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Di- and Trinuclear Di-*tert*-butylphosphido-Bridged Complexes of Palladium. Synthesis and X-ray Structures of $[Pd(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2(Pd\text{-}Pd)$ and Mixed-Valence $Pd_3(\mu\text{-}t\text{-}Bu_2P)_3(CO)_2Cl$

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Reaction of $[Pd(CO)Cl]_n$ with Li-t-Bu_2P in THF at -78 °C produces a mixture of compounds from which the trinuclear phosphido-bridged complex $Pd_3(\mu\text{-}t\text{-}Bu_2P)_3(CO)_2Cl$ (**2**) can be isolated in low yield (12%). Treatment of the supernatant with excess PMe_3 permits isolation of the dimer $[Pd(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**1**) (44%). The structures of both **1** and **2** have been determined by single-crystal X-ray diffraction studies. The molecular structure of **1** consists of a short Pd-Pd bond (Pd-Pd = 2.571 (1) Å) that is bridged by two Bu_2P^- units. Each Pd also bears a terminal PMe_3 ligand. The molecular structure of **2** consists of a triangle of Pd atoms in which the three Pd-Pd bonds are bridged by t-Bu_2P^- units. Two Pd atoms bear a single terminal CO group while the third is bonded to a chloride ligand. The Pd, P, Cl, C, and O atoms are all virtually in the same plane. Crystal data for **1**: $C_{22}H_{54}P_4Pd_2$, M_r 655.4, tetragonal, $P4_2/m$, $a = 9.376$ (1) Å, $b = 9.376$ (1) Å, $c = 18.591$ (4) Å, $V = 1634.3$ (5) Å^3, $D_{calcd} = 1.33$ g cm^{-3}, $Z = 2$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 12.87 cm^{-1}. Methods: MULTAN, difference Fourier, full-matrix least squares. Refinement of 940 reflections ($I > 3\sigma(I)$) out of 1506 observed ($3° < 2\theta < 48°$) gave R and R_w values of 0.0465 and 0.0613, respectively. Data/parameter ratio = 13.06; highest peak in final difference Fourier = 0.503 e Å^{-3}. Crystal data for **2**: $C_{26}H_{54}ClO_2P_3Pd_3$, M_r 846.3, orthorhombic, *Pnma*, $a = 17.816$ (1) Å, $b = 18.055$ (2) Å, $c = 11.676$ (4) Å, $V = 3755.8$ (5) Å^3, $D_{calcd} = 1.50$ g cm^{-3}, $Z = 4$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 16.20 cm^{-1}. Methods used were as for **1**. Refinement of 1587 reflections ($I > 3\sigma(I)$) out of 2970 observed ($3° < 2\theta < 46°$) gave R and R_w values of 0.0439 and 0.0532, respectively. Data/parameter ratio = 8.35; highest peak in final difference Fourier = 0.965 e Å^{-3}.

