}C\{^1H,^{31}P\}$ NMR (toluene-d_8, 125.7 MHz): δ 28.1 (CH), 25.5 (CH_2), 25.1 (CH_2), 24.5 (CH_2), 20.4 (CH_3), 19.2 (CH_3), 10.6 (CH_3).

In Situ Generation of (DIPPP)Pd(CO)$_n$ (*n* = 1, 2) and (DIPPP)Pd(C_2H_4). (DIPPP)Pd(CO)$_2$ (2). A toluene solution of complex **1a** (40 mg, 0.06 mmol) was transferred into a NMR tube and pressurized with 40 psi of CO. The initial clear yellow solution became colorless within a few seconds. IR (toluene): 2002, 1961 cm^{-1} (ν_{CO}). $^{31}P\{^1H\}$ NMR (toluene-d_8, 121 MHz): 29.9 ppm. $^{13}C\{^1H,^{31}P\}$ NMR (toluene-d_8, 125.7 MHz): δ 26.4 (CH), 23.7 (CH_2), 22.6 (CH_2), 18.9 (CH_3), 17.8 (CH_3). $^1H\{^{31}P\}$ NMR (toluene-d_8, 499.9 MHz): 1.52 (sept, 7 Hz, 4H), 1.45 (m, 2H), 1.02 (d, 7 Hz, 12H), 0.99 (m, 4H), 0.92 (d, 7.0 Hz, 12H).

(DIPPP)Pd(CO) (3). A solution of complex **2**, generated as described above, was exposed to a nitrogen atmosphere for 3 min. The clear solution turned yellow-orange, and the IR and NMR spectra were recorded immediately. IR (toluene): 1953 cm^{-1} (ν_{CO}). $^{31}P\{^1H\}$ NMR (toluene-d_8, 499.9 MHz): 23.7 ppm. When ^{13}CO was used, ν^{13}_{CO} 1924 cm^{-1} was measured and a doublet was observed in the $^{31}P\{^1H\}$ NMR ($^2J_{PC}$ = 32 Hz).

(DIPPP)Pd(C_2H_4) (4). A toluene-d_8 solution of complex **1a** (40 mg, 0.06 mmol) was transferred into a NMR tube and pressurized with 40 psi of ethylene. $^{31}P\{^1H\}$ NMR (toluene-d_8, 121 MHz): 33.3 ppm.

Reactions of Complexes 1a and 1b with Alcohols. In Situ Generation of the Complexes [(DIPPP)PdH(PCy_3)][OR] (5a−e) and [(DIPPP)PdH(PEt_3)][OR] (6a−e). Complex **1a** (20 mg, 0.03 mmol) was dissolved in toluene-d_8 (0.5 mL), and 5 molar equiv of *p*-cyanophenol was added to the solution. The initial yellow color became colorless instantaneously. The NMR data displayed in Table 1 are in agreement with the formula [(DIPPP)PdH(PCy_3)][OR] (**5a**, R = *p*-NCC_6H_{40}). Attempts to isolate the new complex failed because the reaction reverses in the absence of excess alcohol.

The reactions of **1a** with phenol and 2,2,2-trifluoroethanol were carried out in a similar manner, but with the addition of 20 and 100 equiv of each alcohol, respectively. In the case of fluoroethanol and methanol, complex **1a** was dissolved in the neat alcohols. Similar reactions were carried out with the same substrates and complex **1b.** Selected $^{31}P\{^1H\}$ NMR data are shown in Table 1.

Synthesis of [(DIPPP)PdH(PCy_3)][OTf] (7). A solution of **1a** (0.33 g, 0.5 mmol) in 30 mL of diethyl ether was treated with 1 equiv of triflic acid (50 μL, 0.57 mmol). A white solid precipitated almost instantaneously. The mixture was stirred for 3 h before the precipitate was separated by filtration. The solid was dissolved in a 50:50 mixture of toluene and pentane. After 30 min at room temperature, the product separated as an oil. Diethyl ether was added dropwise to redissolve it, and the resulting solution was left overnight at room temperature. Off-white crystals suitable for X-ray diffraction were obtained in 60% yield. Anal. Calcd for $C_{34}H_{68}F_3O_3P_3PdS$: C, 50.2; H, 8.4; S, 3.9, Found C, 50.2; H, 8.2; S, 4.2. Selected spectroscopic data: IR (Nujol mull) 1951 cm^{-1} (ν_{Pd-H}); $^{31}P\{^1H\}$ NMR (toluene-d_8, 121 MHz) AMX spin system, δ_A 41.4, δ_X 14.0, δ_M 36.7, $^2J_{AX}$ = 308 Hz, $^2J_{MX}$ = 40 Hz, $^2J_{AM}$ = 24 Hz; ^1H NMR (toluene-d_8, 300 MHz) δ −7.6 ppm (ddd, Pd−H, $^2J_{H-P(trans)}$ = 171 Hz, $^2J_{H-P(cis)}$ = 16 and 7 Hz); $^{13}C\{^1H,^{31}P\}$ NMR (toluene-d_8, 125.7 MHz) δ 37.6 (CH), 31.0 (CH_2), 28.4 (CH), 27.7 (CH_2), 27.3 (CH), 26.6 (CH_2), 22.6 (CH_2), 21.2 (CH_3), 19.1 (CH_3), 18.9 (CH_2), 18.2 (CH_2), 17.7 (CH_3), 16.9 (CH_2).

Synthesis of [{(DIPPP)Pd]$_2$(μ-H)(μ-CO)}][OPh] (8). Complex [(DIPPP)PdH(PCy_3)][OPh] (**5b**) was generated as described above, and the solution was pressurized with 40 psi of CO. After 48 h, a red solution was obtained. NMR studies revealed quantitative conversion into complex **8**. IR (toluene): 1793 cm^{-1} (ν_{CO}). $^{31}P\{^1H\}$ NMR (toluene-d_8, 121 MHz): 21.6 ppm. When **8** was generated with ^{13}CO, this resonance splits into a doublet with $^2J_{PC}$ = 32 Hz. ^1H NMR (toluene-d_8, 300 MHz): −5.50 ppm (quintet, 1 H, Pd−H−Pd, $^2J_{HP}$ = 40 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75 MHz): 250.3 (quintet, $^2J_{PC}$ = 32 Hz).

