Synthesis and Reactivity of (PCP) Palladium Hydroxy Carbonyl and Related Complexes toward CO_2 and Phenylacetylene

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{2,6-Bis[(di-*tert*-butylphosphino)methyl]phenyl}palladium hydroxide, PCPPdOH, undergoes a fast insertion of CO_2 to give the bicarbonate complex (PCP)PdO_2COH. It also reacts with CO to give a mononuclear hydroxy carbonyl complex, (PCP)PdCOOH. The Pd−C bond of this is unreactive toward olefins. The complex undergoes a slow conversion to the formate complex, (PCP)PdO_2CH, via a decarboxylation to give the hydride, which undergoes a fast normal insertion of CO_2 to give the formate. The hydride, (PCP)PdH, reacts with phenyl acetylene to give the acetylide complex, (PCP)PdCCPh, in a C−H exchange reaction. This is similarly obtained from the reaction of (PCP)PdMe or (PCP)PdPh with phenyl acetylene.

Introduction

Metallocarboxylic acids, or hydroxy carbonyl compounds, have been proposed as intermediates in a number of reactions such as the methoxy carbonylation of 1-alkynes[1] and the reduction of CO_2 with H_2, as well as in electrochemical reduction[2] and the water gas shift reaction,[3] but reports on their isolation and characterization are relatively few.[4] The reported reactivity of hydroxy carbonyl compounds include decarboxylation reactions to give the corresponding hydride and nucleophilic substitution reactions on the coordinated CO unit.[4h] Mononuclear palladium hydroxy carbonyl compounds have not been isolated, as opposed to their platinum analogues.[4f,h] However, they have been proposed to be involved in the hydroxy carbonylation of aryl halides,[5] and it has also been shown that alkoxy carbonyl compounds can undergo insertion of alkene followed by β-elimination to give unsaturated esters.[6] We have an interest in the carboxylation of hydrocarbons, and one possible way to generate unsaturated carboxylic acids would be insertion of alkene into a palladium hydroxy carbonyl moiety in a similar fashion. Recently, a palladium hydroxy carbonyl compound based on a {2,6-bis[(diisopropylphosphino)methyl]-phenyl} ligand framework was reported.[7] The complex could not be isolated and underwent decarbonylation to give a dinuclear, CO_2-bridged unit.

We were interested in tuning the behavior of such (PCP)Pd systems, and here we report on the synthesis of a stable mononuclear palladium hydroxy carbonyl compound based on the {2,6-bis[(di-*tert*-butylphosphino)methyl]phenyl} ligand that could be characterized in the solid state. We also report on its reactivity and that of the related hydride, especially with respect to C−H bond activation of phenyl acetylene in a σ-bond metathesis type of reaction.

Experimental Section

General Procedures and Materials. All experiments were carried out using standard high-vacuum line or Schlenk techniques or in a glovebox under nitrogen.[8] Solvents were dried over and distilled from Na/benzophenone prior to use. If nothing else is stated, all commercially available reagents were used as received from Aldrich. Complexes **1**,[9] **4**,[10] **7**, and **8**[11] were prepared according to literature. NMR measurements were performed in C_6D_6 unless otherwise stated. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz (^1H). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^1H, ^{13}C NMR) or using H_3PO_4 as an external reference (^{31}P). Elemental analyses was performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Coupling constants are given in Hz.

Preparation of $PCP^{tBu}PdO_2COH$ (2). In a sealable NMR tube **1** (3.2 mg) was dissolved in C_6D_6 (0.6 mL). The solution was pressurized with approximately 4 atm of CO_2. Within minutes the

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Table 1. Crystal Data for 2, 3, and 4

	2	**3**	**4**
formula	$C_{25}H_{44}O_3P_2Pd$	$C_{25}H_{44}O_2P_2Pd$	$C_{24}H_{44}P_2Pd$
fw	560.93	544.94	500.93
space group	*Pbca*	*C*2/*c*	$I4_1cd$
a/Å	15.7850(3)	30.3983(11)	16.36170(10)
b/Å	16.3154(4)	12.8608(7)	16.36170(10)
c/Å	21.8306(3)	15.4378(9)	19.3825 (3)
α/deg	90	90	90
β/deg	90	111.773(4)	90
γ/deg	90	90	90
V/Å^3	5622.22(19)	5604.8(5)	5188.80(9)
Z	8	8	8
D_{calcd}/g cm^{-3}	1.323	1.292	1.282
μ/mm^{-1}	0.80	0.79	0.85
θ range/deg	2.27−32.73	2.68−32.66	2.49−33.08
no. of reflns collected	35 760	24 782	51 183
no. of unique reflns	9186	9536	9643
$R(F)$ $(I > 2\sigma(I))^a$	0.038	0.052	0.033
$wR(F^2)$ (all data)^b	0.093	0.186	0.095
S^c	0.91	1.55	1.02
R_{int}	0.061	0.027	0.053