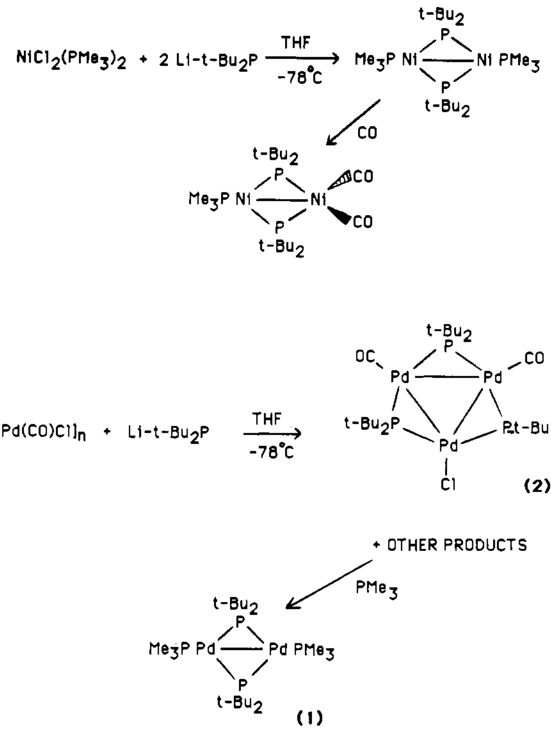
Introduction

As part of a general study of the steric effects of bulky phosphido and arsenido ligands in transition-metal chemistry, we recently reported the synthesis and structures of a series of dinuclear Ni(I) complexes.[1] In particular, we observed that the symmetrical dinuclear compound $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ reacts readily with CO to give an unusual asymmetric complex $(PMe_3)Ni(\mu\text{-}t\text{-}Bu_2P)_2Ni(CO)_2$ in which two CO ligands replace a single PMe_3 group at one end of the molecule while the other PMe_3 cannot be replaced. Several analogues of this unusual asymmetric complex have also been reported.[1]

In order to gain more insight into bulky phosphido complexes of the Ni triad, we attempted the synthesis of some new Pd phosphido complexes. We report here details of the synthesis and structures of two new di-*tert*-butylphosphido complexes of Pd: $[Pd(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**1**) and $Pd_3(\mu\text{-}t\text{-}Bu_2P)_2(CO)_2Cl$ (**2**) (see Scheme I). To the best of our knowledge, **1** is the first dinuclear metal-metal-bonded phosphido-bridged complex of palladium reported. In addition, **2** is the first carbonyl derivative of a palladium phosphide and also the first palladium cluster complex that bears *terminal* instead of bridging CO ligands. The reaction chemisty of **1** differs from that of its Ni analogue since it does not react with CO, C_2H_4, or H_2 under mild conditions.

Several palladium phosphido complexes are known. These include $[Pd_3Cl(PPh_2)_2(PR_3)_3][BF_4]$ (R = Et, Ph)[2,3] and $[PdCl(\mu\text{-}PR'_2)(PR_3)]_2$ (R_3 = Et_3, HPh_2 and R' = Ph; R_3 = Et_3, Ph_3, HMe_2 and R' = Me)[4] recently reported by Dixon and co-workers. Meek and coworkers have also described dinuclear complexes of Pd(II) of the type $[PdCl(\mu\text{-}RP(CH_2)_3PPh_2)]_2$ (R = Cy, Ph), in which the organophosphido group is attached to a chelate chain.[5] In addition, a number of heterometallic phosphido complexes of Pd are known, for example, $(CO)_4M(\mu\text{-}PCy_2)_2Pd(PPh_3)$ (M = Mo, W) recently described by Loeb and Stephan.[6]

Scheme I. Synthesis of New Palladium Phosphido Complexes



Results and Discussion

Synthesis. Reaction of $[Pd(CO)Cl]_n$[7] with Li-t-Bu_2P[8] in THF at -78 °C produces a deep red solution from which the trinuclear complex $Pd_3(\mu\text{-}t\text{-}Bu_2P)_3(CO)_2Cl$ (**2**) can be isolated in fairly low yield (12%). The supernatant from the initial workup contains more palladium species, which we have been unable to characterize fully. However, the addition of excess PMe_3 to the supernatant permits the isolation of the dimer $[Pd(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**1**) in reasonable yield (44%) (see Scheme I). Spectroscopic data for

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[7] Dell'Amico, D. B.; Calderazzo, F.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 137.
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Table I. Crystal Structure Parameters for Complexes **1** and **2**

