

Table 2. Selected interatomic bond distances (Å) and angles (°) with estimated standard deviations in parentheses

W—P(1)	2.481 (3)	W—C(1)	1.993 (8)
W—P(2)	2.533 (4)	W—C(2)	1.968 (8)
W—P(3)	2.439 (3)	W—C(3)	2.018 (9)
P(2)—C(231)	1.876 (8)	P(3)—C(231)	1.845 (8)
(P—C(phenyl))	1.836 (5)	(P(1)—C(phenyl))	1.846 (5)
(C—O)	1.154 (8)	C(232)—N(1)	1.471 (11)
C(231)—C(232)	1.544 (10)	C(233)—N(1)	1.583 (17)
C(233)—C(234)	1.377 (11)	C(234)—C(235)	1.292 (26)
P(1)—W—P(2)	99.1 (2)	P(2)—W—P(3)	67.9 (2)
P(1)—W—P(3)	165.1 (1)	P(3)—W—C(2)	93.5 (3)
P(1)—W—C(2)	99.2 (3)	P(2)—C(231)—P(3)	96.6 (4)
C(1)—W—C(3)	169.2 (2)	P(3)—C(231)—C(232)	119.7 (6)
P(2)—C(231)—C(232)	120.1 (6)	W—C(3)—O(3)	175.0 (5)
W—C(1)—O(1)	172.8 (6)	C(232)—N(1)—C(233)	103.7 (9)
W—C(2)—O(2)	175.4 (5)		
C(231)—C(232)—N(1)	108.8 (7)		

1.544 (10) Å in contrast to the same distance in free vdpp 1.327 (6) Å (Schimdbaur, Herr & Riede, 1985). The angle P(2)—C(231)—P(3) is considerably reduced from 119.0 (3) to 96.6 (4)°; the C atom does not retain its planar *sp*² configuration upon addition since the deviation of this atom from the plane of its attached atoms [P(3), P(2) and C(232)] is 0.486 (6) Å. The angle at C(232) [C(231)—C(232)—N(1)], an initially *sp*² C atom, is now 108.8 (7)°, typical of an *sp*³ configuration. Steric effects are apparent for two of the carbonyl groups which are bent slightly away from the diphosphine chelate leading to a C(1)—W—C(3) angle of 169.2 (2)°.

We thank the SERC for support and the Xunta de Galicia for a scholarship (to JMV).

References

- BLAGG, A. HUTTON, A. T., SHAW, B. L. & THORNTON-PETT, M. (1985). *Inorg. Chim. Acta*, **100**, L33–L36.
- COLQUHOUN, I. J. & MCFARLANE, W. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1915–1921.
- COOPER, G. R., HASSAN, F., SHAW, B. L. & THORNTON-PETT, M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 614–616.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
- SCHIMDBAUR, M., HERR, R. & RIEDE, J. (1985). *Organometallics*, **4**, 1208–1213.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

one P atom of the chelated diphosphine and a carbonyl *trans* to the other. The W—C distances are not significantly different at 1.993 (8), 1.968 (8) and 2.018 (9) Å and are comparable to those in other tungsten(0) carbonyl complexes (Blagg, Hutton, Shaw & Thornton-Pett, 1985); the two W—P(vdpp) distances are significantly different: 2.439 (3) Å (*trans* to P) and 2.533 (4) Å (*trans* to C), and reflect the differing *trans* influence of the phosphine and carbonyl ligands. Because of the bite restriction of the diphosphine chelate the equatorial valence angles at the W atom are not equal, ranging from 67.9 (2) to 99.2 (3)°, although the W atom remains in the plane defined by the three P atoms (sum of angles 359.7°). The C—C bond distance of the diphosphine is

Acta Cryst. (1990). **C46**, 56–58

Structure of [Bis(diphenylphosphino)methane]bis(trifluoroacetato)palladium(II)

BY DONALD J. WINK

Department of Chemistry, New York University, New York, New York 10003, USA

(Received 11 January 1989; accepted 5 May 1989)