Catalytic Isomerization of 1-Pentene. The isomerization of 1-pentene to 2- pentene was followed by ^1H NMR spectroscopy. A solution containing 20 mg of **1a**, 42 mg of 1-pentene, and 60 mg of CF_3CH_2OH in 600 μL of benzene-d_6 was loaded into a 5 mm NMR tube. After the sample was heated to 80 °C in the NMR probe, the isomerization rate was determined by integrating the intensities of the olefinic protons of 1-pentene and 2-pentene, respectively. To determine the effect of phosphine concentration on the rate of olefin isomerization, the experiment was repeated in the presence of 10 mg of PCy_3.

Catalytic Experiments. *o*-Dichlorobenzene (0.2 g, internal standard), phenol (1.4 g, 14.9 mmol), and complex **1a** (20 mg, 0.03 mmol), **1b** (15 mg, 0.03 mmol), or **7** (24 mg, 0.03 mmol) were dissolved in 60 mL of toluene. The solution was loaded into a 100 mL Hastelloy C autoclave under a nitrogen atmosphere. The autoclave was pressurized with ethylene (300 psi) and CO (600 psi) and then heated at 100 °C for about 2 h. The content of the reactor was analyzed by GC on a HP-5890 chromatograph using a Quadrex 30 m × 320 μm cyanopropyl methyl silicone capillary column. Conversion of phenol into

Table 2. Crystallographic Data for 1a and 7

	1a	7
formula	$C_{33}H_{67}P_3Pd$	$C_{33}H_{68}F_3O_3P_3SPd$
fw	663.22	813.30
cryst syst	noncentrosymmetric	monoclinic
space group	*Cc* (No. 9)	$P2_1/n$
a (Å)	13.174(1)	16.137(1)
b (Å)	16.175(1)	22.431(1)
c (Å)	16.872(1)	11.362(1)
β (deg)	96.233(3)	103.738(1)
V (Å^3)	3574	3995
Z	4	4
D_{calcd} (g cm^{-3})	1.232	1.357
cryst size (mm)	0.06 × 0.11 × 0.85	0.2 × 0.33 × 0.25
μ(Mo Kα) (cm^{-1})	6.63	6.72
2θ range (deg)	2.4−48.9	2.6−48.4
temp (°C)	−41	−54
cryst to plate dist (mm)	83	85
no. of frames	45	46
oscillation range, deg/frame	4.0	4.0
exposure, min/frame	8.0	4.0
no. of rflns collected	9803	19 804
no. of indep rflns	2812	4803
final *R* index	0.039	0.036
goodness of fit on *F*	1.52	1.17
largest Δ/σ	0.31	0.08
data to param ratio	8.16	11.62
largest diff, e Å^{-3}	0.40	0.57

Table 3. Selected Bond Distances (Å) for 1a and 7

1a		7	
Pd(1)−P(1)	2.300(1)	Pd(1)−P(1)	2.2925(10)
Pd(1)−P(2)	2.307(2)	Pd(1)−P(2)	2.3721(9)
Pd(1)−P(3)	2.313(2)	Pd(1)−P(3)	2.340(1)
P(1)−C(1)	1.856(8)	Pd(1)−H(1)	1.532(39)
P(1)−C(11)	1.869(8)	P(1)−C(1)	1.823(4)
P(1)−C(21)	1.863(8)	P(1)−C(11)	1.846(4)
P(2)−C(3)	1.865(7)	P(1)−C(21)	1.833(3)
P(2)−C(31)	1.894(9)	P(2)−C(3)	1.825(4)
P(2)−C(41)	1.849(8)	P(2)−C(31)	1.848(4)
P(3)−C(51)	1.884(6)	P(2)−C(41)	1.858(4)
P(3)−C(61)	1.877(7)	P(3)−C(51)	1.855(4)
P(3)−C(71)	1.883(6)	P(3)−C(61)	1.851(3)
		P(3)−C(71)	1.850(3)

phenyl propionate was 70% for complex **1a**, 72% for complex **1b**, and 100% for complex **7**.

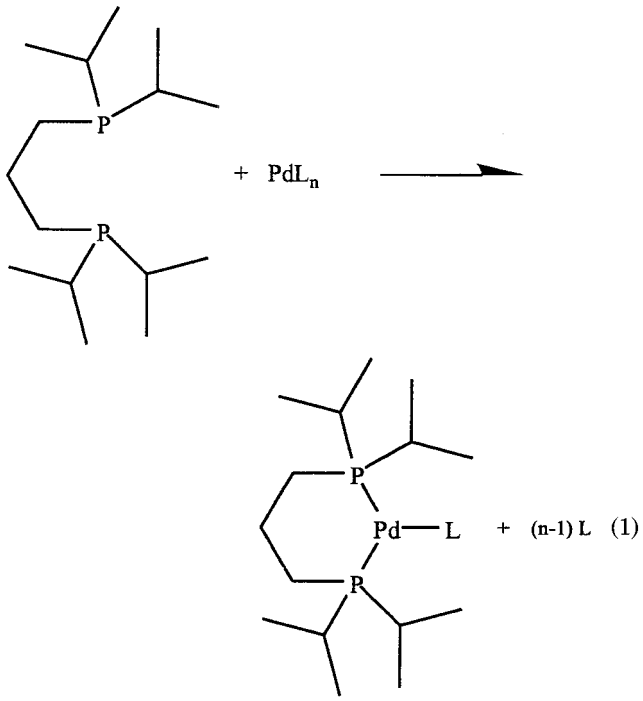
Crystal Structure Determination. The X-ray crystallographic analyses were based on the data collected on a Rigaku RU300 R-AXIS IIc image plate area detector using Mo Kα radiation with a graphite monochromator. Tables 2 and 3 display the main crystallographic data, bond distances, and bond angles for the molecules of complexes **1a** and **7**.

X-ray Analysis of 1a. At a crystal to plate distance of 83 mm, a total of 45 frames were collected with an oscillation range of 4.0°/frame. A total of 9803 data were collected from 2.4° < 2θ < 48.9°. After the 3086 duplicates were merged (2.4% *R*(merge)), 2812 unique reflections with $I > 3.0\sigma(I)$ remained for the analysis. The structure was solved by automated Patterson analysis (PHASE) and consists of one molecule in a general position. The hydrogen atoms were idealized with a C−H bond length of 0.95 Å but were omitted for the C3 bridging atoms. The acentric space group indicates an optically pure enantiomorph, which was established from an *R* value test (0.0589/0.0597 vs 0.0711/0.0722). Refinement was by full-matrix least squares on *F*; the final refinement cycle included 341 parameters, with a data/parameter ratio of 8.16, and resulted in $R = 0.039$ and $R_w = 0.039$ with an error of fit of 1.52. The maximum shift/error was 0.31, and the largest residual density on the final difference map was 0.40 e/Å^3, near Pd.

