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Anomalous carbonylation of $[Pd(dppm)(O_2CCF_3)]_2$ to give an asymmetric μ-CO complex

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Abstract

The reactive palladium dimer, $[Pd(dppm)(O_2CCF_3)]_2$, is carbonylated to $[Pd(dppm)(O_2CCF_3)]_2(\mu\text{-CO})$ in a reversible reaction with $K = c.\ 7.2(2) \times 10^4$ atm^{-1} ($P_{1/2} = c.$ 2.4 Torr). This is significantly larger than is expected based on the $\lambda_{max} = 280$ nm in the electronic spectrum. The product can be isolated in analytically pure form by crystallization under a CO atmosphere. It forms crystals in the monoclinic space group *Cc* with $a = 18.584(5)$, $b = 28.65(1)$, $c = 11.164(3)$ Å and $\beta = 95.16(2)°$. The structure is significantly distorted. The bonding about the two palladium atoms is quite asymmetric. While one is close to a square planar geometry with a Pd–C(O) distance of 1.90(2) Å, the other is significantly pyramidalized and has a longer (2.00(2) Å) bond to the bridging CO. The Pd–Pd distance is only 2.896(2) Å, much shorter than that usually observed for formally non-bonded Pd atoms.

Introduction

The strategy of incorporating trifluoroacetate into a palladium compound is very useful in synthetic [1, 2] and catalytic [3] processes. One explanation for this is the lability of the ligand. But trifluoroacetate also exerts a significant direct influence on complex structure. This is demonstrated by the extremely short Pd–O bonds in the monomer $Pd(dppm)(O_2CCF_3)_2$ [4] and the short Pd–Pd bond in the dimer $[Pd(dppm)(O_2CCF_3)]_2$ [2]. This paper describes equilibrium and crystallographic studies that demonstrate that these structural effects correlate with unusual reactivity in the reaction of the dimer with CO.

Experimental

Synthesis of (μ^2-carbonyl)[bis(bis(diphenylphosphino)methane)][bis(trifluoroacetato)]dipalladium(II)

Samples of the carbonyl complex are prepared by bubbling CO through a solution or a slurry of the dimer, which dissolves as carbonylation occurs. A sample for elemental analysis was prepared by carbonylation in CH_2Cl_2 followed by slow admixture of diethyl ether under a CO atmosphere. IR (cm^{-1}, CH_2Cl_2): 1720 (ν_{CO}). NMR data are reported for a $CDCl_3$ solution prepared from the dimer under *c.* 200 Torr of ^{13}CO: ^{1} NMR: δ 7.69, 7.56, 7.39–7.19 (40 H, br, m, C_6H_5); δ 3.25–3.17, δ 2.82–2.71 (4H, m, CH_2). ^{13}C NMR: δ 229.6 (qn, $^2J_{PC} = 5.6$ Hz, μ-CO); δ 160.6 (qu, $^2J_{FC} = 36$ Hz, CF_3CO_2); δ 133.5, 131.0, 128.8 (C_6H_5); δ 115.38 (qu, $^1J_{FC} = 291$ Hz, CF_3CO_2); δ 23.5 (m, CH_2). ^{31}P NMR (reference, 85% H_3PO_4): δ 22.5 (d, $^2J_{PC} = 5.5$ Hz). *Anal.* Calc. for $C_{55}H_{44}O_5F_6P_4Pd_2$: C, 53.46; H, 3.75. Found: C, 53.27; H, 3.59%.

Equilibrium measurements

Samples of the dimer in DMA (*c.* 1.5×10^{-4} M) were placed in a 1-cm quartz cell fitted with a Teflon stopcock. The system was then opened to a ballast system consisting of a 2-liter flask. Air was removed *in vacuo* and then the system was charged with the appropriate pressure of carbon monoxide. The solution was stirred vigorously under the CO atmosphere for a minimum of 3 h and then was closed off and removed to the spectrophotometer. The reference wavelength of 465 nm was used in the data analysis. Following the procedure discussed by James and coworkers [5], plots of $\log[(A_0 - A_{CO})/(A - A_{CO})]$ versus log[CO], where A = absorbance at a given pressure of CO, A_0 = absorbance in the absence of CO, and A_{CO} = absorbance under a pressure of 1 atmosphere of CO, were used to determine K.

