Triply Bridging Alkyne Complexes of Palladium

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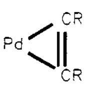
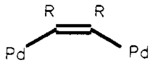
The first triply bridging alkyne complexes of palladium have been prepared and characterized. Reaction of the alkynes RCCR (R = CO_2Me or CO_2Et) with $[M_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ gives $[M_3(\mu_3\text{-}\eta^2\text{-}RCCR)(O_2CCF_3)(\mu\text{-dppm})_3]^+$, M = Pd or Pt, and the structure of one derivative, $[Pd_3(\mu_3\text{-}\eta^2\text{-}RCCR)(O_2CCF_3)(\mu\text{-dppm})_3]^+$, R = CO_2Me, has been determined crystallographically. The trifluoroacetate ligand in the alkyne complexes is easily replaced by chloride to give $[M_3(\mu_3\text{-}\eta^2\text{-}RCCR)Cl(\mu\text{-dppm})_3]^+$. NMR studies show that the alkyne is rigidly bonded in all the palladium and platinum complexes. For palladium, but not for platinum, the electronegative alkyne substituents are necessary prerequisites to the isolation of stable alkyne complexes.

Introduction

The chemistry of alkynes with palladium complexes is extremely rich and useful, but few alkyne complexes have been isolated. Known complexes include mononuclear and binuclear alkyne complexes with structural types A–C[1-4]



A



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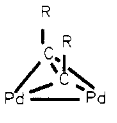

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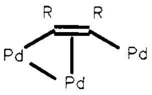
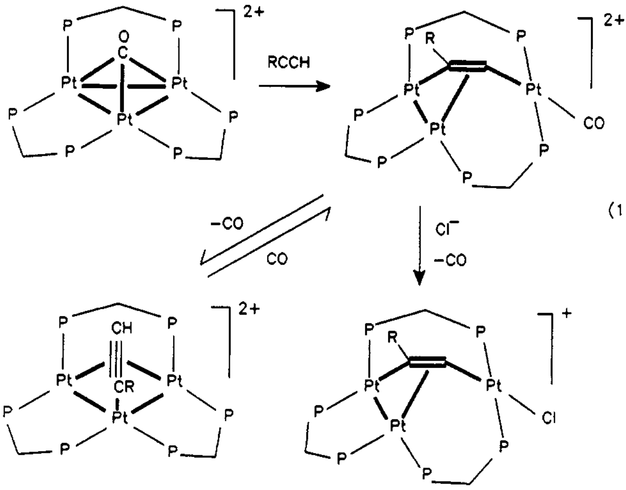


D

as well as alkynyl and μ-alkynediyl complexes.[5] However, there are no higher nuclearity palladium alkyne complexes, and hence no triply bridging alkyne complexes are known.[1-5] This article reports the first trinuclear palladium alkyne complexes, which have the $Pd_3(\mu_3\text{-}\eta^2\text{-}RCCR)$ structural type D. Similar platinum complexes have been reported earlier,[6] but the palladium analogs with simple alkynes (RCCR with R = H, alkyl, aryl) could not be prepared and characterized at that time. However, the complexes having $M_3(\mu^3\text{-}\eta^2\text{-}RCCR)$ groups with R = CO_2Me or CO_2Et are more stable and have now been characterized for both M = Pd and Pt.

Results and Discussion

The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ reacts easily with alkynes such as HCCH or MeCCH to give the 46-electron complex $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)(CO)(\mu\text{-dppm})_3]^{2+}$ and then, by reversible loss of the carbonyl ligand, the 44-electron cluster $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)(\mu\text{-dppm})_3]^{2+}$ or, by displacement of carbonyl, the 46-electron cluster $[Pt_3Cl(\mu_3\text{-}\eta^2\text{-}RCCH)(\mu\text{-dppm})_3]^{2+}$ (eq 1).[6] However, attempts to prepare similar tripalladium complexes from $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ have been unsuccessful since rapid breakup of the cluster occurs instead. This observation is consistent with the greater difficulty of preparing other alkyne complexes of palladium compared to platinum.[1-4]



(1)

Since most known alkyne complexes of palladium carry electronegative substituents on the alkyne,[1-4] it seemed likely that the reactions of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1a**) with acetylenedicarboxylic esters might give more stable alkyne complexes. It should be noted that in the trifluoroacetate salt of **1a** one trifluoroacetate is bound weakly to the Pd_3 triangle, and so the complex may be more properly represented as $[Pd_3(O_2CCF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3](CF_3CO_2)$, whereas **1a** is certainly the correct representation of the hexafluorophosphate salt; for simplicity, both will be represented by **1a**.[6,7] Reaction of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3](CF_3CO_2)_2$ (**1a**), dppm = $Ph_2PCH_2PPh_2$,[5] with the alkynes RCCR, R = CO_2Me or CO_2Et, followed by treatment with NH_4PF_6, gave the new complexes $[Pd_3(\mu_3\text{-}\eta^2\text{-}RCCR)(O_2CCF_3)(\mu\text{-dppm})_3][PF_6]$ (**2a** and **2b**) in >90% yield (Scheme I).

