

Platinum Dimers Bridged by Diphenylphosphinocyclopentadienyl Ligands. Molecular Structures and NMR Studies of Two Isomeric Forms of the Complexes $[\text{Pt}_2\text{R}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$

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Abstract: Reactions of $[\text{PtClR}(\text{cod})]$ with $\text{TiC}_5\text{H}_4\text{PPh}_2$ yield dimeric complexes of the type $[\text{Pt}_2\text{R}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ (**1a**, R = Me; **1b**, R = Et; **1c**, R = Np; **1d**, R = Ph). The crystal structure of **1a** has been determined. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.155$ (2) Å, $b = 14.696$ (3) Å, $c = 21.080$ (5) Å, $\beta = 90.02$ (2)°, $V = 3146.0$ (11) Å³, and $Z = 4$. Least-squares refinement converged at $R = 0.0490$ and $R_w = 0.0550$ based on 6340 reflections with $F > 4.0\sigma(F)$. The molecular structure reveals a structure of the type $[\text{Pt}_2\text{Me}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-}\eta^1\text{-}1,1\text{-C}_5\text{H}_4\text{PPh}_2)]$, in which the cyclopentadienyl group of one dppc ligand coordinates in the usual η^5 mode, whereas the other is bound in η^1 fashion, with both platinum and phosphorus attached to the same carbon atom giving a spirocyclic structure and a four-membered Pt_2PC ring containing a Pt→Pt dative bond. The dimers are fluxional in solution at ambient temperature, but the solid-state structure of **1a** is consistent with the NMR parameters obtained in solution at low temperature for all the complexes. A minor species is detected in solution for **1c** and **1d**, which is consistent with a symmetrical dimer of the type $[\text{Pt}_2\text{R}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$. Crystals of **1d** were obtained by slow evaporation of an ether solution and the crystal structure was determined. This compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.256$ (4) Å, $b = 13.693$ (5) Å, $c = 14.687$ (7) Å, $\alpha = 95.52$ (3)°, $\beta = 109.68$ (3)°, $\gamma = 101.87$ (3)°, $V = 1869.7$ (13) Å³, and $Z = 2$. Least-squares refinement converged at $R = 0.0221$ and $R_w = 0.0266$ based on 6759 reflections with $F > 6.0\sigma(F)$. The molecular structure reveals that both cyclopentadienyl groups are indeed bonded in η^5 fashion, but the molecule is distorted and does not possess a center of symmetry. An equilibrium between the two forms in solution is proposed, and the symmetrical dimer, or a closely related analogue, is suggested to be an intermediate in the fluxional process observed for the unsymmetrical dimer at ambient temperature.

Introduction

There has been considerable interest in recent years in the construction of homo- and heterometallic complexes through the use of unsymmetrical, bidentate ligands. One such is the diphenylphosphinocyclopentadienyl (dppc) ligand, which typically coordinates to one metal by means of the η^5 -cyclopentadienyl group and to a second through the phosphino group. This ligand has proved particularly versatile in the synthesis of complexes containing dissimilar metals.¹ These include complexes prepared from the commercially available bis(diphenylphosphino)ferrocene (dppf) fragment,²⁻²¹ as well as those prepared from one²²⁻³¹ or two³²⁻³⁸ dppc (or dimethylphosphinocyclopentadienyl (dmppc)) ligands by consecutively attaching the two metal centers. Several dicobalt, dirhodium, and diiridium complexes bridged by dppc or dmppc ligands have also been prepared.³⁹⁻⁴³

Many of these complexes have been characterized by X-ray diffraction methods, and in each case the cyclopentadienyl group is attached to the metal in the η^5 mode. In a previous communication we reported the structure of $[\text{Pt}_2\text{Ph}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$,⁴⁴ in which the cyclopentadienyl rings are also bonded to platinum in η^5 fashion. We have shown that the cyclopentadienyl group of the dppc ligand can coordinate in several different modes, however.⁴⁵ In this paper we will describe the unexpected structure of $[\text{Pt}_2\text{Me}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ in the solid state, which is adopted by each complex of the type $[\text{Pt}_2\text{R}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ in solution, and its relationship to that reported previously for its phenyl analogue.⁴⁴

Results and Discussion

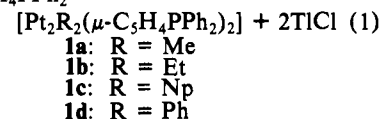
Addition of 1 mol equiv of $\text{TiC}_5\text{H}_4\text{PPh}_2$ to a benzene solution of $[\text{PtClR}(\text{cod})]$ (R = Me, Et, Np, Ph; cod = 1,5-cyclooctadiene) at 25 °C under an argon atmosphere results in the formation of a precipitate of TiCl and a clear yellow solution. Filtration, or purification by passing the solution through a short alumina

Table I. ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR Parameters for **1a-d**^a

	1a (-50 °C)	1b (-40 °C)	1c ^b (-50 °C)	1d ^c (-60 °C)
δP_1	-13.3 d	-13.7 d	-16.0 d	-21.0 d
δP_2	16.8 d	15.8 d	11.4 d	12.7 d
¹ J(P ₁ ,Pt ₁)	4147	4338	4224	4085
¹ J(P ₂ ,Pt ₂)	3969	4281	4396	3589
² J(P ₁ ,Pt ₂)	305	358	365	351
² J(P ₂ ,Pt ₁)	126	140	118	105
³ J(P ₁ ,P ₂)	20	19	21	22
δPt_1	-4278 dd	-4252 d	-4266 d	-4103 d
δPt_2	-3389 dd	-3369 dd	-3387 dd	-3045 dd
¹ J(Pt ₁ ,Pt ₂)	1134	1180	1154	1100

^a Recorded in CDCl₃ solution. Chemical shifts are relative to external 85% H₃PO₄ (³¹P) or K₂PtCl₄ (¹⁹⁵Pt), positive shifts representing deshielding. Coupling constants are in hertz. ^b A minor species is observed in CD₂Cl₂ solution at -90 °C at $\delta\text{P} -1.0$, $\delta\text{Pt} -3763$, ¹J(Pt,P) 5840 Hz. ^c A minor species is observed at $\delta\text{P} -1.6$, $\delta\text{Pt} -3512$, ¹J(Pt,P) 5690 Hz.

column, followed by solvent removal produces $[\text{Pt}_2\text{R}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ in good yield (eq 1). The reaction can be carried



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Table II. ^1H NMR parameters for **1a-d**^a