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Results and discussion

The synthesis of the palladium dimer from palladium acetate, dppm and trifluoroacetic acid has been reported by Krafft *et al.* [2]; it can also be made by the condensation of $Pd(dppm)(O_2CCF_3)_2$ [4] with $Pd_2(dba)_3$ (dba = dibenzylideneacetone) in the presence of additional dppm in methylene chloride. The electronic spectrum of the compound is also similar to other palladium dppm dimers, with bands at 418, 325 and 280 nm, though this last band, which has been shown to correlate with the reaction with CO, is at higher energy than has been observed before [5].

One of the most important reactions in the chemistry of Pd(I) dimers is the reversible insertion of small molecules into the metal–metal bond. The bis(trifluoroacetate)dimer is indeed an excellent substrate for carbonylation, with a rapid uptake of CO accompanied by a slight darkening of the solution (eqn. (1)). This reaction, which has been briefly described elsewhere [1c, 2], can be quantitatively followed by monitoring the appearance of bands at 465, 376 and 303 nm for the μ-CO dimer.

$$[Pd(dppm)(O_2CCF_3)]_2 + CO \longrightarrow [Pd(dppm)(O_2CCF_3)]_2(\mu\text{-}CO) \quad (1)$$

The carbonylation is an equilibrium process [6]. Spectrophotometric titration gives an equilibrium constant for the reaction as written of $7.2(2)\times10^4$ atm^{-1}. This means this complex binds CO much better than would be expected based on the qualitative correlation between K and λ_{max} [5]. Unfortunately, we have been unable to determine whether this is due to changes in k_1 or k_{-1} because decarbonylation kinetics are complicated by non-first order behavior.

The carbonyl dimer can be isolated as analytically pure orange–red prisms under an atmosphere of carbon monoxide. The crystals were subject to an X-ray diffraction study. Experimental details are given in Table 1, with important bond lengths and angles in Table 2 and atomic positions and equivalent isotropic thermal parameters in Table 3. A perspective drawing of the complex is provided in Fig. 1. The structure is complicated by disorder of both the CF_3 groups, which were modeled by two orientations of a rigid F_3 set.

The structure deviates from a symmetric μ-CO structure with non-bonded palladium centers in several ways. There is a close contact (2.896(2) Å) between the two Pd atoms. While this is still beyond the distance typically associated with a Pd–Pd bond (e.g. 2.699(5) Å for $[Pd(dppm)Br]_2(\mu\text{-}CO)$ [7]) it is nevertheless considerably shorter than the shortest reported Pd–Pd non-bonded contact, 2.959(2) Å in $Pd_2(dppm)_3$ [8]. In addition, the two palladium coordination environments are quite different. That about Pd1 is quite planar with a mean deviation from the plane of 0.02 Å. However, the environment about Pd2, with a mean deviation from the least-squares plane of 0.37 Å, is distorted towards a tetrahedron, with angles of 160.5(7) and 154.1(2)° for O–Pd–C and P–Pd–P, respectively. as shown in a side-on view of the molecular core (Fig. 2). In addition, Pd2 has longer bonds to the coordinated phosphorus ligands and to the bridging CO. The C–O vector is, though, still oriented perpendicularly to the Pd–Pd bond and is not to be considered a semi-bridging CO [9].

TABLE 1. Experimental details of crystal structure determination

Crystal data	
Empirical formula	$C_{57}H_{44}F_6O_5P_4Pd_2$
Formula weight	1234.91
Habit	red–orange block
Size (mm)	0.20×0.20×0.30
Crystal system	monoclinic
Lattice parameters	
a (Å)	18.514(4)
b (Å)	28.638(7)
c (Å)	11.459(7)
β (°)	95.18(3)
Volume (Å^3)	6051(4)
Space group	Cc (No. 9)
Z	4
Intensity measurements	
Diffractometer	Rigaku AFC6S
Radiation	Mo Kα (λ = 0.71069 Å)
F(000)	1136
Temperature (°C)	25
$2\theta_{max}$ (°)	50.2
Data collected	$+h$, $+k$, $\pm l$
Reflections measured	5693
Unique (R_{int})	5504 (0.006)
Transmission factors	0.82–1.10
Scan rate (°/min)	4.0
Scan type	ω–2θ
Structure solution and refinement	
Observations ($I > 3.00\sigma(I)$)	3024
Variables	363
Reflections/variable	8.3
Residuals	
R	0.062
R_w	0.075
Goodness of fit	1.61
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$; $w = 4F_o^2/\sigma^2(F_o)$