X-ray Analysis of 7. At a crystal-to-plate distance of 85 mm, a total of 46 frames were collected with an oscillation range of 4.0°/frame. A total of 19 408 data were collected from 2.6° < 2θ < 48.4°. After the 5648 duplicates were merged (3.0% *R*(merge)), 4803 unique reflections with $I > 3.0\sigma(I)$ remained for the analysis. The structure was solved by direct methods (MULTAN). The asymmetric unit consists of one ion pair in a general position. The hydrogen atoms were idealized with a C−H bond length of 0.95 Å; the Pd−H distance was set to 1.6 Å and refined. Refinement was done by full-matrix least squares on F^2. All non-hydrogen atoms were successfully refined anisotropically, and all hydrogen atoms were refined isotropically. The final refinement cycle included 410 parameters, with a data/parameter ratio of 11.62, and resulted in $R = 0.036$ and $R_w = 0.036$ with an error of fit of 1.17. The maximum shift/error was 0.08, and the largest residual density on the on the final difference map was 0.57 e/Å^3, suggesting a second orientation of the triflate.

Results and Discussion

Palladium(0) Complexes. The reaction of Pd(PEt$_3$)$_3$ and Pd(PCy$_3$)$_2$ with DIPPP provides a convenient entry into the (DIPPP)PdPR$_3$ (**1a**, R = Cy; **1b**, R = Et) system (eq 1). Both complexes are easily characterized on the



1a , L= PCy$_3$, n=2
1b , L= PEt$_3$, n=3

basis of their ^{31}P NMR spectra, where they both exhibit an AX$_2$ pattern. For example, the value of J_{AX} in complex **1a** (81 Hz) compares well to the value reported for (DIPPP)Pd(P^{i}Pr$_2$^{n}Bu) (84 Hz).[5] Complex **1a** was further characterized by X-ray diffraction methods. The molecular structure of **1a** in the solid state (Figure 1) shows the expected trigonal-planar coordination around the metal center formed by the three phosphorus atoms. Whereas the atomic distances appear to be within the normal range for this type of compound (Table 3), the P(1)−Pd−P(2) (101.95(6)°) bite angle is rather short when compared with other molecules containing the

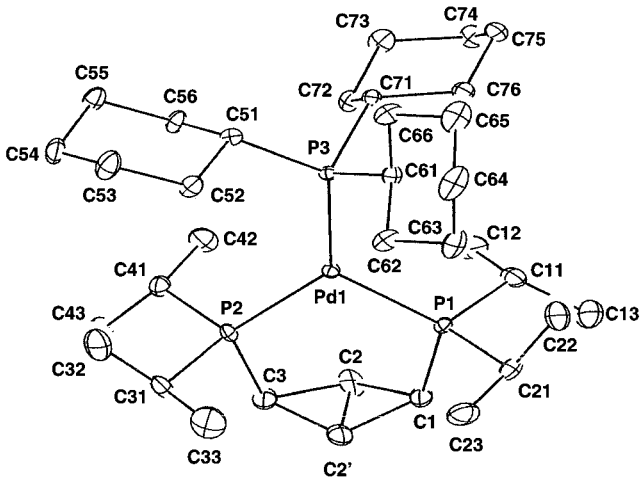
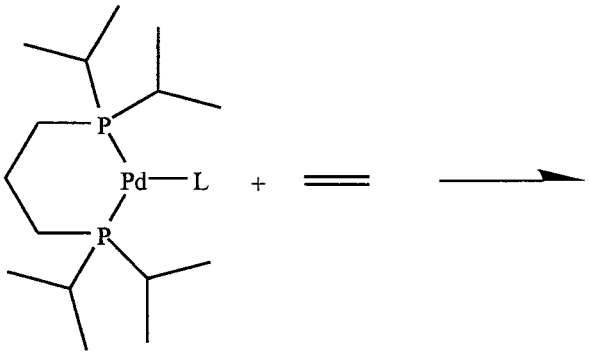


Figure 1. View of the molecular structure of complex **1a**, showing propane bridge disorder.

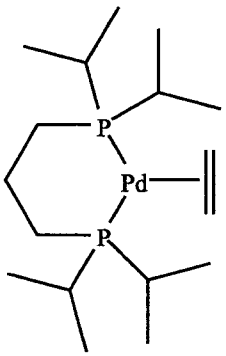
same fragment. For example, the dimeric complex $[(DIPPP)Pd]_2(\mu\text{-H})(\mu\text{-CO})][Cl]$[8] presents a 126.1(2)° value for that angle. This could be explained in terms of the steric hindrance between the cyclohexyl groups in PCy_3 and the isopropyl fragments on the DIPPP ligand. Surprisingly, the Pd is nearly planar with hydrogen atoms of the isopropyl groups yielding an 180° cone angle.

The complexes **1a** and **1b** instantaneously react with CO to produce $(DIPPP)Pd(CO)_2$ (**2**) ($^{31}P\{^1H\}$ NMR, δ 29.9 ppm; IR (toluene), ν_{CO} 2002, 1961 cm^{-1}). The monocarbonyl complex (DIPPP)Pd(CO) (**3**) ($^{31}P\{^1H\}$ NMR, δ 23.7 ppm; IR (toluene), ν_{CO} 1953 cm^{-1}) was observed when a solution of complex **3** was briefly purged with nitrogen to remove the carbon monoxide. When the reaction is performed in the presence of ^{13}CO, no coupling of ^{13}C to ^{31}P is observed in the ^{31}P NMR spectra of **3**, even at temperatures as low as −80 °C. Additionally, no resonance could be assigned to the palladium carbonyl moiety in the ^{13}C NMR spectra of **3** at temperatures as low as −80 °C. The lack of coupling and the lack of a discrete resonance in the ^{13}C NMR spectra are probably due to the fast exchange of carbon monoxide bonded to palladium in complex **3** and free CO in solution. Milstein[5,8] has previously suggested the existence of **2** and **3**. The related complex (BDPP)Pd-$(CO)_2$ (BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) has been proposed by Elsevier.[9] (D^tBPE)$Pd(CO)_2$ (D^tBPE = bis(di-*tert*-butylphosphino)ethane) has been structurally characterized by Porschke.[10] To have an independent confirmation of the assignments for complexes **2** and **3**, we prepared samples of both complexes by reacting $\{(DIPPP)Pd\}_2(\mu\text{-H})_2\}$[11] with CO. The spectroscopic features previously described for **2** and **3** are identical with those obtained when prepared by this independent reaction. Attempts to isolate **2** or **3** failed due to the loss of carbon monoxide.