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. $^c S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Table 2. Selected Angles and Distances for the Complexes Studied

	2	**3**	**4**
Pd−C	2.005	2.070	2.072
Pd−P1	2.305	2.297	2.258
Pd−P2	2.319	2.300	
Pd−X^a	2.121	2.056	
P−Pd−P	164.46	165.6	167.89

^{a} X denotes the binding atom of the ligand in the fourth position.

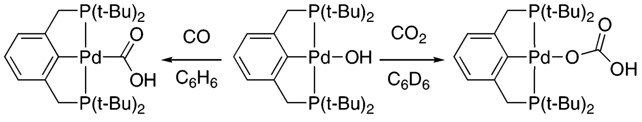
corresponding carbonate complex was formed. After slow evaporation of the solvent, crystals suitable for X-ray diffraction studies formed as colorless prisms. Anal. Found: C, 53.6; H, 8.0. $C_{25}H_{44}O_3P_2Pd$ requires: C, 53.5; H, 7.9. ^{1}H NMR (C_6D_6): δ 6.99 (t, J_{HH} = 7.5, 1H), 6.88 (d, J_{HH} = 7.8, 2H), 2.91 (vt, J_{PH} = 8, 4H), 1.31 (vt, J_{PH} = 13, 36H). ^{31}P{^{1}H} NMR: δ 73.1. ^{13}C{^{1}H} NMR: δ 162.5 (s), 154.0 (s), 151.9 (t, J_{PC} = 10), 124.9 (s), 122.5 (vt, J_{PC} = 20), 34.8 (vt, J_{PC} =14.5), 33.5 (vt, J_{PC} = 20), 29.3 (vt, J_{PC} = 7).

Preparation of PCP^{tBu}PdCOOH (3). In a Strauss flask PCP^{tBu}-PdOH (**1**) (0.068 g; 0.13 mmol) was dissolved in C_6H_6, and this solution was stirred in an atmosphere of CO for 2 h. The solvent was removed, and the solid was washed with pentane. This left a gray, amorphous solid that was used without further purification (0.032 g; 0.059 mmol; 45%). Slow diffusion of pentane into a benzene solution gave crystals suitable for X-ray diffraction studies. ^{1}H NMR (C_6D_6): δ 7.13 (t, $^3J_{HH}$ = 5, 1H), 7.12 (d, $^3J_{HH}$ = 5, 2H), 3.27 (vt, $^2J_{PH}$ = 7, 4H), 1.27 (vt, $^3J_{PH}$ = 13, 36H). ^{31}P{^{1}H} NMR: δ 79.3. ^{13}C{^{1}H} NMR: δ 213.4 (s), 172.4 (s), 151.2 (t), 125.2 (s), 122.2 (s), 121.1 (t, J_{PC} = 9), 38.7 (vt, J_{PC} = 21), 35.0 (vt, J_{PC} = 15), 29.5 (s).

Reaction of 4 with CO_2. In a sealable NMR tube **4** was dissolved in C_6D_6 (0.6 mL). The tube was pressurized with approximately 4 atm of CO_2. The reaction was complete in less than 1 h, giving PCP^{tBu}PdO$_2$CH, **5**, as the sole product. ^{1}H NMR (C_6D_6): δ 9.08 (t, J_{PH} = 1.7, 1H), 7.00 (t, J_{HH} = 7.5, 1H), 6.89 (d, J_{HH} = 7.5, 2H), 2.92 (vt, J_{PH} = 7.9, 4H), 1.26 (vt, J_{PH} = 13.7, 36H). ^{31}P{^{1}H} NMR: δ 73.9. ^{13}C{^{1}H} NMR: δ 167.6 (s), 154.9 (s), 151,7 (t, J_{PC} = 10.3), 125.0 (s), 122.5 (vt, J_{PC} = 22), 34.8 (vt, J_{PC} = 14), 33.7 (vt, J_{PC} = 21), 29.3 (vt, J_{PC} = 6).