These complexes were stable to air at room temperature, and so it seems that electronegative groups R are important in stabilizing **2**. The trifluoroacetate group in **2a** or **2b** is easily displaced by chloride ions to give the corresponding derivative **3a** or **3b**. The platinum analogs **2c** and **3c** can also be prepared and are related to the known compounds $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)Cl(\mu\text{-dppm})_3][PF_6]$ (**4**), R = H, Me, OEt, of eq 1.[6] Our inability to prepare palladium analogs of **4** shows clearly that the μ_3-alkyne complexes of platinum are much more robust than those of palladium. One other significant difference between the palladium complexes of Scheme I, and the platinum alkyne clusters of eq 1 is that no complexes with a terminal carbonyl could

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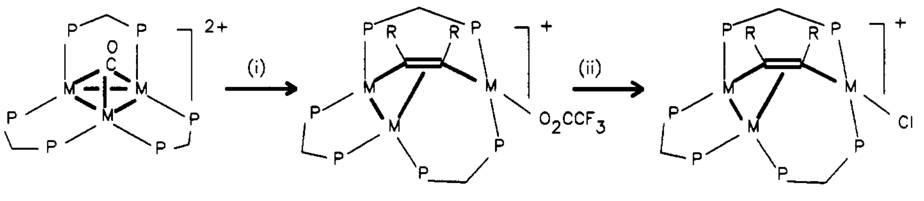
Scheme I



1a, M = Pd
1b, M = Pt

2a, M = Pd, R = CO_2Me
2b, M = Pd, R = CO_2Et
2c, M = Pt, R = CO_2Me
2d, M = Pt, R = CO_2Et

3a, M = Pd, R = CO_2Me
3b, M = Pd, R = CO_2Et
3c, M = Pt, R = CO_2Me
3d, M = Pt, R = CO_2Et

(i) RCCR, -CO. (ii) Cl^-, - $CF_3CO_2^-$

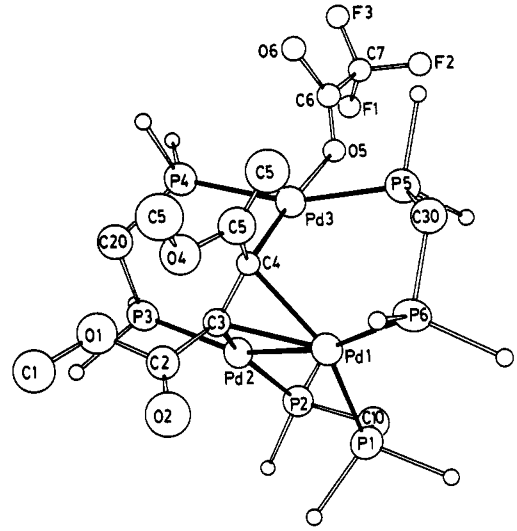


Figure 1. View of the structure of the cation **2a** with the atomic numbering scheme.

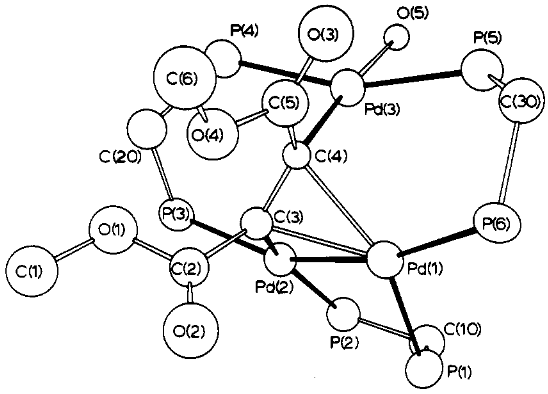


Figure 2. View of the inner coordination sphere of the cation **2a**. For clarity, the phenyl groups of the dppm ligands and all but the ligated oxygen atom of the trifluoroacetate ligand have been omitted.

be identified as intermediates when M = Pd. In one attempt to detect such a species, the isotopically labeled cluster $[Pd_3(\mu_3\text{-}^{13}CO)(\mu\text{-dppm})_3]^{2+}$ was treated with MeO_2CCCCO_2Me but subsequent monitoring by ^{13}C NMR spectroscopy showed only peaks due to the starting material and free ^{13}CO. It is also noteworthy that reaction of **1** as the hexafluorophosphate salts with MeO_2CCCCO_2Me gave complexes which gave NMR spectra very similar to those of complexes **2** and which did not contain CO. It seems likely that a solvent molecule (acetone) coordinates to give the products $[M_3(\mu_3\text{-}\eta^2\text{-}RCCR)(\text{acetone})(\mu\text{-dppm})_3]^{2+}$ in these cases. Otherwise, if no additional ligand were present, the complexes would be 44-electron clusters and would be expected to have 2-fold symmetry.[6] Complex **2a** was inert to further reaction with CO, H_2, HCCH, or MeO_2CCCCO_2Me at room temperature.

