Thermal and Electrochemical C-X Activation (X = Cl, Br, I) by the Strong Lewis Acid $Pd_3(dppm)_3(CO)^{2+}$ Cluster and Its Catalytic Applications

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Reactivity of $Pd_3(L)^+$ towards halogenated compounds : mechanisms and kinetics (L = CF_3CO_2, PF_6)

I- MECHANISMS

a. Associative pathway

$$Pd_3(L)^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd_3^{2+} + L^- \qquad (1)$$

$$Pd_3^{2+} + RX \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pd_3(RX)^{2+} \qquad (2)$$

$$Pd_3(RX)^{2+} \xrightarrow{k_3} Pd_3(X)^+ + R^+ \qquad (3)$$

When L = PF_6, $Pd_3(L)^+$ is completly dissociated in solution and the mechanism is limited to steps (2) and (3).

b. Dissociative pathway

$$Pd_3(L)^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd_3^{2+} + L^- \qquad (1)$$

$$RX \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} R^+ + X^- \qquad (4)$$

$$Pd_3^{2+} + X^- \xrightarrow{k_3'} Pd_3(X)^+ \qquad (5)$$

As above, with L = PF_6, equilibrium (1) is not taken into account.

II- KINETICS

a. Associative pathway

α. L = PF₆

Assuming the stationary state for $Pd_3(RX)^{2+}$,

$$\frac{d[Pd_3(RX)^{2+}]}{dt} = k_2[Pd_3^{2+}][RX] - k_{-2}[Pd_3(RX)^{2+}] - k_3[Pd_3(RX)^{2+}] = 0 \qquad (6)$$

from which, it can be written :

$$[Pd_3(RX)^{2+}] = \frac{k_2}{k_{-2} + k_3}[Pd_3^{2+}][RX] \qquad (7)$$

The rate of the reaction can be defined as :

$$v = -\frac{d[Pd_3^{2+}]}{dt} = k_2[Pd_3^{2+}][RX] - k_{-2}[Pd_3(RX)^{2+}] \qquad (8)$$

From (6),

$$v = k_3[Pd_3(RX)^{2+}] \qquad (9)$$

and, finally,

$$\boxed{v = k[Pd_3^{2+}][RX]} \qquad (10)$$

with $k = \frac{k_2 k_3}{k_{-2} + k_3}$

Application 1 : spectrophometric studies of the reactivity of alkyl halides

In the case where $[RX] >> [Pd_3^{2+}]$, [RX] does not vary along the period of the experiment ; at any time,

$$[RX] \approx [RX]_0 \qquad (11)$$

So,

$$v = -\frac{d[Pd_3^{2+}]}{dt} = k[Pd_3^{2+}][RX]_0 \qquad (12)$$

When integrated,

$$\frac{1}{[RX]_0}\mathrm{Ln}\frac{[Pd_3^{2+}]}{[Pd_3^{2+}]_0} = -kt \tag{13}$$

If A corresponds to the absorbance at the maximum of absorption in the spectra of Pd_3^{2+} :

$$\boxed{\frac{1}{[RX]_0}\mathrm{Ln}\frac{A}{A_0} = -kt} \tag{14}$$

Application 2 : voltammetric studies of the reactivity of acid chlorides

With stoechiometric amounts of Pd_3^{2+} and RCOCl,

$$[RCOCl] = [Pd_3^{2+}] \tag{15}$$

and, from (10),

$$v = k[Pd_3^{2+}]^2 \tag{16}$$

Then,

$$\frac{d[Pd_3^{2+}]}{[Pd_3^{2+}]^2} = -kdt \tag{17}$$

$$\frac{1}{[Pd_3^{2+}]_0} - \frac{1}{[Pd_3^{2+}]} = -kt \tag{18}$$

$$\frac{1}{[Pd_3^{2+}]_0}(1 - \frac{[Pd_3^{2+}]_0}{[Pd_3^{2+}]}) = -kt \tag{19}$$

$$\frac{1}{[Pd_3^{2+}]_0}(1 - \frac{(i_{p1})_0}{(i_{p1})}) = -kt \tag{20}$$

where i_{p1} is the symbol for the peak current at the first reduction step of Pd_3^{2+}.

β. L = $CF_3CO_2^-$

The step 1 of the associative pathway is no more neglected.

Bodenstein approximation can be applied both to $Pd_3(RX)^{2+}$ and Pd_3^{2+} :

$$\frac{d[Pd_3(RX)^{2+}]}{dt} = k_2[Pd_3^{2+}][RX] - k_{-2}[Pd_3(RX)^{2+}] - k_3[Pd_3(RX)^{2+}] = 0 \tag{6}$$

$$\frac{d[Pd_3{}^{2+}]}{dt} = k_1[Pd_3(L)^+] - k_{-1}[Pd_3{}^{2+}][L^-] - k_2[Pd_3{}^{2+}][RX] + k_{-2}[Pd_3(RX)^{2+}] = 0 \quad (21)$$

from which, it can be obtained

$$[Pd_3(RX)^{2+}] = \frac{k_2}{k_{-2} + k_3}[Pd_3{}^{2+}][RX] \quad (22)$$

$$[Pd_3{}^{2+}] = \frac{k_1[Pd_3(L)^+]}{k_{-1}[L^-] + \frac{k_2 k_3}{k_{-2} + k_3}[RX]} \quad (23)$$

The rate of the reaction is defined as :

$$v = -\frac{d[Pd_3(L)^+]}{dt} = k_1[Pd_3(L)^+] - k_{-1}[Pd_3{}^{2+}][L^-] \quad (24)$$