Preparation of PCP^{tBu}PdCCPh (6). In a round bottomed flask **4** (50 mg; 0.0998 mmol) was dissolved in C_6H_6 (15 mL). Phenylacetylene (0.13 mL; 1.18 mmol) was added, and the solution was left stirring for 2 days. After evaporation of all volatile components and recrystallization in acetone, **6** was isolated (44 mg, 0.085 mmol, 85%). ^{1}H NMR (C_6D_6): δ 7.63 (d, J_{HH} = 7.6, 2H), 7.18 (t, J_{HH} = 7.5, 2H), 7.12 (m, 3H) 7.00 (t, J_{HH} = 7.1, 1H), 3.23 (vt, J_{PH} = 8.0, 4H), 1.34 (vt, J_{PH} = 13.7, 36H). ^{31}P{^{1}H} NMR: δ 80.3; ^{13}C{^{1}H}: δ 152.1 (t, J_{PC} = 10.2), 130.9 (s), 128.3 (s), 128.1 (s), 127.9 (s), 125.0 (s), 124.6 (s), 121.4 (vt, J_{PC} = 21.8), 118.5 (s), 118.3 (t, J_{PC} = 2.9), 37.8 (vt, J_{PC} = 20.4), 34.9 (vt, J_{PC} = 17.2), 29.5 (vt, J_{PC} = 6.6).

Scheme 1



3 **1** **2**

Crystallography. Intensity data were collected with an Oxford Diffraction Xcalibur 3 system using ω-scans and Mo Kα (λ = 0.71073 Å) radiation.[12] Intensity data were extracted and integrated using Crysalis RED.[13] The structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.[14] Non-H atoms were refined with anisotropic displacement. All hydrogen atoms were constrained to parent sites, using a riding model. Crystal data and details about data collection are given in Table 1. Selected bond distances and angles are given in Table 2. All crystallographic data are available in CIF format and are given in the Supporting Information.

Reaction of 7 and 8 with PhCCH. In a sealable NMR tube **7** or **8** was dissolved in C_6D_6 (0.6 mL). PhCCH (3.5 μL) was added, and the tube was heated to 80 °C. The reaction with **7** to yield **6** was finished after roughly 12 h. The sample of **8** was heated at 100 °C for 14 days until all of the PhCCH was consumed.

Results and Discussion

The palladium hydroxide **1** was prepared as previously described from the corresponding chloride via the nitrate.[9] Terminal palladium hydroxides are rare and include the isopropyl analogue of **1**. Within minutes of pressurizing a sample of **1** in C_6D_6 with 4 atm of CO_2 the corresponding bicarbonate, **2**, was formed, cf. Scheme 1. This reactivity is about the same as that found for other palladium hydroxide complexes,[15] but it is orders of magnitude higher than the corresponding (with the same ligand system) insertion into a Pd−Me bond, which requires heating for 48 h. Compound **2** was isolated and fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The molecular structure shows some unusual arrangement and is given in Figure 1. The phenyl group of the ligand backbone is tilted in comparison to what is commonly found for pincer complexes. Also, the benzylic carbons are not in the plane of the phenyl ring and neither is the palladium. The phenyl ring is forced out of position by one of the t-Bu groups of a neighboring complex. The carbonate groups of two neighboring units exhibit hydrogen bonding with an O−H···O distance comparable to other carbonate hydrogen-bonding distances (2.607(4) Å). We were unable to find any signal in the ^{1}H NMR corresponding to the bicarbonate proton,

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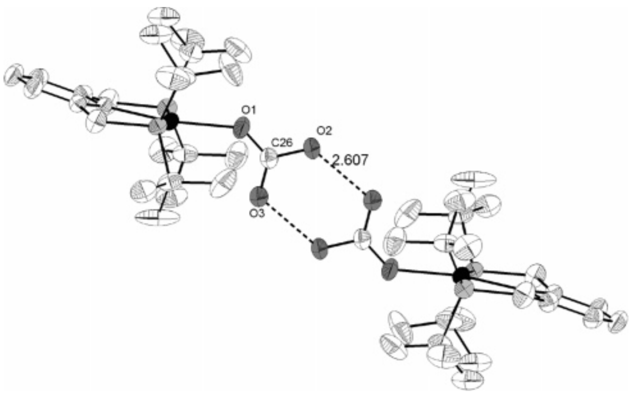


Figure 1. DIAMOND drawing of **2**. Hydrogen atoms are omitted for clarity.

