Formation of Monometallic Bis(bicarbonato) Complexes of Palladium(II) by the Insertion of Carbon Dioxide into Palladium(II)–Hydroxide Bonds

Sanjoy Ganguly, Joel T. Mague, and D. Max Roundhill*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

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Two series of μ-hydroxy-bridged complexes, $[Pd(\mu\text{-}OH)L_2]_2(BF_4)_2$ and $[Pd(\mu\text{-}OH)(L\text{-}L)]_2(BF_4)_2$, have been prepared by treating $PdCl_2L_2$ (L = PPh_3, PPh_2Me) and $PdCl_2(L\text{-}L)$ (L-L = $Ph_2PCH_2CH_2PPh_2$(dppe), $Cy_2PCH_2CH_2PCy_2$-(dcpe)) with silver tetrafluoroborate in aqueous acetone solvent. These μ-hydroxy complexes react with carbon dioxide in aqueous acetone to give the bis(bicarbonato) complexes $Pd(OC(O)OH)_2L_2$ and $Pd(OC(O)OH)_2(L\text{-}L)$. $Pd(OC(O)OH)_2$dppe crystallizes in the monoclinic space group, *Cc* (No. 9), with $a = 10.410$ (1) Å, $b = 15.703$ (2) Å, $c = 16.365$ (2) Å, $\beta = 100.22$ (1)°, $V = 2633$ (2) Å^3 and $Z = 4$. The structure was refined with 3130 unique and 2730 observed ($I \geq 3\sigma(I)$) data to give $R = 0.021$ and $R_w = 0.028$.

Introduction

Complexes between the late transition metals and hard ligands such as hydroxide and amide are becoming of increasing interest.[1] Our interest in hydroxide complexes of palladium(II) has been increased recently because of our discovery that the cationic hydroxy bridged complex $[Pd(\mu\text{-}OH)dppe]_2^{2+}$ (dppe = 1,2-bis-(diphenylphosphino)ethane) acts as a homogeneous catalyst for the hydration of diethyl maleate to diethyl malate.[2] This result, combined with the relatively small number of μ-hydroxide complexes of palladium that are known, has caused us to focus on expanding the number of bridged hydroxy complexes of palladium(II) that are known and to develop a better understanding of their reaction chemistry with small unsaturated molecules.[3]

Experimental Section

Infrared spectra were recorded on a Mattson Cygnus 100 FT-IR spectrometer with the samples placed between sodium chloride plates as Nujol mulls. Nuclear magnetic resonance spectra were recorded on either a Bruker AC200 or on a GE Omega 400 spectrometer with the compounds dissolved in CDCl_3. Fast atom bombardment (FAB) mass spectra were obtained using a Kratos Concept 1H spectrometer with a *m*-nitrobenzyl alcohol matrix. Conductance measurements were made in nitromethane solvent using an Industrial Instruments Conductivity bridge (Model RC 16BC) with platinized electrodes. Spectral grade nitromethane was obtained from MCB Reagents and dried over molecular sieves prior to use. The water used for the measurement of the cell constant of the conductivity cell was obtained from a continuous distillation apparatus and distilled under nitrogen prior to use. The cell constant *k* was obtained using an 0.1 M aqueous solution of potassium chloride ($\Lambda_M = 128.96$ Ω^{-1} cm^2 mol^{-1}). The value was found to be 0.413 cm^{-1}.

For each of the dipalladium complexes, four separate conductivity measurements were made for each complex. In each case, the four concentrations in nitromethane solution were 6×10^{-3}, 1×10^{-3}, 6×10^{-4}, and 6×10^{-5} M. The molar conductivity Λ_M of each complex (1–4) was calculated according to the formula

$$\Lambda_M = k/M\Omega$$

where *k* is the cell constant, *M* is molar concentration, and Ω is resistance. The equivalent conductivities Λ_e for complexes 1–4 were then calculated, and their value at the different concentrations plotted against the square root of the equivalent concentrations ($c^{1/2}$). Extrapolation of these data gave the value Λ_0, the conductivity at infinite dilution, as the intercept.

The conductivity difference was then plotted against $c^{1/2}$ to give a straight line of slope B.[4]

All palladium complexes were prepared under an atmosphere of argon using Schlenk techniques, and all solvents were purged with nitrogen prior to use. Silver tetrafluoroborate, triphenylphosphine, and dppe were purchased from Aldrich Chemicals. Methyldiphenylphosphine was obtained from K & K Laboratories, and 1,2-bis(dicyclohexylphosphino)-ethane (dcpe) from Strem Chemicals. Carbon dioxide was purchased from Airco Inc. and used as received. The complexes $PdCl_2(L\text{-}L)$ (L-L = dppe, dcpe)[5] and $PdCl_2L_2$ (L = PPh_3, PMePh_2)[6] were synthesized according to literature procedures. Satisfactory microanalytical data on the new complexes could not be obtained because of their hygroscopic properties. The data were consistently low, indicative of occluded water or carbon dioxide.