The structure of $\mathbf{2a}[PF_6]\cdot MeOH\cdot H_2O$ has been determined crystallographically and views of the cation are shown in Figures 1 and 2. Selected bond distances and angles are given in Table I. There is only one Pd–Pd bond [Pd(1)–Pd(2) = 2.673 (3) Å], the other Pd–Pd distances being too long for any bonding to be present [Pd(1)–Pd(3) = 3.188 (3) Å, Pd(2)–Pd(3) = 3.329 (3) Å]; this is to be expected for a 46-electron cluster if each palladium atom is to have a 16-electron configuration.[6] The RCCR group is σ-bonded to Pd(2) and Pd(3) [Pd(2)–C(3) = 1.99 (3) Å, Pd(3)–C(4) = 2.07 (2) Å] and π-bonded to Pd(1) [Pd(1)–C(3) = 2.16 (3) Å, Pd(1)–C(4) = 2.21 (3) Å] and hence acts as a 4-electron ligand. A consequence of this bonding mode is that molecules **2** and **3** have low symmetry and the two R, three metal (Pd or Pt), and six P atoms are all nonequivalent. The trifluoroacetate group is present as a terminal ligand bonded to Pd(3). This is clearly shown by the structure determination, but the CF_3CO_2 group was disordered and only the oxygen donor atom is shown in Figure 2. The structure may be compared with those of $[Pt_3Cl(HCCH)(\mu\text{-dppm})_3]^+$ and $[Pt_3(CO)(EtOCCH)(\mu\text{-dppm})_3]^{2+}$, and selected data are given in Table II.[6] While most of the bond distances and angles involving the M_3C_2 core atoms (M = Pd or Pt) are similar, it is noted that the dihedral angle M(2)–C(3)–C(4)–M(3), which gives a measure of the distortion of these atoms from planarity and hence deviation from the ideal $M_3(\mu_3\text{-}\eta^2\text{-}RCCR)$ geometry, is considerably less [–19 (3)°] for **2a** than for **4** or **5** [–27.4 (5) or –30 (1)°, respectively].

The absence of symmetry in the clusters is maintained in solution, as is easily demonstrated by NMR spectroscopy. Thus each of the complexes **2** and **3** gave six ^{31}P resonances for the nonequivalent dppm phosphorus atoms (partial overlap of peaks occurred in several cases). In all cases, separate resonances were observed in the ^1H NMR spectra due to the nonequivalent substituents R (Me or Et) and, when R = Et, the OCH_2 protons were diastereotopic and gave rise to well-defined "AB" spectra. For complex **2c**, the ^{195}Pt NMR spectrum was recorded and gave three well-resolved resonances due to the nonequivalent platinum atoms (Figure 3). The spectra were unchanged between –80 and +60 °C. Typical data are listed

Table I. Selected Bond Distances (Å) and Angles (deg)