	1	**2**
	Description of Crystal	
color	red	dark red
habit	prism	plate
max cryst dimens, mm	0.40 × 0.38 × 0.28	0.35 × 0.28 × 0.25
	Unit Cell	
crystal system	tetragonal	orthorhombic
space group	$P4_2/m$	*Pnma*
unit cell params		
a, Å	9.376 (1)	17.816 (1)
b, Å	9.376 (1)	18.055 (2)
c, Å	18.591 (4)	11.676 (4)
V, Å^3	1634.3 (5)	3755.8 (5)
molecules per unit cell	2	4
formula	$C_{22}H_{54}P_4Pd_2$	$C_{26}H_{54}ClO_2P_3Pd_3$
mol wt	655.4	846.3
D_{calcd}, g cm^{-3}	1.33	1.50
μ_{calcd}, cm^{-1}	12.87	16.20
	Data Collection	
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
scan technique	$\theta/2\theta$	$\theta/2\theta$
scan width, deg	0.8 + 0.35(tan θ)	0.8 + 0.35(tan θ)
range of indices *h*,*k*,*l*	+10,+10,+21	+19,+19,+12
2θ range, deg	3.0–48.0	3.0–46.0
no. of reflcns measd	1506	2970
std reflcns		
intens	328; 15$\bar{4}$	3,10,1; $\bar{1}$88
orientation	165; 4$\bar{1}$7	188; 2$\bar{6}$10
decay of stds, %	12.0	<1
min. % transmissn		77.90
max. % transmissn		99.14
av % transmissn		88.98
agreement factor for avgd reflcns		
F_o	0.025	
intens	0.024	
	Structure Determination	
no. of reflcns used ($I > 3\sigma(I)$)	940	1587
no. params varied	72	190
data/param ratio	13.06	8.35
shift/error ratio	0.171	0.177
esd of an observn of unit wt	4.972	3.066
R	0.0465	0.0439
R_w	0.0613	0.0532

Table II. Positional Parameters for **1**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Pd	0.6023 (1)	0.0913 (1)	0.000	3.51 (2)
P1	0.500	0.000	0.1045 (2)	4.04 (8)
P2	0.7769 (5)	0.2559 (5)	0.000	5.7 (1)
C1	0.389 (1)	0.124 (1)	0.1622 (6)	6.4 (3)
C2	0.481 (2)	0.218 (2)	0.213 (1)	11.6 (5)
C3	0.273 (2)	0.043 (2)	0.207 (1)	12.0 (5)
C4	0.315 (2)	0.221 (2)	0.1071 (9)	9.7 (4)
C5	0.906 (3)	0.261 (3)	0.075 (1)	17.3 (9)*
C6	0.716 (5)	0.433 (5)	0.000	20 (2)*

[a] Starred values denote isotropically refined atoms. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

1 is relatively straightforward with the $^{31}P\{^1H\}$ NMR spectrum consisting of two triplets at δ 289.0 and −26.6 (relative to H_3PO_4), the former being assigned to the phosphido groups bridging a metal–metal bond. Although **1** is isostructural with its Ni analogue,[1] it does not possess the same reactivities. Thus, there is no reaction of **1** in THF with CO (60 psi, 90 °C), ethylene (60 psi, 80 °C), or H_2 (60 psi, 80 °C).

X-ray Structure of 1. Molecules of **1** crystallize in the tetragonal space group $P4_2/m$ with two molecules in the unit cell. The molecule possesses crystallographically imposed $2/m$ symmetry such that Pd, P2, and C6 lie on a mirror plane and P1 lies on a 2-fold axis of rotation. A view of **1** is shown in Figure 1 and crystallographic details are given in Table I. Positional parameters, bond lengths, and bond angles for **1** are given in Tables II–IV, respectively. The structural parameters for the molecule all fall within reasonable limits. Thus, the Pd–P1 (phosphido) distance (2.329 (3) Å) may be compared with those in other phosphido-bridge systems (ca. 2.3 Å).[4-6] The terminal Pd–P (phosphine) distances (2.250 (5) Å) are also normal. Interestingly, the Pd–Pd distance of 2.571 (1) Å is quite short for a Pd–Pd bond of order one.[9] However, Pd–Pd bonds have been observed as short as 2.5310 (9) Å in $[Pd_2(MeNC)_4][PF_6]_2$[10] and have been invoked for lengths well over 3 Å.[9]

