Inorg. Chem. **1994,** *33,* 6242−6246

Polynuclear Homo- or Heterometallic Palladium(II)−Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 2. Synthesis and Crystal Structure of $[(C_6F_5)_2Pt(\mu\text{-}P(C_6H_5)_2)_2Pd(P(C_6H_5)_3)]\cdot 2C_6H_6$

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Received April 13, 1994[®]

The tetranuclear complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M = Pt (**A**) or Pd (**B**)) react with PPh_3 in acetone affording $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2MCl(PPh_3)]$ (M = Pt (**1**), Pd (**2**)). However, when such reactions are carried out in CH_2Cl_2 or $CHCl_3$/MeOH, the dinuclear complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2ML]$ (L = PPh_3, M = Pt (**3**), Pd (**4**); L = PPh_2Et, M = Pd (**5**)) are obtained. Complexes **3** and **4** can also be obtained by reacting **A** and **B**, respectively, with $O_3ClOAgPPh_3$ in CH_2Cl_2. The ^{31}P NMR indicates that **3**−**5** display Pt→M donor−acceptor bonds while **1** or **2** does not show this type of metal−metal bond. The reaction of **3** or **4** with neutral or anionic monodentate ligands L′ renders dinuclear derivatives $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2ML'(PPh_3)]^{n-}$ ($n = 1$: M = Pt, L′ = Br (**6**); M = Pd, L′ = CN (**7**). $n = 0$: M = Pt, L′ = Py (**8**), CO (**9**); M = Pd, L′ = Py (**10**)) in which the M center is four-coordinate and no Pt→M bond is present. The structure of **4** has been determined by a single-crystal X-ray diffraction study. Crystals are monoclinic, space group *C*2/*m*, with $a = 16.774(5)$ Å, $b = 19.404(4)$ Å, $c = 19.416(4)$ Å, $\beta = 111.54(3)°$, and $Z = 4$. The structure was refined to 5051 data, giving a traditional *R*-factor of 0.0456. The Pt−Pd distance is 2.657(1) Å.

Introduction

The ability of phosphido (PR_2^-) groups to act as bridging ligands and stabilize polynuclear transition metal complexes is well known.[1−6] Moreover, ligands of this type are sufficiently flexible so as to be able to bridge a range of metal−metal distances within the polynuclear framework, from the shorter distances that arise in the presence of metal−metal bonds[2−4,6] to the longer distances when no type of metal−metal interaction is present.[5]

Recently we synthesized the polynuclear phosphido complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M = Pt, Pd) which according to their ^{31}P NMR spectra do not contain Pt−M bonds.[1] In this paper we report on the reactivity of these complexes toward monodentate phosphines (PPh_3, PPh_2Me) which produces, as expected, the cleavage of the bridging $M(\mu\text{-}Cl)_2M$ system and renders, depending on the solvent, dinuclear complexes with or without donor−acceptor Pt→M bonds.

Results and Discussion

Reactions of $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M = Pt (A); M = Pd (B)). Complexes **A** and **B** react with triphenylphosphine, (molar ratio 1:2) in acetone, yielding, after appropriate treatment, the dinuclear anionic derivatives $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2MCl(PPh_3)]$ (M = Pt (**1**); M = Pd (**2**)) (Scheme 1, a). The $M(\mu\text{-}Cl)_2M$ (M = Pt, Pd) bridging system is cleaved and from ^{31}P NMR spectra (see below) it can be inferred that no Pt−M bonds are present in the products.

Moreover, we noted that although **2** is yellow in the solid state (as in acetone solution), its solutions in CH_2Cl_2 or $CHCl_3$ and MeOH are purple and the addition of an excess of NBu_4Br gives a yellow solution. Exploring this behavior further, we carried out the reactions of **A** and **B** with phosphines in CH_2Cl_2 or $CHCl_3$/MeOH and found that under appropriate conditions (see Experimental Section), not only does the cleavage of the bridging system take place, but so also does the elimination of NBu_4Cl, with formation of the dinuclear neutral complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2ML]$ (M = Pt, L = PPh_3 (**3**); M = Pd, L = PPh_3 (**4**), PPh_2Me (**5**)) (Scheme 1, c). The separation of NBu_4Cl takes place very easily in CH_2Cl_2/MeOH when M = Pd, but refluxing followed by treatment of the mixture with water is needed for the total elimination of NBu_4Cl for M = Pt (**3**). On the other hand, the formation of **3** and **4** can be more easily achieved if **A** or **B** is reacted in CH_2Cl_2 with $O_3ClOAgPPh_3$ since the precipitation of AgCl takes place and **3** or **4** is formed in very high yield (Scheme 1, b).

These neutral complexes **3**−**5** are very strongly colored, and their ^{31}P NMR spectra indicate that the phosphido ligands bridge the metal centers, which form Pt→M bonds (see below). The molecular structure of **4** has been established by X-ray studies and confirms the NMR structural data, as will be discussed later.