	1a (-50 °C)	1b (-40 °C)	1c (-50 °C)	1d (-60 °C)
C_5H_4	4.61 ^b	4.60 ^b	3.84 ^b	4.63 ^b
	4.85 ^b	4.73 ^b	4.86 ^b	5.05 ^b
	5.71 ^c	5.77 ^c	5.53 ^c	5.58 ^c
	6.32 ^b	6.38 ^b	5.96 ^b	6.02 ^b
	6.39 ^c	6.38 ^b	6.16 ^c	6.14 ^c
	6.42 ^c	6.38 ^c	6.51 ^b	6.20 ^c
	6.49 ^b	6.61 ^c	6.51 ^c	6.42 ^b
	6.77 ^c	6.79 ^c	6.70 ^c	6.54 ^c
CH_2		0.61 br	<i>d</i>	
		0.81 br	1.37 br	
		1.68 br	2.20 br	
		1.98 br	2.63 br	
CH_3	0.30 d (1.8, J_{PH} 91)	1.00	0.47	
	0.88 d (2.3, J_{PH} 88)	1.15	0.67	

^aRecorded in CDCl_3 solution. Chemical shifts are relative to the residual solvent resonance. Coupling constants are in hertz. ^b ^1H resonances due to the η^5 ring. ^c ^1H resonances due to the η^1 ring. ^dResonance not observed.

out in ethereal solvents, though less cleanly, or in pentane, when the reaction proceeds cleanly but more slowly due to the low

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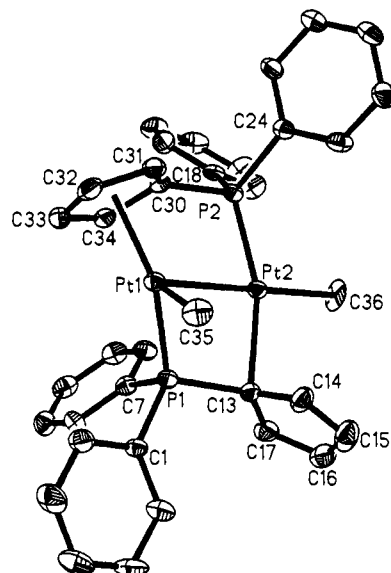


Figure 1. Projection view of the molecular structure of **1a**, showing the atom labeling scheme.

solubility of $[\text{PtClR}(\text{cod})]$ in this solvent. The products are air-stable, yellow solids, which give yellow to orange solutions in most organic solvents. They decompose only very slowly in solution.

The complexes **1a-d** are fluxional in solution at ambient temperature, two broad, featureless resonances being observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1a-c**, whereas no signals are detected at all in the spectrum of **1d**. A single resonance is observed at high temperature (vide infra), but cooling to $-50\text{ }^\circ\text{C}$ allows the observation of two distinct ^{31}P resonances in each case, each of which exhibits short- and long-range coupling to ^{195}Pt (Table I). The ^{31}P resonances are separated by ca. 30 ppm, and in the ^{195}Pt NMR spectra the signals are approximately 1000 ppm apart, indicating that the two platinum centers are in very different environments. In each case the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra exhibit two sets of resonances for the organic groups attached to platinum, separate resonances for every hydrogen and carbon of the cyclopentadienyl rings (Tables II and III), and extremely complex aromatic regions, which can only be accounted for in terms of all four phosphino phenyls being nonequivalent.

In most instances the complexes are obtained as powders, but crystals of the methyl derivative **1a** were obtained from benzene solution. The molecular structure of **1a** has been determined and is shown in Figure 1. Selected bond lengths and angles are presented in Table IV. The dimeric unit is of a most unexpected and unsymmetrical nature. One dppe ligand functions in the usual η^5 -cyclopentadienyl mode, such that one platinum center has a $\text{Pt}(\eta^5\text{-Cp})\text{RL}$ -type coordination, but the second dppe moiety is coordinated in a quite different manner. The cyclopentadienyl

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Table III. $^{13}\text{C}\{^1\text{H}\}$ NMR Parameters for **1a-d**^a

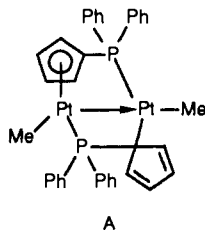
	1a (-50 °C)	1b (-40 °C)	1c (-50 °C)	1d (-60 °C)
C_5H_4	47.3 dd (61, 36) ^c 81.9 d (65) ^d 93.2 t (12) ^c 100.3 d (13) ^c 105.3 br s ^c 107.4 d (7) ^c 118.0 d (11) ^{d,e} (int 2)	46.9 dd (60, 37) ^c 84.7 d (66) ^d 93.8 t (11) ^c (J_{CH} 177) 98.1 d (13) ^c (J_{CH} 176) 105.8 d (4) ^c (J_{CH} 174) 108.7 d (8) ^c (J_{CH} 177) 116.9 d (11) ^d (J_{CH} 161) 118.3 d (10) ^d (J_{CH} 168) 124.0 d (11) ^d (J_{CH} 157) 129.0 ^d	47.5 dd (59, 38) 80.7 d (64) 90.2 d (6) 100.1 d (9) 107.1 d (8) 107.7 d (11) 117.4 d (9) 120.4 d (11) 125.9 d (6) b	b 82.3 d (66) 96.5 t (10) 97.5 d (13) 105.6 d (4) 107.5 d (7) 111.4 d (10) 120.9 d (10) 121.1 d (12) b
CH_2		-11.8 (J_{PtC} 772) 16.4 (J_{PtC} 865)	14.4 (J_{PtC} 816) b	
CH_3	-36.5 (J_{PtC} 800) -2.8 (J_{PtC} 870)	21.8 25.6	31-35 br	
$\text{C}(\text{CH}_3)_3$			30.0 43.9	

^a Recorded in CDCl_3 solution. Chemical shifts are relative to the residual solvent resonance. Coupling constants are in hertz and are to ^{31}P unless stated. ^b Not observed. ^c ^{13}C resonances due to the η^5 ring. ^d ^{13}C resonances due to the η^1 ring. ^e In CD_2Cl_2 solution at -50 °C this is resolved into two doublets at 117.8 (12) and 118.8 (11).