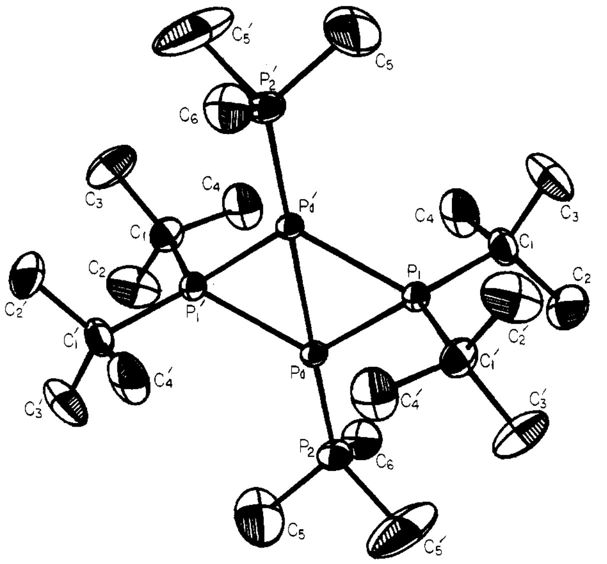

Figure 1. ORTEP view of **1** showing the atoms at the 50% probability level.

Table III. Bond Distances (Å) for **1**[a]

Pd–P1	2.329 (3)	C1–C2	1.56 (2)
Pd–P2	2.250 (5)	C1–C3	1.57 (2)
P1–C1	1.893 (13)	C1–C4	1.53 (2)
P2–C5	1.85 (3)	Pd–Pd'	2.571 (2)
P2–C6	1.76 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg) for **1**[a]

Pd'–Pd–P1	56.49 (6)	Pd–P2–C6	114 (2)
Pd'–Pd–P2	178.4 (1)	C5–P2–C5'	98 (1)
P1–Pd–P1'	112.98 (9)	C5–P2–C6	101 (1)
P1–Pd–P2	123.50 (6)	P1–C1–C2	113 (1)
Pd–P1–Pd'	67.0 (1)	P1–C1–C3	113 (1)
Pd–P1–C1	118.3 (4)	P1–C1–C4	103.5 (9)
Pd–P1–C1'	118.1 (4)	C2–C1–C3	109 (1)
C1–P1–C1'	110.9 (5)	C2–C1–C4	109 (1)
Pd–P2–C5	119.7 (9)	C3–C1–C4	109 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Characterization of 2. Although **2** is produced in low yield (the presence of one chloride and two CO ligands can not be easily rationalized), it is an interesting example of a mixed-valence trinuclear palladium phosphido complex. Although it is a neutral compound, it may be regarded as essentially isoelectronic with cationic complexes such as $[Pd_3Cl(PPh_2)_2(PEt_3)_3]^+BF_4^-$ recently described by Dixon and co-workers.[2,3] To our knowledge, **2** is the first cluster complex of Pd that has terminal instead of bridging CO ligands. The $^{31}P\{^1H\}$ NMR spectrum consists of a doublet and triplet both shifted downfield (δ 280.1 and 207.5), consistent with the structure in the solid state (see below). The presence of terminal carbonyl ligands is indicated by two strong peaks in the infrared spectrum at 2035 and 2030 cm^{-1} (hexane solution). Relatively few carbonyls of palladium are known,[9] and in the few

Table V. Positional Parameters for **2**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Pd1	0.40018 (6)	0.16693 (5)	0.57791 (8)	3.40 (2)
Pd2	0.34084 (8)	0.250	0.7756 (1)	3.26 (3)
P1	0.3481 (2)	0.1257 (2)	0.7470 (3)	3.50 (7)
P2	0.4464 (3)	0.250	0.4444 (4)	3.8 (1)
Cl	0.2944 (3)	0.250	0.9633 (4)	5.3 (1)
O1	0.4248 (7)	0.0222 (6)	0.458 (1)	7.6 (3)
C1	0.4167 (8)	0.0757 (8)	0.503 (1)	4.6 (3)
C2	0.2558 (9)	0.0757 (9)	0.727 (1)	6.1 (4)
C3	0.2165 (9)	0.120 (1)	0.630 (2)	8.1 (5)
C4	0.266 (1)	−0.006 (1)	0.692 (2)	7.9 (5)
C5	0.209 (1)	0.082 (1)	0.838 (2)	8.6 (5)
C6	0.4171 (8)	0.0748 (8)	0.841 (1)	5.3 (4)
C7	0.377 (1)	0.053 (1)	0.956 (1)	8.0 (5)
C8	0.4815 (9)	0.130 (1)	0.864 (2)	7.6 (5)
C9	0.451 (1)	0.005 (1)	0.783 (2)	9.3 (5)
C10	0.553 (1)	0.250	0.440 (2)	4.8 (5)
C11	0.576 (1)	0.250	0.571 (2)	7.8 (7)
C12	0.584 (1)	0.181 (1)	0.380 (2)	8.7 (5)
C13	0.400 (1)	0.250	0.297 (2)	5.9 (6)
C14	0.421 (1)	0.319 (1)	0.228 (1)	11.0 (7)
C15	0.316 (2)	0.250	0.325 (2)	12 (1)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Bond Distances (Å) for **2**[a]

