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Notes

Synthesis of a Novel Palladium(0) Carbonyl Complex Containing a Tridentate Phosphorus Ligand. X-ray Crystal Structure of [Pd(CO)($CH_3C(CH_2PPh_2)_3$)]

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There are a few palladium(0) complexes which are described in the literature,[1–3] especially when they simultaneously contain CO and phosphine ligands. In addition, there is a limited number of X-ray crystal structures.[2,3] However, such complexes have been recognized to be involved in numerous carbonylation reactions.[4]

Due to their low stability, these species are usually generated *in situ* by adding an excess of an appropriate phosphine ligand to a solution of either an easily reducible palladium salt such as $Pd(OAc)_2$[4] or a preformed isolable Pd(0) complex such as $Pd(dba)_2$.[5] The complex [Pd(CO)(PPh_3)$_3$], which has been prepared by Hidai[1] but not fully characterized by an X-ray structure, appears to be representative of this class of compounds. It seemed therefore interesting to us to isolate and authenticate a Pd(0) complex containing the same donor atom set as Hidai's compound. This objective was successfully achieved by using the triphosphine[6] $MeC(CH_2PPh_2)_3$ (triphos), which stabilizes the new complex [Pd(CO)(triphos)] (**1**). Actually, like all tripodal polyphosphines, triphos forms metal complexes which are generally much more stable than those containing comparable monodentate ligands. As a matter of fact, it is worth mentioning that the Ni(0)[7] and Pd(0)[2,3] derivatives [Ni(SO_2)(triphos)] and [Pd(NP_3)] (NP_3 = $N(CH_2CH_2PPh_2)_3$) have previously been synthesized.

We report here a synthetic procedure for and a single-crystal X-ray analysis of [Pd(CO)(triphos)] (**1**). This complex has been isolated and fully characterized by an X-ray crystal and molecular structure. Clearly, three phosphorus atoms and the CO ligand complete to 18 electrons the coordination sphere of the palladium(0) center which lies in a distorted tetrahedral environment.

Table I. Crystallographic Data for [Pd(CO)($CH_3C(CH_2PPh_2)_3$)]

$C_{42}H_{39}OP_3Pd$	M_r = 759.09
a = 10.222(2) Å	$Pc2_1n$ (No. 33)
b = 17.221(5) Å	λ = 0.710 69 Å
c = 20.613(3) Å	ρ_{calcd} = 1.39 g·cm^{-3}
V = 3629(1) Å^3	μ = 6.65 cm^{-1}
Z = 4	$R(F_o)^a$ = 0.0288
T = 20 °C	$R_w(F_o)^b$ = 0.0327

[a] $R(F_o) = \sum(||F_o|-|F_c||)/\sum|F_o|$. [b] $R_w(F_o) = [\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table II. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters (U(eq))