Abstract. [Pd(C₂F₃O₂)₂(C₂₅H₂₂P₂)], *M*_r = 720.86, monoclinic, *P*2₁/*n*, *a* = 10.459 (2), *b* = 13.592 (2), *c* = 20.927 (2) Å, β = 90.46 (1)°, *V* = 2974.8 (7) Å³, *Z* = 4, *D*_x = 1.61 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 7.89 cm⁻¹, *F*(000) = 1448, *T* = 296 K, *R* = 0.069 for 3195 unique data with *I* > 3σ(*I*). The refinement of the structure was complicated by disorder of one of the trifluoromethyl groups, which was treated by the introduction of two partially occupied rigid rotors. The molecular structure consists of a pseudo-square plane with remarkably short Pd—P bonds [2.219 (3)

and 2.233 (3) Å] and a narrow O—Pd—O angle [84.4 (4)°], which are ascribed to the weak *trans* influence of the trifluoroacetate and the strong *trans* influence of the phosphine.

Introduction. We have conducted the synthesis of a simple molecular palladium trifluoroacetate, [Pd(Ph₂PCH₂PPh₂)(O₂CCF₃)₂], which is of interest as a catalyst and cluster precursor, stabilized by the dppm ligand (McAuliffe, 1988; Puddephatt, 1983). This strategy has already been used for the construc-

Table 1. Fractional positional and equivalent isotropic thermal parameters

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
Pd	0-15867 (8)	0-20552 (7)	0-20242 (4)	2-71 (4)
P1	0-3644 (3)	0-2103 (3)	0-2290 (1)	2-9 (1)
P2	0-2634 (3)	0-2552 (3)	0-1157 (1)	2-8 (1)
F1*	0-031 (1)	0-1317 (6)	0-4160 (4)	6-5 (3)
F2*	-0-045 (1)	-0-0085 (3)	0-3880 (5)	7-1 (4)
F3*	-0-1419 (4)	0-1245 (6)	0-3603 (5)	7-4 (4)
F1A†	-0-135216	0-033353	0-360139	10 (1)
F2A†	-0-037872	0-040555	0-415837	13 (1)
F3A†	-0-058739	0-173560	0-388315	12 (1)
F4*	-0-275 (1)	0-1619 (6)	0-1392 (5)	8-4 (4)
F5*	-0-247 (1)	0-3172 (5)	0-1521 (4)	8-9 (4)
F6*	-0-253 (1)	0-2560 (8)	0-0576 (2)	7-0 (3)
F4A†	-0-241729	0-328186	0-093407	10 (1)
F5A†	-0-263102	0-234099	0-175059	5-7 (5)
F6A†	-0-269654	0-172907	0-080485	11 (1)
O1	0-0821 (9)	0-1757 (6)	0-2917 (4)	3-9 (4)
O2	0-087 (1)	0-0106 (9)	0-2814 (6)	8-1 (8)
O3	-0-0292 (8)	0-2172 (7)	0-1739 (4)	4-5 (5)
O4	-0-023 (1)	0-192 (1)	0-0704 (6)	9-3 (9)
C1	0-412 (1)	0-283 (1)	0-1599 (5)	3-2 (5)
C2	0-055 (1)	0-086 (1)	0-3067 (6)	4-1 (7)
C3	-0-028 (2)	0-084 (1)	0-369 (1)	7 (1)
C4	-0-074 (1)	0-213 (1)	0-1192 (7)	4-2 (7)
C5	-0-213 (1)	0-240 (1)	0-1171 (7)	4-7 (7)
C11	0-443 (1)	0-090 (1)	0-2283 (6)	3-4 (6)
C12	0-568 (1)	0-082 (1)	0-2516 (7)	4-3 (7)
C13	0-625 (2)	-0-009 (1)	0-2481 (8)	6 (1)
C14	0-558 (2)	-0-089 (1)	0-2220 (7)	5-4 (9)
C15	0-439 (2)	-0-082 (1)	0-2008 (7)	4-4 (7)
C16	0-380 (1)	0-007 (1)	0-2034 (6)	4-2 (7)
C21	0-413 (1)	0-2746 (8)	0-2993 (6)	3-3 (6)
C22	0-347 (1)	0-261 (1)	0-3545 (6)	4-4 (7)
C23	0-389 (2)	0-302 (2)	0-4098 (8)	7 (1)
C24	0-499 (2)	0-362 (2)	0-4094 (9)	8 (1)
C25	0-562 (2)	0-377 (2)	0-354 (1)	8 (1)
C26	0-519 (2)	0-333 (1)	0-2984 (7)	5-6 (8)
C31	0-210 (1)	0-367 (1)	0-0797 (6)	3-5 (6)
C32	0-144 (2)	0-436 (1)	0-1184 (7)	5-4 (8)
C33	0-106 (2)	0-526 (1)	0-0939 (9)	7 (1)
C34	0-135 (2)	0-549 (1)	0-0319 (8)	6 (1)
C35	0-195 (2)	0-484 (1)	-0-0063 (8)	7 (1)
C36	0-231 (2)	0-393 (1)	0-0173 (7)	6 (1)
C41	0-304 (1)	0-168 (1)	0-0539 (5)	3-1 (5)
C42	0-234 (1)	0-087 (1)	0-0436 (6)	3-6 (6)
C43	0-266 (2)	0-023 (1)	-0-0047 (7)	5-1 (8)
C44	0-369 (2)	0-046 (1)	-0-0438 (7)	5-3 (8)
C45	0-436 (1)	0-126 (1)	-0-0348 (6)	4-7 (7)
C46	0-409 (1)	0-186 (1)	0-0159 (6)	3-9 (6)