The presence of a pyramidalization about one palladium, with elongated Pd–P and Pd–C bonds (compared to the adjacent square planar center) is consistent with the build-up of charge density at the distorted center. There is no ready explanation for why this occurs, though it is interesting to point out that the structure can be viewed as an intermediate in the dissociation of trifluoroacetate to give [Pd$_2$(μ-dppm)$_2$(μ-CO)(O$_2$CFF$_3$)]$^+$[O$_2$CCF$_3$]$^-$, which is isoelectronic with the several M$_2$L$_3$X$_2$(μ-CO) complexes known [10] which have undisputed Pd–Pd bonds. Dissociation may merely be prevented in the present

TABLE 2. Selected bond distances (Å) and angles (°) for [Pd(dppm)(O$_2$CCF$_3$)]$_2$(μ-CO)

Pd1–Pd2	2.896(2)
Pd1–P1	2.329(6)
Pd1–P2	2.309(6)
Pd1–O2	2.17(1)
Pd1–C1	1.90(2)
Pd2–P3	2.366(6)
Pd2–P4	2.377(6)
Pd2–O4	2.17(2)
Pd2–C1	1.99(2)
P1–C2	1.85(2)
P2–C3	1.82(2)
P3–C2	1.81(2)
P4–C3	1.80(2)
O1–C1	1.20(3)
Pd2–Pd1–P1	94.0(2)
Pd2–Pd1–P2	84.4(2)
Pd2–Pd1–O2	134.0(4)
Pd2–Pd1–C1	43.0(7)
P1–Pd1–P2	177.9(2)
P1–Pd1–O2	96.1(4)
P1–Pd1–C1	89.7(6)
P2–Pd1–O2	85.9(4)
P2–Pd1–C1	88.2(6)
O2–Pd1–C1	173.8(7)
Pd1–Pd2–P3	91.7(2)
Pd1–Pd2–P4	94.7(2)
Pd1–Pd2–O4	119.9(4)
Pd1–Pd2–C1	40.7(6)
P3–Pd2–P4	154.1(2)
P3–Pd2–O4	96.9(4)
P3–Pd2–C1	86.4(6)
P4–Pd2–O4	101.6(4)
P4–Pd2–C1	82.4(6)
O4–Pd2–C1	160.5(7)
Pd1–P1–C2	112.0(7)
Pd1–P2–C3	114.8(7)
Pd2–P3–C2	112.4(8)
Pd2–P4–C3	111.4(6)
Pd1–C1–Pd2	96(1)
Pd1–C1–O1	134(2)
Pd2–C1–O1	129(2)
P1–C2–P3	118(1)
P2–C3–P4	111(1)
O2–C4–O3	127(2)
O2–C4–C5	112(2)
O3–C4–C5	120(2)
O4–C6–O5	130(2)
O4–C6–C7	117(2)
O5–C6–C7	113(2)

TABLE 3. Atomic positional and isotropic thermal parameters for [Pd(dppm)(O$_2$CCF$_3$)]$_2$(μ-CO)[a]