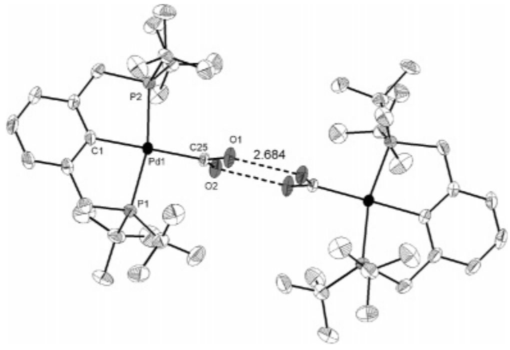
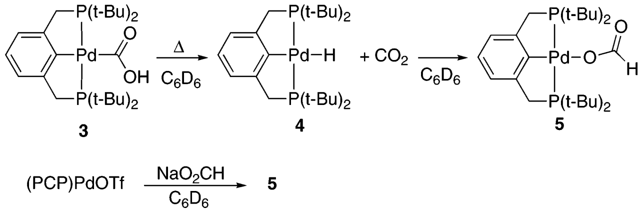


Figure 2. DIAMOND drawing of **3**. Hydrogen atoms are omitted for clarity.

possibly due to exchange of that proton with adventitious water in the solvent or a fast monomer−dimer equilibrium in solution, but the ^{13}C NMR signal for the bicarbonate was located at 162.5 ppm. The insertion of CO_2 into a palladium oxygen bond is a well-known reaction,[16] but there are few reports on any structurally characterized mononuclear palladium bicarbonate complexes.[17] We have earlier reported on the isolation of a bicarbonate complex from the reaction between carbonic acid and palladium methyl complexes.[18]

Carbon monoxide reacts in the same way as was previously reported for making hydroxycarbonyls of the platinum group metals,[4f,h] resulting in a gray solid that was identified as the hydroxycarbonyl compound **3**, cf. Scheme 1. This is a slightly thermally sensitive compound that was characterized by multinuclear NMR and X-ray crystallography. It failed to give a satisfactory elemental analysis due to thermal decomposition. The COOH group gives a characteristic ^{13}C NMR signal at 213 ppm. In the solid state **3** consists of hydrogen-bonded dimers formed from symmetry equivalent complexes. The molecular structure is given in Figure 2. The O−O distance is 2.684(9) Å, indicating a fairly strong hydrogen bond well within the range commonly seen for hydroxy carbonyl compounds and only slightly longer than what is expected for carboxylic acids. It is also markedly shorter than the corresponding platinum analogue. The dimeric structure is slightly bent (5.4°), and the distances between the two closest carbons of the *tert*-butyl groups differ noticeably between the two sides of the dimer (3.666 vs 4.479 Å for the closest distance). The complex has a distorted square planar arrangement, and as is almost always seen in PCP complexes, it exhibits the typical bent-back P−Pd−P angle (165.5°) because of the limitations from the rigid ligand backbone. When heating a benzene solution of **3**, it decomposes by loss of CO_2, forming **4**. This is seen as a new signal in the ^{31}P NMR spectrum at 95 ppm. All spectral features fit well with those reported for **4** in the literature and were also compared with an independently synthesized sample (vide infra). The elimination of CO_2 from **3** is not reversible since the reaction of **4** with CO_2 does not produce the hydroxycarbonyl but rather the formate complex, **5**, in a normal insertion that parallels our previously studied reaction of PCP^{tBu}PdMe.[11] Thus, heating **3** in a closed vessel slowly converts it into **5** through loss of CO_2 followed by normal insertion into the palladium hydride bond. These reactions are summarized in Scheme 2. The reactivity of **3** is in stark contrast to that reported for the corresponding isopropyl complex PCP^{i-Pr}PdCOOH. In that case the hydroxycarbonyl could not be isolated but only detected in solution under carbon monoxide pressure. It is reported that when the pressure of CO is removed, the complex loses carbon monoxide to re-form the palladium hydroxide, which reacts with a remaining hydroxy carbonyl under loss of water, forming a CO_2-bridged dimer, which could be isolated and characterized.[7] For **3**, there is no evidence of a monomer−dimer equilibrium in solution, and attempts to make the dimeric analogue by reacting **1** with **3** were unsuccessful. The difference in behavior is most likely due to the higher steric hindrance of the *tert*-butyl groups in **3**, making it thermodynamically favorable to lose CO_2 and obtain the small hydride in the fourth position as opposed to the larger hydroxide group. The unwillingness of **3** to dimerize can also be explained by steric factors. Many metal hydroxy carbonyls with open coordination sites decompose by loss of CO_2,[4a] but for palladium and platinum complexes with two trans-bound phosphines and a phenyl group trans to the hydroxy carbonyl the preferred decomposition route is normally through loss of carbon monoxide.[4f,h,7] To investigate the reactivity of the Pd−C bond of **3**, it was reacted with methyl acrylate, phenyl acetylene, and ethylene, but no insertion products were detected in any of these reactions. This seems to rule out a reactivity pattern where a new C−C bond could be formed from a hydroxy carbonyl in a similar fashion as reported for an alkoxy carbonyl as mentioned in the Introduction. The olefins gave a mixture of unidentified decomposition products, but the reaction with phenyl acetylene gave a main product at 80 ppm in the ^{31}P NMR spectrum in addition to minor (20%) decomposition products. The main product displays two characteristic peaks at around 118 ppm corresponding to the sp-hybridized carbons, and it was shown to be the acetylide complex, **6**. The peak at 118.3 displays a typical triplet pattern due to coupling with the phosphorus atoms and can hence be assigned to the sp carbon bonded to the palladium. An HMBC 2D-NMR showed that the peak at 118.5 corresponds to the sp carbon next to the phenyl ring. Compound **6** could never be obtained in an analytically pure state; it always contained small amounts of an insoluble hydrocarbon, presumably the phenyl acetylene polymer, thus giving a higher carbon analysis than expected.