* Occupancy = 0-65.

† Occupancy = 0-35. Positional parameters calculated to be 30° from the other set of F atoms.

tion of trimetallic palladium and platinum clusters (Ferguson, Lloyd, Manojlovic-Muir, Muir & Puddephatt, 1986; Lloyd & Puddephatt, 1984; Manojlovic-Muir, Muir, Lloyd & Puddephatt, 1983) and we are studying the use of these lower nuclearity compounds directly in the activation of small molecules and the synthesis of heterometallic clusters. The structure contains several remarkable features that demonstrate the effect of the weakly basic trifluoroacetate ligand on structure and bonding.

Experimental. Trifluoroacetate is introduced by the reaction of palladium acetate with two equivalents of the acid in the presence of the diphosphorus ligand in dry methylene chloride. Recrystallization from CH₂Cl₂/Et₂O gave samples suitable for crystal-structure studies.

Table 2. Selected intramolecular distances and angles

Distances are in Å, angles in °. E.s.d. in the least significant figure is given in parentheses.

Pd	O3	2-055 (8)	P2	C41	1-81 (1)		
Pd	O1	2-079 (8)	P2	C1	1-84 (1)		
Pd	P1	2-219 (3)	O1	C2	1-29 (2)		
Pd	P2	2-233 (3)	O2	C2	1-21 (2)		
P1	C21	1-78 (1)	O3	C4	1-23 (2)		
P1	C1	1-82 (1)	O4	C4	1-19 (2)		
P1	C11	1-83 (1)	C2	C3	1-57 (2)		
P2	C31	1-79 (1)	C4	C5	1-51 (2)		
O3	Pd	O1	84-4 (4)	C31	P2	Pd	116-4 (4)
O3	Pd	P1	173-4 (3)	C41	P2	C1	107-0 (5)
O3	Pd	P2	102-4 (3)	C41	P2	Pd	120-0 (4)
O1	Pd	P1	99-3 (3)	C1	P2	Pd	94-1 (4)
O1	Pd	P2	170-1 (3)	C2	O1	Pd	119-4 (8)
P1	Pd	P2	73-3 (1)	C4	O3	Pd	128-1 (8)
C21	P1	C1	108-1 (6)	P1	C1	P2	92-9 (5)
C21	P1	C11	108-4 (6)	O2	C2	O1	129 (1)
C21	P1	Pd	119-5 (4)	O2	C2	C3	120 (1)
C1	P1	C11	110-5 (6)	O1	C2	C3	111 (1)
C1	P1	Pd	95-2 (4)	O4	C4	O3	130 (1)
C11	P1	Pd	114-2 (4)	O4	C4	C5	118 (1)
C31	P2	C41	109-6 (6)	O3	C4	C5	112 (1)
C31	P2	C1	107-4 (6)				