Table IV. Selected Bond Lengths (Å) and Angles (deg) for **1a**

Bond Lengths			
Pt(1)-Pt(2)	2.723 (1)	Pt(1)-P(1)	2.202 (2)
Pt(1)-C(30)	2.372 (8)	Pt(1)-C(31)	2.333 (10)
Pt(1)-C(32)	2.362 (13)	Pt(1)-C(33)	2.411 (11)
Pt(1)-C(34)	2.315 (9)	Pt(1)-C(35)	2.069 (12)
Pt(2)-P(2)	2.189 (2)	Pt(2)-C(13)	2.217 (8)
Pt(2)-C(36)	2.118 (13)	P(1)-C(13)	1.806 (9)
P(2)-C(30)	1.809 (9)	C(13)-C(14)	1.409 (15)
C(13)-C(17)	1.460 (14)	C(14)-C(15)	1.337 (19)
C(15)-C(16)	1.381 (26)	C(16)-C(17)	1.359 (20)
C(30)-C(31)	1.408 (13)	C(30)-C(34)	1.435 (13)
C(31)-C(32)	1.423 (17)	C(32)-C(33)	1.390 (20)
C(33)-C(34)	1.402 (15)		
Bond Angles			
Pt(2)-Pt(1)-P(1)	68.1 (1)	Pt(2)-Pt(1)-C(35)	99.4 (3)
P(1)-Pt(1)-C(35)	89.9 (3)	Pt(1)-Pt(2)-P(2)	82.2 (1)
Pt(1)-Pt(2)-C(13)	82.9 (2)	Pt(1)-Pt(2)-C(36)	175.7 (4)
P(2)-Pt(2)-C(13)	162.1 (2)	P(2)-Pt(2)-C(36)	99.0 (4)
C(13)-Pt(2)-C(36)	96.5 (5)	Pt(1)-P(1)-C(13)	110.1 (3)
Pt(2)-P(2)-C(30)	101.1 (3)	Pt(2)-C(13)-P(1)	87.2 (3)
C(14)-C(13)-C(17)	104.9 (9)	C(13)-C(14)-C(15)	109.5 (12)
C(14)-C(15)-C(16)	109.0 (14)	C(15)-C(16)-C(17)	109.7 (13)
C(13)-C(17)-C(16)	106.6 (12)	C(31)-C(30)-C(34)	106.3 (8)
C(30)-C(31)-C(32)	107.6 (10)	C(31)-C(32)-C(33)	109.4 (11)
C(32)-C(33)-C(34)	107.1 (10)	C(30)-C(34)-C(33)	109.1 (9)

group functions as an η^1 ligand and the five-membered ring is 1,1-substituted by phosphorus and platinum, giving a spirocyclic arrangement. The η^1 -cyclopentadienyl lies approximately trans to the phosphino group of the second dppc ligand (P(2)-Pt(2)-C(13) 162.1 (2)°, with the methyl group in a cis position. The remaining coordination site at this distorted square-planar platinum center is occupied by a metal-metal bond. The Pt-Pt distance is 2.723 (1) Å. Without the metal-metal bond the two platinum(II) centers would be 18- and 14-electron fragments, respectively. Thus, we conclude that the metal-metal bond is in fact a dative bond, the 18-electron center acting as a two-electron donor to the more electron-deficient platinum center (see below).



A

Such a dative bond between two platinum(II) centers has been proposed previously for the $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$ cation, in which the Pt-Pt distance is 2.769 Å.⁴⁶ In that case both platinum

centers achieve a formal electron count of 16, whereas in the present instance Pt(1) and Pt(2) become 18- and 16-electron centers, respectively.

For the η^5 -cyclopentadienyl ring the Pt-C distances show the type of variation frequently observed for such groups (ranging from 2.315 (9) to 2.411 (11) Å),⁴⁷ and the C-C distances exhibit only slight differences, lying between 1.390 (20) and 1.435 (13) Å. The η^1 ring exhibits longer and unequal C-C distances for the sp^3 carbon (C(13)-C(14) = 1.409 (15) and C(13)-C(17) = 1.460 (14) Å), whereas C(14)-C(15) (1.337 (19) Å) and C(16)-C(17) (1.359 (20) Å) are essentially double bonds, and C(15)-C(16) is of an intermediate nature. The P(1)-Pt(1)-C(35) angle is 89.9 (3)°.

Of particular interest is the four-membered Pt_2PC ring. The Pt(1)-P(1) and P(1)-C(13) distances are unremarkable, and the Pt(2)-C(13) bond is only slightly long at 2.217 (8) Å. The Pt(1)-P(1)-C(13) angle is almost exactly tetrahedral, whereas the Pt(2)-C(13)-P(1) angle is closed to 87.2 (3)°. The angles at platinum are both less than 90°; the Pt(1)-Pt(2)-C(13) angle is 82.9 (2)°, whereas the Pt(2)-Pt(1)-P(1) angle is quite acute at 68.1 (1)°. We have observed a Pt-Pt-P angle of 73.5 (1)° in the related platinum(I) dimer $[\text{Pt}_2(\text{CO})_2(\mu\text{-}\eta^1\text{-1,1-C}_5\text{H}_4\text{PPh}_2)_2]$,⁴⁵ and an angle of 77.2 (1)° was found in $[\text{Pt}_2\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\mu\text{-SPEt}_2)_2]$.⁴⁸ In the present instance there is a short contact of 2.79 Å between Pt(2) and P(1), which is less than the sum of the van der Waals radii. It is uncertain whether this represents a bonding interaction or is simply a consequence of the presence of the four-membered ring and the acute angle at Pt(1). In $[\text{Pt}_2(\text{CO})_2(\mu\text{-}\eta^1\text{-1,1-C}_5\text{H}_4\text{PPh}_2)_2]$, where the same four-membered ring is involved, the corresponding distance is 2.90 Å, however.⁴⁵ It may be that the bulkier η^5 -cyclopentadienyl group on Pt(1) in **1a** necessitates the smaller Pt-Pt-P angle and, hence, the shorter Pt(2)-P(1) distance.