We have also investigated the interaction of **1a** and **1b** with ethylene (eq 2), both leading to the formation of the same complex, $(DIPPP)Pd(C_2H_4)$ (**4**). This complex



1a , L= PCy_3, n=2
1b , L= PEt_3, n=3



+ L (2)

has been described previously by Fryzuk.[11] The exchange between free ethylene in solution and coordinated ethylene is responsible for the absence of coupling between the hydrogen nuclei of ethylene and the phosphorus of the DIPPP ligand. No coupling is observed, even at −80 °C. In the presence of α-olefins, no olefin complex was detected. Ethylene is cleanly displaced by carbon monoxide, giving **2** and **3** (Scheme 1).

Palladium(II) Complexes. Reaction of **1a** and **1b** with alcohols and phenols cleanly generates complexes of the general composition $[(DIPPP)PdH(PR_3)][OR]$ (**5**, **6**). Attempts to isolate these complexes proved to be unsuccessful, due to the decomposition to $(DIPPP)Pd(PR_3)$ and alcohol. Despite this, all the complexes were fully characterized by ^1H and ^{31}P NMR (Table 1). Thus, the ^1H NMR spectrum of $[(DIPPP)PdH(PCy_3)][OPh]$ displays a resonance centered at −7.8 ppm (ddd), assigned to the hydride group (Figure 2). The splitting of the hydride resonance occurs due to coupling with a phosphorus atom of the DIPPP ligand occupying a trans position relative to the hydride (J_{H-P} = 171 Hz) and both the *cis* phosphorus nuclei of the PCy_3 and DIPPP

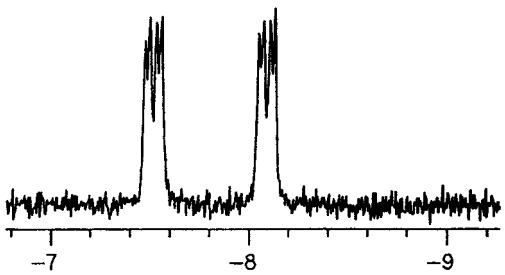
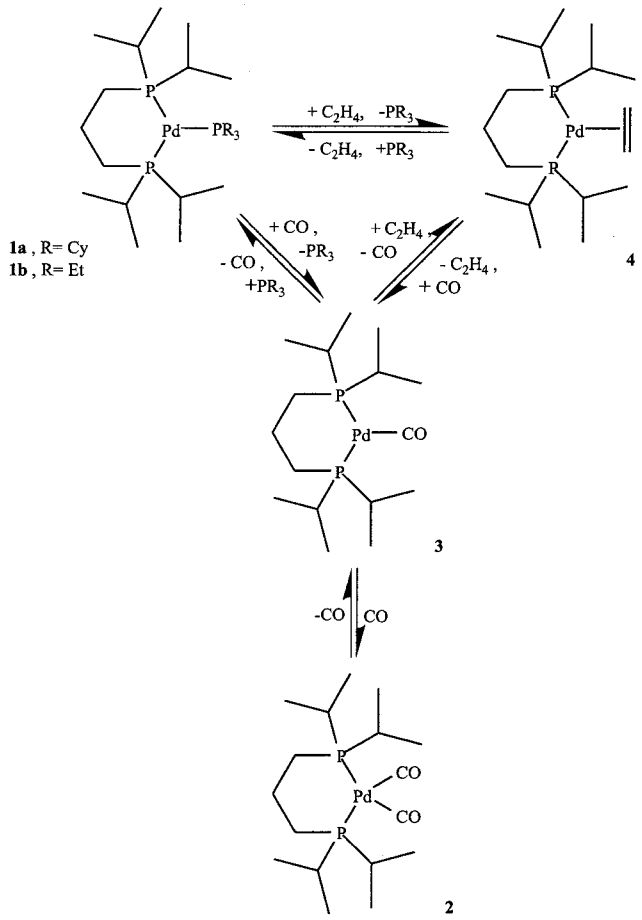


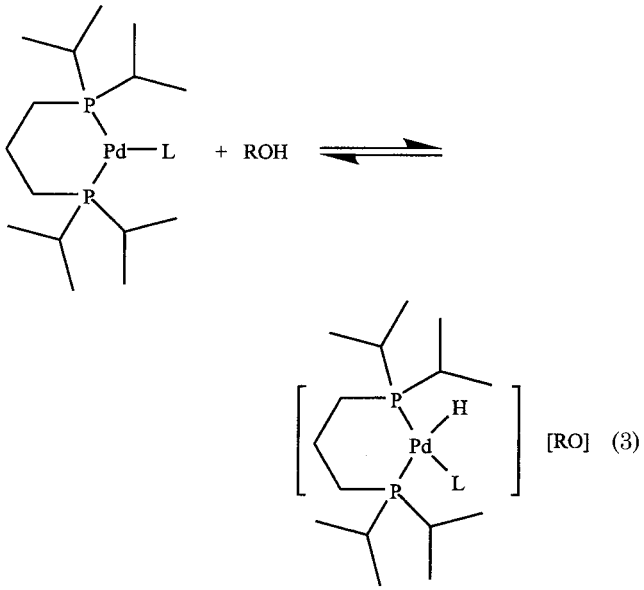
Figure 2. ^1H NMR upfield hydride resonance for the complex $[(DIPPP)PdH(PCy_3)]OPh$.