A colorless block approximately 0.25 × 0.40 × 0.30 mm in size was used for data collection on a Rigaku AFC6 diffractometer (Mo K α radiation, graphite monochromator) using ω -2 θ scans with a variable scan width $\Delta\omega = 0.85^\circ + 0.30^\circ \tan\theta$ and scan rate 32.0° min⁻¹. Lattice parameters were determined from 25 reflections in the range 32.8 < 2 θ < 41.4°. The crystal system was confirmed by a check of equivalent reflections and the space-group determination was obtained from an analysis of systematically absent reflections (*h*0*l*: *h* + *l* = 2*n* + 1; 0*k*0: *k* = 2*n* + 1) and Laue symmetry. A total of 5842 reflections, to a maximum 2 θ of 50.1°, were collected, *h* 0→18, *k* 0→20, *l* -29→23. Of 5521 unique reflections ($R_{\text{int}} = 0.035$), 3195 had $I > 3\sigma(I)$ and were used in structure solution and refinement. The structure was solved by Patterson methods (Calabrese, 1972) and the other non-H atoms were located with the *DIRDIF* program (Beurskens *et al.*, 1984) and Fourier difference techniques. H atoms were included in calculated positions with isotropic thermal parameters at 120% of the neighboring C atom. After partial refinement of the structure (isotropic thermal parameters) an idealized absorption correction was applied to the data (*DIFABS*, Walker & Stuart, 1983; transmission factors 0.89–1.11).

Full-matrix least-squares refinement of the structure, using the *TEXSAN* computing package of computer programs (Molecular Structure Corporation, 1987), was conducted on the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o/\sigma^2(F_o^2)$ (with constraints as noted) until convergence. Neutral-atom scattering factors and anomalous-dispersion effects, for inclusion in F_{calc} , were taken from *International Tables for X-ray Crystallography* (1974).

It became apparent in the initial stages of refinement that there is severe disorder associated with both CF₃ groups. It is possible to model this by simply introducing six independent F atoms with 50% occupancy at each site and allowing them to refine without constraints. Low *R* values ($\approx 5\%$) and small residual peaks ($<0.6 \text{ e } \text{Å}^{-3}$) in Fourier difference maps are thereby obtained, but the structure contains chemically unreasonable bond lengths and angles at the disordered groups. A more chemically reasonable result was obtained, and is reported here, by the introduction of rigid rotors, two per site, with fixed C—F bond lengths and angles and group occupancies adjusted manually to minimize peaks in the final difference map. Convergence, with refinement of positional and anisotropic thermal parameters for all non-H and non-F atoms, was judged from the non-halide parameters (maximum shift/e.s.d. <0.1); $R = 0.069$, $wR = 0.102$. The final difference map contains large positive and negative peaks in the region of the F atoms, but no peaks above $0.5 \text{ e } \text{Å}^{-3}$ occur elsewhere.

Atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are given in Table 1, along with occupancies for the atoms in the disordered groups.* Selected bond lengths and angles are presented in Table 2. A drawing of the molecular structure, showing only the major orientation of the disordered groups, is given in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles, torsion angles and least-squares-planes details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52202 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

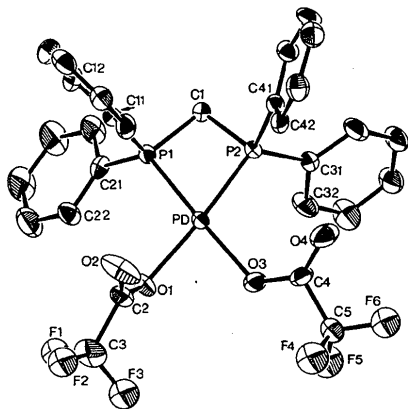


Fig. 1. ORTEP drawing (Johnson, 1965) of [Pd(dppm)(O₂CCF₃)₂] showing the major orientation of the F atoms and atomic numbering. Thermal ellipsoids are given at the 30% probability level. Atomic numbering for the phenyl rings is sequential in the pattern C(x1)...C(x6), following the scheme indicated for each ring.

