Inorg. Chem. **2002**, *41*, 6032–6037

Inorganic Chemistry
Article

Dianionic Platinadiphospholene Complexes

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Received February 5, 2002

1,2,3,4-Tetraphenyl-1,2-dihydrodiphosphetene **1** reacts with lithium or sodium naphthalenide to afford the corresponding dianionic salts **2** and **3**. An X-ray crystal structure analysis shows that dianion **3** of general formula $[(\mathbf{1})^{2-}{}_2Na_3(DME)_2, Na(DME)_3]$ is a polymeric structure consisting of $[(\mathbf{1})^{2-}{}_2Na_3(DME)_2]$ units which are connected together through one sodium atom. Reaction of the dianionic lithium salt **2** with $[Pt(COD)Cl_2]$ affords the $\mathbf{4[Li(2.2.1)]_2}$ complex, after the addition of 2 equiv of (2.2.1) cryptate. The overall geometry around platinum in $\mathbf{4[Li(2.2.1)]_2}$ can be described as distorted square planar, and only the diastereomer (1-*R*, 2-*S*, 3-*R*, 4-*S*) is formed. X-ray data indicate that no delocalization takes place within each platinadiphospholene unit and that complex $\mathbf{4[Li(2.2.1)]_2}$ must be regarded as the coordination of two molecules of dianion **2** onto a Pt^{2+} center. Reaction of the dianionic sodium salt **3** with 1 equiv of $[Pt(COD)Cl_2]$ produces the $\mathbf{4[Na(DME,Et_2O)]_2}$ complex which adopts a pseudotetrahedral geometry around platinum (θ between interplane angles = 35°), the two cationic units $[Na(DME, Et_2O)]$ being located along a C_2 axis. Four weak interactions exist between the sodium cations and the phosphorus atoms. Only the (1-*S*, 2-*S*, 3-*S*, 4-*S*) diastereomer is formed. Bond distances in the diphospholene units of $\mathbf{4[Na(DME,Et_2O)]_2}$ are close to that of dianion **3** indicating that, like in $\mathbf{4[Li(2.2.1)]_2}$, the complex can be described as a platinum (+2) dianionic species.

Introduction

Since their initial discovery in 1963,[1] dithiolene complexes have aroused a continuous interest from coordination chemists because of their ability to exist in several oxidation states with various metallic centers. Homo- and heteroleptic dithiolene complexes have found a widespread use in many domains including the preparation of superconducting molecular materials and the synthesis of complexes having well-defined optical, electric, and magnetic properties as well as in the elaboration of efficient models for metalloenzymes.[2] So far, this chemistry has found no parallel with other heteroatoms besides sulfur. In this perspective, a still unanswered question concerns the possible replacement of sulfur by phosphorus. Indeed, the isoelectronic analogy between phosphido $[R_2P]$ and [RS] fragments suggests that *cis*-1,2-bis(diphosphinyl)ethene ligands such as $\mathbf{A}^{2-}$, which are the reduced forms of 1,4-diphosphabutadienes **A**, might be used as appropriate equivalents of dithiolenes ligands (Chart 1).

Though our knowledge is still limited, some metalladiphospholene complexes are known.[3] Two iridadiphospholene complexes were characterized in solution by NMR spectroscopy, and zirconium, tin, and boron derivatives of benzo analogues of ligand $\mathbf{A}^{2-}$ were structurally characterized.[4] In 1992, some of us investigated the synthesis of nickel and platinum diphosphetene complexes.[5] From these two last studies, it clearly appeared that, like the dithiolenes, these dianionic phosphorus ligands exhibit a “noninnocent” character. Depending on the nature and the electronic properties of the metal fragment to which they are coordinated, they

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10.1021/ic020103d CCC: $22.00

Chart 1

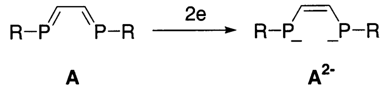
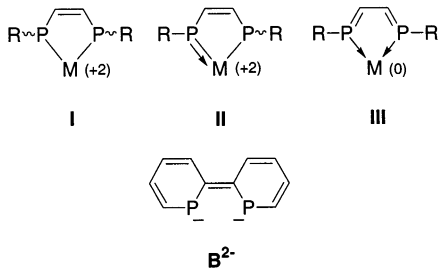


Chart 2



can either act (according to the covalent model) as a (1 + 1) electron donor (form **I**, Chart 2), the metal having here a formal oxidation state of +2, as a (1 + 3) electron donor (form **II**, oxidation state of the metal: +2) when one lone pair at phosphorus is also engaged in the bonding, or as a (2 + 2) electron donor (form **III**) if the metal is considered zerovalent.[6] Given this background and on the basis of our recent studies on dianionic biphosphinine ligands $\mathbf{B}^{2-}$,[7] which are closely related systems, we decided to explore the synthesis of dianionic complexes of these *cis*-1,2-bis(diphosphinyl)ethene ligands.