Atom	x	y	z	B_{eq}
Pd(1)	0	0.15836(5)	0	2.81(7)
Pd(2)	−0.1470(1)	0.18337(6)	−0.0849(2)	2.81(7)
P(1)	−0.0048(3)	0.1966(2)	0.1785(5)	3.2(3)
P(2)	0.0024(3)	0.1226(2)	−0.1802(5)	2.9(3)
P(3)	−0.1616(3)	0.2279(2)	0.0853(5)	3.1(3)
P(4)	−0.1282(3)	0.1737(2)	−0.2860(5)	3.1(3)
O(1)	−0.0272(8)	0.2461(5)	−0.115(1)	3.8(7)
O(2)	0.0504(9)	0.0952(5)	0.072(1)	3.9(7)
O(3)	0.149(1)	0.1374(8)	0.102(2)	8(1)
O(4)	−0.2350(8)	0.1347(5)	−0.066(1)	3.9(7)
O(5)	−0.1867(9)	0.1149(6)	0.115(1)	4.8(2)
C(1)	−0.047(1)	0.2099(7)	−0.078(2)	3(1)
C(2)	−0.099(1)	0.2108(8)	0.208(2)	4(1)
C(3)	−0.036(1)	0.1571(8)	−0.304(2)	3(1)
C(4)	0.115(1)	0.101(1)	0.102(2)	4(1)
C(5)	0.161(2)	0.047(1)	0.127(3)	13(3)
C(6)	−0.235(1)	0.1153(9)	0.027(2)	4(1)
C(7)	−0.300(2)	0.084(1)	0.044(2)	6(2)
C(11)	0.042(1)	0.2510(8)	0.200(2)	3.6(4)
C(12)	0.081(1)	0.2682(8)	0.115(2)	4.1(5)
C(13)	0.117(1)	0.313(1)	0.128(2)	5.6(6)
C(14)	0.117(1)	0.334(1)	0.231(2)	5.5(6)
C(15)	0.075(2)	0.317(1)	0.315(3)	7.3(8)
C(16)	0.043(1)	0.2732(9)	0.301(2)	4.4(5)
C(21)	0.026(1)	0.1617(8)	0.301(2)	3.5(5)
C(22)	−0.010(1)	0.1194(9)	0.324(2)	4.3(5)
C(23)	0.017(1)	0.088(1)	0.412(2)	5.4(6)
C(24)	0.081(2)	0.096(1)	0.472(2)	6.3(7)
C(25)	0.124(2)	0.138(1)	0.455(2)	6.3(6)
C(26)	0.092(1)	0.1697(8)	0.363(2)	4.8(5)
C(31)	0.094(1)	0.1084(9)	−0.205(2)	4.4(5)
C(32)	0.140(1)	0.144(1)	−0.240(2)	5.0(5)
C(33)	0.214(2)	0.139(1)	−0.248(3)	6.5(7)
C(34)	0.242(1)	0.092(1)	−0.228(2)	5.6(6)
C(35)	0.203(2)	0.058(1)	−0.190(2)	5.3(6)
C(36)	0.127(1)	0.0669(9)	−0.185(2)	4.4(5)
C(41)	−0.044(1)	0.0673(7)	−0.193(2)	3.0(4)
C(42)	−0.091(1)	0.0544(8)	−0.111(2)	3.9(5)
C(43)	−0.133(1)	0.0153(8)	−0.120(2)	4.3(5)
C(44)	−0.127(1)	−0.012(1)	−0.216(2)	5.9(6)
C(45)	−0.083(1)	−0.0012(9)	−0.297(2)	5.5(6)
C(46)	−0.038(1)	0.0387(7)	−0.293(2)	3.3(4)
C(51)	−0.249(1)	0.2266(7)	0.149(2)	2.8(4)
C(52)	−0.256(1)	0.2303(8)	0.266(2)	4.8(5)
C(53)	−0.320(1)	0.228(1)	0.312(2)	5.7(6)
C(54)	−0.379(1)	0.223(1)	0.239(2)	6.0(6)
C(55)	−0.378(2)	0.218(1)	0.121(3)	6.7(7)
C(56)	−0.306(1)	0.2214(9)	0.078(2)	5.1(5)
C(61)	−0.146(1)	0.2890(8)	0.061(2)	4.1(5)
C(62)	−0.116(1)	0.318(1)	0.146(2)	5.7(6)
C(63)	−0.103(2)	0.365(1)	0.123(3)	9(1)
C(64)	−0.130(2)	0.378(2)	0.011(4)	11(1)
C(65)	−0.169(2)	0.357(2)	−0.072(4)	12(1)
C(66)	−0.169(2)	0.306(1)	−0.047(3)	7.1(7)
C(71)	−0.181(1)	0.1337(8)	−0.381(2)	3.3(4)
C(72)	−0.222(1)	0.0999(8)	−0.333(2)	4.5(5)
C(73)	−0.267(1)	0.069(1)	−0.408(2)	5.8(6)

(*continued*)

TABLE 3. (*continued*)