Table 3. Selected angles (°) in *d*⁸ [Pd(diphosphine)X₂] complexes

Complex	P—Pd—P	X—Pd—X	Reference
[Pd(dppm)Cl ₂]	72.68 (3)	93.63 (3)	Steffen & Palenik (1976)
[Pd(dppm)(SCN) ₂]	73.33 (5)	92.97 (7)	Palenik, Mathew, Steffen & Beran (1975)
[Pd(dppm)(O ₂ CCF ₃) ₂]	73.4 (1)	84.5 (3)	This work
[Pd(dppe)Cl ₂]	85.82 (5)	94.19 (7)	Palenik <i>et al.</i> (1975)
[Pd(dppp)Cl ₂]	90.58 (5)	90.78 (5)	Palenik <i>et al.</i> (1975)

Discussion. The structure of the bidentate dppm ligand bound to palladium is similar to that in other complexes of this ligand when both P atoms are bound to a single metal. The Pd—P distances, 2.217 (3) to 2.233 (3) Å, are extraordinarily short for any kind of Pd—P bond, undoubtedly because of the poor *trans* influence of the O₂CCF₃ ligand. It is very surprising that the corresponding O—Pd—O angle is just 84.4 (4)°. One would expect the angle to be opened up, as in the case of most of the other planar four-coordinate *d*⁸ dppm complexes (McAuliffe, 1988) (Table 3). The reason for the smaller angle *trans* to the dppm in the present case is unclear, but may be due to the relatively strong *trans* influence of a phosphine ligand favoring a rigorously *trans* geometry with a simple and small σ donor.

We thank the Research Challenge Fund of New York University for financial support and are grateful to Drs John Dewan and Joseph Ferrara for helpful conversations.

References

- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., PARTHASARATHI, V., BRUINS SLOT, H. J. & HALTIWANGER, R. C. (1984). *DIRDIF*. Tech. Rep. 1984/1. Crystallography Laboratory, Univ. of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- CALABRESE, J. C. (1972). PhD Thesis, Univ. of Wisconsin, USA.
- FERGUSON, G., LLOYD, B. R., MANOJLOVIC-MUIR, LJ., MUIR, K. W. & PUDDEPHATT, R. J. (1986). *Inorg. Chem.* **25**, 4190–4197.
- International Tables for X-ray Crystallography* (1974). Vol IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- LLOYD, B. R. & PUDDEPHATT, R. J. (1984). *Inorg. Chim. Acta*, **90**, L77–L78.
- MCAULIFFE, C. A. (1988). *Comprehensive Inorganic Chemistry*, Vol. 2, edited by G. WILKINSON, R. D. GILLARD & J. A. MCCLEVERTY, pp. 989–1066. New York: Pergamon Press.
- MANOJLOVIC-MUIR, LJ., MUIR, K. W., LLOYD, B. R. & PUDDEPHATT, R. J. (1983). *J. Chem. Soc. Chem. Commun.* pp. 1336–1337.
- Molecular Structure Corporation (1987). *TEXSAN User's Manual*. Longmire Drive, College Station, Texas.
- PALENIK, G. J., MATHIEW, M., STEFFEN, W. L. & BERAN, G. (1975). *J. Am. Chem. Soc.* **97**, 1059–1066.
- PUDDEPHATT, R. J. (1983). *Chem. Soc. Rev.* **12**, 99–127.
- STEFFEN, W. L. & PALENIK, G. J. (1976). *Inorg. Chem.* **15**, 2432–2439.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.