Reactions of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2MPPh_3]$ (M = Pt, Pd). The strongly colored CH_2Cl_2 solutions of **3** and **4** react with anionic or neutral ligands; the color of the solution fades to yellow, yielding dinuclear anionic (**6**, **7**) or neutral complexes (**8**−**10**) in which the M center is four-coordinate (see Scheme 1, d). From the ^{31}P NMR spectra it can be inferred that as for **1** and **2** no Pt→M bonds are present in these complexes. Although the reaction between **3** and CO, in CH_2Cl_2, yields the stable yellow carbonyl derivative **9** ($\nu(co) = 2101\ cm^{-1}$), **4** reacts with CO under similar conditions, giving a brown solid ($\nu(co) = 2119\ cm^{-1}$) which could not be fully characterized

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[®] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

(1) Part 1: Forniés, J.; Fortuño, C.; Navarro, R.; Martínez, F.; Welch, A. J. *J. Organomet. Chem.* **1990**, *394*, 643.

(2) Loeb, S. J.; Taylor, H. A.; Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1977.

(3) Blum, T.; Braunstein, P.; Tiripicchio, A.; Tiripicchio Camellini, M. *Organometallics* **1989**, *8*, 2504.

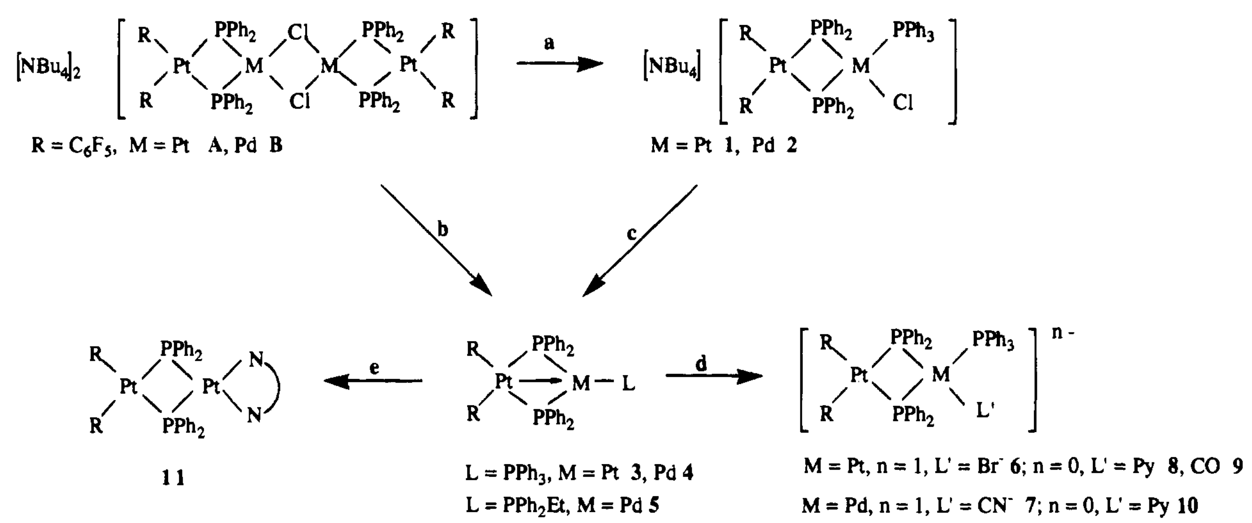
(4) Powell, J.; Couture, C.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem.* **1989**, *28*, 3437.

(5) Carty, A. J.; Hartstock, F.; Taylor, N. C. *Inorg. Chem.* **1982**, *21*, 1349.

(6) Morrison, E. D.; Harley, A. D.; Marcelli, M. A.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 1407.

0020-1669/94/1333-6242$04.50/0

Scheme 1



a: PPh_3 in acetone; b: $O_3ClOAgPPh_3$ in CH_2Cl_2; c: $CH_2Cl_2/CH_3OH/H_2O$; d: L in acetone or CH_2Cl_2; e: 1,10 phen.H_2O in CH_2Cl_2.

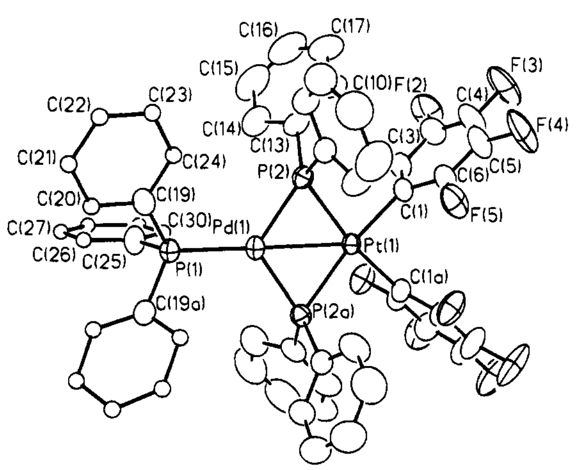


Figure 1. Computer drawing of one molecule of compound **4** from the X-ray crystal structure. Atomic sites that were refined anisotropically are represented by their 35% probability ellipsoids. Other atoms are drawn as small circles.