Pd1–Pd1′	3.000 (5)	C2–C3	1.553 (13)
Pd1–Pd2	2.949 (6)	C2–C4	1.541 (15)
Pd1–P1	2.305 (2)	C2–C5	1.545 (13)
Pd1–P2	2.315 (2)	C6–C7	1.552 (12)
Pd1–C1	1.888 (10)	C6–C8	1.575 (13)
Pd2–P1	2.273 (10)	C6–C9	1.570 (12)
Pd2–Cl	2.343 (10)	C10–C11	1.58 (2)
P1–C2	1.890 (9)	C10–C12	1.532 (1)
P1–C6	1.859 (9)	C13–C14	1.530 (12)
P2–C10	1.900 (12)	C13–C15	1.53 (2)
P2–C13	1.909 (11)	C1–O1	1.109 (10)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

examples of terminal coordination found in mononuclear complexes, it has been noted that ν_{CO} is generally above 2100 cm^{-1}.[9] The lower ν_{CO} frequency found in **2** may be due to the electron-rich phosphido units.

X-ray Structure of 2. Molecules of **2** crystallize in the orthorhombic space group *Pnma* with four molecules in the unit cell. Crystallographic data for **2** are collected in Table I, and a view of 2 is given in Figure 2. Positional parameters, bond lengths, and bond angles are presented in Tables V–VII, respectively. The molecule lies on a crystallographically imposed mirror plane that contains the atoms Pd2, Cl, P2, C10, C11, C13, and C15. As for **1**, the structural parameters of **2** all appear to be normal. The Pd–Pd distances are all notably larger than that found in **1** (average 2.975 Å) although they are still within acceptable limits for Pd–Pd single bonds.[9] The phosphido units adopt fairly symmetrical bridging positions with the Pd–P distances (2.298 Å average) slightly shorter than that observed in **1**. The Pd, P, and Cl atoms and the CO ligand are all virtually in the same plane.[11]

Experimental Section

All operations were performed under oxygen-free nitrogen or under vacuum. Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane and tetrahydrofuran were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Instruments: IR, Perkin-Elmer 1330; NMR, FT-80 (^{31}P, 32.384 MHz), Nicolet NT 360 (^{1}H, 361.084 MHz). IR spectra were recorded as Nujol mulls on NaCl disks or in solution (matched KBr cells). NMR spectra were recorded in C_6D_6 at ambient temperature and are in ppm referenced to Me_4Si (δ = 0.0, ^{1}H) and 85% H_3PO_4(aq) (δ = 0.0, ^{31}P). Melting points were in sealed capillaries under nitrogen (1 atm) and are uncorrected. $[Pd(CO)Cl]_n$[7] and Li-*t*-Bu_2P[8] were prepared as previously described.