Distances			
Pd(2)–Pd(1)	2.637 (3)	Pd(1)–Pd(3)	3.188 (3)
Pd(2)–Pd(3)	3.329 (3)	P(1)–Pd(1)	2.308 (9)
P(6)–Pd(1)	2.363 (8)	C(3)–Pd(1)	2.156 (26)
C(4)–Pd(1)	2.205 (25)	Pd(1)–Pd(2)	2.637 (3)
P(2)–Pd(2)	2.341 (8)	P(3)–Pd(2)	2.296 (9)
C(3)–Pd(2)	1.987 (26)	P(4)–Pd(3)	2.363 (9)
P(5)–Pd(3)	2.350 (9)	C(4)–Pd(3)	2.070 (24)
O(5)–Pd(3)	2.220 (16)	C(10)–P(1)	1.814 (30)
C(111)–P(1)	1.811 (26)	C(121)–P(1)	1.803 (23)
C(10)–P(2)	1.834 (29)	C(211)–P(2)	1.811 (25)
C(221)–P(2)	1.805 (25)	C(20)–P(3)	1.824 (30)
C(311)–P(3)	1.829 (23)	C(321)–P(3)	1.821 (28)
C(20)–P(4)	1.859 (29)	C(411)–P(4)	1.801 (27)
C(421)–P(4)	1.839 (24)	C(30)–P(5)	1.788 (28)
C(511)–P(5)	1.792 (22)	C(521)–P(5)	1.794 (25)
C(30)–P(6)	1.887 (28)	C(611)–P(6)	1.819 (24)
C(621)–P(6)	1.826 (23)	O(1)–C(1)	1.517 (32)
C(2)–O(1)	1.383 (31)	C(2)–O(2)	1.163 (30)
C(3)–C(2)	1.517 (35)	C(4)–C(3)	1.346 (31)
C(5)–C(4)	1.524 (38)	O(3)–C(5)	1.185 (31)
O(4)–C(5)	1.290 (32)	C(6)–O(4)	1.419 (33)
C(7)–O(5)	1.202 (33)	C(7)–O(6)	1.387 (37)
C(8)–C(7)	1.502 (9)		
Angles			
P(1)–Pd(1)–Pd(2)	81.8 (2)	P(6)–Pd(1)–Pd(2)	166.8 (2)
P(6)–Pd(1)–P(1)	109.4 (3)	C(3)–Pd(1)–Pd(2)	47.7 (7)
C(3)–Pd(1)–P(1)	120.8 (7)	C(3)–Pd(1)–P(6)	125.7 (7)
C(4)–Pd(1)–Pd(2)	72.3 (6)	C(4)–Pd(1)–P(1)	153.9 (7)
C(4)–Pd(1)–P(6)	96.6 (7)	C(4)–Pd(1)–C(3)	35.9 (8)
P(2)–Pd(2)–Pd(1)	101.9 (2)	P(3)–Pd(2)–Pd(1)	146.3 (2)
P(3)–Pd(2)–P(2)	110.9 (3)	C(3)–Pd(2)–Pd(1)	53.3 (7)
C(3)–Pd(2)–P(2)	154.6 (8)	C(3)–Pd(2)–P(3)	94.5 (8)
P(5)–Pd(3)–P(4)	159.6 (3)	C(4)–Pd(3)–P(4)	87.7 (7)
C(4)–Pd(3)–P(5)	97.2 (7)	O(5)–Pd(3)–P(4)	94.5 (5)
O(5)–Pd(3)–P(5)	82.8 (4)	O(5)–Pd(3)–C(4)	173.8 (8)
C(10)–P(1)–Pd(1)	112.2 (10)	C(111)–P(1)–Pd(1)	117.9 (8)
C(121)–P(1)–Pd(1)	114.9 (7)	C(10)–P(2)–Pd(2)	104.2 (10)
C(211)–P(2)–Pd(2)	119.0 (8)	C(221)–P(2)–Pd(2)	118.0 (8)
C(20)–P(3)–Pd(2)	110.1 (10)	C(311)–P(3)–Pd(2)	109.9 (7)
C(321)–P(3)–Pd(2)	123.2 (8)	C(20)–P(4)–Pd(3)	124.1 (10)
C(411)–P(4)–Pd(3)	118.1 (8)	C(421)–P(4)–Pd(3)	103.7 (7)
C(30)–P(5)–Pd(3)	121.0 (10)	C(511)–P(5)–Pd(3)	114.2 (7)
C(521)–P(5)–Pd(3)	106.6 (7)	C(30)–P(6)–Pd(1)	106.1 (9)
C(611)–P(6)–Pd(1)	124.2 (8)	C(621)–P(6)–Pd(1)	114.3 (7)
C(2)–O(1)–C(1)	113.5 (22)	O(2)–C(2)–O(1)	120.3 (3)
C(3)–C(2)–O(1)	107.6 (24)	C(3)–C(2)–O(2)	132.0 (29)
Pd(2)–C(3)–Pd(1)	79.0 (9)	C(2)–C(3)–Pd(1)	118.6 (19)
C(2)–C(3)–Pd(2)	121.1 (19)	C(4)–C(3)–Pd(1)	74.0 (16)
C(4)–C(3)–Pd(2)	118.0 (19)	C(4)–C(3)–C(2)	120.8 (23)
Pd(3)–C(4)–Pd(1)	96.4 (10)	C(3)–C(4)–Pd(1)	70.0 (16)
C(3)–C(4)–Pd(3)	118.8 (19)	C(5)–C(4)–Pd(1)	120.4 (18)
C(5)–C(4)–Pd(3)	114.2 (19)	C(5)–C(4)–C(3)	124.2 (24)
O(3)–C(5)–C(4)	123.7 (29)	O(4)–C(5)–C(4)	113.5 (27)
O(4)–C(5)–O(3)	121.8 (30)	C(6)–O(4)–C(5)	116.8 (25)
C(7)–O(5)–Pd(3)	123.2 (14)	O(6)–C(7)–O(5)	127.4 (19)
C(8)–C(7)–O(5)	118.2 (21)	C(8)–C(7)–O(6)	114.4 (22)

Table II. Selected Bond Distances (Å) and Angles (deg) in Complexes 2a, 4, and 5[a]

	2a	4	5
M(1)–M(2)	2.637 (2)	2.623 (1)	2.631 (2)
M(1)···M(3)	3.188 (3)	3.205 (1)	3.232 (2)
M(2)···M(3)	3.329 (3)	3.426 (1)	3.277 (2)
M(1)–C(3)	2.16 (3)	2.25 (1)	2.17 (3)
M(1)–C(4)	2.20 (3)	2.21 (1)	2.21 (3)
M(2)–C(3)	1.99 (3)	2.02 (1)	2.05 (3)
M(3)–C(4)	2.07 (2)	2.08 (1)	1.99 (3)
C(3)–C(4)	1.35 (3)	1.38 (2)	1.40 (4)
M(2)–C(3)–C(4)	118 (2)	117.3 (7)	119 (2)
M(3)–C(4)–C(3)	119 (2)	119.2 (7)	112 (2)
C(3)–M(2)–P(2)	154.6 (8)	153.3 (3)	152 (2)
C(4)–M(3)–X[b]	173.8 (8)	176.9 (6)	165 (1)
M(2)–C(3)–C(4)–M(3)	-19 (3)	-27.4 (5)	-30 (1)

[a] M = Pd in 2a, M = Pt in 4 and 5. [b] X = O (of CF_3CO_2), Cl, C (of CO) in 2a, 4, and 5, respectively.