(8) Portnoy, M.; Frolow, F.; Milstein, D. *Organometdllics* **1991**, *10*, 3960.
(9) Tóth, I.; Elsevier, C. J. *Organometallics* **1994**, *13*, 2118.
(10) Trebbe, R.; Goddard, R.; Rufinska, A.; Seevogel, K.; Porschke, K. *Organometallics* **1999**, *18*, 2466.
(11) Fryzuk, M.; Lloyd, B.; Clentsmith, G.; Rettig, S. *J. Am. Chem. Soc.* **1994**, *116*, 3804.

Scheme 1



ligand (J_{H-P} = 17 and 7 Hz). Similar patterns have been reported for the related complexes [(DIPPP)$_2$PdH][Cl][5] and [PdH(PPh$_3$)$_3$][BPh$_4$].[4b] In all the cases studied, metal protonation is a reversible process, indicated by detection of both the Pd(0) and Pd(II) compounds in the reaction mixture (eq 3).



(3)

The equilibrium constant for the reaction depicted in eq 3 depends on the value of the pK_a of the alcohol or phenol. For example, only 5 equiv of *p*-cyanophenol (pK_a = 8) is required to convert >99% of (DIPPP)Pd(PCy$_3$) (**1a**) into [(DIPPP)PdH(PCy$_3$)][OR]. In contrast, MeOH (pK_a = 16.0) must be the solvent to observe the formation of the cationic Pd hydride.

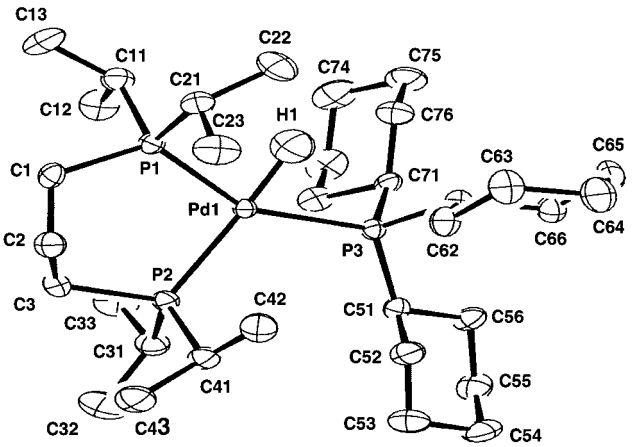


Figure 3. Molecular geometry of complex **7** (cation only).

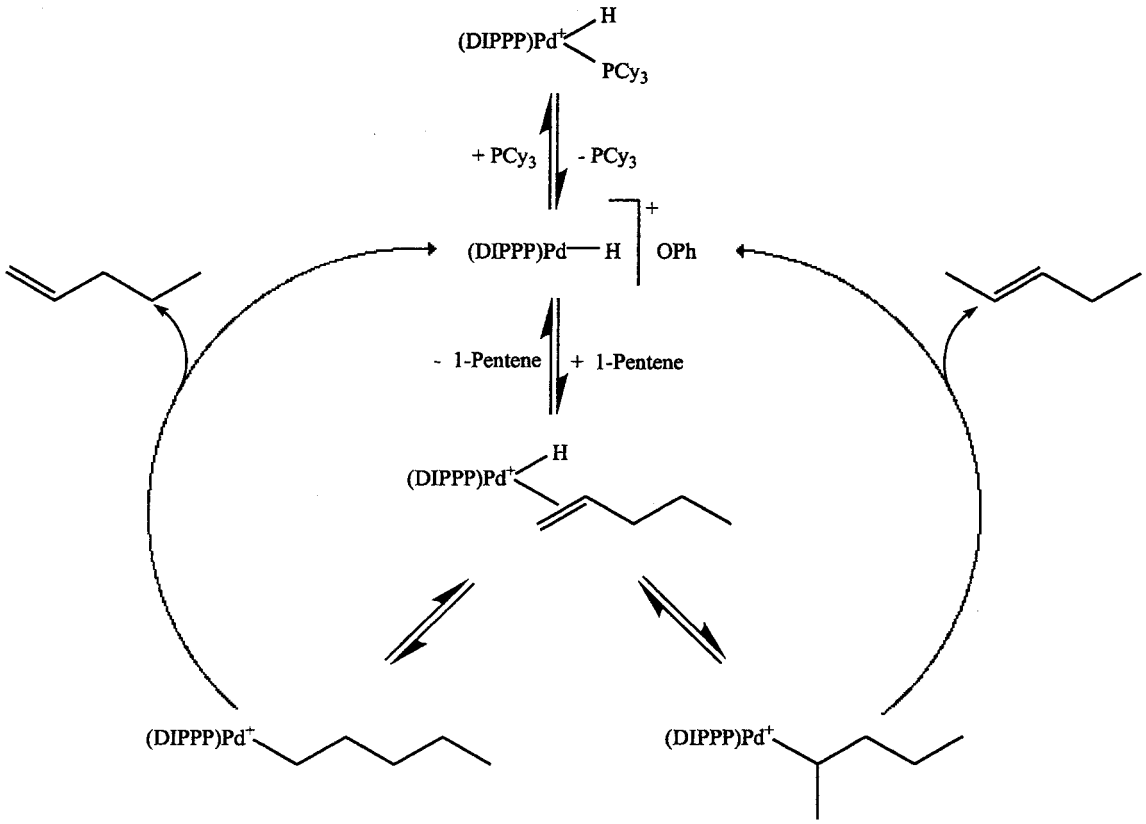
Even though we were not able to isolate any [(DIPPP)PdH(PCy$_3$)][OR] complexes, we have prepared an analogous compound (**7**) by reaction of (DIPPP)Pd(PCy$_3$) and triflic acid. The spectroscopic properties of this complex are completely similar to those of complexes **5** and **6**. The X-ray structure of **7** (Figure 3) reveals the expected square-planar geometry of the complex. The angles around the palladium center show significant deviation from orthogonality (H−Pd−P(1) = 79°, P(1)−Pd−P(2) = 97.69°, P(2)−Pd−P(3) = 110°). The refined hydrogen atom is located in the PdP$_3$ plane, and the Pd−H bond distance is 1.532(39) Å. This value compares well with those reported for other structurally characterized palladium hydrides: 1.51(1) and 1.57(2) Å for *trans*-[Pd(PCy$_3$)$_2$(H)(H$_2$O)]BF$_4$[12] and [Pd(PCy$_3$)$_2$(H)(OPh)]·PhOH,[4a] respectively. The P−Pd−P angle encompassing the hydride is highly acute (152°), suggesting a large van der Waals interaction between the isopropyl groups of the ligand and the cyclohexyl groups of the PCy$_3$.