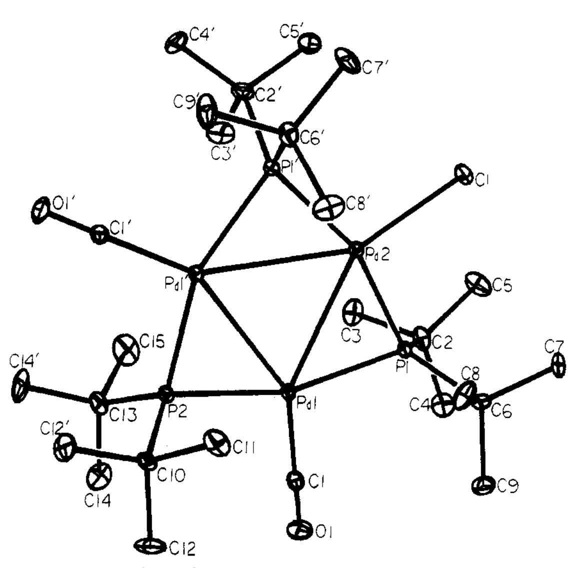

Figure 2. ORTEP view of **2**.

Table VII. Bond Angles (deg) for **2**[a]

Pd1′–Pd1–Pd2	59.43 (4)	Pd1–P2–C10	112.0 (3)
Pd1′–Pd1–P1	108.84 (6)	Pd1–P2–C13	116.9 (3)
Pd1′–Pd1–P2	49.61 (7)	C10–P2–C13	114.1 (6)
Pd1′–Pd1–C1	150.74 (7)	Pd1–C1–O1	178.4 (9)
Pd2–Pd1–P1	49.42 (7)	P1–C2–C3	103.7 (6)
Pd2–Pd1–P2	108.97 (7)	P1–C2–C4	112.8 (8)
Pd2–Pd1–C1	149.57 (7)	P1–C2–C5	109.3 (7)
P1–Pd1–P2	158.33 (7)	C3–C2–C4	100.7 (9)
P1–Pd1–C1	100.2 (3)	C3–C2–C5	109.0 (1)
P2–Pd1–C1	101.4 (3)	C4–C2–C5	110.9 (9)
Pd1′–Pd2–Pd1	61.15 (4)	P1–C6–C7	111.1 (6)
Pd1–Pd2–P1	50.38 (7)	P1–C6–C8	105.7 (6)
Pd1′–Pd2–P1	111.52 (7)	P1–C6–C9	113.9 (7)
Pd1–Pd2–Cl	149.20 (7)	C7–C6–C8	109.9 (9)
P1′–Pd2–P1	161.87 (7)	C7–C6–C9	110.4 (9)
P1–Pd2–Cl	99.1 (3)	C8–C6–C9	105.7 (9)
Pd1–P1–Pd2	80.20 (7)	P2–C10–C11	103.5 (8)
Pd1–P1–C2	113.5 (3)	P2–C10–C12	111.9 (7)
Pd1–P1–C6	114.1 (3)	C11–C10–C12	110.4 (8)
Pd2–P1–C2	116.1 (3)	C12′–C10–C12	108.8 (8)
Pd2–P1–C6	116.0 (3)	P2–C13–C14	111.6 (7)
C2–P1–C6	113.1 (4)	P2–C13–C15	103.3 (9)
Pd1′–P2–Pd1	80.78 (6)	C14′–C13–C14	109.0 (9)
C14–C13–C15	110.6 (9)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Synthesis of $[Pd(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (1) and $Pd_3(\mu\text{-}t\text{-}Bu_2P)_3(CO)_2Cl$ (2). Li-*t*-Bu_2P (4.56 mL of a 0.71 M THF solution, 3.2 mmol) was added dropwise to a suspension of $[Pd(CO)Cl]_n$ (0.55 g, 3.2 mmol) in THF (30 mL) at −78 °C. The mixture quickly darkened and was allowed to warm to room temperature over a period of 1 h. The mixture was stirred at room temperature (3 h), and volatile materials were removed under vacuum. The material was extracted with hexane (2 × 20 mL), leaving a black residue, and volatile materials were again removed under vacuum. The residue was extracted with hexane (2 × 15 mL), and the filtered, combined extracts were concentrated under vacuum (ca. 5 mL). Cooling (−40 °C) produced dark red crystals of **2**, which were collected and dried under vacuum. The black residue of the reaction mixture was partially redissolved in THF (40 mL), and PMe_3 (2 mL) was added to it. The mixture was stirred (16 h) during which time the color changed from black to red and most of the residue dissolved. Volatile materials were removed under vacuum, and the residue was extracted with hexane (3 × 20 mL). The filtered, combined extracts were reduced in volume under vacuum (ca. 25 mL) and cooled (−40 °C),

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(9) See: Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Comprehensive Organometallic Chemistry*, 4th ed.; Wilkinson, G., Stone, F. G. A.; Able, E. W., Eds.; Pergamon: Oxford, England, 1984; p 266 and references therein.