Bis[(μ-hydroxy)bis(triphenylphosphine)palladium(II)] Tetrafluoroborate, $[Pd(\mu\text{-}OH)(PPh_3)_2]_2(BF_4)_2$ (1). This complex was prepared according to literature procedures.[7] IR: ν(OH) 3560 cm^{-1} (m). ^{1}H NMR: δ 2.2 s (O*H*). ^{31}P{^{1}H} NMR: δ 37.7 s. Mass spectrum: *m/z* 770.3 (Pd_2(OH)_2(PPh_3)_2), 647.3 (PdOH(PPh_3)_2), 630.2 (Pd(PPh_3)_2), 370.0 (Pd(PPh_3)).

Bis[(μ-hydroxy)bis(methyldiphenylphosphine)palladium(II)] Tetrafluoroborate, $[Pd(\mu\text{-}OH)(PMePh_2)_2]_2(BF_4)_2$ (2). Silver tetrafluoroborate (0.14 g, 0.72 mmol) in acetone (10 mL) containing 5% of water was added dropwise to a vigorously stirred dichloromethane or acetonitrile solution (15 mL) of PdCl_2(PMePh_2)_2 (0.20 g, 0.35 mmol). The stirring was continued for 4 h at 25 °C. The reacting mixture was then allowed to settle, the silver chloride formed removed by filtration, and the filtrate evaporated to dryness on a rotary evaporator. The solid product was extracted with dichloromethane (2 mL) and recrystallized by the slow addition of cold pentane to yield the complex as a green-yellow hygroscopic precipitate. Yield: 0.14 g (60%). IR: ν(OH) 3510 cm^{-1} (s). ^{1}H NMR: δ 2.1 s (O*H*). ^{31}P{^{1}H} NMR: δ 26.5 s. Mass spectrum: *m/z* 646.0 (Pd_2(OH)_2(PMePh_2)_2), 522.9 (Pd(OH)(PMePh_2)_2), 506.0 (Pd(PMePh_2)_2), 305.0 (Pd(PMePh_2)).

Bis[(μ-hydroxy)(1,2-bis(diphenylphosphino)ethane)palladium(II)] Tetrafluoroborate, $[Pd(\mu\text{-}OH)(Ph_2PCH_2CH_2PPh_2)]_2(BF_4)_2$ (3). This complex was prepared by a procedure similar to that used for 2 with PdCl_2(dppe) (0.20 g, 0.35 mmol) in acetonitrile (15 mL) and silver tetrafluoroborate (0.15 g, 0.76 mmol) in acetone (10 mL) containing 5% of water. The complex was isolated by the dropwise addition of dry pentane to a stirred solution of the filtrate in dichloromethane (2 mL) to give the complex as a colorless hygroscopic precipitate. Yield: 0.16 g (37%). IR: ν(OH): 3565 cm^{-1} (s). ^{1}H NMR: δ 2.5 s (O*H*) ^{31}P{^{1}H}

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(6) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596–9.
(7) Bushnell, G. W.; Dixon, K. R. *Can. J. Chem.* **1972**, *50*, 3694–9.

NMR: δ 74.2 s. Mass spectrum: m/z 1026.0 (Pd$_2$(OH)(dppe)$_2$), 645.0 (Pd$_2$(OH)$_2$dppe), 522 (Pd(OH)dppe)), 504 (Pd(dppe)).

Bis[(μ-hydroxy)(1,2-bis(dicyclohexylphosphino)ethane)palladium-(II)] Tetrafluoroborate, Pd(μ-OH)(Cy$_2$PCH$_2$CH$_2$PCy$_2$)]$_2$(BF$_4$)$_2$ (4). Silver tetrafluoroborate (0.13 g, 0.67 mmol) in acetone (10 mL) containing 5% water was added dropwise to a vigorously stirred solution of PdCl$_2$-(dcpe) (0.20 g, 0.33 mmol) in dichloromethane (15 mL). After 1 h at 25 °C, the solution was centrifuged to remove the major portion of the silver chloride formed. After a further 18 h the solution was filtered to remove a dark precipitate comprising a mixture of silver and silver chloride. The colorless solution was evaporated to dryness and placed under high vacuum for 5 h. The solid residue was extracted with dry dichloromethane (2 mL), which was poured into stirred pentane to give the complex as colorless hygroscopic microcrystals. Yield: 0.13 g (30%). IR: ν(OH) 3606 cm^{-1} (m). ^{1}H NMR: δ 1.8 s (OH) ^{31}P{^{1}H} NMR: δ 103.2 s. Mass spectrum: m/z 669.4 (Pd$_2$(OH)$_2$(dcpe)), 546.0 (Pd(OH)dcpe), 528.2 (Pd(dcpe)).