since it decomposes rapidly by losing CO, yielding the starting material, **4**. This lack of stability has been observed for other carbonyl palladium(II) containing complexes.[7]

The reaction of **3** with a neutral didentate ligand (1,10-phenanthroline) results in the displacement of the PPh_3 yielding **11** (Scheme 1, e). Complexes of this type can be obtained directly by reacting **A** or **B** with didentate chelating ligands such as bipy, phen or dppm; the molecular structure of **11** obtained by this latter method has been reported previously[1] and indicates that no Pt−Pt interactions are present in this compound, in accord with the ^{31}P NMR data.

Crystal Structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(PPh_3)]\cdot 2C_6H_6$ (4). The structure of one molecule of complex **4** is shown in Figure 1. Crystal data are summarized in Table 1, and a list of selected distances and angles is given in Table 2.

The structure of **4** consists of a heterodinuclear compound formed by two fragments which, neglecting the Pt→Pd bond, can be described as (a) a distorted square planar platinum environment formed by two C_6F_5 groups (mutually cis) and two phosphido groups and (b) a distorted triangular palladium environment formed by the two phosphido bridging groups and a triphenylphosphine. The two coordination environments share an edge containing the P atoms of the bridging PPh_2 ligands. The Pt, Pd and P(1) atoms are located in a crystallographic mirror plane. The square-planar platinum environment (C(1), C(1a), P(2), P(2a), plane 1, in which an "a" appended to an atom name signifies transformation by the crystallographic

Table 1. Crystal Data for $(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(PPh_3)\cdot 2C_6H_6$

formula	$PtPdC_{66}H_{47}F_{10}P_3$
fw	1424.5
space group	$C2/m$ (No. 12)
a, Å	16.774(5)
b, Å	19.404(4)
c, Å	19.416(4)
β, deg	111.54(3)
V, Å^3	5878(3)
Z	4
d_{calcd}, g/cm^3	1.609
μ(Mo Kα), cm^{-1}	29.6
radiation (graphite monochromated)	Mo Kα (λ_α = 0.710 73 Å)
temp, °C	22 ± 2
R_w[a]	0.1053
R[b]	0.0456 (for $F_o^2 \geq 2\sigma(F_o^2)$)

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(PPh_3)\cdot 2C_6H_6$[a]

Pt(1)−Pd(1)	2.6571(9)	Pt(1)−C(1)	2.077(6)
Pt(1)−P(2)	2.354(2)	Pd(1)−P(2)	2.243(2)
Pd(1)−P(1)	2.272(2)	P(1)−C(25)	1.812(10)
P(1)−C(19)	1.831(7)	P(2)−C(13)	1.815(8)
P(2)−C(7)	1.821(7)		
C(1)−Pt(1)−C(1a)	84.7(4)	C(1)−Pt(1)−P(2a)	169.8(2)
C(1)−Pt(1)−P(2)	85.1(2)	P(2a)−Pt(1)−P(2)	105.05(9)
C(1)−Pt(1)−Pd(1)	137.3(2)	P(2)−Pt(1)−Pd(1)	52.75(4)
P(2)−Pd(1)−P(2a)	112.83(9)	P(2)−Pd(1)−P(1)	123.46(4)
P(2)−Pd(1)−Pt(1)	56.68(4)	P(1)−Pd(1)−Pt(1)	177.84(7)
C(25)−P(1)−C(19)	105.5(3)	C(19)−P(1)−C(19a)	102.8(5)
C(25)−P(1)−Pd(1)	110.4(3)	C(19)−P(1)−Pd(1)	115.7(2)
C(13)−P(2)−C(7)	105.1(3)	C(13)−P(2)−Pd(1)	127.1(3)
C(7)−P(2)−Pd(1)	118.9(2)	C(13)−P(2)−Pt(1)	116.8(2)
C(7)−P(2)−Pt(1)	115.0(2)	Pd(1)−P(2)−Pt(1)	70.57(6)

[a] Symmetry transformation used to generate equivalent atoms: (a) $x, -y, z$.

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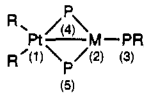
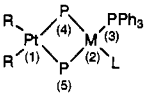
(7) Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1985**, *4*, 1912.