(10) Goldberg, S. Z.; Eisenberg, R. *Inorg. Chem.* **1976**, *15*, 535.

(11) Deviations (Å) through the least-squares plane: Pd(1) −0.046 (1), Pd(2) 0.031 (1), P(1) 0.042 (4), P(2) −0.198 (5), Cl −0.060 (6), C(1) 0.023 (14), O(1) 0.094 (12).

producing red crystals of **1**, which were collected and dried under vacuum. The supernatant was further concentrated and cooled to yield additional amounts of **1**: yield 0.47 g (44% based on Pd); mp 171–175 °C dec. IR: (Nujol mull, NaCl plates) 1462 s, 1415 m, 1372 m, 1349 s, 1290 w, 1274 m, 1168 br, m, 1013 m, 931 br, s 840 w, 807 m, 713 m, 665 m cm^{-1}. ^{1}H NMR (361.084 MHz): δ 1.427 (t, 36 H, μ-P(*t-Bu*)$_2$), 1.410 (t, 18 H, P*Me*$_3$). ^{31}P{^{1}H} NMR (32.384 MHz): δ 289.0 (t, $^2J_{P-P}$ = 41 Hz, μ-*P*(t-Bu)$_2$), −26.6 (t, $^2J_{P-P}$ = 41 Hz, *P*Me$_3$). For 2: yield 0.11 g (12% based on Pd); mp 170–173 °C dec. IR: (hexane solution, KBr cells) 2035 s, sh, 2030 s cm^{-1}; (Nujol mull, NaCl plates) 2040 s, sh, 2035 s, 1359 m, 1168 m, 1016 m, 809 m cm^{-1}. ^{1}H NMR (361.089 MHz): δ 1.455 (t, 36 H, μ-P(*t-Bu*)$_2$), 1.110 (d, 18 H, $^3J_{P-H}$ = 15 Hz, μ-P(*t-Bu*)$_2$). ^{31}P{^{1}H} NMR (32.384 MHz): δ 280.1 (d, $^2J_{P-P}$ = 119 Hz, μ-*P*(t-Bu)$_2$), 207.5 (t, $^2J_{P-P}$ = 119 Hz, μ-*P*(t-Bu)$_2$). Anal. Calcd for $C_{26}H_{54}ClO_2P_3Pd_3$: *C*, 36.90; H, 6.43; P, 10.98. Found: C, 37.02; H, 6.58; P, 10.79.

X-ray Experimental Data. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C using graphite-monochromated Mo Kα radiation. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS.[12] For each structure, the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (MULTAN)[13] and successive cycles of difference Fourier maps followed by least-squares refinement.

1. Crystals were grown from hexane solutions (−40 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 22 and 32°. Examination of the diffraction symmetry and the systematic absence 00l, l = $2n + 1$, indicated a choice of the tetragonal space groups $P4_2$ and $P4_2/m$. The space group $P4_2/m$ was chosen to be the correct one on the basis of successful refinement of the structure. Data were collected in the $+h,+k,+l$ octant between 2θ values of 3 and 48°. The check reflections indicated a 12.0% decrease in intensity over the course of data collection, and hence an anisotropic correction was applied. A Ψ scan of four reflections having χ values between 80 and 90° showed that no absorption correction was necessary, and none was applied. The observed structure factors of equivalent reflections were averaged with agreement factors of 0.025 for intensity and 0.024 on F_o. All non-hydrogen atoms except for C5 and C6 were refined anisotropically. Hydrogen atoms were not located, but their contributions were included in the refinements. Data with intensities less than $3\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor of $P = 0.05$ was used in the final stages of refinement.[14] The atoms were refined to final values of 0.0465 and 0.0613 for R and R_w, respectively. The maximum peak in the final difference Fourier map had a height of 0.503 e/Å^3 and was located 0.963 Å from Pd.