The structure of **1a** revealed by X-ray diffraction accounts for the low-temperature NMR data found for **1a-d**. The existence of one platinum center bearing an η^5 -cyclopentadienyl group (formally 18-electron) and one with an η^1 -cyclopentadienyl moiety (formally 16-electron, including the Pt-Pt bond) readily explains the large differences in ^{31}P and ^{195}Pt chemical shifts, the platinum with the η^5 -Cp and its attached phosphorus being significantly shielded relative to their electron-deficient counterparts. Although platinum-platinum couplings are notoriously difficult to interpret,⁴⁹

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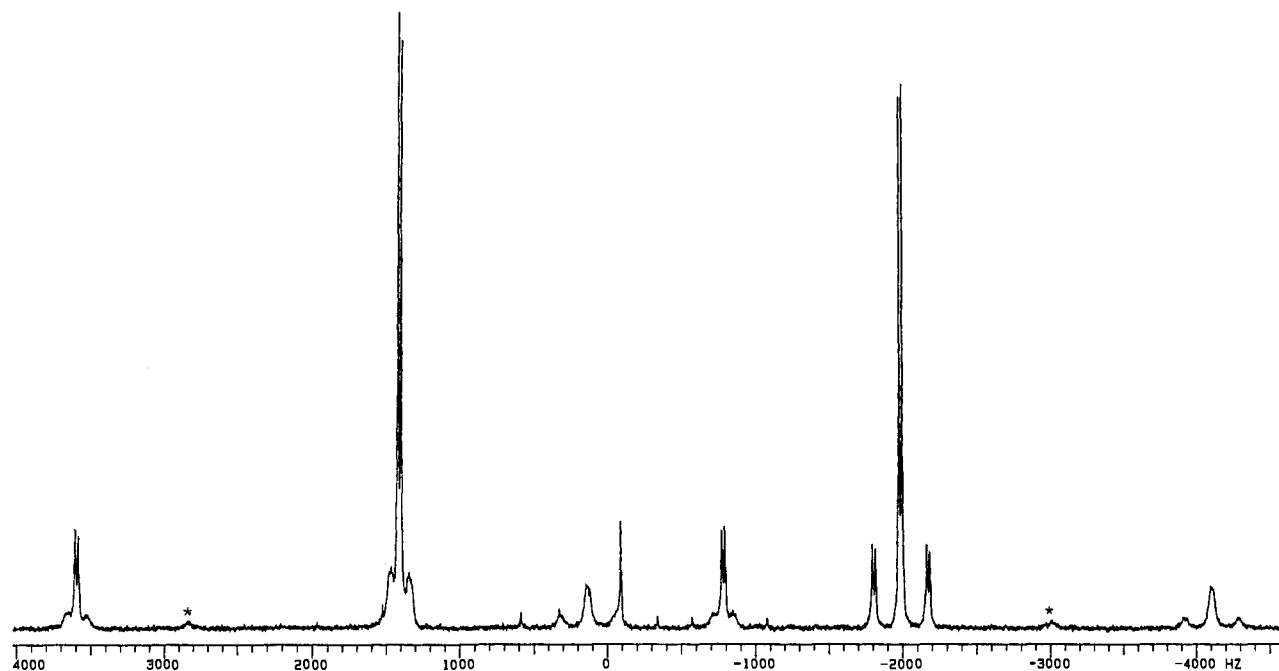


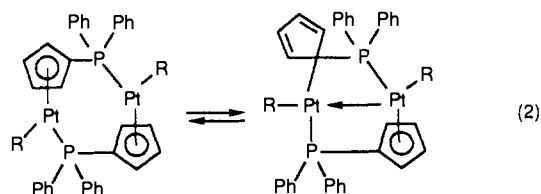
Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1c** in CD_2Cl_2 solution at -90°C . ^{195}Pt satellites for the symmetrical isomer are denoted by asterisks.

the values of 1100–1200 Hz are certainly indicative of the presence of a metal–metal bond. These are considerably larger than the $^1J(\text{Pt},\text{Pt})$ value of 332 Hz found in the $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$ cation,⁴⁶ indicating a greater degree of s-character in the metal–metal bond in **1a**. This, in addition to the shorter bond length, suggests a stronger dative bond in this case. In **1a–d** both $^1J(\text{Pt},\text{P})$ couplings are large, but the magnitude of $^2J(\text{P}_1,\text{Pt}_2)$ is approximately three times that of $^2J(\text{P}_2,\text{Pt}_1)$ (Table I). This reflects the existence of two possible two-bond coupling paths between P_1 and Pt_2 , whereas there is only one between P_2 and Pt_1 (coupling through the η^5 -cyclopentadienyl moiety will be minimal owing to the lack of s-electron density in the η^5 -cyclopentadienyl–platinum interaction).

In the low-temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra two sets of signals are observed for the organic groups attached to platinum. Again there is a significant difference in the shielding of these nuclei. For example, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1a** the two methyl carbons are found at -36.5 and -2.8 ppm, the former showing a remarkably high degree of shielding. Similarly, in **1b** the CH_2 groups attached to platinum resonate at -11.8 and 16.4 ppm (Table III). In the ^1H NMR spectra of **1b** and **1c** the CH_2 groups are diastereotopic, due to the lack of symmetry of the molecule, and four resonances for the methylene hydrogens are detected in each complex (Table II). This lack of symmetry is also responsible for the existence of eight ^1H and ten ^{13}C resonances for the cyclopentadienyl groups. The ^1H signals have been assigned to individual rings on the basis of ^1H – ^1H homonuclear correlation (COSY) experiments (coupling only being observed between the hydrogens on the same ring). Also, ^{13}C – ^1H heteronuclear correlation experiments for **1a** and **1b** have allowed the carbons to be assigned to individual rings (resonances at 129.5 for **1a** and 129.0 for **1b**, hidden in the aromatic region, were identified in this manner). The methine carbons on the η^5 ring exhibit greater shielding, while the chemical shifts of those on the η^1 ring are characteristic of olefinic carbons. In each complex the phosphorus-bearing carbon of the η^5 ring appears as a doublet at 80–85 ppm, whereas that of the η^1 ring is a doublet of doublets at 45–50 ppm. In the ^1H NMR spectra the two most shielded hydrogens are α to the phosphorus (vide infra) on the η^5 ring, and the next most shielded is an α -hydrogen on the η^1 ring. The remaining signals lie between 6 and 7 ppm and are therefore more typically olefinic. The low-temperature NMR data are clearly consistent with the solid-state structure of **1a**.

In the $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of **1c** and **1d** a minor species may be observed at low temperatures. In each case this appears as a singlet with ^{195}Pt satellites in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and as a doublet in the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum, with $^1J(\text{Pt},\text{P})$ values of 5840 and 5690 Hz, respectively (Table I). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1c** at -90°C is shown in Figure 2. Observation of only one signal for the minor species suggests that it is a symmetrical dimer, and the magnitudes of the one-bond coupling constants are very similar to that found for $[\text{Pt}(\eta^5\text{-C}_5\text{H}_5)\text{Ph}(\text{PPh}_3)]$.⁵⁰ This suggests that the minor species is of the form $[\text{Pt}_2\text{R}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ ($\text{R} = \text{Np}, \text{Ph}$), and integration of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicates that it is present to the extent of about 5% in each case. As the temperature is raised the signals due to the unsymmetrical dimer start to broaden and the minor species is no longer distinguishable.