Scheme 2



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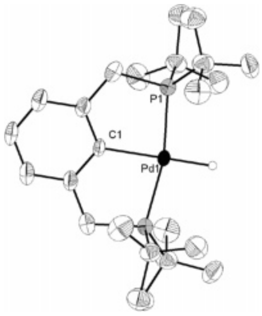
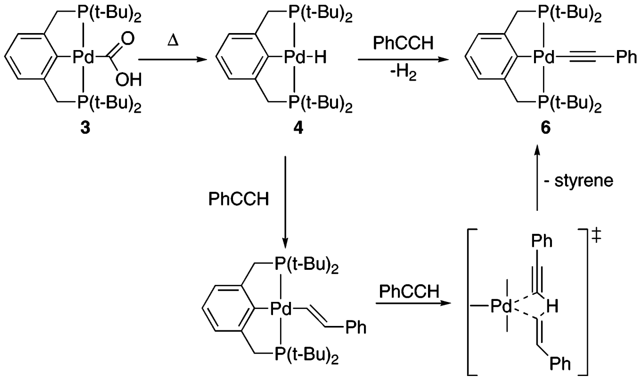


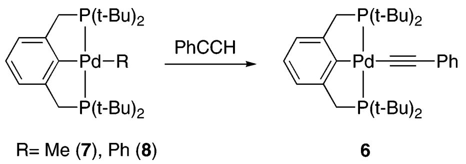
Figure 3. DIAMOND drawing of **4**. Hydrogen atoms, except for the hydride, are omitted for clarity.