Bis(bicarbonato)bis(triphenylphosphine)palladium(II), Pd(OC(O)-OH)$_2$(PPh$_3$)$_2$ (5). Complex 1 (0.06 g, 0.04 mmol) was stirred in a mixture containing dichloromethane (5 mL) and acetone (10 mL) containing 5% water. Carbon dioxide was bubbled through this solution for 2 h. The solvents were removed under vacuum on a rotary evaporator. The solid residue was dissolved in dichloromethane (2 mL) and recrystallized as orange microcrystals by layering with pentane. IR: ν(OH) 2725 (s), 2672 cm^{-1} (m); ν(OCO$_2$) 1690 (w), 1600 (m), 1310 (m), 890 (s), 845 cm^{-1} (m). ^{1}H NMR: δ 11.6 s (OH); δ 11.2 s (OH) (cis and trans isomers). ^{31}P{^{1}H} NMR: δ 30.1 s; δ 23.7 s; mixture of cis and trans isomers. Mass spectrum: m/z 796 (Pd(OC(O)OH)$_2$(PPh$_3$)$_2$(CO$_2$)), 752 (Pd(OC(O)-OH)$_2$(PPh$_3$)$_2$), 631 (Pd(PPh$_3$)$_2$), 367 (Pd(PPh$_3$)).

Bis(bicarbonato)bis(methyldiphenylphosphine)palladium(II), Pd(OC-(O)OH)$_2$(PPh$_2$Me)$_2$ (6). Complex 2 (0.07 g, 0.057 mmol) was stirred in a mixture comprising dichloromethane (5 mL) and acetone (10 mL) containing 5% water. Carbon dioxide was bubbled through this solution for 5 h. The solvents were removed on a rotary evaporator, and the residue was extracted into dichloromethane (2 mL). This solution was slowly poured into stirred diethyl ether to give the complex as a yellow solid in quantitative yield. IR: ν(OH) 2731 (m), 2671 cm^{-1} (s); ν(OCO$_2$) 1734 (s), 1630 (m), 1320 (m), 790 cm^{-1} (w). ^{1}H NMR: δ 11.6 s (OH); δ 11.3 s (OH) (cis and trans isomers). ^{31}P{^{1}H} NMR: δ 24.3 s; δ 22.0 s; mixture of cis and trans isomers. Mass spectrum: m/z 672 (Pd(OC-(O)OH)$_2$(PPh$_2$Me)$_2$(CO$_2$)), 628 (Pd(OC(O)OH)$_2$(PPh$_2$Me)$_2$), 506 (Pd-(PPh$_2$Me)$_2$), 306 (Pd(PPh$_2$Me)).

Bis(bicarbonato)(1,2-bis(diphenylphosphino)ethane)palladium(II), Pd-(OC(O)OH)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) (7). Complex 3 (0.08 g, 0.065 mmol) was stirred in a mixture comprising dichloromethane (5 mL) and acetone (10 mL) containing 5% water. Carbon dioxide was bubbled through this solution for 1 h. The solvents were removed on a rotary evaporator, and the residue was extracted into aqueous acetone. Slow evaporation gave the complex as yellow crystals in quantitative yield. IR: ν(OH) 2680 (s), 2660 cm^{-1} (m); ν(OCO$_2$) 1700 (w), 1630 (m), 1410 (m), 1300 (s), 850 cm^{-1} (m). ^{1}H NMR: δ 11.7 (OH). ^{31}P{^{1}H} NMR: δ 72.8 s. Mass spectrum: m/z 670 (Pd(OC(O)OH)$_2$(dppe)(CO$_2$)), 626 (Pd(OC(O)-OH)$_2$(dppe)), 566 (Pd(OC(O)OH)(dppe)), 504 (Pd(dppe)).

Bis(bicarbonato)(1,2-bis(dicyclohexylphosphino)ethane)palladium-(II), Pd(OC(O)OH)$_2$(Cy$_2$PCH$_2$CH$_2$PCy$_2$) (8). Complex 4 (0.065 g, 0.05 mmol) was stirred in a mixture comprising dichloromethane (5 mL) and acetone (10 mL) containing 5% water. Carbon dioxide was bubbled through this solution for 8 h. The solvents were removed on a rotary evaporator, and the residue was extracted into aqueous acetone. Slow evaporation gave the complex as a yellow solid in quantitative yield. IR: ν(OH) 2700 (m), 2670 cm^{-1} (s); ν(OCO$_2$) 1655 (m), 1610 (m), 1300 (s), 840 cm^{-1} (w). ^{1}H NMR: δ 11.2 s (OH). ^{31}P{^{1}H} NMR: δ 109.6 s. Mass spectrum: m/z 694 (Pd(OC(O)OH)$_2$(dcpe)(CO$_2$)), 650 (Pd(OC(O)-OH)$_2$(dcpe)), 590 (Pd(OC(O)OH)(dcpe)), 527 (Pd(dcpe)).

X-ray Crystallography. An irregular yellow crystal of **7** measuring 0.23 × 0.36 × 0.33 mm, crystallized from aqueous acetone containing a small quantity of dichloromethane, was mounted on a thin glass fiber and coated with a thin layer of epoxy cement. General procedures for unit cell determination and data collection on the CAD-4 diffractometer have been published[8] while details specific to this structure are given in Table I. The C-centered monoclinic cell indicated by the CAD-4 software was confirmed by the observed 2/m diffraction symmetry and by the systematic absences seen in an initial partial data set. The additional systematic absence, $h0l$ for $l = 2n + 1$, observed in the final data set is

(8) Mague, J. T.; Lloyd, C. L. *Organometallics* **1988**, *7*, 983–93.