By considering equation (21),

$$v = k_2[Pd_3{}^{2+}][RX] - k_{-2}[Pd_3(RX)^{2+}] \quad (25)$$

and equation (6) :

$$v = k_3[Pd_3(RX)^{2+}] \quad (26)$$

Then,

$$v = \frac{k_3 k_2}{k_{-2} + k_3}[Pd_3{}^{2+}][RX] \quad (27)$$

$$v = \frac{k_3 k_2}{k_{-2} + k_3} \frac{k_1[Pd_3(L)^+][RX]}{k_{-1}[L^-] + \frac{k_2 k_3}{k_{-2} + k_3}[RX]} \quad (28)$$

and, finally,

$$\boxed{v = \frac{k_1[Pd_3(L)^+][RX]}{\frac{k_{-2} + k_3}{k_3 k_2} k_{-1}[L^-] + [RX]}} \quad (29)$$

Moreover,

$$\frac{k_{-2}+k_3}{k_3k_2}k_{-1}[L^-] >> [RX] \tag{30}$$

So,

$$\boxed{v = \frac{k_3k_2}{k_{-2}+k_3}\frac{k_1[Pd_3(L)^+][RX]}{k_{-1}[L^-]} = k*\frac{[Pd_3(L)^+][RX]}{[L^-]}} \tag{31}$$

with $$k^* = \frac{k_3k_2}{k_{-2}+k_3}\frac{k_1}{k_{-1}}$$

Application 1 : spectrophometric studies of the reactivity of alkyl halides

● If, at t = 0, $[Pd_3(L)^+]_0 = [RX]_0 = a$, equation (31) becomes

$$v = k*\frac{[Pd_3(L)^+]^2}{[L^-]} = -\frac{d[Pd_3(L)^+]}{dt} = \frac{d(a-x)}{dt} = \frac{dx}{dt} = k*\frac{(a-x)^2}{(a+x)} \tag{32}$$

where x is the concentration of cluster which has reacted, (a-x) the concentration of unreacted cluster and (a+x) the concentration of L^- (L = CF_3CO_2 ; $[L^-]_0$ = a, as the intial solid compound, $[Pd_3(dppm)_3(CO)(L)](L)$, releases one free L^- in solution).

So,

$$\frac{(a+x)}{(a-x)^2}dx = k*dt \tag{33}$$

$$\frac{(a+x)}{(a-x)^2} = \frac{a}{(a-x)^2} - \frac{(a-x)}{(a-x)^2} + \frac{a}{(a-x)^2} \tag{34}$$

$$k*\int dt = \int\frac{(a+x)}{(a-x)^2}dx = 2a\int\frac{1}{(a-x)^2}dx - \int\frac{1}{(a-x)}dx \tag{35}$$

and

$$k*t + K = \frac{2a}{(a-x)} + Ln(a-x) \tag{36}$$

$$K = 2 + Lna \tag{37}$$

$$k*t = \frac{2a}{(a-x)} + Ln\frac{(a-x)}{a} - 2 \tag{38}$$

Finally,

$$\boxed{k * t = \frac{2A_0}{A} + Ln\frac{A}{A_0} - 2 = kt} \tag{39}$$

● If, at t = 0, $[RX]_0 >> [Pd_3(L)^+]_0 = a$, equation (31) becomes

$$v \approx k * [RX]_0 \frac{[Pd_3(L)^+]}{[L^-]} \tag{40}$$

So,

$$v = k * [RX]_0 \frac{[Pd_3(L)^+]}{[L^-]} = \frac{dx}{dt} = k * [RX]_0 \frac{(a-x)}{(a+x)} \tag{41}$$

$$\frac{(a+x)}{(a-x)} dx = k * [RX]_0 dt \tag{42}$$

$$\frac{(a+x)}{(a-x)} = \frac{a}{(a-x)} - \frac{(a-x)}{(a-x)} + \frac{a}{(a-x)} \tag{43}$$

$$k * [RX]_0 \int dt = \int \frac{(a+x)}{(a-x)} dx = 2a \int \frac{1}{(a-x)} dx - \int dx \tag{44}$$

$$-k * [RX]_0 t + K = 2aLn(a-x) + x \tag{45}$$

$$K = -2aLna \tag{46}$$

$$-k * [RX]_0 t = 2aLn\frac{(a-x)}{a} + x \tag{47}$$

$$-k * [RX]_0 t = 2aLn\frac{(a-x)}{a} + a - (a-x) \tag{48}$$

$$-k * [RX]_0 t = 2aLn\frac{a-x}{a} + a(1 - \frac{a-x}{a}) \tag{49}$$

$$-k * [RX]_0 t = a(2Ln\frac{A}{A_0} + 1 - \frac{A}{A_0}) \tag{50}$$

At the end,

$$\boxed{-k*t=\frac{a}{[RX]_0}(2Ln\frac{A}{A_0}+1-\frac{A}{A_0})} \quad (51)$$

<u>b. Dissociative pathway</u> (L = PF_6 and $CF_3CO_2^-$)

Bodenstein approximation can be applied to X^- as a reactive intermediate species :

$$\frac{d[X^-]}{dt}=k_2'[RX]-k_{-2}'[R^+][X^-]-k_3'[Pd_3^{2+}][X^-]=0 \quad (52)$$

from which :

$$[X^-]=\frac{k_2'[RX]}{k_{-2}'[R^+]+k_3'[Pd_3^{2+}]} \quad (53)$$

which can be simplified to

$$[X^-]=\frac{k_2'[RX]}{k_3'[Pd_3^{2+}]} \quad (54)$$

as R^+ is a low-concentration reactive species.