Table 3. Relevant ^{31}P NMR Data[a,b]

		$\delta(P_3)$	$\delta(P_4,P_5)$	J_{13}	J_{23}	J_{14} or J_{15}	J_{24} or J_{25}	J_{34} or J_{35}
M = Pt, $PR_3 = PPh_3$ (**3**)		60.8(t)	240.0(d)	136	5414	1223.8	2986.8	55.5
M = Pd, $PR_3 = PPh_3$ (**4**)		41.8(t)	226.8(d)	188.9		1345.3		25.6
M = Pd, $PR_3 = PPh_2Et$ (**5**)	room temp	41.1(s)	230.1(s)	183.7		1345.2		*c*
	−60 °C	47.1(t)	235.5(d)	191.6		1368.5		20.4

[a] Recorded in $CDCl_3$ solution; *J* values in hertz. [b] Abbreviations: d = doublet, s = singlet, t = triplet. [c] See text.

Table 4. Relevant ^{31}P NMR Data[a]

	$\delta(P_3)$	$\delta(P_4)$	$\delta(P_5)$	J_{14}	J_{15}	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}
M = Pt, L = Cl^- (**1**)[b]	24.8					2009					
M = Pd, L = Cl^- (**2**)	19.6	−141.0	−138.9	*c*	*c*				7.9	354.6	226.3[d]
M = Pt, L = Br^- (**6**)[e]	24.2					2031.7					
M = Pd, L = CN^- (**7**)	20.9	−154.2	−126.9	1604.4	1726.6				*f*	317.5	185.7
M = Pt, L = Py (**8**)	22.5	−150.7	−139.6	1880.0	*g*	2008.5	2228.0	*g*	*f*	292.6	154.9
M = Pt, L = CO (**9**)	19.2	−121.1	−109.7	1695.2	1270.9	1920.0	1946.6	1842.8	*f*	210.0	132.5
M = Pd, L = Py (**10**)[h]	17.7										

[a] Recorded in HDA solution; *J* values in hertz. [b] Second order spectrum (ABX spin system). Neither of the two expected AB quartets can be identified, and the spectrum cannot be analyzed. Signals due to PPh_2^- appear in the −130 and −165 ppm range. $J_{AX} + J_{BX} = 350.6$ Hz. [c] J_{14} and J_{15} cannot be independently evaluated. The separation between platinum satellites is 1790.7 Hz. [d] $|J_{45}|$. [e] See footnote *b*. Signals due to PPh_2^- appear around −145 ppm. $J_{AX} + J_{BX} = 351.5$ Hz. [f] Not observed. [g] The signal due to P(5) does not clearly show two pairs of platinum satellites. The observed satellites are broad, indicating that $^1J_{Pt(1)-P(5)} \approx {}^1J_{Pt(2)-P(5)}$ with a separation of 1762.9 Hz. [h] See footnote *b*. Signals due to PPh_2^- in the −128 and −150 ppm range. $J_{AX} + J_{BX} = 302.8$ Hz.

mirror), the triangular palladium environment (P(1), P(2), P(2a), plane 2) and the PtP_2Pd ring (plane 3) are planar; the dihedral angle formed by plane 1 and plane 2 is 9.8(2)° while the dihedral angles formed by plane 1−plane 3 and plane 2−plane 3 are respectively 5.8(2) and 3.99(5)°. Atom C(1) lies essentially in the same plane as Pt(1), P(2) and P(2a); its deviation from the plane of the latter three atoms is 0.010(6) Å. The most remarkable feature in this structure is the short Pt-Pd distance, 2.657(1) Å, in the range found in other Pd or Pt complexes with metal−metal bonds,[8−10] although in the latter cases the metal centers display a formal oxidation state of (I) and are bonded covalently while in **4**, both metal centers display a formal oxidation state of (II) and the metal−metal bond must be donor−acceptor (Pt→Pd) in nature.

The Pt−P−Pd angles are very small 70.57(6)°, similar to those shown by other phosphido ligands that bridge metal−metal bonds,[2−4,6,8,11] pointing to the existence of a Pt→Pd bond. A concomitant effect is that the intracycle angles at the metal atoms are larger than 90° (P(2)−Pt(1)−P(2a), 105.05(9)°; P(2)−Pd(1)−P(2a), 112.83(9)°). This molecule provides another example of the flexibility of a bridging phosphido ligand, which is able to adapt to the steric requirements of the metal centers that it bridges. It is worthwile to compare the Pt−P−Pd angles in **4** with those found in $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$, **11** (102.7(1) and 103.2 (1)°), a dinuclear compound without any bonding interaction between the metal centers (Pt••Pt 3.585(1)Å).[1] Although we believe that this compound does posses a Pt→Pd donor−acceptor bond, our judgement is partially based on the broad consistency among the features of **4** (both structural and ^{31}P NMR) and between **4** and other compound possessing similar bonds. Nevertheless, if consider alone and without further context, the geommetrical features of **4** could also be interpreted in terms of a strong PtP_2Pd bridging interaction not driven primarily by metal−metal bonding.