Table I. Crystallographic Data for [Pd(OCO$_2$H)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]

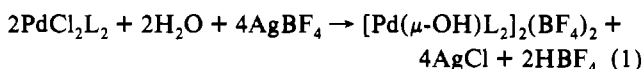| formula	C$_{28}$H$_{26}$O$_6$P$_2$Pd	Z	4
fw	626.9	T, °C	23
space group	Cc (No. 9)	λ, Å	0.710 73^a
a, Å	10.410 (1)	d_{obsd} (d_{calcd}), g cm^{-3}	1.56 (1.58)
b, Å	15.703 (2)	μ, cm^{-1}	8.54
c, Å	16.365 (2)	trans coeff	0.97–1.00
β, deg	100.22 (1)	R^b	0.021
V, Å^3	2633 (2)	$R_w{}^c$	0.028

^{a} Mo Kα graphite monochromated. ^{b} $R = \sum||F_o| - |F_c||)/\sum|F_o|$. ^{c} $R_w = [\sum w(F_o - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ where $w = 1/(\sigma_F)^2$, $\sigma_F = \sigma(F^2)/2F$, and $\sigma(F^2) = [(\sigma_I)^2 + (0.04F^2)^2]^{1/2}$.

consistent with the space groups Cc and $C2/c$. The measured density of 1.56 g cm^{-3} together with these possible space groups clearly indicated that the species present was mononuclear and that $Z = 4$. The raw data were corrected for Lorentz and polarization effects and a 1.6% decay in the intensity standards. An empirical absorption correction was applied.[9] Scattering factors include the real and imaginary corrections for anomalous dispersion.[10] All calculations were performed using the Enraf-Nonius MolEN system.[11]

The indication that $Z = 4$ together with the observed intensity distribution strongly indicated the space group to be Cc, a choice confirmed by the successful refinement. The position of the palladium atom was determined by direct methods (MULTAN 11/82)[12] and the atoms of the dppe ligand were located from successive cycles of full-matrix, least-squares refinement followed by difference Fourier synthesis. At this point, the major peaks remaining in the difference map suggested that the remainder of the molecule consisted of two bicarbonate ligands. Inclusion of these and further refinement allowed the location of many of the hydrogen atoms of the dppe ligand. These were included as fixed contributions with isotropic thermal parameters 20% larger than those of the attached carbon atoms. The difference map at this point showed small peaks consistent with hydrogen atoms bound to O(4) and O(6), but all attempts to refine them were unsuccessful. On the other hand, the absence of any significant features elsewhere in the map (residual peaks +0.29 to –0.09 e/Å^3) makes it extremely unlikely that any cationic species remain undiscovered. We therefore conclude that the palladium complex is electrically neutral and that the anionic ligands are, in fact, bicarbonate and not carbonate despite our inability to crystallographically confirm this. Final positional parameters are given in Table II while additional crystallographic data are provided as Supplementary Material (Tables S1–S6).

Results and Discussion

Bridged Hydroxy Complexes. The dihalide palladium(II) complexes PdCl$_2$L$_2$ (L = PPh$_3$, PPh$_2$Me) and PdCl$_2$(L-L) (L-L = dppe, dcpe) are prepared by treating palladium(II) chloride with equimolar amounts of triphenylphosphine, methyldiphen-ylphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), and 1,2-bis(dicyclohexylphosphino)ethane (dcpe). These complexes can be converted into the deliquescent μ-hydroxy complexes [Pd(μ-OH)L$_2$]$_2$(BF$_4$)$_2$ and [Pd(μ-OH)(L-L)]$_2$(BF$_4$)$_2$ by treating the dihalide complexes with silver tetrafluoroborate in aqueous acetone using the procedure previously reported for [Pd(μ-OH)-(PPh$_3$)$_2$]$_2$(BF$_4$)$_2$.[7] (eq 1). The yield of these μ-hydroxy complexes

$$2PdCl_2L_2 + 2H_2O + 4AgBF_4 \rightarrow [Pd(\mu\text{-}OH)L_2]_2(BF_4)_2 +$$
$$4AgCl + 2HBF_4 \quad (1)$$

range from 30% to 60%. The lower yields are obtained when the solution darkens, presumably due to the formation of elemental silver and/or palladium. The addition of hydroxide ion to the

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(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B. Cromer, D. T. *Ibid.*; Table 3.2.1.

(11) MolEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.

(12) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. MULTAN80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. University of York, England, 1980.
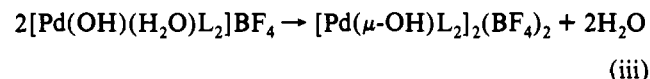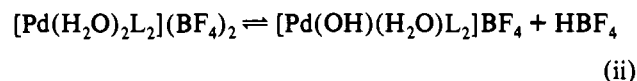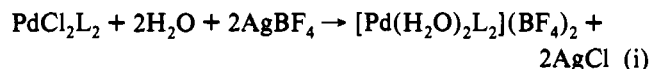
Table II. Positional Parameters (Esd) for Pd(OCO$_2$H)$_2$(dppe)