The rate can be written as follows :

$$v=-\frac{d[Pd_3^{2+}]}{dt}=k_3'[Pd_3^{2+}][X^-] \quad (55)$$

and, finally,

$$v=-\frac{d[Pd_3^{2+}]}{dt}=-\frac{d[RX]}{dt}=k_2'[RX] \quad (56)$$

which, after integration, leaves

$$\boxed{Ln\frac{[RX]}{[RX]_0}=-k_2't} \quad (57)$$

As stated in the text, at any given time reaction time, $[Pd_3^{2+}]$ is lower with L = $CF_3CO_2^-$ than with PF_6. So, one can predict that (54) and, consequently, (57) applies over a shorter period of time.

Application 2 (the dissociative case is only observed within the reactivity of acid chlorides

For any experiment, it can be written :

$$[RCOCl]_0 - [RCOCl] = [cluster]_0 - [cluster] \tag{58}$$

As

$$\frac{i_{p1}}{(i_{p1})_0} = \frac{[cluster]}{[cluster]_0} \tag{59}$$

Finally, by transposing the above relations into equation 57,

$$\boxed{Ln(1-(1-\frac{i_{p1}}{(i_{p1})_0})\frac{[cluster]_0}{[RCOCl]_0}) = -k_2\text{'}t} \tag{60}$$

Table 1.

Entry	Experimental peak	Relative intensity	assignment	Calculated peak
1	659	53.8	$Pd_2(dppm)(Cl)(CO)$	660.7
2	674.7	69.2		
3	734.7	59.2	$Pd_3(dppm)_3$	736.2
4	766	39.5		
5	888.5	36.5		
6	981.6	100	$Pd_2(dppm)_2$	981.6
7	1087.5	19.2	$Pd_3(dppm)_2$	1088.1
8	1122	16.1	$Pd_3(dppm)_2(Cl)$	1123.5
9	1164	14.6		
10	1208	12.3		
11	1285.5	19		
12	1395.4	7.6	$Pd_2(dppm)_3(CO)$	1394
13	1470.4	75.4	$Pd_3(dppm)_3$	1472.4
14	1499.4	21.3	$Pd_3(dppm)_3(CO)$	1500.4
15	1585.2	13.4	$Pd_3(dppm)_3(CO)(BF_4)$	1587.2
16	1612.3	70.4	$Pd_3(dppm)_3(ClAg)$	1615.7

Table 2. Crystal data and structure refinement for $C_{76}H_{66}OP_6Pd_3$ PF_2O_2 PF_6 $3(C_7H_8)$

Empirical formula	C97 H90 F8 O3 P8 Pd3	
Formula weight	2022.65	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 10.8603(1) Å	α= 90°.
	b = 37.0351(2) Å	β= 91.24°.
	c = 21.3783(2) Å	γ = 90°.
Volume	8596.61(12) $Å^3$	
Z	4	
Density (calculated)	1.563 Mg/m^3	
Absorption coefficient	0.839 mm^{-1}	
F(000)	4104	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.20 to 27.49°.	
Index ranges	-11<=h<=14, -48<=k<=46, -27<=l<=24	
Reflections collected	34960	
Independent reflections	18307 [R(int) = 0.0282]	
Completeness to theta = 27.49°	92.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18307 / 3 / 667	
Goodness-of-fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1007	
R indices (all data)	R1 = 0.0606, wR2 = 0.1059	
Largest diff. peak and hole	1.569 and -0.647 e.$Å^{-3}$	

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $C_{76}H_{66}OP_6Pd_3$ PF_2O_2 PF_6 $3(C_7H_8)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	-161(1)	1428(1)	3469(1)	21(1)
Pd(2)	-213(1)	1397(1)	2257(1)	21(1)
Pd(3)	770(1)	866(1)	2909(1)	21(1)
P(1)	-1059(1)	1993(1)	3511(1)	22(1)
P(2)	-1057(1)	1964(1)	2102(1)	22(1)
P(3)	65(1)	1136(1)	1281(1)	21(1)
P(4)	1026(1)	493(1)	2041(1)	29(1)
P(5)	1002(1)	535(1)	3828(1)	22(1)
P(6)	155(1)	1218(1)	4485(1)	21(1)
P(7)	-2607(1)	800(1)	2917(1)	34(1)
P(8)	-2467(1)	1856(1)	7897(1)	47(1)
F(1)	-1434(3)	2004(1)	7441(1)	74(1)
F(2)	-1743(2)	2012(1)	8485(1)	69(1)
F(3)	-3172(3)	2234(1)	7841(1)	122(1)
F(4)	-3469(2)	1708(1)	8367(1)	71(1)
F(5)	-3242(3)	1719(1)	7314(1)	108(1)
F(6)	-1775(3)	1487(1)	7950(1)	82(1)
F(8)	-3936(2)	963(1)	2918(1)	51(1)
F(9)	-3014(2)	399(1)	2877(1)	62(1)
O(1)	2288(2)	1557(1)	2847(1)	33(1)
O(2)	-2047(2)	864(1)	3528(1)	46(1)
O(3)	-2050(2)	902(1)	2341(1)	52(1)
C(1)	-669(3)	2242(1)	2794(1)	26(1)
C(2)	48(3)	643(1)	1380(1)	25(1)
C(3)	105(3)	724(1)	4472(1)	22(1)
C(4)	-471(1)	2282(1)	4147(1)	23(1)
C(5)	-981(1)	2243(1)	4733(1)	25(1)
C(6)	-486(1)	2431(1)	5242(1)	31(1)
C(7)	518(1)	2657(1)	5164(1)	33(1)