These observations suggest there is an equilibrium between $[\text{Pt}_2\text{R}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ and $[\text{Pt}_2\text{R}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-}\eta^1\text{-}1,1\text{-C}_5\text{H}_4\text{PPh}_2)]$ in solution (eq 2). For **1a** and **1b** the equilibrium



lies sufficiently far to the right-hand side that the symmetrical form is not detected in solution at any temperature. When the solvent is removed rapidly from a solution of **1a** or **1d** by rotary evaporation, however, the solid-state ^{31}P NMR spectrum of the resulting powder shows the presence of both species, the unsymmetrical form again predominating.

Slow evaporation of an ether solution of **1d** resulted in the formation of orange crystals, which were of suitable quality to perform an X-ray diffraction study. The molecular structure of the resulting complex is shown in Figure 3. Selected bond lengths and angles are presented in Table V. The dimer is of the form $[\text{Pt}_2\text{Ph}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$, but it does not possess a center of symmetry, in contrast to the related complex $[\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$.^{39,40} In the latter, the two P atoms, the two Rh atoms, and the centroids of the two cyclopentadienyl rings adopt a “chair” conformation, whereas in $[\text{Pt}_2\text{Ph}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ the two P

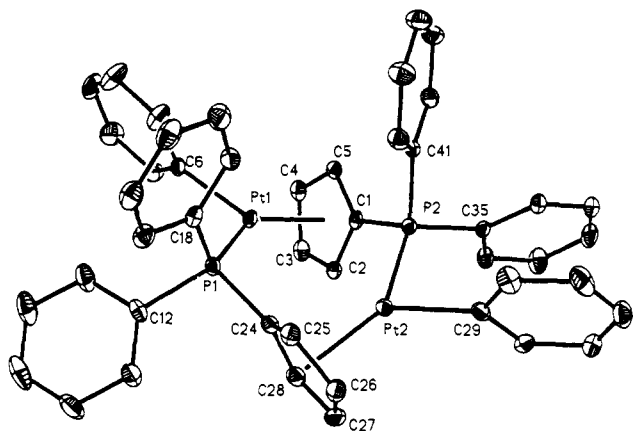


Figure 3. Projection view of the molecular structure of **1d**, showing the atom labeling scheme.

atoms, the two Pt atoms, and the centroids of the rings constitute a distorted "boat". The platinum–platinum separation is 4.21 Å, similar to the rhodium–rhodium distance of 4.30 Å found in $[\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$,^{39,40} which indicates the absence

of any metal–metal interaction. The two Pt–P and two Pt–C(Ph) distances are nearly identical, and the Pt–C(Cp) distances show the usual variation (2.303–2.446 for one ring, and 2.308–2.474 for the other) found for η^5 -cyclopentadienyls of platinum and palladium,⁴⁷ the Pt–Cp(centroid) distances being 2.034 and 2.070 Å. There are, likewise, only small differences in the bond lengths and angles within the cyclopentadienyl rings. The two P–Pt–C(Ph) angles of 96.8 (1)° and 87.0 (2)° are indicative of the distortion of the molecule.

Isolation of crystals of the symmetrical form of **1d** is doubtless dependent on using a different solvent, and on the more favorable equilibrium position compared with **1a**. Although still the minor component in solution, $[\text{Pt}_2\text{Ph}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ apparently crystallizes preferentially and slow crystallization allows the equilibrium to be continuously re-established and a good yield of the symmetrical form to be obtained. In contrast, the more rapid growth of crystals of **1a** (and from a different solvent), or solvent removal by rotary evaporation to give **1a** or **1d** as a powder, yields a product distribution more representative of that observed in solution.

As mentioned above, the ^1H NMR signals associated with the cyclopentadienyl moieties in $[\text{Pt}_2\text{R}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-}\eta^1\text{-1,1-C}_5\text{H}_4\text{PPh}_2)]$ could be assigned to individual rings by means of