atom	x/a	y/b	z/c	U(eq),[a] Å^2
Pd(1)	0.06653(3)	–0.1322	–0.06946(2)	0.0331
P(1)	0.1230(1)	–0.12234(9)	0.04173(6)	0.0349
P(2)	–0.0322(1)	–0.00797(8)	–0.06233(6)	0.0342
P(3)	0.2695(1)	–0.07751(8)	–0.09893(6)	0.0325
C(1)	0.1583(5)	–0.0188(3)	0.0606(2)	0.0363
C(2)	0.0988(5)	0.0615(3)	–0.0412(2)	0.0361
C(3)	0.3213(5)	–0.0105(3)	–0.0341(2)	0.0387
C(4)	0.2109(5)	0.0312(3)	0.0041(2)	0.0333
C(5)	0.2716(6)	0.1047(3)	0.0345(3)	0.0415
C(11)	0.0024(7)	–0.2217(4)	–0.1136(4)	0.0572
O(11)	–0.0283(8)	–0.2736(4)	–0.1412(4)	0.0973
C(111)	0.2692(5)	–0.1730(3)	0.0717(3)	0.0429
C(112)	0.3269(6)	–0.1576(4)	0.1315(4)	0.0611
C(113)	0.4313(7)	–0.1988(6)	0.1525(5)	0.0756
C(114)	0.4779(7)	–0.2594(6)	0.1154(6)	0.0781
C(115)	0.4240(8)	–0.2759(5)	0.0575(5)	0.0759
C(116)	0.3194(6)	–0.2320(4)	0.0345(3)	0.0545
C(121)	0.0073(5)	–0.1494(3)	0.1053(2)	0.0388
C(122)	0.0014(6)	–0.1165(4)	0.1661(3)	0.0509
C(123)	–0.0858(6)	–0.1420(5)	0.2122(3)	0.0599
C(124)	–0.1677(7)	–0.2034(5)	0.1980(4)	0.0660
C(125)	–0.1625(6)	–0.2376(4)	0.1379(3)	0.0605
C(126)	–0.0762(5)	–0.2110(4)	0.0919(3)	0.0480
C(211)	–0.1569(5)	0.0085(3)	0.0005(3)	0.0410
C(212)	–0.2243(5)	–0.0550(4)	0.0229(3)	0.0483
C(213)	–0.3246(6)	–0.0463(5)	0.0691(3)	0.0591
C(214)	–0.3525(7)	0.0261(5)	0.0930(3)	0.0659
C(215)	–0.284(1)	0.0891(5)	0.0716(4)	0.0796
C(216)	–0.1876(8)	0.0799(4)	0.0262(4)	0.0665
C(221)	–0.1094(5)	0.0409(3)	–0.1315(2)	0.0379
C(222)	–0.1667(6)	–0.0031(4)	–0.1798(3)	0.0547
C(223)	–0.2250(7)	0.0321(5)	–0.2327(3)	0.0635
C(224)	–0.2284(7)	0.1116(5)	–0.2381(4)	0.0613
C(225)	–0.1716(7)	0.1552(4)	–0.1909(4)	0.0624
C(226)	–0.1140(6)	0.1212(3)	–0.1377(3)	0.0504
C(311)	0.4114(4)	–0.1399(3)	–0.1112(2)	0.0336
C(312)	0.5358(5)	–0.1238(4)	–0.0900(3)	0.0466
C(313)	0.6388(6)	–0.1744(4)	–0.1021(3)	0.0552
C(314)	0.6170(6)	–0.2420(4)	–0.1354(3)	0.0499
C(315)	0.4924(7)	–0.2590(4)	–0.1577(3)	0.0524
C(316)	0.3897(6)	–0.2089(3)	–0.1449(3)	0.0460
C(321)	0.2826(5)	–0.0146(3)	–0.1713(2)	0.0346
C(322)	0.3924(6)	0.0291(4)	–0.1842(3)	0.0515
C(323)	0.3980(7)	0.0774(4)	–0.2377(3)	0.0574
C(324)	0.2922(8)	0.0830(4)	–0.2787(3)	0.0630
C(325)	0.1839(7)	0.0403(4)	–0.2659(3)	0.0570
C(326)	0.1784(5)	–0.0091(4)	–0.2134(3)	0.0457

[a] $U(eq) = [U(11)U(22)U(33)]^{1/3}$.

Experimental Section

[$Pd(dba)_2$], where dba is dibenzylideneacetone, was prepared according to the literature procedure.[8] The triphos ligand was synthetized as previously described.[6] All the solvents were purified, distilled, and stored under nitrogen.[9]

In a 100-mL hastelloy-steel autoclave were introduced 0.575 g (1 mmol) of [$Pd(dba)_2$] and 0.625 g of triphos (1 mmol). The autoclave