atom	x	y	z	$B,^a$ Å^2
Pd	0.356	0.16279 (1)	0.586	2.867 (3)
P(1)	0.42243 (9)	0.23724 (5)	0.70052 (5)	2.94 (1)
P(2)	0.50882 (9)	0.23463 (6)	0.53547 (5)	3.28 (2)
O(1)	0.2913 (3)	0.0871 (2)	0.4796 (2)	4.80 (6)
O(2)	0.2050 (3)	0.1094 (2)	0.6390 (2)	3.79 (5)
C(1)	0.5705 (4)	0.2957 (2)	0.6921 (2)	3.72 (7)
C(2)	0.5559 (4)	0.3263 (2)	0.6024 (3)	4.01 (7)
C(3)	0.1870 (4)	0.1170 (3)	0.4362 (2)	4.15 (8)
O(3)	0.1530 (4)	0.1874 (3)	0.4499 (2)	6.41 (8)
O(4)	0.1258 (5)	0.0736 (4)	0.3824 (3)	11.5 (1)
C(4)	0.2225 (4)	0.0307 (2)	0.6605 (2)	3.48 (7)
O(5)	0.1354 (4)	−0.0040 (2)	0.6897 (2)	6.88 (9)
O(6)	0.3224 (4)	−0.0040 (2)	0.6507 (3)	6.82 (9)
C(111)	0.3005 (4)	0.3151 (2)	0.7136 (2)	3.29 (6)
C(112)	0.1875 (4)	0.3245 (2)	0.6550 (2)	3.86 (7)
C(113)	0.0953 (5)	0.3848 (3)	0.6677 (3)	4.69 (9)
C(114)	0.1166 (5)	0.4358 (3)	0.7368 (3)	5.15 (9)
C(115)	0.2268 (5)	0.4263 (3)	0.7940 (3)	5.9 (1)
C(116)	0.3208 (5)	0.3661 (3)	0.7831 (3)	5.27 (9)
C(121)	0.4510 (4)	0.1747 (2)	0.7943 (2)	3.31 (6)
C(122)	0.3428 (5)	0.1428 (3)	0.8240 (3)	4.42 (8)
C(123)	0.3613 (6)	0.0899 (3)	0.8928 (3)	5.4 (1)
C(124)	0.4854 (6)	0.0708 (3)	0.9324 (3)	5.8 (1)
C(125)	0.5904 (5)	0.1027 (3)	0.9040 (3)	5.4 (1)
C(126)	0.5754 (5)	0.1540 (3)	0.8349 (3)	4.52 (9)
C(211)	0.6567 (4)	0.1737 (2)	0.5403 (2)	3.46 (6)
C(212)	0.6710 (4)	0.0946 (3)	0.5784 (3)	4.27 (8)
C(213)	0.7870 (5)	0.0503 (3)	0.5814 (4)	5.7 (1)
C(214)	0.8876 (4)	0.0837 (4)	0.5487 (3)	5.8 (1)
C(215)	0.8738 (5)	0.1618 (4)	0.5116 (3)	6.3 (1)
C(216)	0.7600 (5)	0.2075 (4)	0.5079 (3)	5.7 (1)
C(221)	0.4718 (4)	0.2708 (3)	0.4294 (2)	4.41 (8)
C(222)	0.4877 (6)	0.3557 (4)	0.4082 (3)	5.9 (1)
C(223)	0.4683 (7)	0.3778 (5)	0.3238 (3)	7.9 (1)
C(224)	0.4343 (7)	0.3189 (5)	0.2643 (3)	8.5 (2)
C(225)	0.4177 (6)	0.2362 (5)	0.2850 (3)	6.9 (1)
C(226)	0.4377 (5)	0.2107 (4)	0.3672 (3)	5.5 (1)

^{a} Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

reaction mixture increases the amounts of these dark precipitates and significantly decreases the yield of the μ-hydroxy complexes. The highest yields are obtained when pure oxygen-free water is added to the acetone. The detrimental effect of hydroxide ion may be due to replacement of the phosphine ligands by hydroxide, followed by decomposition of the resulting hydroxy complex to elemental palladium. A plausible pathway for the formation of these hydroxy bridged complexes from PdCl$_2$L$_2$ is shown in Scheme I. This proposed scheme involves the intermediacy of the dicationic diaquo complex Pd(H$_2$O)$_2$L$_2{}^{2+}$, formed after the removal of the chloride ligands from palladium. A water ligand bonded to a dicationic metal ion is expected to be acidic, and loss of a proton from one of the coordinated waters will give the monocationic intermediate [Pd(OH)(H$_2$O)L$_2$]$^+$. This intermediate, which is a monomeric hydroxy complex, is expected to be unstable to associative dimerization, because a lone electron pair on the coordinated terminal hydroxide can act as a ligand to a second palladium(II) center to give a bridging hydroxide. These associative dimerization reactions involve the substitution of a weakly bound ligand at each metal center (scheme I, reaction iii). This substitution of a water molecule at each palladium(II) center results in the formation of the doubly hydroxy-bridged palladium(II) cation dimer [Pd(μ-OH)L$_2$]$_2{}^{2+}$.