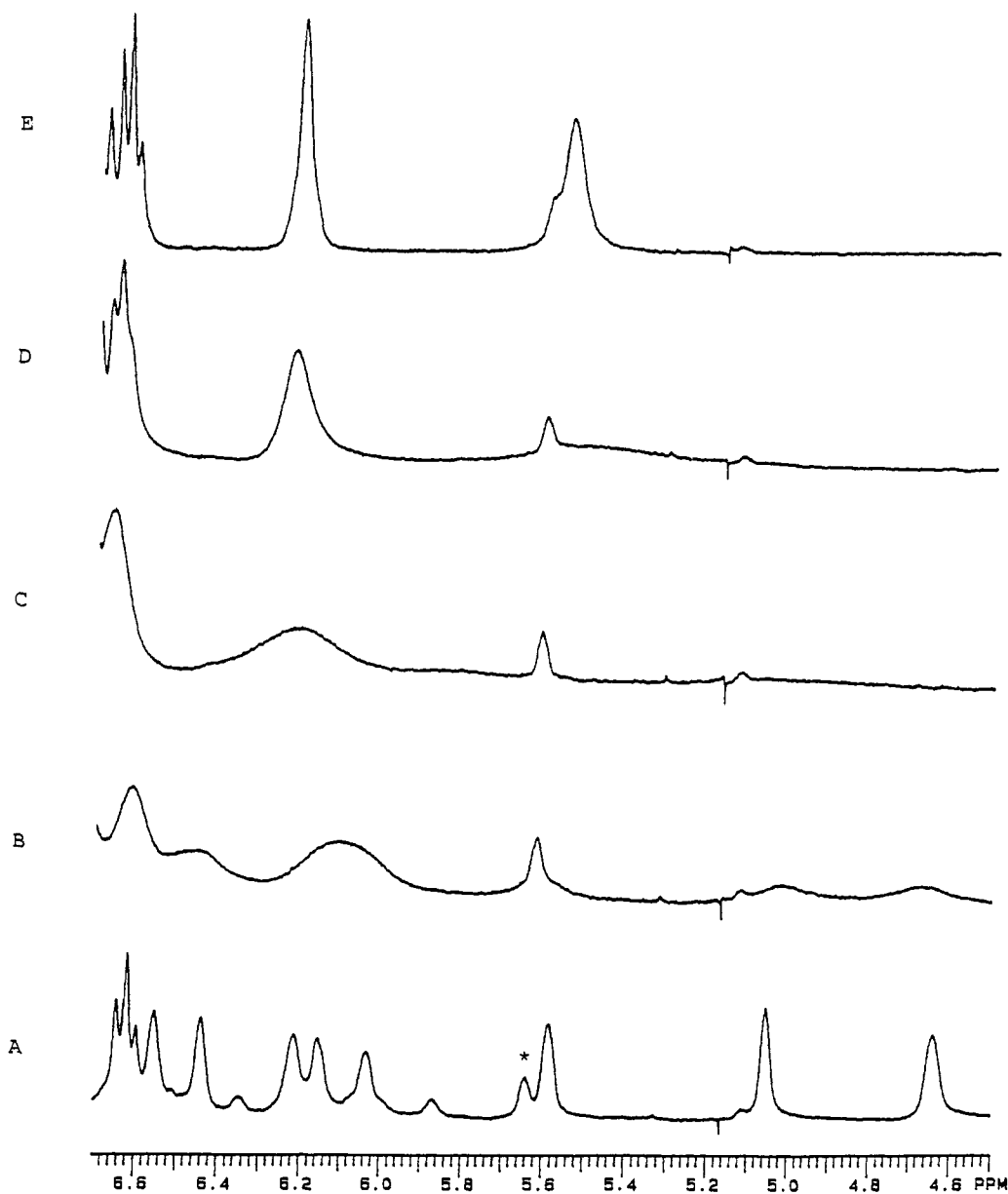


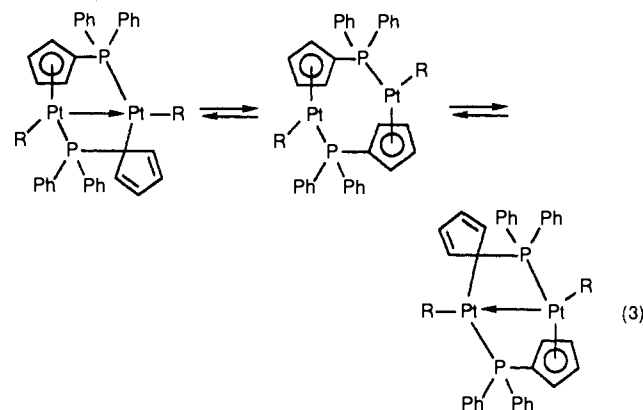
Figure 4. Variable-temperature ^1H NMR spectra of **1d** in CDCl_3 solution: (A) $-60\text{ }^\circ\text{C}$; (B) $-20\text{ }^\circ\text{C}$; (C) $0\text{ }^\circ\text{C}$; (D) $+20\text{ }^\circ\text{C}$; (E) $+50\text{ }^\circ\text{C}$. The signal marked with an asterisk is due to free cyclooctadiene.

Table V. Selected Bond Lengths (Å) and Angles (deg) for **1d**

Bond Lengths			
Pt(1)-P(1)	2.198 (1)	Pt(1)-C(1)	2.350 (3)
Pt(1)-C(2)	2.392 (3)	Pt(1)-C(3)	2.446 (4)
Pt(1)-C(4)	2.303 (4)	Pt(1)-C(5)	2.335 (4)
Pt(1)-C(6)	2.025 (4)	Pt(2)-P(2)	2.200 (2)
Pt(2)-C(24)	2.380 (4)	Pt(2)-C(25)	2.370 (4)
Pt(2)-C(26)	2.308 (6)	Pt(2)-C(27)	2.445 (5)
Pt(2)-C(28)	2.474 (5)	Pt(2)-C(29)	2.018 (4)
P(1)-C(24)	1.808 (5)	P(2)-C(1)	1.803 (4)
C(1)-C(2)	1.433 (6)	C(1)-C(5)	1.420 (7)
C(2)-C(3)	1.394 (6)	C(3)-C(4)	1.425 (7)
C(4)-C(5)	1.429 (6)	C(24)-C(25)	1.432 (6)
C(24)-C(28)	1.439 (5)	C(25)-C(26)	1.416 (7)
C(26)-C(27)	1.407 (6)	C(27)-C(28)	1.408 (8)
Bond Angles			
P(1)-Pt(1)-C(6)	96.8 (1)	P(2)-Pt(2)-C(29)	87.0 (2)
Pt(1)-P(1)-C(24)	112.4 (1)	Pt(2)-P(2)-C(1)	111.0 (1)
C(2)-C(1)-C(5)	107.8 (4)	C(1)-C(2)-C(3)	109.5 (4)
C(2)-C(3)-C(4)	106.4 (4)	C(3)-C(4)-C(5)	109.7 (4)
C(1)-C(5)-C(4)	106.2 (4)	C(25)-C(24)-C(28)	107.3 (4)
C(24)-C(25)-C(26)	106.7 (3)	C(25)-C(26)-C(27)	109.6 (5)
C(26)-C(27)-C(28)	107.7 (4)	C(24)-C(28)-C(27)	108.2 (4)

^1H - ^1H homonuclear correlation experiments. Variable-temperature studies of **1a** and **1d** allowed the hydrogens α and β to the phosphino groups to be determined. ^1H NMR spectra for **1d** at several temperatures are shown in Figure 4. Eight distinct cyclopentadienyl signals due to the unsymmetrical dimer are observed at -60°C , and the two minor resonances at 5.88 and 6.35 ppm are consistent with $[\text{Pt}_2\text{Ph}_2(\mu-\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$. The cyclopentadienyl signals broaden above -50°C , the four signals originally observed at 6.02–6.42 ppm coalesce at -20°C , and the other four coalesce at 0°C . At $+50^\circ\text{C}$ two relatively sharp signals are observed. **1a** behaves in a broadly similar manner, two signals for the methyls and eight resonances for the cyclopentadienyl hydrogens being observed at temperatures below -20°C . As the temperature is raised the signals broaden, the four resonances clustered at 6.32–6.49 ppm coalesce at $+10^\circ\text{C}$ into a broad line at 6.45 ppm, the methyl signals coalesce at $+40^\circ\text{C}$, and the other four cyclopentadienyl signals coalesce at $+50^\circ\text{C}$. At $+90^\circ\text{C}$ there is a single methyl resonance and a relatively sharp singlet at 6.42 ppm, but the resonance at 5.39 ppm remains broad. In each case we assign the signals clustered at 6.0–6.5 ppm to the hydrogens β to the phosphino group, since they are farthest removed from the site of substitution, and the remaining resonances to the α -hydrogens. Thus at higher temperatures all four α -hydrogens and all four β -hydrogens, as well as the two methyls in the case of **1a**, are equivalent, consistent with a symmetrical averaged structure.