C(8)	1027(1)	2696(1)	4578(1)	35(1)
C(9)	533(1)	2509(1)	4069(1)	31(1)
C(10)	-2718(1)	2025(1)	3577(1)	24(1)
C(11)	-3407(1)	1722(1)	3697(1)	38(1)
C(12)	-4692(1)	1747(1)	3754(1)	51(1)
C(13)	-5264(1)	2080(1)	3667(1)	44(1)
C(14)	-4586(1)	2388(1)	3557(1)	43(1)
C(15)	-3293(1)	2361(1)	3511(1)	38(1)
C(16)	-395(1)	2208(1)	1448(1)	25(1)
C(17)	618(1)	2439(1)	1524(1)	31(1)
C(18)	1158(1)	2585(1)	993(1)	36(1)
C(19)	703(1)	2508(1)	394(1)	39(1)
C(20)	-312(1)	2277(1)	320(1)	34(1)
C(21)	-875(1)	2130(1)	847(1)	28(1)
C(22)	-2702(1)	2029(1)	1993(1)	26(1)
C(23)	-3511(1)	1750(1)	2069(1)	39(1)
C(24)	-4796(1)	1822(1)	2051(1)	54(1)
C(25)	-5201(1)	2168(1)	1958(1)	53(1)
C(26)	-4409(1)	2446(1)	1865(1)	46(1)
C(27)	-3148(1)	2386(1)	1878(1)	39(1)
C(28)	1491(1)	1251(1)	895(1)	24(1)
C(29)	1972(1)	1033(1)	439(1)	41(1)
C(30)	3022(1)	1153(1)	114(1)	60(1)
C(31)	3543(1)	1484(1)	252(1)	56(1)
C(32)	3045(1)	1701(1)	711(1)	42(1)
C(33)	2022(1)	1582(1)	1041(1)	30(1)
C(34)	-1131(1)	1198(1)	675(1)	27(1)
C(35)	-2336(1)	1157(1)	857(1)	53(1)
C(36)	-3295(1)	1218(1)	425(1)	76(2)
C(37)	-3018(1)	1316(1)	-196(1)	63(1)
C(38)	-1830(1)	1358(1)	-363(1)	44(1)
C(39)	-880(1)	1304(1)	68(1)	34(1)
C(40)	2622(1)	511(1)	1696(1)	21(1)
C(41)	3536(1)	740(1)	1947(1)	26(1)
C(42)	4689(1)	762(1)	1665(1)	39(1)
C(43)	4929(1)	555(1)	1131(1)	43(1)

C(44)	4016(1)	325(1)	880(1)	41(1)
C(45)	2863(1)	303(1)	1162(1)	30(1)
C(40*)	2327(1)	422(1)	1756(1)	30(3)
C(41*)	3275(1)	647(1)	1999(1)	37(3)
C(42*)	4466(1)	633(1)	1745(1)	43(3)
C(43*)	4710(1)	393(1)	1248(1)	46(3)
C(44*)	3762(1)	168(1)	1005(1)	44(3)
C(45*)	2571(1)	182(1)	1259(1)	42(3)
C(46)	741(1)	20(1)	2071(1)	23(1)
C(47)	1647(1)	-246(1)	2031(1)	40(1)
C(48)	1316(1)	-610(1)	2028(1)	52(2)
C(49)	80(1)	-708(1)	2066(1)	38(1)
C(50)	-826(1)	-443(1)	2107(1)	44(1)
C(51)	-495(1)	-79(1)	2109(1)	34(1)
C(46*)	225(1)	26(1)	2105(1)	17(2)
C(47*)	1031(1)	-273(1)	2112(1)	33(3)
C(48*)	552(1)	-627(1)	2103(1)	39(3)
C(49*)	-732(1)	-682(1)	2088(1)	36(3)
C(50*)	-1539(1)	-384(1)	2082(1)	33(3)
C(51*)	-1060(1)	-30(1)	2090(1)	28(3)
C(52)	2553(1)	517(1)	4171(1)	27(1)
C(53)	2763(1)	319(1)	4728(1)	33(1)
C(54)	3925(1)	330(1)	5021(1)	41(1)
C(56)	4866(1)	532(1)	4760(1)	44(1)
C(57)	4660(1)	725(1)	4208(1)	41(1)
C(58)	3490(1)	713(1)	3912(1)	31(1)
C(59)	473(1)	66(1)	3810(1)	27(1)
C(60)	-790(1)	-3(1)	3788(1)	34(1)
C(61)	-1211(1)	-356(1)	3722(1)	39(1)
C(62)	-373(1)	-641(1)	3680(1)	44(1)
C(63)	872(1)	-572(1)	3694(1)	50(1)
C(64)	1309(1)	-218(1)	3761(1)	42(1)
C(65)	1608(1)	1361(1)	4843(1)	23(1)
C(66)	2025(1)	1709(1)	4699(1)	29(1)
C(67)	3060(1)	1849(1)	5000(1)	36(1)
C(68)	3700(1)	1640(1)	5447(1)	38(1)