NMR Spectra. As for other phosphido-bridged complexes, the $^{31}P\{^1H\}$ NMR spectra of the present systems give important structural evidence. The most relevant data for the complexes reported here are collected in Tables 3 and 4, along with the atom numbering scheme for assignment of the resonances and coupling constants. Literature data indicate that the ^{31}P chemical shifts of the bridging phosphido ligands are dependent on the presence or absence of a metal−metal bond supported by these ligands. So, although this is not conclusive, the data reported show that for most μ-PR_2 ligands bridging a metal−metal bond, the phosphorus chemical shift is downfield (δ from +50 to +300 ppm), while for the same type of ligands bridging two metal centers without a metal−metal bond, the resonances appear upfield (δ from +50 to −200 ppm).[12,13] However, it has been suggested that since exceptions do occur,[14,15] this type of correlation can be made only for closely related series of compounds supported by X-ray crystallography.

The ^{31}P NMR spectra of **3**−**5** can be interpreted in terms of a first order spin system model. Both sets of signals (μ-PPh_2 and PR_3) are well separated by ca. 180 ppm and show platinum satellites (see Table 3). The resonances due to μ-PPh_2 groups appear downfield, indicating the presence of Pt−M bonds in all cases. Moreover, the J_{23} in **1** is large (5414 Hz) which, as for other cases, indicates a weak trans influence of the metal−metal bond and hence suggests relatively weak Pt→Pt donation.[2,4,6,16] The assignment of J_{14} (or J_{15}) and J_{24} (or J_{25}) in **3**

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(8) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448.

(9) Skapski, A. C.; Troughton, P. G. H. *J. Chem. Soc. A* **1969**, 2772.

(10) Forniés, J.; Martínez, F.; Navarro, R.; Redondo, A.; Tomás, M.; Welch, A. J. *J. Organomet. Chem.* **1986**, *316*, 351.

(11) Braunstein, P.; Jesús, E.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1992**, *31*, 411.

(12) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186.

(13) Carty, A.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27.

(14) Rosen, R. P.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J. P.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846.

(15) Jones, R. A.; Wright, T. C.; Atwood, J. C.; Hunter, W. E. *Organometallics* **1983**, *2*, 470.

(16) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

Table 5. Relevant ^{19}F NMR Data

complex		$\delta(F_o)$	$\delta(F_m)$	$\delta(F_p)$	$^3J_{Pt-F}$, Hz
1^a		−113.2 (4 F)	−165.9 (4 F)	−166.9 (1 F), −167.0 (1 F)	317.5
2^a		−113.2 (2 F), −113.4 (2 F)	−165.4 (4 F)	−166.2 (1 F), −166.3 (1 F)	≈327.7
3^b		−119.3 (4 F)	−165.4 (4 F)	−162.8 (2 F)	302.4
4^b		−118.8 (4 F)	−164.4 (4 F)	−162.0 (2 F)	303.8
5^b		−117.2 (4 F)	−162.9 (4 F)	−160.6 (2 F)	305.9
6^a		−108.3 (2 F), −108.6 (2 F)	−161.2 (2 F), −161.3 (2 F)	−162.2 (1 F), −162.4 (1 F)	350.6, 281.5
7^a	room temp	−113.6 (4 F)	−166.3 (4 F)	−167.4 (2 F)	≈344.4
	−60 °C	−113.7 (2 F), −114.3 (2 F)	−165.2 (4 F)	−166.0 (2 F)	317.4, 329.2
8^b		−116.4 (2 F), −116.9 (2 F)	−166.3 (6 F)		331.0, 329.8
9^b	room temp	−116.6 (4 F)	−165.5 (4 F)	−165.0 (2 F)	339.4
	−55 °C	−116.7 (4 F)	−164.9 (4 F)	−164.1 (1 F), −164.4 (1 F)	332.6
10^a		−113.5 (2 F), −114.2 (2 F)	−165.9 (6 F)		288.2, 306.4

[a] Solvent: HDA. [b] Solvent: $CDCl_3$.

is made on the basis of the large trans influence of the pentafluorophenyl groups[17] and on the value of J_{14} or J_{15} in complexes **4** and **5**. J_{13} is observed in all cases. The NMR spectrum of **5** at room temperature does not show coupling between phosphido and phospine P atoms (J_{34}) although this coupling can be observed in the low temperature NMR spectrum (−60 °C). A similar behavior has been described previously for $[(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2ML_n]$ (M = Ni, Pt).[18]

For complexes **1**, **2**, and **6**−**10**, two well separated sets of signals, due to PPh_2 and PPh_3, can be observed (see Table 4). The resonances due to the bridging PPh_2 groups appear at very high field, indicating the absence of metal−metal bonds in the complexes. The ^{31}P NMR spectra of **7**−**9** can be easily analyzed in terms of first order spin systems (AMX), with the corresponding platinum satellites. Complexes **1**, **2**, **6**, and **10** show second order ^{31}P NMR spectra (ABX spin system), and only for **2** can one of the two expected AB quartets be identified and the analysis of the spectrum carried out. For complexes **1**, **6**, and **10** neither of the two expected AB quartets in the high field region could be identified preventing the full analysis of the spectra. In Table 4 are given the range of chemical shifts. However, the resonances due to PPh_3 ($\delta(P_3)$) in these complexes appear as four signals (i.e., a typical pattern of the X part of an ABX spin system) from which ($J_{AX} + J_{BX}$) can be measured.