Atom	x	y	z	B_{eq}
C(74)	−0.266(2)	0.076(1)	−0.527(2)	6.1(6)
C(75)	−0.230(2)	0.108(1)	−0.576(3)	6.5(7)
C(76)	−0.188(1)	0.139(1)	−0.505(2)	5.4(6)
C(81)	−0.143(1)	0.2273(7)	−0.359(2)	3.5(4)
C(82)	−0.090(1)	0.250(1)	−0.422(2)	5.6(6)
C(83)	−0.105(2)	0.295(1)	−0.478(3)	6.8(7)
C(84)	−0.172(2)	0.314(1)	−0.465(3)	7.1(7)
C(85)	−0.225(2)	0.293(1)	−0.407(3)	7.4(8)
C(86)	−0.205(1)	0.254(1)	−0.354(2)	5.4(6)
F(1)	0.2316(3)	0.049(1)	0.118(2)	11.3(3)
F(2)	0.136(1)	0.0076(5)	0.083(2)	11.3(6)
F(3)	0.151(1)	0.047(1)	0.2420(5)	11.3(6)
F(1A)	0.1140	0.0202	0.1765	13(1)
F(2A)	0.1944	0.0225	0.0527	13(1)
F(3A)	0.2101	0.0616	0.2129	13(1)
F(4)	−0.3622(6)	0.1075(6)	0.042(1)	8.9(4)
F(5)	−0.294(1)	0.0583(5)	0.141(1)	8.9(4)
F(6)	−0.304(1)	0.0555(5)	−0.047(1)	8.9(4)
F(4A)	−0.2780	0.0400	0.0483	7.9(8)
F(5A)	−0.3361	0.0920	0.1374	7.9(8)
F(6A)	−0.3463	0.0893	−0.0506	7.9(8)

[a] Occupancy for F1–F3: 0.60; F1A–F3A: 0.40; F4–F6: 0.70; F4A–F6A: 0.30.

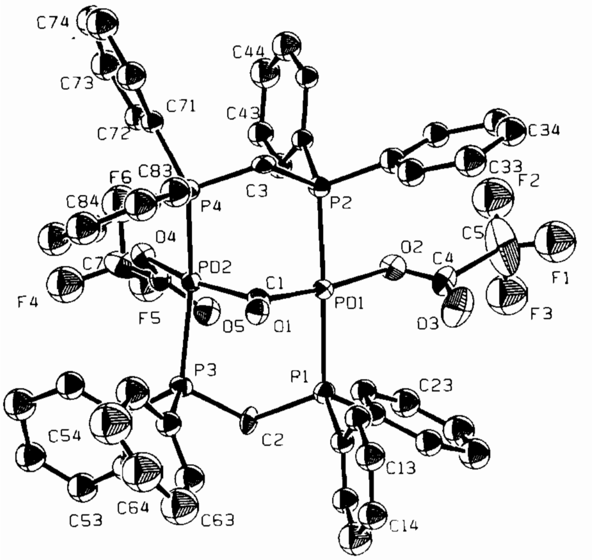

Fig. 1. ORTEP drawing of the solid state structure of $[Pd(dppm)(O_2CCF_3)]_2(\mu\text{-}CO)$. Thermal ellipsoids are shown at 30% probability and H atoms and the minor rotamer of the disordered CF_3 groups are omitted for clarity. Atom numbering for the phenyl rings follows the sequence C(x1)..C(x6) according to the pattern shown for C(x3) and C(x4). Labels are omitted for C6 and C7.

case by the fact that the dppm ligands cannot reach the positions required for a $XL_2M(\mu\text{-}CO)MLX$ stoichiometry.

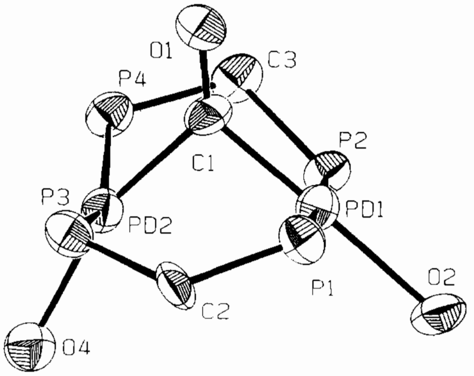

Fig. 2. View of the core of $[Pd(dppm)(O_2CCF_3)]_2(\mu\text{-}CO)$ with thermal ellipsoids at 50% probability illustrating the asymmetry of the two metal ligand environments.

Supplementary material

Tables of the hydrogen atom positional and thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, complete bond distances and angles, torsional angles, relevant least-squares planes and a listing of observed and structure factor amplitudes for the carbonyl dimer are available from the authors.

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