Similarly, the ^{31}P signals for **1d** broaden and coalesce at $+35^\circ\text{C}$ and, although decomposition occurs at elevated temperatures, heating a $\text{C}_2\text{H}_2\text{Cl}_4/\text{C}_6\text{D}_6$ solution of **1d** allows observation of a broad signal with ^{195}Pt satellites at $+80^\circ\text{C}$, which becomes sharp at $+120^\circ\text{C}$ ($\delta_{\text{P}} -3.0$, $^1J(\text{Pt},\text{P})$ 4350 Hz, $^2J(\text{Pt},\text{P})$ 155 Hz). The value of $^1J(\text{Pt},\text{P})$ is considerably smaller than that observed for $[\text{Pt}_2\text{R}_2(\mu-\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ at low temperature, and a long-range Pt–P coupling is observed, ruling out the possibility that it is the symmetrical η^5 form that is observed at higher temperatures. The $^1J(\text{Pt},\text{P})$ value is greater than either of the values found in the unsymmetrical form, however. If there is an equilibrium between the two forms at 120°C , and the $^1J(\text{Pt},\text{P})$ and $^2J(\text{Pt},\text{P})$ coupling constants are weighted averages of those found for the two forms, then the values obtained would indicate a 3:1 mixture of the unsymmetrical and symmetrical dimers. We propose that the symmetrical isomer is an intermediate in a fluxional process that interconverts the η^5 and η^1 rings of the unsymmetrical dimer, which would be accompanied by a reversal of the direction of the Pt–Pt dative bond, and it is of sufficiently low energy to be observed as a minor component at low temperature (eq 3). It is a larger component of the equilibrium mixture at higher temperatures, but since interconversion is rapid under these conditions it cannot be distinguished as a separate species. The free energy of acti-



vation, ΔG^\ddagger , for the interconversion of the unsymmetrical and symmetrical forms is 12.4 ± 0.4 kcal/mol at 35°C .⁵¹

It may be noted that in the low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of each complex (see Figure 2, for example) the satellites that arise from coupling with Pt_1 ($^1J(\text{P}_1,\text{Pt}_1)$ and $^2J(\text{P}_2,\text{Pt}_1)$) are broader than those due to Pt_2 . Also, the resonance due to Pt_1 is significantly broader than that due to Pt_2 in each of the ^{195}Pt NMR spectra. These observations indicate a shorter T_1 for Pt_1 and suggest there is greater motion of the 18-electron platinum center compared with its 16-electron counterpart. This might indicate that the first step in the fluxional process takes place at the 18-electron center, perhaps involving slippage of the η^5 -cyclopentadienyl toward η^3 coordination prior to cleavage of the metal–metal bond and opening of the structure toward the symmetrical η^5 form.

Conclusion

The dppc-bridged platinum dimers $[\text{Pt}_2\text{R}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ can exist in two forms, and each has been isolated and structurally characterized. In one both cyclopentadienyl groups are bonded in η^5 fashion, whereas in the second case one ring coordinates in the η^1 mode and there is a dative bond between the two platinum centers. The two isomers are in equilibrium in solution and can be identified by NMR spectroscopy at low temperatures, the unsymmetrical one predominating. At higher temperatures the molecules are fluxional, and we suggest that the symmetrical dimer is an intermediate in the interconversion of the unsymmetrical forms.

Experimental Section

All reactions were carried out under an atmosphere of argon, either in a Vacuum Atmospheres controlled-atmosphere box or by using standard Schlenk techniques. NMR spectra were recorded on a Varian XL-300 FT NMR spectrometer. Microanalyses were performed by Atlantic Microlab, Inc, Norcross, GA. $\text{TiC}_5\text{H}_4\text{PPh}_2$ ²⁵ was prepared by an established method. The compounds $[\text{PtClR}(\text{cod})]$ ($\text{R} = \text{Me}, \text{Et}, \text{Np}, \text{Ph}$) were prepared from $[\text{PtR}_2(\text{cod})]$ by treatment with $\text{CH}_3\text{COCl}/\text{CH}_3\text{OH}$ in ether.^{52–54} Previously unreported $^{13}\text{C}\{^1\text{H}\}$ NMR data follow (couplings to ^{195}Pt in hertz are given in parentheses). $[\text{PtEt}_2(\text{cod})]$: δ 15.9 (34) CH_3 ; 19.5 (838) $\text{Pt}-\text{CH}_2$; 29.8, CH_2 ; 99.3 (47) CH . $[\text{PtClEt}(\text{cod})]$: δ 16.3 (19) CH_3 ; 19.2 (606) $\text{Pt}-\text{CH}_2$; 27.7 (26) and 31.8 (25) CH_2 ; 82.8 (235) and 114.5 (20) CH . $[\text{PtNp}_2(\text{cod})]$: δ 29.7 CH_2 ; 35.5 (50) $\text{C}(\text{CH}_3)_3$; 36.0 (883) $\text{Pt}-\text{CH}_2$; 36.6 $\text{C}(\text{CH}_3)_3$; 100.4 (45) CH . $[\text{PtClNp}(\text{cod})]$: δ 27.6 (26) and 31.9 (26) CH_2 ; 33.9 (29) $\text{C}(\text{CH}_3)_3$; 35.8 $\text{C}(\text{CH}_3)_3$; 37.8 (659) $\text{Pt}-\text{CH}_2$; 82.9 (232) and 116.1 (18) CH .

Preparation of $[\text{Pt}_2\text{Me}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ (1a**).** To a solution of $[\text{PtClMe}(\text{cod})]$ (0.353 g, 1.00 mmol) in benzene (25 mL) was added $\text{TiC}_5\text{H}_4\text{PPh}_2$ (0.460 g, 1.10 mmol) in small portions. The mixture was stirred for 2 days and then filtered through a glass frit. The filtrate was collected and the solvent and free cyclooctadiene were removed in vacuo, leaving the product as a yellow solid (0.437 g, 88%). Anal. Calcd for

(51) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded between -100 and $+120^\circ\text{C}$ in CD_2Cl_2 , CDCl_3 , or $\text{C}_2\text{H}_2\text{Cl}_4/\text{C}_6\text{D}_6$ solution. ΔG^\ddagger was calculated at the coalescence temperature T_c by using the equation $\Delta G^\ddagger = 0.00457T_c(9.97 + \log T_c/\Delta\nu)$. Martin, M. L.; Delpuech, J.-J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; p 340.