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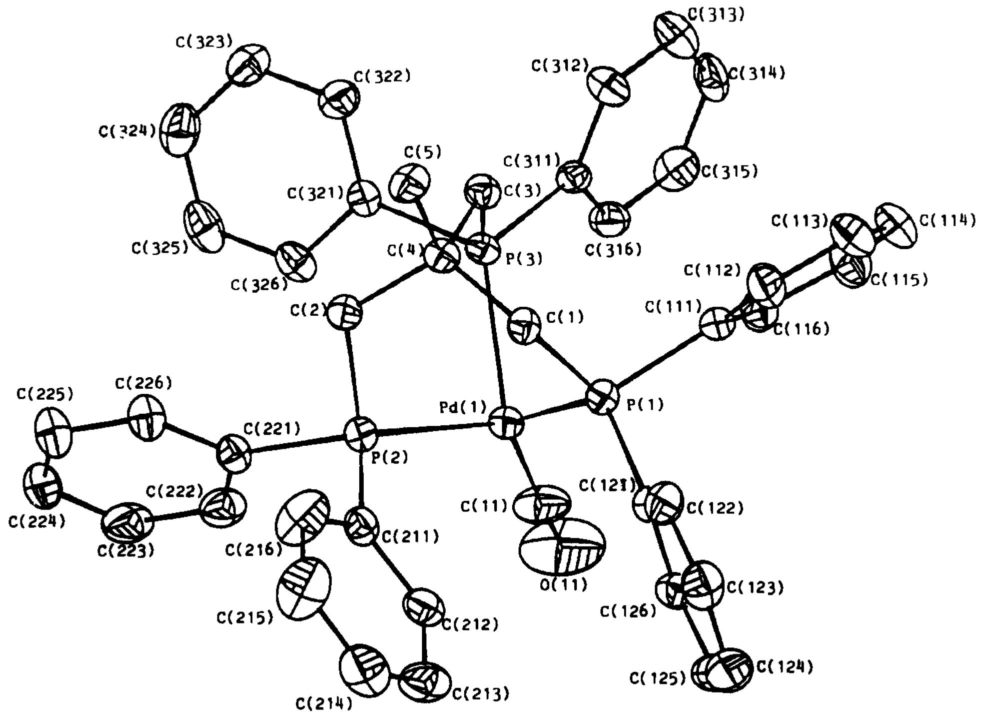

Figure 1. Perspective view of [Pd(triphos)(CO)] (**1**), showing the numbering scheme. Thermal parameters are shown at the 20% level.

Table III. Selected Bond Distances and Angles for **1**

	Distances (Å)		
Pd(1)-P(1)	2.370(1)	Pd(1)-P(3)	2.358(1)
Pd(1)-P(2)	2.370(1)	Pd(1)-C(11)	1.906(6)
	Angles (deg)		
P(2)-Pd(1)-P(1)	88.80(5)	C(11)-Pd(1)-P(1)	127.1(3)
P(3)-Pd(1)-P(1)	90.35(4)	C(11)-Pd(1)-P(2)	127.8(2)
P(3)-Pd(1)-P(2)	91.72(5)	C(11)-Pd(1)-P(3)	120.2(2)

was sealed, evacuated under vacuum, filled with 20 mL of toluene, and then pressurized with 1.6 MPa (51 mmol) of carbon monoxide. The reactor was stirred during 15 h at 100 °C and then cooled to room temperature. The solution was directly transferred through a bridge in a Schlenk tube under a CO atmosphere. The reactor was opened and dried under a CO stream. Fine yellow needles were put in a Schlenk tube, washed with toluene to remove dba, and dried *in vacuo*. The yield in isolated product was approximetely 30%. Anal. Found (calcd): C, 66.24 (66.39); H, 5.12 (5.14); P, 12.01 (12.25); Pd, 13.02 (14.01). Infrared (KBr dispersion): 1919 cm^{-1} (s, ν_{CO}).

Crystal Data

A selected crystal was set up on an automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table I. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs)[10] were applied.

Computations were performed by using CRYSTALS[11] adapted on a MicroVax II. Atomic factors for neutral Pd, P, C, O, and H atoms were taken from ref 12. Anomalous dispersion was taken into account. The position of the Pd atom was determined by Harker vector analysis of a three-dimensional Patterson map. All remaining non-hydrogen atoms were located on successive difference electron density maps. Hydrogen atoms were found on difference electron density maps, but they were introduced in the refinement as fixed contributors in calculated positions. Their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they were attached. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements with approximation to the normal matrix were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycle was $w = w'[1 - \Delta F/6\sigma(F_o)^2]^2$, where $w' = 1/\sum_1^3 A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$, where x was $F_c/F_c(\max)$.[13] Models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ having values listed in Table I. Criteria for a satisfactory complete analysis were the ratios of root-mean-square shift to standard deviation being less than 0.1 and no significant feactures in final difference maps. Atomic coordinates are given in Table II. Selected interatomic distances and angles appear in Table III.