Herein, we report on the structural characterization of one of these dianionic ligands as well as on the synthesis of its homoleptic dianionic platinum complex.

Results and Discussion

A first series of experiments was carried out with the dilithium salt of tetraphenyl derivative **2** which is readily available by the cleavage of the P−P bond of 1,2-dihydrodiphosphetene, **1**,[8] with lithium metal (Scheme 1).[9] As a prerequisite, to gain structural information, we focused our efforts on crystallizing dianionic ligand **2**. Unfortunately, despite many attempts, using different solvents and experimental conditions, no suitable crystals of dianion **2** could be grown. More satisfying results were obtained by using disodium salt **3** which can be prepared by reacting 2 equiv of sodium naphthalenide with diphosphetene **1** in THF or dimethoxyethane as solvent at room temperature. The use of naphthalenide was preferred because it avoids side reactions which can occur when metallic sodium is used in excess. Like with lithium, the formation of dianion **3** is evidenced by a downfield shift in ^{31}P NMR spectroscopy (δ(DME): −2.7 ppm vs −35.0 ppm for **1**).

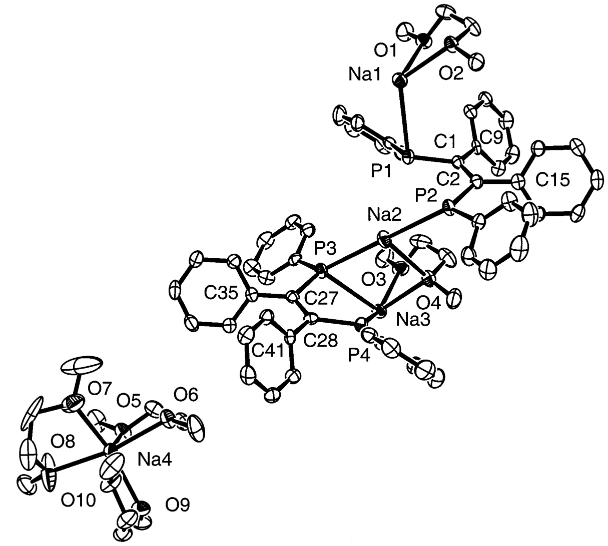
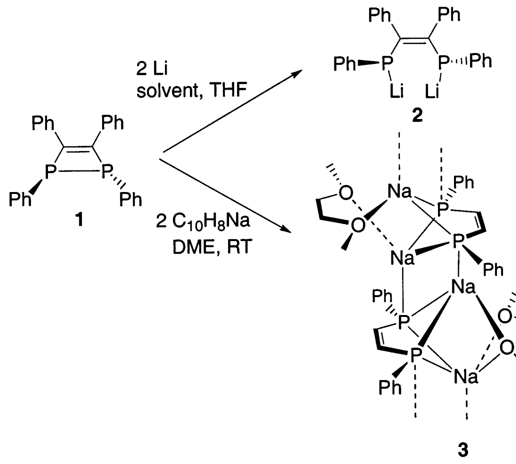


Figure 1. ORTEP drawing of dianion **3**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Important bond distances [Å] and angles [deg]: Na1−P1, 2.951(2); P1−C1, 1.827(4); C1−C2, 1.385(5); C2−P2, 1.818(4); P1−Na1, 2.951(2); P2−Na2, 2.864(2); P3−Na2, 2.860(2); Na2−O4, 2.603(3); Na2−P3, 2.860(2); O4−Na3, 2.386(3); Na3−O3, 2.406(3); P3−C27, 1.817(4); C27−C28, 1.387(5); P4−C28, 1.823(4). Na1−P1−C1, 103.9(1); P1−C1−C2, 117.6(3); C1−C2−P2, 118.0(3); C2−P2−Na2, 111.8(1); P2−Na2−P3, 177.23(7); Na2−P3−C27, 112.5(1); P3−C27−C28, 117.2(3); C27−C28−P4, 117.9(3); C28−P4−Na3, 108.5(1); P3−Na3−P4, 62.10(5); Na3−O4−Na2, 91.4(1); O4−Na2−P3, 93.07(8); Na2−P3−Na3, 77.22(6).