2. Crystals were grown from hexane solutions (−40 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24 and 28°. Examination of the diffraction symmetry and the systematic absences $0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$, indicated a choice of the orthorhombic space groups *Pnma* and $Pn2_1a$. The space group *Pnma* (No. 62) was chosen to be the correct one on the bases of successful refinement of the structure. Data were collected in the $+h,+k,+l$ octant between 2θ values of 3 and 46°. The check reflections indicated <1% decrease in intensity over the course of data collection; hence, no correction was applied. A Ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 77.9% and a maximum transmission of 99.1%. An empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not located but their contribution was included in the refinements. Data with intensities less than $3\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor of $P = 0.06$ was used in the final stages of refinement.[14] The atoms were refined to final values of 0.0439 and 0.0532 for R and R_w respectively. The maximum peak in the final difference Fourier map had a height of 0.965 e/Å^3 and was located 1.215 Å from Pd1. Supplementary material for **1** and **2** is available.[15] Scattering factors were taken from ref 16.

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Registry No. **1**, 111025-75-3; **2**, 111025-74-2; [Pd(CO)Cl]$_n$, 28551-87-3; Pd, 7440-05-3.

Supplementary Material Available: Tables of thermal parameters for **1** and **2** (2 pages); tables of structure factors for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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(12) B. A. Frenz and Associates, College Station, TX 77840, 4th edition, 1981.

(13) Germain, G.; Main, P.; Wolfson, M. M. *Acta. Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

(14) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-square refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4(|F_o|)^2/[\sum(|F_o|)^2]^2$, where $[\sum(|F_o|)^2]^2 = [S^2(C + R^2B) + (P(|F_o|)^2)^2]/L_p{}^2$, where S^2 is the scan rate squared, C is the total background count, R^2 is the ratio of scan time to background count squared, and L_p is the Lorentz–polarization factor.

(15) See paragraph at end of paper regrading supplementary material.

(16) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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Bimetallic Lanthanide Complexes of the Calixarenes: Europium(III) and *tert*-Butylcalix[8]arene

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Addition of a 2 M quantity of $Eu(DMF)_8(ClO_4)_3$ to a solution of the macrocyclic octaphenol *tert*-butylcalix[8]arene in dimethylformamide (DMF) containing triethylamine results in the deposition of yellow crystals of the neutral complex $[Eu_2(LH_2)(DMF)_5]\cdot 4DMF$ ($L = C_{88}H_{104}O_8{}^{8-}$, the octaanion of *tert*-butylcalix[8]arene). The crystals are triclinic, space group $P\bar{1}$, with $a = 21.954$ (6) Å, $b = 17.511$ (11) Å, $c = 17.315$ (10) Å, $\alpha = 76.91$ (5)°, $\beta = 72.86$ (4)°, and $\gamma = 84.14$ (4)°. A single-crystal X-ray structure determination has shown the ligand to adopt a "pinched" conformation with near-twofold rotational symmetry, both europium atoms being encompassed by the ligand in essentially identical environments. The europium atoms are bridged by two phenoxide donor atoms of the macrocyclic ligand and by a solvent (DMF) molecule. Each is also independently bound to two solvent molecules and three phenolic groups, giving eight-coordination in a geometry best described as bicapped trigonal prismatic. One of the capping groups on each europium is believed to be a neutral (protonated) phenolic donor of the calixarene. R was 0.056 for 15 137 "observed" reflections.

The calixarenes[1] are a class of macrocyclic molecules obviously well-suited to act as receptors for both neutral and cationic species.[2] The ready availability of larger species such as calix[6]arene and calix[8]arene (Figure 1) suggests that it should be of particular

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