These (μ-hydroxy)dipalladium(II) complexes are characterized by a single resonance in the ^{31}P{^{1}H} NMR spectrum. The ^{1}H NMR spectrum shows a broad resonance for the hydroxyl group in the region δ 1.5–2.5. The position of this resonance is poorly defined, however, because, like other OH resonances, its chemical shift is dependent on the polarity of the solution. The hydroxyl ligand is identified in the infrared spectrum of the complexes

Scheme I

$$PdCl_2L_2 + 2H_2O + 2AgBF_4 \rightarrow [Pd(H_2O)_2L_2](BF_4)_2 +$$
$$2AgCl \quad (i)$$

$$[Pd(H_2O)_2L_2](BF_4)_2 \rightleftharpoons [Pd(OH)(H_2O)L_2]BF_4 + HBF_4$$
$$(ii)$$

$$2[Pd(OH)(H_2O)L_2]BF_4 \rightarrow [Pd(\mu\text{-}OH)L_2]_2(BF_4)_2 + 2H_2O$$
$$(iii)$$

[Pd(μ-OH)L$_2$]$_2{}^{2+}$ and [Pd(μ-OH)(L-L)]$_2{}^{2+}$ by the presence of a bond due to ν(OH) in the 3500–3600-cm^{-1} region.

The bimetallic structures of these dicationic complexes are supported by their fast atom bombardment (FAB) mass spectra. In each case the more intense peak is observed at a mass value (m/z) that corresponds to the monomer. These respective peaks are found at m/z values of 647.3, 522.9, 522 and 546.0 for L = PPh$_3$ and PPh$_2$Me and L-L = dppe and dcpe, respectively. In each case we observe a fragment that is due to the species PdL$_2$ or Pd(L-L). This observation is a consequence of the complex being a dication; therefore, the major peaks for [Pd(μ-OH)L$_2$]$_2{}^{2+}$ and [Pd(μ-OH)(L-L)]$_2{}^{2+}$ are found at the half-mass value because $z = 2$ in the expression m/z. The weaker peaks found in the mass spectra at the higher m/z values result from a dimer capturing an electron to give the monocations [Pd(OH)L$_2$]$_2{}^+$ and [Pd(OH)(L-L)]$_2{}^+$. As a result, the value for z in the expression m/z is now 1, and the observed mass value now becomes the true mass of the fragment.

The conductivity data in Table III support the formulation of these complexes as 2:1 electrolytes like the complex [Pd(μ-OH)(PPh$_3$)$_2$]$_2$(BF$_4$)$_2$.[7] Slope B, which is given by $(\Lambda_0 - \Lambda_e)/c^{1/2}$ has been considered to be a reasonable indicator of the ion type. For metal complexes that are 2:1 electrolytes in nitromethane solution, this slope usually has a numerical value in the range 400–600.[13] Our values in Table III show values that are significantly higher than this, ranging from 692 to 1116. These values are, however, in agreement with the reported value for the complex [Pd(μ-OH)(PPh$_3$)$_2$]$_2$(BF$_4$)$_2$, which has been reported to have a slope of about 1000.[7] These high conductivity values are a likely consequence of the presence of hydroxyl groups in the complexes, with the hydroxyl groups contributing to the conductivity by a proton transfer pathway with the nitromethane solvent.

Bicarbonato Complexes. When carbon dioxide is bubbled through solutions of these μ-hydroxy complexes, the bis(bicarbonato)palladium(II) complexes Pd(OC(O)OH)$_2$L$_2$ (L = PPh$_3$, PPh$_2$Me) and Pd(OC(O)OH)$_2$(L-L) (L-L = dppe, dcpe) are formed (eq 2). The ^{1}H NMR spectra show resonances for the

$$[Pd(\mu\text{-}OH)L_2]_2{}^{2+} + 4CO_2 + 2H_2O \rightarrow$$
$$2Pd(OC(O)OH)_2L_2 + 2H^+ \quad (2)$$
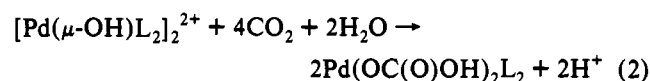
OH group of the bicarbonate ligands in the range δ 11–12. For the complexes Pd(OC(O)OH)$_2$L$_2$ the ^{31}P{^{1}H} NMR spectra show two singlet resonances that result from the presence of both the cis and the trans isomers in solution. The ^{1}H NMR spectrum of **6** (L = PPh$_2$Me) shows a distorted triplet at δ 1.2 and a doublet at δ 1.9. These multiplicities for the methyl groups of the complexed methyldiphenylphosphine are representative of complexes having the phosphine ligands mutually trans and cis, respectively. These resonances are in a ratio of 3:2. In the ^{31}P{^{1}H} NMR spectrum of **6** the peaks at δ 24.3 and 22.0 are in a 3:2 ratio; hence, the downfield peak of the pair can be assigned to

(13) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587–91.