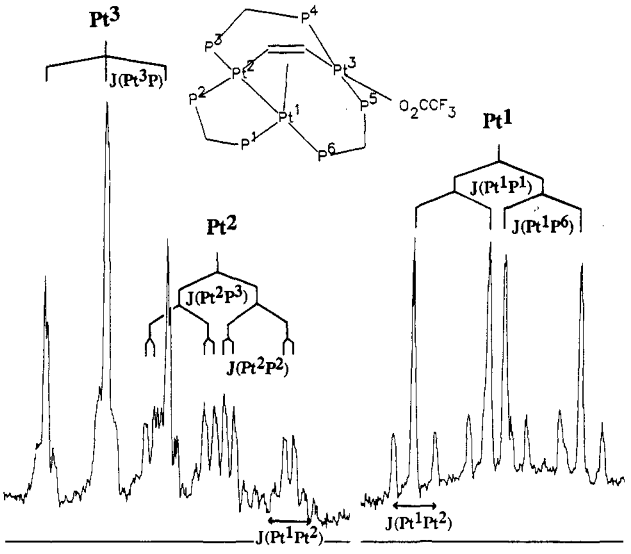


Figure 3. ^{195}Pt NMR spectrum (64.3 MHz) of complex **2c**.

in the Experimental Section and clearly indicate that the structure determined for **2a** in the solid state is maintained in solution. Hence, the M_3(RCCR) unit is rigidly bonded and not fluxional in these complexes. Similar spectra have been observed for some other triplatinum complexes such as **4** and **5**. However, in some other related complexes, such as $[Pt_3(CH{=}CH_2)(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-dppm})_3]^+$, the alkyne ligand is fluxional such that the complex appears to have 2-fold symmetry in the high-temperature NMR spectra.[6] Since palladium complexes are often more labile than their platinum analogs, fluxionality of the palladium alkyne clusters might be expected but was not observed.

The structure of acetylene on a Pd(111) surface at 150 K has been investigated by vibrational spectroscopy and is suggested to be present as distorted $Pd_3(\mu_3\text{-}\eta^2\text{-}HCCH)$ units with the alkyne carbons $sp^{2.5}$ hybridized and with d(CC) = 1.42 (4) Å.[8] This is very similar to the structure observed for **2a**, which may therefore be considered as a model for acetylene chemisorbed on a palladium(111) surface and which gives credence to the proposed surface structure.[8]

Experimental Section

NMR spectra were recorded by using a Varian XL200 (^{1}H) or XL300 (^{31}P and ^{195}Pt) instrument, and references were TMS (^{1}H), H_3PO_4 (^{31}P), and aqueous K_2PtCl_4 (^{195}Pt). FAB mass spectra were recorded by using a Finnigan MAT 8230 spectrometer, with samples prepared as mulls in oxalic acid/3-mercapto-1,2-propanediol. IR spectra were recorded as Nujol mulls. The complexes $[Pd_3(\mu_3\text{-CO})(O_2CCF_3)(\mu\text{-dppm})_3][CF_3CO_2]$, $[Pd_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$, $[Pt_3(\mu_3\text{-CO})(O_2CCF_3)(\mu\text{-dppm})_3][CF_3CO_2]$, and $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ were prepared by the literature methods.[6,7,15]

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Table III. Summary of X-ray Structure Determination

compd	$C_{83}H_{72}F_9O_6P_7Pd_3{\cdot}CH_3OH{\cdot}H_2O$
fw	1922.5
cryst syst, space group	monoclinic, *C*2/*c* (No. 15)
cell dimens	
a (Å)	44.074 (5)
b (Å)	15.890 (3)
c (Å)	26.748 (4)
β (deg)	108.18 (1)
cell vol (Å^3), *Z*	17798.2, 8
density (g·cm^{-2}) (obsd, calc)	1.45 (5), 1.435
F(000)	7760
approx cryst dimens (mm)	0.11 × 0.16 × 0.25
no. of faces; face indices	6; {200}, {002}, (−1,−1,0), (1,−1,0)
scan widths (before, after)	0.148, 0.148
scan mode, width (deg)	$\omega-2\theta$, $1.0 + 0.14 \tan\theta$
index	$-43 \le h \le 43$, $-2 \le k \le 15$, $-2 \le l \le 26$
θ ranges (deg)	$0 \le 2\theta \le 100$
scan speed (deg·min^{-1})	1.648–4.12
no. of data, no. of standards coll	11 618, 249
abs coeff (cm^{-1})	63.74
no. of unique data	9141
no. of observ, no. of variables	3519 ($I > 3\sigma(I)$), 352
final model: *R* and R_w	0.0826, 0.0913