C(69)	3295(1)	1294(1)	5585(1)	37(1)
C(70)	2246(1)	1157(1)	5292(1)	30(1)
C(71)	-985(1)	1313(1)	5076(1)	21(1)
C(72)	-686(1)	1493(1)	5633(1)	25(1)
C(73)	-1590(1)	1568(1)	6066(1)	30(1)
C(74)	-2815(1)	1463(1)	5940(1)	34(1)
C(75)	-3110(1)	1281(1)	5387(1)	39(1)
C(76)	-2197(1)	1208(1)	4957(1)	32(1)
C(77)	1333(3)	1413(1)	2859(1)	27(1)
C(78*)	-2400(20)	3384(6)	2078(6)	91(6)
C(79*)	-2553(10)	3331(4)	2777(5)	83(6)
C(80*)	-3720(10)	3339(3)	3000(5)	47(4)
C(81*)	-3912(10)	3289(4)	3623(5)	173(18)
C(82*)	-2936(11)	3232(3)	4023(5)	62(5)
C(83*)	-1769(11)	3224(3)	3800(5)	78(6)
C(84*)	-1577(10)	3273(4)	3177(5)	87(8)
C(78)	-3845(7)	3382(3)	3799(5)	84(3)
C(79)	-3112(4)	3352(1)	3211(2)	60(2)
C(80)	-1857(5)	3295(2)	3266(2)	79(3)
C(81)	-1157(4)	3269(1)	2736(2)	79(2)
C(82)	-1712(4)	3299(1)	2150(2)	69(2)
C(83)	-2968(4)	3357(1)	2095(2)	76(3)
C(84)	-3668(4)	3383(1)	2626(2)	62(2)

Table 4. Bond lengths [Å] and angles [°] for $C_{76}H_{66}OP_6Pd_3$ PF_2O_2 PF_6 $3(C_7H_8)$.

Pd(1)-C(77)	2.105(3)
Pd(1)-P(1)	2.3114(8)
Pd(1)-P(6)	2.3246(8)
Pd(1)-Pd(2)	2.5940(3)
Pd(1)-Pd(3)	2.6170(3)
Pd(2)-C(77)	2.095(3)
Pd(2)-P(2)	2.3137(8)
Pd(2)-P(3)	2.3252(8)
Pd(2)-Pd(3)	2.6238(3)
Pd(3)-C(77)	2.119(3)
Pd(3)-P(5)	2.3252(8)
Pd(3)-P(4)	2.3347(8)
P(1)-C(10)	1.8134(10)
P(1)-C(4)	1.8335
P(1)-C(1)	1.843(3)
P(2)-C(22)	1.8127(10)
P(2)-C(16)	1.8240
P(2)-C(1)	1.842(3)
P(3)-C(28)	1.8203
P(3)-C(34)	1.8287
P(3)-C(2)	1.837(3)
P(4)-C(40*)	1.5727(11)
P(4)-C(46)	1.7802(10)
P(4)-C(2)	1.838(3)
P(4)-C(40)	1.9002(12)
P(4)-C(46*)	1.9429(11)
P(5)-C(52)	1.8239(11)
P(5)-C(59)	1.8312
P(5)-C(3)	1.841(3)
P(6)-C(65)	1.8165(10)
P(6)-C(71)	1.8235
P(6)-C(3)	1.832(3)
P(7)-O(3)	1.434(2)

P(7)-O(2)	1.447(2)
P(7)-F(9)	1.551(2)
P(7)-F(8)	1.565(2)
P(8)-F(6)	1.563(3)
P(8)-F(5)	1.573(3)
P(8)-F(2)	1.578(3)
P(8)-F(4)	1.593(2)
P(8)-F(1)	1.600(2)
P(8)-F(3)	1.599(3)
O(1)-C(77)	1.167(4)
C(4)-C(9)	1.3889
C(4)-C(5)	1.3891
C(5)-C(6)	1.3889
C(6)-C(7)	1.3890
C(7)-C(8)	1.3889
C(8)-C(9)	1.3890
C(10)-C(11)	1.3770
C(10)-C(15)	1.3971
C(11)-C(12)	1.4070
C(12)-C(13)	1.3915
C(13)-C(14)	1.3801
C(14)-C(15)	1.4137
C(16)-C(17)	1.4012
C(16)-C(21)	1.4067
C(17)-C(18)	1.3980
C(18)-C(19)	1.3919
C(19)-C(20)	1.4024
C(20)-C(21)	1.4038
C(22)-C(23)	1.3686
C(22)-C(27)	1.4248
C(23)-C(24)	1.4211
C(24)-C(25)	1.3658
C(25)-C(26)	1.3602
C(26)-C(27)	1.3878
C(28)-C(29)	1.3787
C(28)-C(33)	1.3878

C(29)-C(30)	1.4196
C(30)-C(31)	1.3790
C(31)-C(32)	1.3876
C(32)-C(33)	1.4005
C(34)-C(35)	1.3823
C(34)-C(39)	1.3892
C(35)-C(36)	1.3956
C(36)-C(37)	1.4153
C(37)-C(38)	1.3551
C(38)-C(39)	1.3817
C(40)-C(45)	1.4044
C(40)-C(41)	1.4045
C(41)-C(42)	1.4045
C(42)-C(43)	1.4044
C(43)-C(44)	1.4044
C(44)-C(45)	1.4042
C(40*)-C(45*)	1.4149
C(40*)-C(41*)	1.4149
C(41*)-C(42*)	1.4150
C(42*)-C(43*)	1.4149
C(43*)-C(44*)	1.4150
C(44*)-C(45*)	1.4149
C(46)-C(51)	1.3952
C(46)-C(47)	1.3953
C(47)-C(48)	1.3952
C(48)-C(49)	1.3952
C(49)-C(50)	1.3951
C(50)-C(51)	1.3953
C(46*)-C(51*)	1.4099
C(46*)-C(47*)	1.4099
C(47*)-C(48*)	1.4098
C(48*)-C(49*)	1.4099
C(49*)-C(50*)	1.4100
C(50*)-C(51*)	1.4098
C(52)-C(58)	1.3780
C(52)-C(53)	1.4106