The reaction of the cationic complexes **5** and **6** with olefins seems to be negligible, since no new resonances are shown in the NMR spectra of the reaction mixture. However, upon heating at 80 °C, it was possible to observe the slow isomerization of 1-pentene into 2-pentene, which suggests a very facile olefin insertion/β-hydrogen elimination mechanism (Scheme 2). The presence of added phosphine partially inhibits this isomerization process (Figure 4), indicating that phosphine dissociation must occur before the rate-determining step.

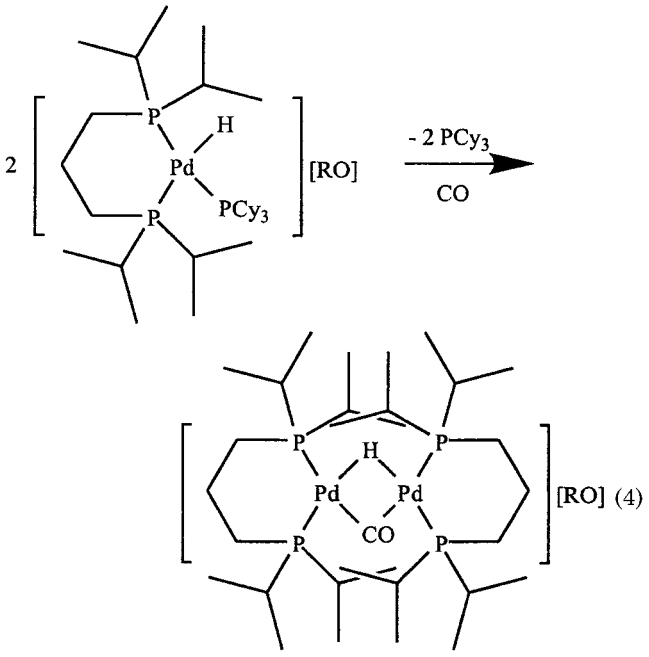
The reaction of [(DIPPP)PdH(PCy$_3$)][OPh] with CO gives a mixture of (DIPPP)Pd(CO)$_2$ and [(DIPPP)Pd(μ-H)(μ-CO)Pd(DIPPP)][OPh] (**8**). The main feature in ^{1}H NMR of complex **8** at room temperature is the hydride resonance, split as a quintet at −5.5 ppm with a J_{H-P} value of 40 Hz. The coupling pattern is attributed to the presence of four equivalent phosphorus atoms. Fast exchange is also observed for the carbonyl resonance of [(DIPPP)Pd(μ-H)(μ-^{13}CO)Pd(DIPPP)][OPh] at 250.3 ppm. The resonance of the carbonyl is split into a quintet due to coupling with four equivalent phosphorus atoms with

(12) Leoni, P.; Sommovigo, M.; Pasquali, M.; Midollini, S.; Braga, D.; Sabatino, P. *Organometallics* **1991**, *10*, 1038.

Scheme 2



a J_{C-P} value of 32 Hz. Variable-temperature studies by ^1H and ^{13}C NMR spectroscopy revealed that the exchange, which accounts for the equivalence of all four phosphorus atoms, cannot be frozen at temperatures as low as −80 °C. The mechanism of formation of **8** could first involve dissociation of PhOH from [(DIPPP)PdH(PCy$_3$)][OPh], followed by displacement of PCy$_3$ by CO to give (DIPPP)Pd(CO)$_2$ and finally protonation by PhOH to give the binuclear compound **8** (eq 4). Even



(4)

though the unsaturated fragment (DIPPP)Pd cannot be detected spectroscopically, a mechanism suggesting its protonation and direct reaction with either **2** or **3** to give complex **8** cannot be ruled out. [(DIPPP)Pd(μ-H)(μ-CO)Pd(DIPPP)][OPh] is totally analogous to the PPh$_3$ derivative [(PPh$_3$)$_2$Pd(μ-H)(μ-CO)Pd(PPh$_3$)$_2$][O$_2$CCF$_3$] previously reported by Zudin.[4c] Milstein[5] and Elsevier[9] later reported analogous complexes with the ligands DIPPP and BDPP, respectively.

The presence of a binuclear palladium hydride of structure **8** has been previously reported in the carbo-

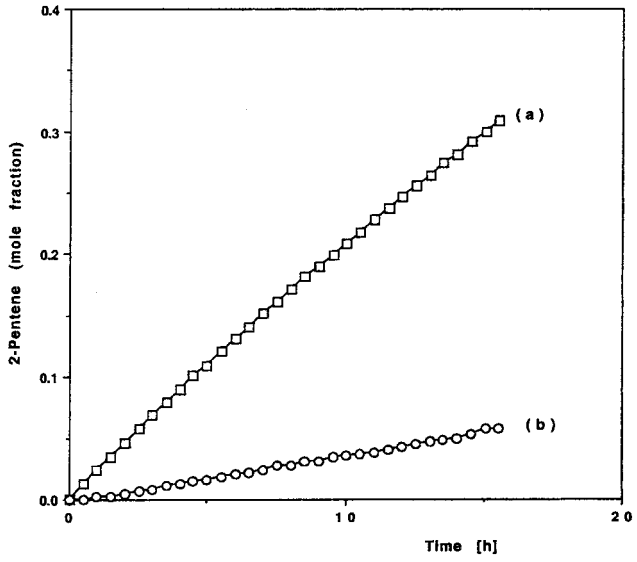


Figure 4. Kinetic profile for the isomerization of 1-pentene into 2-pentene catalyzed by (DIPPP)Pd(PCy$_3$) (**1a**) and CF$_3$CH$_2$OH at 80 °C in C$_6$D$_6$: (a) in the absence of PCy$_3$; (b) in the presence of PCy$_3$. [**1a**]/[PCy$_3$] = 0.85.