Table IV. Selected Atomic Positional (×10^4) and Thermal (×10^3) Parameters

atom	*x*	*y*	*z*	*U* or U_{eq}, Å^2
Pd(1)	1618.9 (5)	3950.6 (15)	2307.0 (9)	39.8 (9)*
Pd(2)	1587.4 (5)	4752.6 (14)	3152.6 (9)	38.6 (9)*
Pd(3)	1182.8 (5)	5588.8 (15)	1995.6 (9)	40.9 (9)*
P(1)	1587 (2)	2792 (5)	2808 (3)	51 (3)*
P(2)	1304 (2)	3795 (5)	3502 (3)	46 (3)*
P(3)	1653 (2)	6011 (5)	3595 (3)	47 (3)*
P(4)	1335 (2)	6831 (5)	2496 (3)	49 (3)*
P(5)	1000 (2)	4707 (5)	1257 (3)	50 (3)*
P(6)	1587 (2)	3510 (5)	1448 (3)	45 (3)*
C(10)	1257 (7)	2868 (18)	3076 (11)	51 (9)
C(20)	1650 (7)	6877 (19)	3147 (11)	53 (10)
C(30)	1274 (7)	4197 (18)	984 (11)	45 (9)
C(1)	2623 (7)	6141 (19)	3294 (12)	63 (10)
O(1)	2266 (5)	5985 (13)	3067 (8)	57 (6)
O(2)	2392 (6)	4691 (14)	2900 (9)	72 (7)
C(2)	2191 (7)	5181 (20)	2870 (11)	37 (8)
C(3)	1830 (6)	5108 (16)	2675 (10)	29 (8)
C(4)	1664 (6)	5308 (15)	2175 (10)	22 (7)
C(5)	1815 (8)	5613 (19)	1767 (13)	48 (9)
O(3)	1666 (5)	5791 (13)	1329 (9)	66 (7)
O(4)	2113 (5)	5801 (12)	1964 (8)	54 (6)
C(6)	2265 (8)	6141 (20)	1614 (13)	67 (11)
O(5)	664 (4)	5773 (10)	1859 (6)	21 (4)
O(6)	633 (7)	7019 (18)	1392 (11)	117 (10)
C(7)	515 (4)	6350 (23)	1610 (13)	120 (17)
C(8)	162 (4)	6391 (12)	1530 (7)	100 (0)
F(1)	12 (7)	5846 (15)	1181 (8)	270 (20)
F(2)	52 (7)	7131 (12)	1371 (10)	281 (21)
F(3)	108 (5)	6227 (14)	1969 (7)	208 (15)
C(111)	1519 (5)	1775 (16)	2488 (9)	45 (9)
C(121)	1936 (5)	2604 (11)	3366 (8)	43 (9)
C(211)	1478 (5)	3438 (13)	4174 (8)	64 (11)
C(221)	888 (6)	4011 (13)	3413 (8)	68 (11)
C(311)	2056 (5)	6077 (12)	4062 (9)	50 (9)
C(321)	1405 (5)	6337 (15)	3993 (10)	51 (9)
C(411)	1029 (6)	7430 (12)	2651 (9)	51 (9)
C(421)	1500 (4)	7499 (13)	2083 (9)	44 (9)
C(511)	729 (5)	3904 (12)	1321 (7)	40 (8)
C(611)	1495 (4)	2440 (14)	1206 (8)	51 (9)
C(621)	1944 (5)	3729 (13)	1263 (6)	48 (9)

[a] Parameters with an asterisk refer to atoms that were refined anisotropically and are given in the form of isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_{ij}U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

[Pd$_3$(O$_2$CCF$_3$)(μ_3-η^2-MeO$_2$CCCCO$_2$Me)(μ-dppm)$_3$][PF$_6$]. To a solution of [Pd$_3$(μ_3-CO)(O$_2$CCF$_3$)(μ-dppm)$_3$][CF$_3$CO$_2$] (0.12 g) in methanol (10 mL) was added MeO_2CCCCO_2Me (9 μL). The color of the solution changed rapidly from purple to brown and a gas (CO) was evolved. The product was obtained as a red precipitate by addition of NH_4PF_6 (0.1 g) in methanol (2 mL) and was recrystallized from $C_2H_4Cl_2$/toluene. Yield: 83%. Anal. Calc for $C_{83}H_{72}F_9O_6P_7Pd_3$: C, 53.2; H, 3.9. Found: C, 53.3; H, 4.1. MS: *m*/*z* = 1726, 1614. Calc for Pd$_3$dppm$_3$(MeO$_2$CCCCO$_2$Me)(CF$_3$CO$_2$)$^+$, Pd$_3$dppm$_3$(MeO$_2$CCCCO$_2$Me)$^+$: *m*/*z* = 1725, 1612. NMR: $\delta(^1H)$ = 2.94, 3.05 (s, each 3 H, MeO); $\delta(^{31}P)$ = 26.5 [*J*(PP) = 96, 43, 24 Hz], 20.7 [*J*(PP) = 435, 97, 21 Hz], 16.9 [*J*(PP) = 435, 95, 22 Hz], −1.4, −2.6, −4.1 (all complex m, each 1 P, dppm).

Similarly, [Pd$_3$(O$_2$CCF$_3$)(μ_3-η^2-EtO$_2$CCCCO$_2$Et)(μ-dppm)$_3$][PF$_6$] was prepared. Yield: 92%. Anal. Calc for $C_{85}H_{76}F_9O_6P_7Pd_3$: C, 53.7; H, 4.0. Found: C, 54.0; H, 4.1. MS: *m*/*z* = 1643. Calc for Pd$_3$dppm$_3$(EtO$_2$CCCCO$_2$Et)$^+$: *m*/*z* = 1642. NMR: $\delta(^1H)$ = 0.84 [t, 3 H, *J*(HH) = 7 Hz, Me], 0.92 [t, 3 H, *J*(HH) = 7 Hz, Me], 2.88, 3.24, 3.40, 3.64 (m, each 1 H, OCH$_2$); $\delta(^{31}P)$ = 25.8, 18.7, 15.9, −1.0, −3.0, −3.9 (m, each 1 P, dppm).