C(53)-C(54)	1.3970
C(54)-C(56)	1.3920
C(56)-C(57)	1.3931
C(57)-C(58)	1.4085
C(59)-C(64)	1.3931
C(59)-C(60)	1.3948
C(60)-C(61)	1.3911
C(61)-C(62)	1.3979
C(62)-C(63)	1.3758
C(63)-C(64)	1.4004
C(65)-C(70)	1.3951
C(65)-C(66)	1.4015
C(66)-C(67)	1.3839
C(67)-C(68)	1.4039
C(68)-C(69)	1.3909
C(69)-C(70)	1.3836
C(71)-C(76)	1.3909
C(71)-C(72)	1.3962
C(72)-C(73)	1.3916
C(73)-C(74)	1.4061
C(74)-C(75)	1.3939
C(75)-C(76)	1.3922
C(78*)-C(79*)	1.522(12)
C(79*)-C(80*)	1.364(7)
C(79*)-C(84*)	1.364(7)
C(80*)-C(81*)	1.364(7)
C(81*)-C(82*)	1.364(7)
C(82*)-C(83*)	1.364(7)
C(83*)-C(84*)	1.364(7)
C(78)-C(79)	1.507(10)
C(79)-C(80)	1.382(3)
C(79)-C(84)	1.382(3)
C(80)-C(81)	1.382(3)
C(81)-C(82)	1.382(3)
C(82)-C(83)	1.382(3)
C(83)-C(84)	1.382(3)

C(77)-Pd(1)-P(1)	112.33(8)
C(77)-Pd(1)-P(6)	118.00(9)
P(1)-Pd(1)-P(6)	108.77(3)
C(77)-Pd(1)-Pd(2)	51.68(9)
P(1)-Pd(1)-Pd(2)	94.51(2)
P(6)-Pd(1)-Pd(2)	156.57(2)
C(77)-Pd(1)-Pd(3)	51.96(8)
P(1)-Pd(1)-Pd(3)	154.90(2)
P(6)-Pd(1)-Pd(3)	96.32(2)
Pd(2)-Pd(1)-Pd(3)	60.464(8)
C(77)-Pd(2)-P(2)	111.83(8)
C(77)-Pd(2)-P(3)	116.42(9)
P(2)-Pd(2)-P(3)	107.93(3)
C(77)-Pd(2)-Pd(1)	52.03(9)
P(2)-Pd(2)-Pd(1)	95.86(2)
P(3)-Pd(2)-Pd(1)	156.20(2)
C(77)-Pd(2)-Pd(3)	51.91(8)
P(2)-Pd(2)-Pd(3)	155.79(2)
P(3)-Pd(2)-Pd(3)	96.08(2)
Pd(1)-Pd(2)-Pd(3)	60.202(8)
C(77)-Pd(3)-P(5)	121.35(8)
C(77)-Pd(3)-P(4)	119.12(8)
P(5)-Pd(3)-P(4)	110.27(3)
C(77)-Pd(3)-Pd(1)	51.47(9)
P(5)-Pd(3)-Pd(1)	93.93(2)
P(4)-Pd(3)-Pd(1)	152.73(2)
C(77)-Pd(3)-Pd(2)	51.07(9)
P(5)-Pd(3)-Pd(2)	151.57(2)
P(4)-Pd(3)-Pd(2)	94.36(2)
Pd(1)-Pd(3)-Pd(2)	59.334(8)
C(10)-P(1)-C(4)	103.6
C(10)-P(1)-C(1)	106.24(11)
C(4)-P(1)-C(1)	104.05(10)
C(10)-P(1)-Pd(1)	118.80(4)
C(4)-P(1)-Pd(1)	114.58(4)
C(1)-P(1)-Pd(1)	108.35(10)

C(22)-P(2)-C(16)	103.9
C(22)-P(2)-C(1)	103.70(11)
C(16)-P(2)-C(1)	104.70(10)
C(22)-P(2)-Pd(2)	121.66(5)
C(16)-P(2)-Pd(2)	113.38(4)
C(1)-P(2)-Pd(2)	107.96(10)
C(28)-P(3)-C(34)	104.3
C(28)-P(3)-C(2)	107.17(11)
C(34)-P(3)-C(2)	101.42(10)
C(28)-P(3)-Pd(2)	115.97(4)
C(34)-P(3)-Pd(2)	118.59(4)
C(2)-P(3)-Pd(2)	107.92(9)
C(40*)-P(4)-C(46)	90.5
C(40*)-P(4)-C(2)	105.11(11)
C(46)-P(4)-C(2)	103.20(10)
C(40*)-P(4)-C(40)	11.6
C(46)-P(4)-C(40)	102.1
C(2)-P(4)-C(40)	101.95(10)
C(40*)-P(4)-C(46*)	106.70(5)
C(46)-P(4)-C(46*)	16.8
C(2)-P(4)-C(46*)	94.14(10)
C(40)-P(4)-C(46*)	118.2
C(40*)-P(4)-Pd(3)	121.99(5)
C(46)-P(4)-Pd(3)	122.03(4)
C(2)-P(4)-Pd(3)	110.79(10)
C(40)-P(4)-Pd(3)	114.41(5)
C(46*)-P(4)-Pd(3)	114.22(4)
C(52)-P(5)-C(59)	105.1
C(52)-P(5)-C(3)	102.26(11)
C(59)-P(5)-C(3)	101.82(10)
C(52)-P(5)-Pd(3)	116.25(4)
C(59)-P(5)-Pd(3)	117.03(4)
C(3)-P(5)-Pd(3)	112.46(10)
C(65)-P(6)-C(71)	104.4
C(65)-P(6)-C(3)	108.81(11)
C(71)-P(6)-C(3)	100.57(9)