The ^{19}F NMR data are given in Table 5 and are consistent with the proposed structures.

In complexes **3**−**5** both C_6F_5 groups are equivalent and appear in all cases as an AA′MXX′ system.

Complexes **1**, **2**, and **6**−**10**, according to the proposed structure, contain two inequivalent C_6F_5 groups. Their ^{19}F NMR spectra do not show the full set of signals expected since some of them are overlapped (see Table 5). However, in all cases either two *o*-F or two *m*-F or two *p*-F can be detected, in good accord with the proposed structure. Furthermore, the intensities of the signals are also in agreement with this structure

Concluding Remarks

The reaction of the tetranuclear derivatives $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ with neutral monodentate ligands produces the cleavage of the $M(\mu\text{-}Cl)_2M$ bridging system, giving dinuclear complexes containing four-coordinate Pt and M centers with bridging PPh_2 and without Pt−M bonds (**1** and **2**). However the elimination of the chloride bonded to M in these complexes (see Scheme 1) renders dinuclear complexes containing three-coordinate M centers and in which a Pt→M donor−acceptor bond completes the electron density of M (**3**−**5**). The presence of such a type of bond requires three-coordination on M since the reaction of these complexes with neutral or anionic ligands renders complexes with four coordinated M and without Pt→M bonds (**6**−**10**).

Experimental Section

C, H and N analyses, IR spectra, ^{19}F and ^{31}P NMR spectra and conductance measurements were performed as described elsewhere.[1] Literature methods were used to prepare the following starting materials: $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (**A**),[1] $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (**B**);[1] $[O_3ClOAgPPh_3]$.[19]

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

$[NBu_4][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2PtCl(PPh_3)]$ (1). PPh_3 (0.019 g, 0.072 mmol) was added to a solution of 0.100 g (0.036 mmol) of **A** in 20 cm^3 of acetone, and the resulting colorless solution was stirred at room temperature for 17 h. By evaporating almost to dryness and addition of ^{i}PrOH (~5 cm^3), a white solid, which was washed with ^{i}PrOH, was obtained (83% yield). Λ_M: 75 Ω^{-1} cm^2 mol.$^{-1}$ IR (Nujol): 777, 768 cm^{-1};[20] ν(Pt−Cl) 280 cm^{-1}. Anal. Found (calc for $C_{70}ClF_{10}H_{71}NP_3Pt_2$): C, 50.91 (51.43); H, 4.63 (4.38); N, 0.62 (0.86).

$[NBu_4][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2PdCl(PPh_3)]$ (2). Complex **2** was prepared similarly to **1** from **B** (0.100 g, 0.039 mmol), acetone (20 cm^3) and PPh_3 (0.021 g, 0.080 mmol). Yield: 86%. Λ_M: 88 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 779, 770 cm^{-1};[20] ν(Pd−Cl) 280 cm^{-1}. Anal. Found (calc for $C_{70}ClF_{10}H_{71}NP_3PdPt$): C, 53.57 (54.38); H, 4.76 (4.63); N, 0.87 (0.90).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)]$ (3). (a) To a CH_2Cl_2 (~10 cm^3) solution of 0.150 g (0.054 mmol) of **A** was added a $CHCl_3$/MeOH (15 cm^3/5 cm^3) solution of 0.029 g (0.110 mmol) of PPh_3. The colorless solution was refluxed for 30 min, and the resulting dark orange solution was stirred for 5 min with 40 cm^3 of H_2O. After separation of the two layers, the red organic solution was stirred for 5 min with a mixture of 40 cm^3 of H_2O + 10 cm^3 of MeOH. After separation of the two layers, the resulting red solution was treated in a similar way twice and then evaporated to dryness. The red solid was stirred for 2.5 h with 40 cm^3 of MeOH (53% yield).

(b) To a CH_2Cl_2 (15 cm^3) solution of 0.090 g (0.033 mmol) of **A** was added $O_3ClOAgPPh_3$ (0.031 g, 0.066 mmol), and the mixture was stirred at room temperature for 30 min. After separation of the AgCl, the resulting solution was treated with ~15 cm^3 of ^{i}PrOH, partially evaporated and the red solid was washed with ^{i}PrOH. Yield: 72%. IR (Nujol): 789, 779 cm^{-1}.[20] Anal. Found (calc for $C_{54}F_{10}H_{35}P_3Pt_2$): C, 47.68 (47.81); H, 2.99 (2.60).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(PPh_3)]$ (4). (a) To an orange solution of 0.250 g (0.097 mmol) of **B** in CH_2Cl_2 (~2 cm^3) was added 0.051 g (0.194 mmol) of PPh_3, and the mixture was stirred at room temperature for 2 min, after which MeOH (~8 cm^3) was added. After stirring at

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(17) Usón, R.; Forniés, J.; Espinet, P.; Fortuño, C. *J. Chem. Soc., Dalton, Trans.* **1986**, 1849.