Table III. Conductivity Data for the Complexes [Pd(μ-OH)L$_2$]$_2$(BF$_4$)$_2$ and [Pd(μ-OH)(L-L)]$_2$(BF$_4$)$_2$

complex	$\Lambda_M{}^a$	$\Lambda_0{}^b$	$(\Lambda_0 - \Lambda_e)/c^{1/2}$
[Pd(μ-OH)(PPh$_3$)$_2$]$_2$(BF$_4$)$_2$	233	140	1116
[Pd(μ-OH)(PPh$_2$Me)$_2$]$_2$(BF$_4$)$_2$	216	124	692
[Pd(μ-OH)(dppe)]$_2$(BF$_4$)$_2$	193	121	821
[Pd(μ-OH)(dcpe)]$_2$(BF$_4$)$_2$	196	116	728

^{a} Molar conductivity Λ_M (Ω^{-1} cm^2 mol^{-1}) of 10^{-3} M solutions in CH$_3$NO$_2$. ^{b} Plot of equivalent conductivity, Λ_e (Ω^{-1} cm^2 equiv^{-1}) against $c^{1/2}$ (equiv L^{-1}) was extrapolated to give the intercept Λ_0, the equivalent conductivity at infinite dilution.
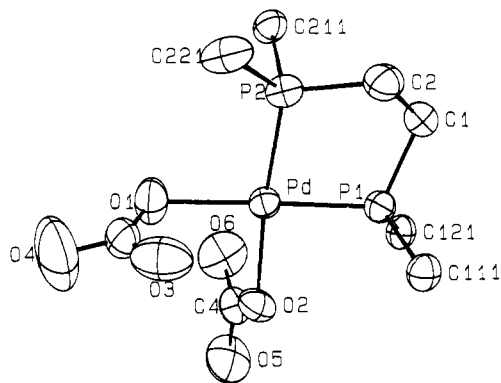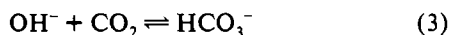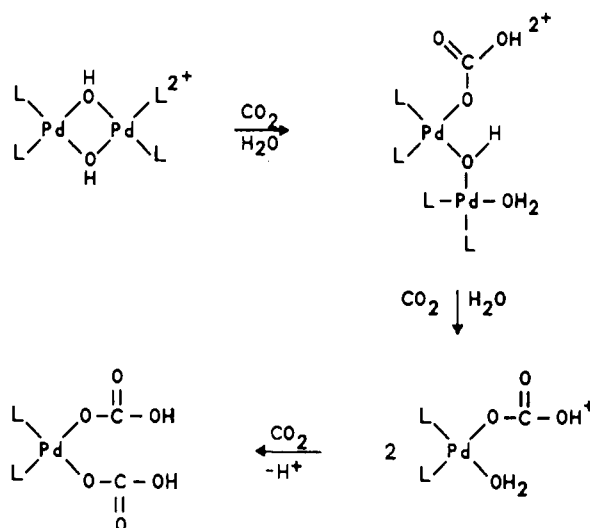

Figure 1. Perspective view of Pd(OCO$_2$H)$_2$(DPPE). Only the ipso carbons of the ligand phenyl groups are shown. Atom C(3) is bonded to atoms O(1), O(2), and O(4). Thermal ellipsoids are drawn at the 50% contour level.

the trans isomer. If in complex **5** (L = PPh$_3$) we can assume that the downfield peak in the ^{31}P{^{1}H} NMR spectrum is due to the trans isomer, the trans:cis isomer ratio in the mixture is 11:9. The infrared spectra of the complexes show the expected bands for the bicarbonate ligand, but the band in the 1700-cm^{-1} region that is primarily due to ν(CO) is rather weak. This band is consistently weak throughout the series of complexes, but as a check that our assigned structures are correct, we have also verified that this infrared band is also weak in a sample of the crystalline material of Pd(OC(O)OH)$_2$dppe that was used for the single crystal structure determination. The band that is primarily due to ν(OH) is found in the 2660–2725-cm^{-1} range. Although these values appear to be rather low for ν(OH), there is precedence for such an assignment in bicarbonato complexes.[14–16] These bicarbonate complexes are the expected products arising from the insertion of carbon dioxide into a palladium hydroxide bond. A rather unexpected feature that is observed in the FAB-MS of these compounds is the presence of a peak that has a m/z value 44 greater than that of the parent ion. This peak results from attachment of a carbon dioxide to the molecular ion fragments. A proposed sequence of reactions leading to the formation of these bis(bicarbonate) complexes are shown in Scheme II. An alternative route that has been discussed by Atwood involves a pathway whereby the hydroxide ion dissociates from the metal center.[17] In the presence of carbon dioxide, this anion will readily form the bicarbonate ion (eq 3), which then coordinates with the cationic palladium center that has been formed. Such a pathway cannot be ruled out in our case.

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \tag{3}$$

(14) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 431–3.
(15) Flynn, B. R.; Vaska, L. *J. Am. Chem. Soc.* **1973**, *95*, 5081–3.
(16) Crutchley, R. J.; Powell, J.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1977**, *24*, L15–L16.
(17) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179–85. The particular reaction studied by these authors is the formation of carboalkoxyiridium complexes by the carbonylation of alkoxyiridium complexes.