C(65)-P(6)-Pd(1)	113.90(4)
C(71)-P(6)-Pd(1)	119.59(4)
C(3)-P(6)-Pd(1)	108.48(9)
O(3)-P(7)-O(2)	123.66(17)
O(3)-P(7)-F(9)	109.20(15)
O(2)-P(7)-F(9)	108.70(15)
O(3)-P(7)-F(8)	107.85(15)
O(2)-P(7)-F(8)	107.78(14)
F(9)-P(7)-F(8)	96.15(13)
F(6)-P(8)-F(5)	91.41(18)
F(6)-P(8)-F(2)	91.90(16)
F(5)-P(8)-F(2)	176.61(18)
F(6)-P(8)-F(4)	89.25(15)
F(5)-P(8)-F(4)	91.60(15)
F(2)-P(8)-F(4)	87.72(13)
F(6)-P(8)-F(1)	90.06(14)
F(5)-P(8)-F(1)	89.79(15)
F(2)-P(8)-F(1)	90.93(15)
F(4)-P(8)-F(1)	178.46(16)
F(6)-P(8)-F(3)	179.81(19)
F(5)-P(8)-F(3)	88.55(19)
F(2)-P(8)-F(3)	88.14(17)
F(4)-P(8)-F(3)	90.95(16)
F(1)-P(8)-F(3)	89.75(16)
P(2)-C(1)-P(1)	109.70(16)
P(4)-C(2)-P(3)	112.51(16)
P(6)-C(3)-P(5)	112.01(15)
C(9)-C(4)-C(5)	120.0
C(9)-C(4)-P(1)	121.7
C(5)-C(4)-P(1)	118.0
C(6)-C(5)-C(4)	120.0
C(5)-C(6)-C(7)	120.0
C(8)-C(7)-C(6)	120.0
C(7)-C(8)-C(9)	120.0
C(4)-C(9)-C(8)	120.0
C(11)-C(10)-C(15)	120.1

C(11)-C(10)-P(1)	120.5
C(15)-C(10)-P(1)	119.4
C(10)-C(11)-C(12)	120.4
C(13)-C(12)-C(11)	119.2
C(14)-C(13)-C(12)	121.1
C(13)-C(14)-C(15)	119.2
C(10)-C(15)-C(14)	119.9
C(17)-C(16)-C(21)	120.4
C(17)-C(16)-P(2)	122.3
C(21)-C(16)-P(2)	117.0
C(18)-C(17)-C(16)	119.0
C(19)-C(18)-C(17)	121.3
C(18)-C(19)-C(20)	119.5
C(19)-C(20)-C(21)	120.1
C(20)-C(21)-C(16)	119.6
C(23)-C(22)-C(27)	120.2
C(23)-C(22)-P(2)	121.2
C(27)-C(22)-P(2)	118.4
C(22)-C(23)-C(24)	119.2
C(25)-C(24)-C(23)	119.5
C(26)-C(25)-C(24)	121.9
C(25)-C(26)-C(27)	120.1
C(26)-C(27)-C(22)	119.0
C(29)-C(28)-C(33)	121.0
C(29)-C(28)-P(3)	121.5
C(33)-C(28)-P(3)	117.3
C(28)-C(29)-C(30)	118.9
C(31)-C(30)-C(29)	120.3
C(30)-C(31)-C(32)	120.2
C(31)-C(32)-C(33)	119.9
C(28)-C(33)-C(32)	119.7
C(35)-C(34)-C(39)	120.1
C(35)-C(34)-P(3)	116.7
C(39)-C(34)-P(3)	123.1
C(34)-C(35)-C(36)	119.5
C(35)-C(36)-C(37)	119.5

C(38)-C(37)-C(36)	119.9
C(37)-C(38)-C(39)	120.7
C(38)-C(39)-C(34)	120.3
C(45)-C(40)-C(41)	120.0
C(45)-C(40)-P(4)	118.9
C(41)-C(40)-P(4)	121.0
C(40)-C(41)-C(42)	120.0
C(43)-C(42)-C(41)	120.0
C(44)-C(43)-C(42)	120.0
C(45)-C(44)-C(43)	120.0
C(44)-C(45)-C(40)	120.0
C(45*)-C(40*)-C(41*)	120.0
C(45*)-C(40*)-P(4)	125.4
C(41*)-C(40*)-P(4)	114.3
C(40*)-C(41*)-C(42*)	120.0
C(43*)-C(42*)-C(41*)	120.0
C(42*)-C(43*)-C(44*)	120.0
C(45*)-C(44*)-C(43*)	120.0
C(40*)-C(45*)-C(44*)	120.0
C(51)-C(46)-C(47)	120.0
C(51)-C(46)-P(4)	115.3
C(47)-C(46)-P(4)	124.6
C(48)-C(47)-C(46)	120.0
C(47)-C(48)-C(49)	120.0
C(50)-C(49)-C(48)	120.0
C(49)-C(50)-C(51)	120.0
C(46)-C(51)-C(50)	120.0
C(51*)-C(46*)-C(47*)	120.0
C(51*)-C(46*)-P(4)	124.9
C(47*)-C(46*)-P(4)	114.8
C(48*)-C(47*)-C(46*)	120.0
C(47*)-C(48*)-C(49*)	120.0
C(48*)-C(49*)-C(50*)	120.0
C(51*)-C(50*)-C(49*)	120.0
C(50*)-C(51*)-C(46*)	120.0
C(58)-C(52)-C(53)	120.4