[Pd$_3$Cl(μ_3-η^2-MeO$_2$CCCCO$_2$Me)(μ-dppm)$_3$][PF$_6$]. Excess NH_4Cl (0.3 g) was added to a solution of [Pd$_3$(O$_2$CCF$_3$)(μ_3-η^2-MeO$_2$CCCCO$_2$Me)(μ-dppm)$_3$][PF$_6$] (0.10 g) in methanol (25 mL). There was an immediate color change to light red. After 15 min, the solvent was evaporated and the residue was extracted with CH_2Cl_2 (6 mL). The product was obtained by evaporation of the solvent and was recrystallized from acetone/pentane to give red needles. Yield: 78%. Anal. Calc for $C_{81}H_{72}ClF_6O_4P_7Pd_3$: C, 54.2; H, 4.0. Found: C, 53.7; H, 3.9. NMR: $\delta(^1H)$ = 2.54 (s, 3 H, Me), 3.52 (s, 3 H, Me); $\delta(^{31}P)$ = 24.0, 21.8, 18.6, −0.5, −2.8, −3.7 (all complex multiplets).

Similarly, [Pd$_3$(Cl(μ_3-η^2-EtO$_2$CCCCO$_2$Et)(μ-dppm)$_3$][PF$_6$] was prepared. Yield: 76%. Anal. Calc for $C_{83}H_{76}ClF_6O_4P_7Pd_3$: C, 54.7; H, 4.2. Found: C, 54.4; H, 4.0. NMR: $\delta(^1H)$ = 0.74 [t, 3 H, *J*(HH) = 7 Hz, Me], 1.22 [t, 3 H, *J*(HH) = 7 Hz, Me], 2.50, 3.04 [each dq, 1 H, ^3J(HH) = 7 Hz, ^2J(HH) = 10 Hz, OCH^{a}H^b], 3.65, 4.15 [each dq, 1 H, ^3J(HH) = 7 Hz, ^2J(HH) = 10 Hz, OCH^{a}H^b]. Note that the OCH$_2$ protons of the ethyl groups are diastereotopic due to the absence of symmetry.

[Pt$_3$(O$_2$CCF$_3$)(μ_3-η^2-MeO$_2$CCCCO$_2$Me)(μ-dppm)$_3$][PF$_6$]. To a solution of [Pt$_3$(O$_2$CCF$_3$)(μ_3-CO)(μ-dppm)$_3$][CF$_3$CO$_2$] (0.11 g) in CH_2Cl_2 (25 mL) was added MeO_2CCCCO_2Me (0.09 mL). The mixture was stirred for 24 h, the solvent was reduced in volume, and the product was precipitated by addition of excess NH_4PF_6 in methanol. Yield: 85%. Anal. Calc for $C_{83}H_{72}F_9O_6P_7Pt_3$: C, 45.9; H, 3.3. Found: C, 45.5; H, 3.5. NMR: $\delta(^1H)$ = 2.48 (s, 3 H, Me), 3.85 (s, 3 H, Me); $\delta(^{31}P)$ = 16.5, 15.9, 3.8, 2.3, −7.2, −14.2 (complex multiplets); $\delta(^{195}Pt)$ (nomenclature as in Figure 1, reference K_2PtCl_4): −2850 [t, ^1J(PtP) = 2750 Hz, ^3J(Pt^{2}Pt^3) = 750 Hz, Pt(3)], −2892 [m, ^1J(PtP) = 3500, 2600 Hz, ^1J(Pt^{1}Pt^2) = 1900 Hz, ^3J(Pt^{2}Pt^3) = 750 Hz, Pt(2)], −3310 [m, ^1J(PtP) = 4075, 3365 Hz, ^1J(Pt^{1}Pt^2) = 1900 Hz, Pt(1)].

Similarly, [Pt$_3$(O$_2$CCF$_3$)(μ_3-η^2-EtO$_2$CCCCO$_2$Et)(μ-dppm)$_3$][PF$_6$] from EtO_2CCCCO_2Et was prepared. Yield: 70%. Anal. Calc for $C_{85}H_{76}F_9O_6P_7Pt_3$: C, 46.4; H, 3.5. Found: C, 45.9; H, 3.4. NMR: $\delta(^1H)$ = 0.87 [t, 3 H, *J*(HH) = 7 Hz, Me], 1.09 [t, 3 H, *J*(HH) = 7 Hz, Me], 2.65, 3.10, 3.56, 4.02 (m, OCH^{a}H^b); $\delta(^{31}P)$ = 17.9, 15.4, 4.8, 1.9, −6.2, −14.1 (m, P of dppm).

[Pt$_3$Cl(μ_3-η^2-MeO$_2$CCCCO$_2$Me)(μ-dppm)$_3$][PF$_6$]. This was prepared in a similar way as the palladium analog. Yield: 65%. Anal. Calc for $C_{81}H_{72}ClF_6O_4P_7Pt_3$: C, 47.2; H, 3.5. Found: C, 47.4; H, 3.6. NMR: $\delta(^1H)$ = 2.83, 3.38 (s, each 3 H, MeO); $\delta(^{31}P)$ = 18.4, 14.9, 4.6, 1.5, −6.2, −13.3 (m, each 1 P, dppm P).