(18) Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1222.

(19) Cotton, F. A.; Falvello, L. R.; Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Ara, I. *Inorg. Chem.* **1987**, *26*, 1366.

(20) X-sensitive mode of the C_6F_5 group: Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *28*, 188.

room temperature for 30 min, dark-violet crystals, which were washed with MeOH, precipitated (83% yield).

(b) Complex **4** can also be prepared (95% yield) by reacting **B** (0.200 g, 0.078 mmol) and $O_3ClOAgPPh_3$ under conditions similar to those used for preparing **3** (method b). IR (Nujol): 788, 778 cm^{-1}.[20] Anal. Found (calc for $C_{54}F_{10}H_{35}P_3PdPt$): C, 51.32 (51.14); H, 2.98 (2.78).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(PPh_2Et)]$ (5). Complex **5** was prepared as complex **3** (method a) by reacting **B** (0.100 g, 0.039 mmol) with PPh_2Me (16 μL, 0.078 mmol) in CH_2Cl_2 (~3 cm^3) at room temperature. Yield: 53%. IR (Nujol): 790, 778 cm^{-1}.[20] Anal. Found (calc for $C_{50}F_{10}H_{35}P_3PdPt$): C, 49.48 (49.23); H, 2.95 (2.89).

$[NBu_4][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2PtBr(PPh_3)]$ (6). To a red solution of 0.060 g (0.044 mmol) of **3** in CH_2Cl_2 (5 cm^3) was added 0.015 g (0.046 mmol) of NBu_4Br, and the resulting pale-yellow solution was stirred at room temperature for 2 min and then evaporated to dryness. The oily yellow residue was treated with ^iPrOH (~10 cm^3), and the resulting yellow solid was washed with ^iPrOH (89% yield). Λ_M: 82 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 777, 769 cm^{-1}.[20] Anal. Found (calc for $BrC_{70}F_{10}H_{71}NP_3Pt_2$): C, 50.06 (50.06); H, 4.46 (4.26); N, 0.83 (0.83).

$[NBu_4][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(CN)(PPh_3)]$ (7). KCN (0.019 g, 0.292 mmol) in MeOH (4 cm^3) was added to a CH_2Cl_2 (20 cm^3) solution of **4** (0.300 g, 0.236 mmol). After 10 min stirring at room temperature NBu_4ClO_4 (0.081 g, 0.237 mmol) was added and the solution was evaporated to dryness. The residue was extracted with 20 cm^3 of CH_2Cl_2 and precipitated with *n*-hexane. Yield: 95%. Λ_M: 88 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 778, 769 cm^{-1};[20] $\nu(C{\equiv}N)$ 2121 cm^{-1}. Anal. Found (calc for $C_{71}F_{10}H_{71}N_2P_3PdPt$): C, 55.77 (55.49); H, 4.52 (4.66); N, 1.79 (1.82).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)(py)]$ (8). To a red solution of 0.075 g (0.055 mmol) of **1** in CH_2Cl_2 (5 cm^3) was added 1.1 cm^3 of a CH_2Cl_2 solution of Py (0.05 M) and the resulting pale-yellow solution was stirred at room temperature for 20 min. Evaporation almost to dryness and addition of ~5 cm^3 of *n*-hexane renders **8** (91% yield). IR (Nujol): 780, 771 cm^{-1}.[20] Anal. Found (calc for $C_{59}F_{10}H_{40}NP_3Pt_2$): C, 49.13 (49.34); H, 2.66 (2.81); N, 0.81 (0.97).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)(CO)]$ (9). Into a red solution of **1** (0.070 g, 0.052 mmol) in CH_2Cl_2 (10 cm^3) was bubbled CO at room temperature for 5 min; *n*-hexane (15 cm^3) was added to the resulting yellow solution. CO was bubbled in again for 30 min and the resulting yellow precipitate was washed with *n*-hexane Yield: 84%. IR (Nujol): 784, 775 cm^{-1};[20] $\nu(C{\equiv}O)$ 2101 cm^{-1}. Anal. Found (calc for $C_{55}F_{10}H_{35}OP_3Pt_2$): C, 48.36 (47.70); H, 2.53 (2.55).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(PPh_3)(py)]$ (10). Complex **10** was obtained similarly to **8**: 0.100 g (0.079 mmol) of **2**, Py (11 μL, 0.11 mmol) and 10 cm^3 of CH_2Cl_2 were used. **10** was precipitated by addition of Et_2O. Yield: 86%. IR (Nujol): 779, 770 cm^{-1}.[20] Anal. Found (calc for $C_{59}F_{10}H_{40}NP_3PdPt$): C, 51.86 (52.59); H, 3.07 (2.99); N, 1.06 (1.04).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ (11). To a red solution of **3** (0.025 g, 0.018 mmol) in CH_2Cl_2 (4 cm^3) was added 1,10-phen·H_2O (0.004 g, 0.002 mmol), and the solution was stirred at room temperature for 15 min. The yellow solution was evaporated almost to dryness and treated with MeOH (15 cm^3) yielding **11**. Yield: 62%.