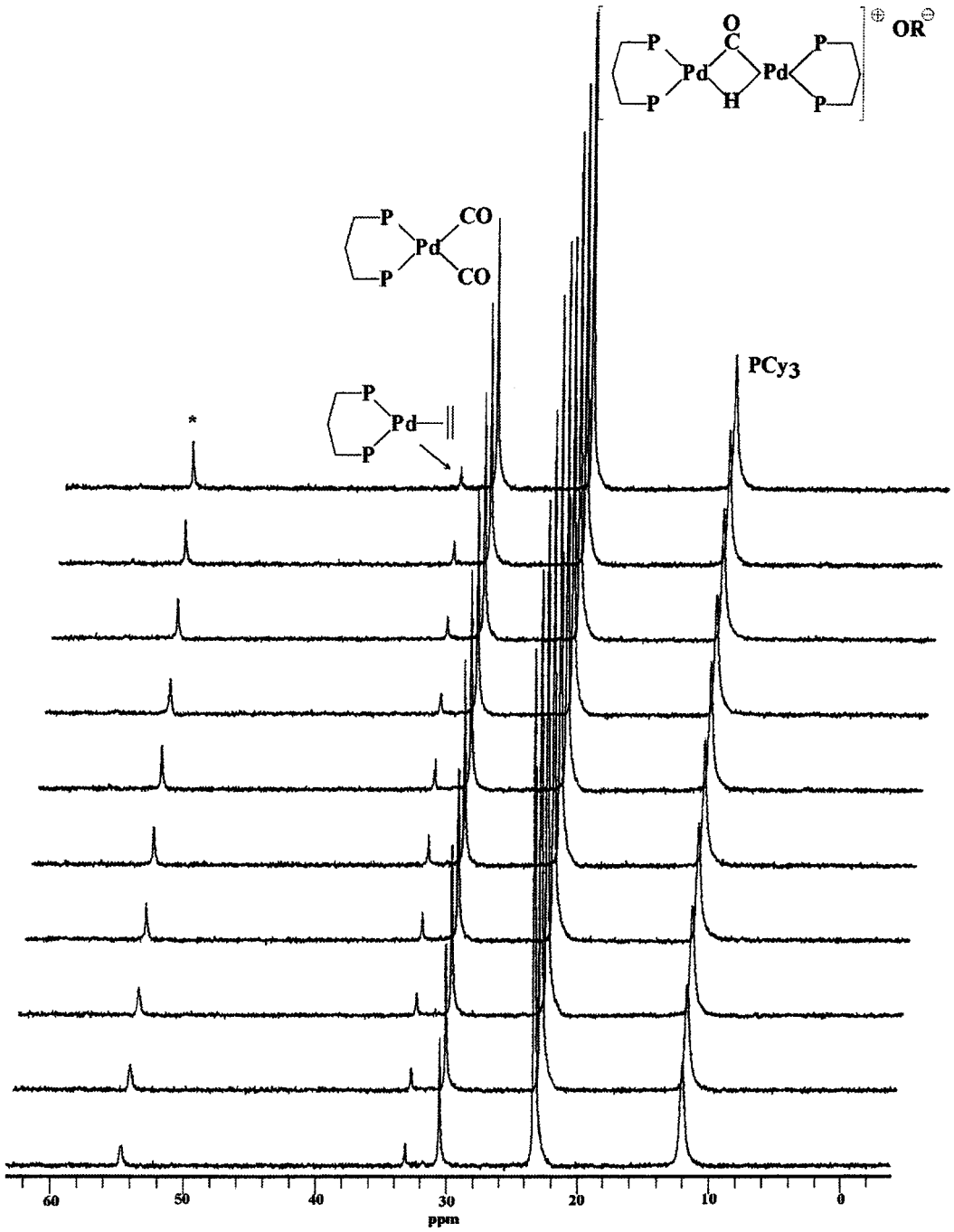


Figure 5. $^{31}P\{^{1}H\}$ NMR monitoring of the catalytic conversion of a mixture of carbon monoxide, ethylene, and phenol into phenyl propionate. The resonance marked with an asterisk has not been identified (elapsed time between spectra 30 min).

nylation of (P−P)PdMeCl to MeCOOMe[13] in the presence of methanol and also in the reaction of (DIPPP)-PdPhCl with methanol.[5] The presence of this bridging hydride in a catalytic transformation has never been proven spectroscopically.

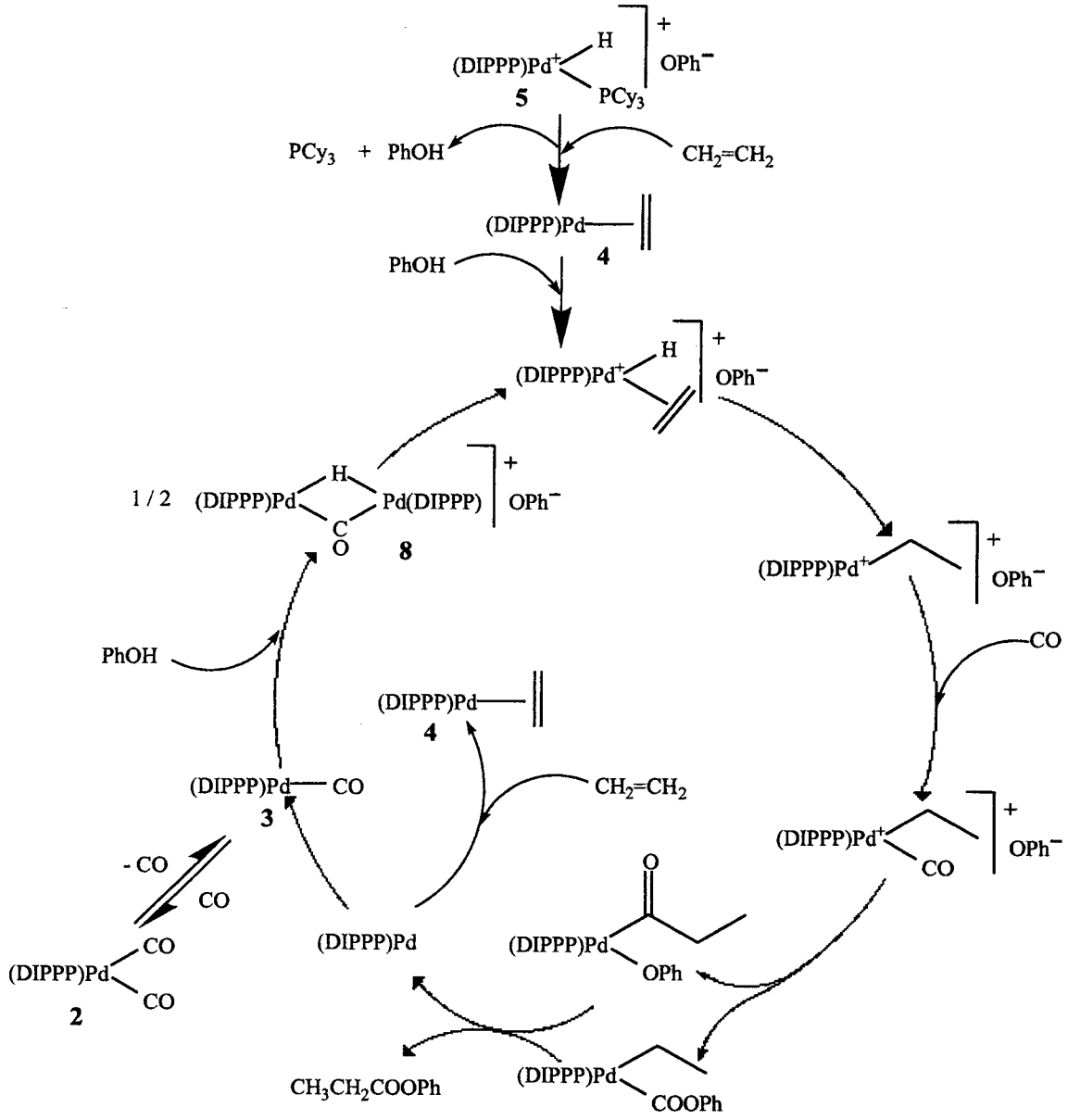
Catalytic Experiments. To establish the participation of **8** in a catalytic transformation, we have studied the carbonylation of ethylene with phenols in the presence of [(DIPPP)PdH(PR_3)][OPh] (R = Cy, Et) as the catalyst (eq 5). We have found that (DIPPP)Pd(PR_3)