C(58)-C(52)-P(5)	120.1
C(53)-C(52)-P(5)	119.3
C(54)-C(53)-C(52)	119.4
C(56)-C(54)-C(53)	120.0
C(54)-C(56)-C(57)	120.6
C(56)-C(57)-C(58)	119.5
C(52)-C(58)-C(57)	120.1
C(64)-C(59)-C(60)	120.1
C(64)-C(59)-P(5)	120.8
C(60)-C(59)-P(5)	118.8
C(61)-C(60)-C(59)	119.7
C(60)-C(61)-C(62)	120.3
C(63)-C(62)-C(61)	119.8
C(62)-C(63)-C(64)	120.6
C(59)-C(64)-C(63)	119.5
C(70)-C(65)-C(66)	119.3
C(70)-C(65)-P(6)	123.1
C(66)-C(65)-P(6)	117.2
C(67)-C(66)-C(65)	120.6
C(66)-C(67)-C(68)	119.6
C(69)-C(68)-C(67)	119.9
C(70)-C(69)-C(68)	120.2
C(69)-C(70)-C(65)	120.4
C(76)-C(71)-C(72)	119.4
C(76)-C(71)-P(6)	118.2
C(72)-C(71)-P(6)	122.3
C(73)-C(72)-C(71)	120.5
C(72)-C(73)-C(74)	119.7
C(75)-C(74)-C(73)	119.7
C(76)-C(75)-C(74)	120.0
C(71)-C(76)-C(75)	120.6
O(1)-C(77)-Pd(2)	134.5(2)
O(1)-C(77)-Pd(1)	134.3(2)
Pd(2)-C(77)-Pd(1)	76.29(12)
O(1)-C(77)-Pd(3)	134.1(3)
Pd(2)-C(77)-Pd(3)	77.02(12)

Pd(1)-C(77)-Pd(3)	76.56(11)
C(80*)-C(79*)-C(84*)	120.0
C(80*)-C(79*)-C(78*)	117.7(9)
C(84*)-C(79*)-C(78*)	122.3(9)
C(81*)-C(80*)-C(79*)	120.0
C(80*)-C(81*)-C(82*)	120.0
C(83*)-C(82*)-C(81*)	120.0
C(84*)-C(83*)-C(82*)	120.0
C(83*)-C(84*)-C(79*)	120.0
C(80)-C(79)-C(84)	120.0
C(80)-C(79)-C(78)	118.6(4)
C(84)-C(79)-C(78)	121.4(4)
C(79)-C(80)-C(81)	120.0
C(80)-C(81)-C(82)	120.0
C(81)-C(82)-C(83)	120.0
C(84)-C(83)-C(82)	120.0
C(83)-C(84)-C(79)	120.0

Symmetry transformations used to generate equivalent atoms:

X-ray structure for $C_{76}H_{66}OP_6Pd_3$ PF_2O_2 PF_6 $3(C_7H_8)$.

Intensity data were collected on a Nonius Kappa CCD at 110 K. The structure was solved by the heavy atom method (SHELXS-97) and refined by full-matrix least-squares methods (SHELXL-97)[1] with the aid of the WINGX program.[2] Except for carbon atoms belonging to two disordered phenyl groups and those from a disordered toluene solvate molecule, non-hydrogen atoms were anisotropically refined. Hydrogen atoms belonging to the complex were included in calculated positions and refined in a riding model with their temperature factors fixed at 1.2 times the Ueq of their parent atoms. The two phenyl groups attached to the P(4) phosphorus atom were found to be disordered over two positions, the occupancies of the pairs of phenyl groups converged to m1= 0.70 and m2=1-m1. These disordered phenyl groups were left isotropic. One toluene solvate molecule was also found to be disordered over two positions (occupancies m1*= 0.71 and m2*=1-m1*). The toluene molecule with the lower occupancy was left isotropic and the methyl hydrogen atoms of these toluene molecules were not located.

Furthermore two additional toluene solvate molecules were located in the Fourier map. These molecules were badly disordered and any tentative to

refined a model failed thus a BYPASS[3] procedure, implemented in the PLATON program,[4] was used to handle this problem. In this procedure the contribution of the solvent (2 toluene molecules) electron density is subtracted to the structure factor. The refinement was done with this solvent-corrected data set. Crystallographic data and selected geometrical parameters for all compounds are reported in Table 1 and Table 2 respectively.

(1) G. M. Sheldrik, SHELX97 (Includes SHELXS-97, SHELXL-97), Release 97-2, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1998.

(2) Farrugia, J. L. *J. Appl. Crystallogr.*, **1999**, *32*, 837.

(3) Van Der Sluis, P.; Spek, A. L. *Acta Crystallogr. Sect. A Found. Crystallogr.* **1990**, *46*, 194.

(4) Spek, A. L. *Acta Crystallogr. Sect. A Found. Crystallogr.* **1990**, *46*, C34.