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Table VI. Crystallographic Data for **1a** and **1d**

	1a	1d
formula	C ₃₆ H ₃₄ P ₂ Pt ₂	C ₄₆ H ₃₈ P ₂ Pt ₂
mol wt	918.8	1042.9
color, habit	yellow, rectangular	golden brown, parallelepiped
space group	P2 ₁ /n	P $\bar{1}$
a, Å	10.155 (2)	10.256 (4)
b, Å	14.696 (3)	13.693 (5)
c, Å	21.080 (5)	14.687 (7)
α , deg	90	95.52 (3)
β , deg	90.02 (2)	109.68 (3)
γ , deg	90	101.87 (3)
cell vol, Å ³	3146.0 (11)	1869.7 (13)
Z	4	2
D(calcd), Mg/m ³	1.940	1.852
temp, K	298	295
radiation	graphite monochromated Mo K α (λ = 0.71073 Å)	graphite monochromated Mo K α (λ = 0.71073 Å)
cryst dimens, mm	0.5 × 0.2 × 0.1	0.25 × 0.38 × 0.63
abs coeff, mm ⁻¹	9.009	7.668
2 θ range, deg	3.5–60.0	3.5–55.0
scan speed, deg/min	3.97–14.65	4.88–29.30
scan range (ω), deg	0.60 plus K α separation	0.60 plus K α separation
independent rflns	9238	8643
obs rflns	6340 ($F > 4.0\sigma(F)$)	6759 ($F > 6.0\sigma(F)$)
absorptn correction	empirical	empirical
R	0.0490	0.0221
R _w	0.0550	0.0266
goodness of fit	1.25	1.14

C₃₆H₃₄P₂Pt₂: C, 47.06; H, 3.73. Found: C, 46.66; H, 3.86. Crystals suitable for X-ray analysis were obtained by slow evaporation of a benzene solution of the complex.

Preparation of [Pt₂Et₂(μ -C₆H₄PPh₂)₂] (1b). [PtClEt(cod)] (0.168 g, 0.456 mmol) and TiCl₃H₄PPh₂ (0.271 g, 0.597 mmol) were mixed in a round-bottomed flask, and benzene (25 mL) was added. The solution immediately became bright yellow. It was stirred for 12 h and then filtered through an alumina column (50 × 30 mm, acidic, Brockman activity I, 80–200 mesh). The filtrate was concentrated, and pentane addition gave a yellow solid, which was filtered and dried in vacuo (0.199 g, 46%). Anal. Calcd for C₃₈H₃₈P₂Pt₂: C, 48.20; H, 4.05. Found: C, 48.29; H, 4.09.

Preparation of [Pt₂Np₂(μ -C₆H₄PPh₂)₂] (1c). This complex was prepared as above from [PtClNp(cod)] (0.090 g, 0.219 mmol) and TiCl₃H₄PPh₂ (0.110 g, 0.243 mmol) and obtained in 46% yield. Anal. Calcd for C₄₄H₃₀P₂Pt₂: C, 51.26; H, 4.89. Found: C, 50.92; H, 4.88.

Preparation of [Pt₂Ph₂(μ -C₆H₄PPh₂)₂] (1d). To a solution of [PtClPh(cod)] (0.550 g, 1.32 mmol) in benzene (50 mL) was added TiCl₃H₄PPh₂ (0.630 g, 1.39 mmol) in small portions. The mixture was stirred for 2 days and then filtered. The filtrate was passed down an alumina column (80 × 10 mm), and the column was washed with an additional 30 mL of benzene. The combined filtrate was evaporated and the residue was dried in vacuo, leaving the product as a yellow solid (0.350 g, 51%). Anal. Calcd for C₄₆H₃₈P₂Pt₂: C, 52.97; H, 3.67. Found: C, 53.96; H, 4.80. Crystals suitable for X-ray analysis were grown from an ether solution under argon.

X-ray Structure Determinations. Single crystals of **1a** and **1d** were mounted on glass fibers in a random orientation. Preliminary exami-

nation was carried out with Mo K α radiation, using a Siemens P3 or R3 automated four-circle diffractometer. Final cell parameters and orientation matrices were obtained by least-squares refinement of 25 automatically centered reflections ($20^\circ < 2\theta < 25^\circ$) in each case. Axial photographs of the three axes were taken to confirm cell lengths and the lattice symmetry. ω -Scans of representative reflections indicated acceptable crystal quality.

Data were collected by using the θ - 2θ scan technique, and the intensities of three standard reflections were measured every 50 reflections. As no significant variation in intensities of the standard reflections was observed during data collection, no decay correction was applied. An empirical absorption correction was applied to the data in each case.

Data reduction and structure solution was achieved by using the SHELXTL PLUS structure solution software package.⁵⁵ The structures were solved by Patterson methods in the space groups P2₁/n and P $\bar{1}$ and were refined successfully in these space groups. The remaining non-hydrogen atoms were located from subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing the function $w(F_o - F_c)^2$. All non-hydrogen atoms were refined anisotropically to convergence. For **1a** all hydrogen atoms were refined isotropically, and for **1d** the hydrogen atoms were included in their idealized calculated positions and were held fixed.

The final difference Fourier maps had maximum electron densities of 3.33 and 1.06 e/Å³ for **1a** and **1d**, respectively, which were close to the platinum atoms. Least-squares planes calculated for the phenyl rings and planar fragments showed very small deviations from planarity. Selected bond distances and angles are given in Tables IV and V. Summaries of crystal data, intensity collection parameters, and final structure refinement parameters are presented in Table VI. Figures 1 and 3 show the projection views and atom labeling schemes for **1a** and **1d**, respectively.

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Registry No. **1a**, 141091-19-2; **1b**, 141091-20-5; **1c** (unsymmetric), 141091-21-6; **1c** (symmetric), 141091-22-7; **1d** (unsymmetric), 141091-23-8; **1d** (symmetric), 124399-71-9; TiCl₃H₄PPh₂, 85320-10-1; PtCl(Me)(cod), 50978-00-2; PtCl(Et)(cod), 68245-69-2; PtCl(Np)(cod), 102307-58-4; PtCl(Ph)(cod), 51177-65-2.

Supplementary Material Available: Tables of atomic coordinates and isotropic displacement coefficients for non-hydrogen atoms, bond lengths and angles, and anisotropic displacement coefficients for non-hydrogen atoms for **1a** and **1d**, hydrogen atom coordinates and isotropic displacement coefficients for **1a**, and calculated hydrogen atom coordinates and isotropic displacement coefficients for **1d** (11 pages); tables of observed and calculated structure factors for **1a** and **1d** (64 pages). Ordering information is given on any current masthead page.

(55) Sheldrick, G. M. Siemens Analytical X-ray Division, Madison, WI, 1989.