$$CH_2{=}CH_2 + CO + ArOH \xrightarrow{\textbf{1a, 1b}} CH_3CH_2COOAr \quad (5)$$

(R = Cy, Et) each catalyze the synthesis of aryl propionates with activities on the order of 10^2 (mol of product)/((mol of catalyst) h) at temperatures around 150 °C. The rate of this transformation was not affected by the nature of PR_3, which is in agreement with the mechanism proposed in Scheme 2: i.e., phosphine dissociation takes place immediately in the presence of CO and ethylene. The rate of the reaction had a direct relation to the nature of the phenol: higher pK_a led to higher turnover frequencies. Methanol and ethanol, neat or in toluene solution, fail to give methyl and ethyl propionates, respectively, when reacted with ethylene in the presence of **1a** and **1b**. The lack of activity can

(13) Tóth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388.

Scheme 3



be attributed to the large pK_a value of methanol and ethanol compared to the pK_a of phenols. The difference in pK_a is probably responsible for the absence of (DIPPP)Pd(L)H^+OR^- complexes when L = ethylene, which we believe necessary to enter the catalytic cycle. In comparison, when L = PEt_3, PCy_3, protonation occurs even with methanol or ethanol.

Using in situ high-pressure NMR techniques, we followed the transformation under conditions identical with those used in our autoclave experiments. We were able to detect, as shown in Figure 5, the complexes (DIPPP)Pd(C_2H_4), (DIPPP)Pd($CO)_2$, and [(DIPPP)Pd(μ-H)(μ-CO)Pd(DIPPP)][OPh] and free PCy_3. The monomeric cationic hydride [(DIPPP)PdH(PR_3)][OPh] was not detected in the reaction mixture. GC analysis of the reaction solution from the high-pressure NMR tube after completion of the experiment confirmed the presence of phenyl propionate.

It is reasonable to assume that the lack of monomeric palladium hydrides, presumed to be the most active component in the catalysis, are due to the much lower acidity of phenols compared with strong acids. However, a similar in situ experiment using [(DIPPP)PdH(PR_3)][OTf] as the catalyst was performed and concluded with results identical with those obtained when [(DIPPP)PdH(PR_3)][OPh] was used as catalyst. In addition, the major species in solution was the binuclear complex **8**. This complex acts as the thermodynamic sink for the palladium complexes involved in the catalytic cycle.

Thus, a possible mechanistic proposal based on the pieces of information described above is depicted in Scheme 3. The cationic hydride **5** would exchange phosphine and olefin to give a transient alkene hydride intermediate. A series of elementary steps would follow: (a) formation of a Pd alkyl complex; (b) CO coordination; (c) formation of an alkyl carboxylate Pd(II) complex or the alternative acyl alkoxy isomer; (d) reductive elimination of the aryl propionate; (e) CO coordination to give complexes **2** and **3**, both equilibrating with **1a**; (f) reaction of **3** with CO and PhOH to provide **8**, the resting state in the catalytic cycle, which further reacts with olefin to start the cycle. We have

not found any evidence to propose a unique intermediate from the alkyl carbonyl intermediate. Both the alkyl carboxylate and the acyl aryloxide find precedent in the literature. Elsevier[13] has proposed the complex (BDPP)-Pd(Me)(COOMe) in the formation of MeCOOMe, whereas Yamamoto has established the existence of acyl aryloxide nickel and palladium intermediates and the corresponding reductive elimination to yield the aryl carboxylates.[14]

Conclusions

The use of basic phosphines such as DIPPP in combination with PCy_3 or PEt_3 makes the palladium metal center very electron rich. Proof of this behavior is the in situ characterization of a variety of isostructural palladium hydrides prepared by simple protonation of (DIPPP)PdPR_3 with alcohols and phenols. The key in this case was the synthesis of monomeric tricoordinated complexes.

It is interesting to note that, in contrast to what one might expect when trying to design a possible active catalyst to functionalize olefins with carbon monoxide, the resting state of the catalyst is far different from the one desired. In the example described in this work, we targeted [(DIPPP)(PR_3)PdH][OR] as the complex most likely to be responsible for the catalytic activity. However, in the presence of CO and ethylene, the only observable monomeric structures were (DIPPP)PdL (L = CO, ethylene). Because of back-bonding between Pd and the olefin, the electronic density at the metal center in complexes such as (DIPPP)Pd(olefin) does not favor the formation of [(DIPPP)(olefin)PdH] [OR] required to enter the catalytic cycle shown in Scheme 3.

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Supporting Information Available: Tables of crystal data and structure refinement parameters, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters and hydrogen coordinates of **1a** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0008833

(14) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.