We suspected the involvement of the palladium hydride in this reaction and decided to investigate the reactivity of **4** in some detail. Thus, **4** was synthesized according to a reported procedure.[10] In addition, we were able to obtain an X-ray crystal structure of **4**, and the molecular structure is given in Figure 3. It forms a monomeric species packed by London forces and the same distorted square planar arrangement as seen earlier. The hydride ligand could not be located in the Fourier map, but its presence was substantiated by the characteristic virtual triplet in the ^{1}H NMR spectrum at −3.76 ppm. The similar PCP^{Ph}PdH has been reported to be dinuclear in the solid state,[19] but again the bulky *tert*-butyl groups seem to prevent dimerization. The steric bulk is probably also what renders complex **4** thermally stable as compared to many other palladium hydrides. As mentioned above, **4** reacts with CO_2 within minutes to give **5** as the sole product. The reactivity of the Pd−H bond is many orders of magnitude higher than that of the corresponding Pd−Me bond. This is in line with the normal reactivity pattern for M−R (R = H, alkyl) bonds in 1,2-insertion reactions and is explained by the stabilization of a concerted transition state that the spherically symmetrical hydrogen s-orbital gives.[20] Compound **5** was identified by comparison with a second sample synthesized through a different route. Thus, PCP^{tBu}PdOTf was reacted with NaO_2CH, giving **5**, which could be characterized by multinuclear NMR spectroscopy, showing a typical formate ^{1}H NMR shift as a triplet at 9.08 ppm. Unfortunately, **5** failed to give X-ray quality crystals and decomposed upon standing, giving reduction to Pd(0).[21] Reaction of **4** with phenyl acetylene gave no insertion but rather the acetylide complex **6** after approximately 24 h reaction at room temperature. This somewhat surprising outcome could be explained by a C−H exchange reaction giving **6** and H_2 as a byproduct. However, no dihydrogen was detected, but the product mixture contained approximately 0.7 equiv of styrene. Also, monitoring the reaction by NMR spectroscopy provided no evidence of any intermediate species. A possible reaction sequence to explain these facts is an initial slow insertion step giving a β-phenylvinyl species that can undergo a fast C−H exchange reaction with a second phenyl acetylene, giving **6** and styrene, as outlined in Scheme 3. Such reaction sequences have been proposed earlier for a rhenium hydride complex.[22] The fact that styrene was present in less than equimolar amounts seems to indicate that there is a parallel C−H exchange reaction directly with the palladium hydride. The small amount of dihydrogen thus formed could possibly escape detection by ^{1}H NMR spectroscopy. The formation of **6** from **3** is therefore proposed to take place via **4**. It can be noted that we observed no formation of styrene in the reaction of **3** to give **6**, suggesting that in this case the reaction does not go via the vinyl compound.

Scheme 3



Scheme 4



We propose that the C−H exchange reaction takes place via a σ-bond metathesis. σ-Bond metathesis reactions have mainly been reported for early transition metals in their highest oxidation state, e.g., Sc(III).[23] However, examples from late transition metals do exist, especially in cases where the alternative oxidative addition−reductive elimination pathway requires access to unstable or unusual oxidation states.[24] In the present case, Pd(IV) is obviously unusual especially in the context of phosphine ligands. To further investigate the possibility of a C−H exchange, (PCP)PdMe, **7**, and (PCP)PdPh, **8**, were reacted with phenyl acetylene, cf. Scheme 4. The reaction with **7** required heating at 80 °C overnight to give **6** and methane. Surprisingly, the phenyl complex reacted even slower. After 14 days at 100 °C there was still approximately 50% of unreacted (PCP)PdPh present. This could be due to an unfavorable equilibrium, but this does not explain the low rate observed. It was difficult to continue the reaction to determine the equilibrium position since phenyl acetylene was consumed by a slow concurrent reaction, which presumably is the radical polymerization. The lower reactivity of **7** as compared to **4** is of course in line with what is expected for a σ-bond metathesis, i.e., the higher the s-character of the bond, the higher the reactivity. One possible explanation for the low reactivity of **8** could be a ground state stabilization by the strong Pd−Ph bond. If the reaction goes via oxidative addition of the C−H bond, this is also expected to be a concerted reaction and should follow the same reactivity trend as a σ-bond metathesis, so this alternative mechanism does not explain the reactivity observed.

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Compound **6** was unreactive toward CO_2 also at elevated temperatures, which is not surprising considering the lack of reactivity previously seen for palladium carbon complexes with sp^2-hybridized carbons.

There seems to be a general reactivity trend for these (PCP) palladium complexes when it comes to insertions. With only one open coordination site, they preferably react with substrates that can undergo direct electrophilic attack without precoordination, such as CO_2, whereas both **4** and **7** are unreactive toward migratory insertion substrates that presumably require a precoordination, such as olefins and CO.[25]

In conclusion we have synthesized the first mononuclear palladium hydroxy carbonyl and tested its reactivity in reactions where it has been suggested to participate. Complex **3** shows no tendency to dimerize and slowly isomerizes to the corresponding formate via CO_2 elimination to give the hydride, which undergoes a normal CO_2 insertion. The Pd−C bond of **3** is unreactive toward unsaturated compounds, ruling out its involvement in a possible route for hydrocarbon carboxylation. The palladium hydride reacts with phenyl acetylene in a C−H exchange reaction to give a palladium acetylide. This is proposed to take place via a σ-bond metathesis. Similar reactions occur between phenyl acetylene and palladium methyl and phenyl complexes.

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Supporting Information Available: All crystallographic material in CIF format. This is available free of charge via the Internet at http://pubs.acs.org.

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