Scheme II

Table IV. Selected Bond Distances (Å) and Interbond Angles (deg) for Pd(OCO$_2$H)$_2$(DPPE)

Bond Distances			
Pd–P(1)	2.2169 (9)	O(2)–C(4)	1.289 (5)
Pd–P(2)	2.223 (1)	C(3)–O(3)	1.195 (6)
Pd–O(1)	2.114 (3)	C(3)–O(4)	1.203 (6)
Pd–O(2)	2.103 (3)	C(4)–O(5)	1.225 (6)
O(1)–C(3)	1.277 (5)	C(4)–O(6)	1.210 (6)

Interbond Angles			
P(1)–Pd–P(2)	84.83 (4)	Pd–O(2)–C(4)	114.6 (3)
P(1)–Pd–O(1)	177.4 (1)	O(1)–C(3)–O(3)	119.1 (4)
P(1)–Pd–O(2)	90.14 (8)	O(1)–C(3)–O(4)	119.2 (5)
P(2)–Pd–O(1)	97.3 (1)	O(3)–C(3)–O(4)	121.7 (5)
P(2)–Pd–O(2)	172.90 (8)	O(2)–C(4)–O(5)	117.0 (4)
O(1)–Pd–O(2)	87.9 (1)	O(2)–C(4)–O(6)	118.6 (4)
Pd–O(1)–C(3)	111.5 (3)	O(5)–C(4)–O(6)	124.4 (4)

Nonbonded Distances			
Pd- -O(3)	2.810 (4)	Pd- -O(6)	2.872 (4)

These bicarbonato complexes of palladium(II) appear to be the favored products with this system, and they are obtained even after prolonged exposure to carbon dioxide during the synthesis. We believe that these compounds are the first example of bis(bicarbonato) complexes where the monodentate ligands are coordinated to a single metal center. This observation contrasts with previous work where bis(μ-hydroxy) complexes of the late transition metals react with carbon dioxide to give the bidentate carbonato complexes.

Structure of Pd(OC(O)OH)$_2$dppe. A perspective view of Pd(OC(O)OH)$_2$(DPPE) is given in Figure 1 while selected bond distances and interbond angles are presented in Table IV. From these it is evident that the palladium atom adopts a square planar geometry and that the anionic ligands are monodentate since the Pd- - -O(3) and Pd- - -O(6) separations are clearly nonbonding. The two Pd–O bond distances are equivalent within experimental error and compare well with that found in *trans*-Pd(Me)(O-C(O)OH)(PEt$_3$)$_2$ (2.13 (2) Å)[16] particularly considering that in the latter the bicarbonate ligand is trans to a methyl group which would be expected to exert a significant trans influence. The distances C(3)–O(1) and C(4)–O(2) are also substantially equivalent and comparable to the corresponding distance (1.27 (4) Å) in the above-mentioned palladium complex. The interpretation of the remaining metrical parameters for the anionic ligands is less certain. The remaining C–O distances within each ligand are equal within experimental error and all are considerably shorter than corresponding distances in *trans*-Pd(Me)(OC(O)-

OH)(PEt$_3$)$_2$[16] and RhH$_2$(O$_2$COH)(PPr$^i_3$)$_2$.[18,19] This coupled with the lack of definitive crystallographic evidence for hydrogen atoms bonded to any of the terminal oxygen atoms raises the question that these ligands are carbonate rather than bicarbonate. Were this to be the case, then either the complex must be Pd(IV), which is very unlikely, or it is an anionic Pd(II) species. This also seems very unlikely in view of the essentially featureless difference map obtained at the end of the refinement and the low R value obtained which argues against the presence of even a small cation. As the spectroscopic data seem most consistent with the formulation of the anionic ligands as bicarbonate, we suggest that the short and virtually identical C–O distances and the failure to locate the O–H hydrogen atoms may be the result of the relatively large thermal motions of the oxygen atoms (which would tend to make the C–O distances appear shorter) and a 2-fold disorder of the {C(O)OH} moieties. A final point concerns the apparent lack of hydrogen bonding which might be expected if

the ligands are indeed bicarbonate and is a significant feature of the structure of *trans*-Pd(Me)(OC(O)OH)(PEt$_3$)$_2$. The shortest intramolecular O- -O contact is 4.471 (6) Å (O(3)- - -O(6)) while the shortest intermolecular contact is 3.356 (8) Å between O(4) and O(5) in a neighboring molecule. Both are clearly too long to be consistent with hydrogen bonding. While this could be taken as evidence against the presence of bicarbonate ligands, given the spectroscopic evidence in favor of bicarbonate, we suggest that the considerably greater bulk of the DPPE ligand as compared with the triethylphosphine ligands in *trans*-Pd(Me)(OC(O)-OH)(PEt$_3$)$_2$ makes it difficult for the molecules in the present structure to get close enough to participate in hydrogen bonding.

Supplementary Material Available: Tables of crystallographic data (Table S1), bond distances (Table S2), bond angles (Table S3), calculated hydrogen positions (Table S4), general displacement parameters (Table S5), and anisotropic displacement parameters (Table S6) (8 pages). Ordering information is given on any current masthead page.

(18) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212–21.
(19) For purposes of comparison, the Pd–O distance in the monodentate bicarbonate complex Pd(Me)(OC(O)OH)(PEt$_3$)$_2$ is 2.13 (2) Å. The Pd–O distances in the bidentate bicarbonate complex RhH$_2$(O$_2$-COH)(PPr$^i_3$)$_2$ are longer at 2.306 (3) and 2.279 (2) Å.