Results and Discussion

Addition of a stoichiometric amount of triphos to a toluene solution of [Pd(dba)$_2$] in the presence of 1 atm of CO generates a yellow powder of **1**. At atmospheric pressure of CO the yield of **1** is very low, but this increases as the CO pressure is increased (*ca.* 30% at 1.6 MPa). The formation of **1** likely proceeds *via* a trigonal Pd(0) species of the formula [Pd(triphos)]. Indeed, the complex [Pd(NP$_3$)][2,3] has recently been described in the literature as containing a palladium atom coordinated by the three phosphorus atoms of the tripodal ligand in a trigonal mode. Treatment of [Pd(NP$_3$)] in benzene solution with CO (1 atm) gives the carbonyl derivative [Pd(CO)(NP$_3$)], ν_{CO} = 1930 cm^{-1}, which was assigned a tetrahedral structure on the basis of its spectroscopic features.

The solubility of **1** in most organic solvents is low so as to preclude meaningful characterization in solution. Thus, the compound was studied by solid-state techniques, particularly by IR spectroscopy in KBr pellets and by an X-ray analysis. The IR spectrum contains the typical absorptions of the triphos ligand and an intense ν_{CO} band at 1919 cm^{-1}, consistent with an electron-rich Pd(0) metal center.

Figure 1 shows the coordination sphere of palladium. The metal center is surrounded by four ligands: one CO and three

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phosphorus atoms from triphos. The geometry can be viewed as a trigonal pyramid since the three P–Pd–C(O) angles are close to 120° and the P–Pd–P angles are near 90°. When compared to those of [Pd(NP$_3$)], the Pd–P distances (see Table III) are significantly longer since they were found to be 2.370(1), 2.370(1), and 2.358(1) Å in this structure (2.298(7) Å in [Pd(NP$_3$)]). This chelating ligand is crowded so that the Pd–P distances are lengthened to remove the steric constraint. Moreover, although C(11) and the three phosphorus atoms form a tetrahedron, the palladium atom does not lie in the center and is shifted out of plane (P(1)–P(2)–P(3)) toward the CO ligand as indicated by the P–Pd–P and P–Pd–C(11) angles values (see Table III).

The only comparable structure in the literature is that of the Ni(0) complex [Ni(triphos)(SO$_2$)], whose geometry was described as a distorted tetrahedron, the S–Ni–P angles being between 117.5(1) and 126.3(1)°.[7] The larger distortion observed for the Ni complex may reasonably be due to steric factors, particularly to the repulsion between the six phenyl substituents on the phosphorus donors and the larger SO$_2$ group.

Several carbonyl-containing palladium and platinum clusters are known in the literature[14] as well as mononuclear species observed under high CO pressures. The two trinuclear palladium and platinum [M$_3$(CO)$_3$(PPh$_3$)$_3$] clusters present ν_{CO} bands at high frequencies (a$_1$ modes at 2074 and 2056 cm^{-1}). The [Pt(CO)$_2$(PPh$_3$)$_2$] complex presents two CO stretchings at 1996 and 1954 cm^{-1}; similarly the ν_{CO} band of [Pd(CO)(PPh$_3$)$_3$] appears at 1955 cm^{-1}. In all these complexes, the retrodonation on the CO ligands is largely weaker than in the derivatives [Pd(CO)(NP$_3$)] (ν_{CO} = 1930 cm^{-1}) and [Pd(CO)(triphos)] under investigation (1919 cm^{-1}). Thus, in complex **1** the three phosphorus atoms exert a great σ-donating effect on the palladium atom inducing an important retrodonation as evidenced by the unusually low CO stretching frequency.

In conclusion, as expected,[15] the use of a tripodal polydentate ligand has allowed the isolation and characterization of a metal species not easily accessible by using monophosphine ligands.

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Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen coordinates, and additional interatomic distances and angles (4 pages). Ordering information is given on any current masthead page.

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