X-ray Structure Determination of Complex 4. Crystals of **4** for X-ray analysis were grown by slow diffusion (14 h) of *n*-hexane into a very concentrated benzene solution of **4** at 6 °C. Diffraction data were taken from a block-like red crystal at room temperature, using routine procedures. An empirical absorption correction was based on ψ-scans of 10 scattering vectors. The solution of the structure was carried out with the comercial program package SHELXTL-PLUS,[21,22] and the final refinement was done by the program Shelxl-93.[23] A summary of important crystal data is given in Table 1.

Structure Solution and Refinement. Systematic absences were consistent with space groups *C*2, *Cm* and *C*2/*m*. We tested all three groups thoroughly, as is detailed in the supplementary material; and as all three gave qualitatively similar results, including for the disordered moieties (vide infra), we conducted the final refinement using the centric group *C*2/*m*.

The crystallographic asymmetric unit comprises two half-molecules of benzene and a half-molecule of complex **4**. The latter sits across a crystallographic mirror, with atoms Pt(1), Pd(1) and P(1) lying on the symmetry element.

We found the triphenylphosphine ligand to be disordered about the mirror plane. The following description of the disorder is best considered with reference to Figure 1. The phosphorus atom sits on the crystallographic mirror. The more distal phenyl group C(19)−C(24) in the figure is disordered two ways, with the two congeners possessing a common *ipso* carbon atom, C(19). A second phenyl site is related to the first by the mirror plane, and thus comprises two disordered congeners as well. N.B.: we use the letter "a" to indicate a symmetry relative and primed atom names to represent a disordered congener. Thus, in Figure 1, atom C(19a) is the mirror image of atom C(19). The occupancies of these congeneric phenyl moieties were set to a ratio of 1:2, to accommodate a random distribution of the acceptable conformations of PPh_3. (A complete description of the model is given as supplementary material.)

The third phenyl site is also disordered two ways, and is located at the mirror plane. One congener, C(25) through C(30), lies in the mirror plane. Its *ipso* (C(25)) and *para* (C(28)) carbon atoms are shared with the second congener, which is roughly perpendicular to the plane. The two congeners of this phenyl group were refined with 50% site occupancy each.

In sum, then, the PPh_3 ligand shows a total of eight potential conformations, of which two are not chemically reasonable, owing to a short contact distance (2.73(4) Å) betwen carbon atoms of two rings. The remaining six conformations are consistent with the geometries of low-energy conformations found in a statistical analysis of structures containing the moiety Ph_3PO.[24] Each of the six phenyl group orientations contributes to at least one of the acceptable overall conformations.

For the final refinement, all non-hydrogen atoms on fully occupied positions in compound **4** were refined anisotropically. The partially occupied sites of the disordered phenyl rings, along with the atoms of the interstitial benzene moieties, were refined isotropically. Similarity restraints and restraints to C_2 symmetry were applied to the phenyl groups of the PPh_3 ligand. Hydrogen atoms were included only for the bridging PPh_2 ligand; nine were located in a difference map and one was placed in a calculated position. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. Loose restraints were applied to three of the C−H distances. In all, 365 parameters were refined to 5051 data and 114 observational restraints. All positive diffraction intensities were used, and the structure was refined to F_o^2. The final, convergent refinement gave the residuals listed in Table 1.

Acknowledgment. We thank the Spanish Comisión Interministerial de Ciencia y Tecnología (project PB 92-0360) for financial support.

Supplementary Material Available: A detailed description of the structural model of compound **4** and its refinement and tables of general crystallographic data, all atomic coordinates, bond lengths and angles, and anisotropic displacement parameters (16 pages). Ordering information is given on any current masthead page.

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(21) Crystallographic calculations were done on a Local Area VAXcluster (VMS V5.5) and on a Hewlett-Packard 715/50 (HP-UX V9.0). Initial data reduction was done by the program REDU4 (Stoe) Release 7.03.

(22) SHELXTL-PLUS Release 4.21/V (© 1990, Siemens Analytical X-ray Instruments, Inc.).

(23) SHELXL-93: FORTRAN-77 program for the refinement of crystal structures from diffraction data. Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation.

(24) Dunitz, J. D. *Trans. Am. Crystallogr. Assoc.* **1984**, *20*, 1.