Similarly, [Pt$_3$Cl(μ_3-η^2-EtO$_2$CCCCO$_2$Et)(μ-dppm)$_3$][PF$_6$] was prepared. Yield: 71%. Anal. Calc for $C_{83}H_{76}ClF_6O_4P_7Pt_3$: C, 47.7; H, 3.7. Found: C, 47.3; H, 3.4. NMR: $\delta(^1H)$ = 0.77 [t, 3 H, *J*(HH) = 7 Hz, Me], 1.12 [t, 3 H, *J*(HH) = 7 Hz, Me], 2.36, 3.82, 3.95, 4.13 (m, OCH^{a}H^b); $\delta(^{31}P)$ = 18.0, 15.8, 4.0, 2.2, −5.8, −15.4 (m, P of dppm).

X-ray Structure Determination. A red crystal was mounted inside a capillary tube under argon. The crystal density was determined to be 1.45 (5) g·cm^{-3} by the neutral buoyancy method using a mixture of carbon tetrachloride and hexane.

The data collection was carried out at ambient temperature (23 °C) on an Enraf-Nonius CAD4F diffractometer using Cu Kα_1 radiation with a nickel filter.[9] Cell constants and an orientation matrix were determined and refined by using the angular settings for 20 high-angle reflections with $40.5 \leq 2\theta \leq 54.1°$. Intensity data were recorded at variable scan speeds chosen so as to optimize counting statistics within a maximum time per datum of 60 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections 400, 020, and 002 were monitored every 180 min of X-ray exposure time and showed no decline over the total period of 222.25 h. In all, 11 618 reflections and 249 standards were recorded. Corrections were made for Lorentz, monochromator and crystal polarization, and background radiation effects, using the Structure Determination Package[10] running on a PDP11/23+ computer. The data were corrected for absorption with the use of an empirical method[11] based on ψ scans ($\psi = 0 \rightarrow 360°$ every 10°) for χ values near 90°. Eight sets of reflections (with θ ranging from 6.6 to 20.4°) gave an absorption profile with maximum and minimum transmission values 99.805–72.586.

The structure was solved by a combination of MULTAN[12] and difference Fourier techniques. Refinement was by full-matrix least-squares techniques on F, using the SHELX-76 software[13] running on a SUN 3/50 workstation. Scattering factors for neutral, non-hydrogen atoms were taken from ref 14. Anisotropic thermal parameters were assigned for all the Pd and P atoms and were refined while the thermal parameters of all the remaining non-hydrogen atoms were refined isotropically. The phenyl rings were constrained to regular hexagons with C–C = 1.392 Å, and the hydrogen atoms attached to the carbon atoms in the cation were placed in idealized positions (C–H = 0.95 Å) and were included for structure factor calculations only. A common temperature factor was assigned to all hydrogen atoms and was refined. At this stage the solvent molecules were found to be disordered. The methanol molecule was found to have three disorder components with site occupancies of 50, 25, and 25%, and the water molecule was found to be disordered with 50% site occupancies. Independent confirmation of methanol was obtained by ^{1}H NMR spectroscopy of the crystalline sample. Individual temperature factors of the C and O atoms were refined in the least squares. The thermal parameters of the atoms in the PF_6^- anion and the CF_3 moiety of the trifluoroacetate anion attached to Pd_3 were high, indicating the possibility of disorder. However, chemically reasonable disorder could not be resolved. The PF_6^- anion was fixed as an ideal octahedran with d(P–F) = 1.600 Å. A common thermal parameter was assigned to the F atoms and refined in the least-squares cycles, whereas the CCF_3 fragment was treated as an ideal tetrahedron with a C–F distance of 1.30 Å. The isotropic thermal parameters of F atoms were refined, and the temperature factor for the C(8) carbon atom was fixed at $U = 0.100$ Å^2.

With the use of 3519 observations with $I > 3.0\sigma(I)$ and utilizing weights of the form $w = k/\sigma^2(F_o) + gF^2$, where $k = 1.0$ and $g = 0.019976$, refinement of 352 variables converged at agreement factors $R = 0.0826$ and $R_w = 0.0913$. The final least-square cycles had a maximum shift/esd of −0.49 for y of C(13). The top 10 peaks in the final difference Fourier synthesis had electron densities in the range 1.16–0.673 e·Å^{-3}; of these, the top peak was found near F(9) at a distance of 1.08 Å, the next two peaks (with electron densities of 0.769 and 0.755 e·Å^{-3}) were found near O(7) and C(12) in the solvent molecules, and the remaining peaks were of no chemical significance.

The summary of X-ray crystal data and experimental details is given in Table III. Selected atomic positional and U_{eq} thermal parameters are shown in Table IV. Tables of atomic coordinates of all the atoms, all the interatomic distances and angles, hydrogen atom parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, weighted least-squares planes, and selected torsion angles have been included in the supplementary material.

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Supplementary Material Available: Tables of atomic coordinates of all the atoms (S1), all the interatomic distances and angles (S2), hydrogen atom parameters (S4), anisotropic thermal parameters (S3), root-mean-square amplitudes of vibration (S6), weighted least-squares planes (S5), and selected torsion angles (S7) (10 pages). Ordering information is given on any current masthead page.

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