Scheme 1



Dianion **3**, which is highly oxygen and moisture sensitive, crystallized out from the crude mixture at room temperature using a mixture of DME/ether (1:1). The structure of **3** is polymeric as can be seen in Figures 1 and 2. In Figure 1, a monomeric unit is presented whereas Figure 2 shows the spatial arrangement of two units. Significant bond lengths and angles are given in the legend of Figure 1, and crystal data and structural refinement details are listed in Table 1. A monomeric unit consists of two molecules of dianion **3**, three sodium atoms (Na1, Na2, and Na3), and two molecules of DME. As can be seen in Figure 1, the fourth sodium atom

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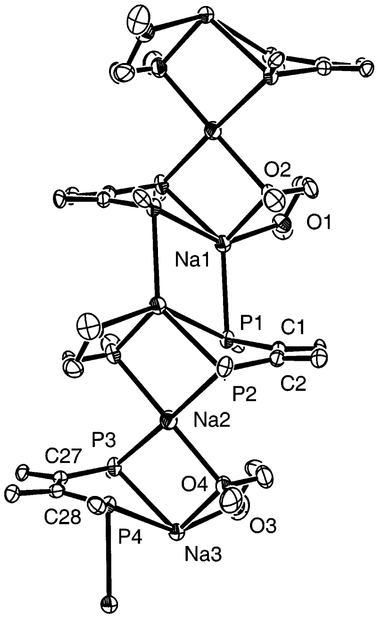


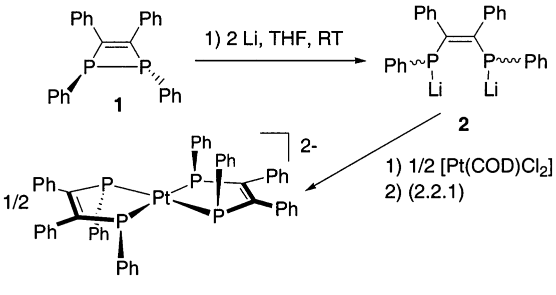
Figure 2. View of the polymeric arrangement of dianion **3**. Ellipsoids are scaled to enclose 50% of the electron density. Five carbon atoms of each phenyl group at phosphorus and carbon atoms and hydrogen atoms are omitted for clarity. Important bond distances [Å] and angles [deg]: P1–C1, 1.862(5); C1–C2, 1.357(6); C2–P2, 1.826(5); P1–Pt1, 2.347(1); P2–Pt1, 2.315(1); P3–Pt1, 2.319(1); P4–Pt1, 2.349(1); P3–C3, 1.807(5); C3–C4, 1.374(7); C4–P4, 1.858(4); Pt1–P1–C1, 105.3(2); P1–C1–C2, 119.3(3); C1–C2–P2, 118.8(3); C2–P2–Pt1, 107.9(2); P1–Pt1–P2, 86.26(4); Pt1–P3–C3, 107.6(2); P3–C3–C4, 119.3(3); C3–C4–P4, 119.0(3); C4–P4–Pt1, 105.2(2); P3–Pt1–P4, 86.57(4); P1–Pt1–P3, 94.17(4); P2–Pt1–P4, 93.02(4); P1–Pt1–P4, 178.76(4); P2–Pt1–P3, 178.71(5).

Table 1. Crystal Data and Structural Refinement Details for the Structure of Dianion **3**

	3
emp formula	$C_{72}H_{90}Na_4O_4P_4.C_{10}H_8$
fw	1459.44
temp, K	150.0(1)
λ (Å)	0.71069
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	15.366(5)
b, Å	16.723(5)
c, Å	17.533(5)
α, deg	93.820(5)
β, deg	104.520(5)
γ, deg	112.250(5)
V, Å^3	3971(2)
Z	2
D_{calcd}, g/cm^3	1.221
μ (cm^{-1})	0.173
h,k,l ranges	−17−17; −19−18; −20−20
cryst size, mm^3	0.22 × 0.10 × 0.08
cryst color and habit	deep red plate
$2\theta_{max}$, deg	24.11
no. reflns measured	19751
no. indep reflns	12590
no. reflns used	8701
R1^a [$I > 2\sigma(I)$]	0.0649
wR2^b [$I > 2\sigma(I)$]	0.1602
Flack param	not applicable
GOF on F^2	1.030
difference peak/hole e Å^{-3}	1.038(0.079)/−0.877 (0.079)

^{a} $R1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

Scheme 2



4 [Li(2.2.1)]$_2$

is coordinated by three molecules of DME. One molecule of naphthalene, which has been omitted for clarity in the ORTEP view, is also present. One molecule of dianion **3** is coordinated to cations Na1 and Na2 through the two phosphorus atoms P1 and P2, respectively. The second molecule of **3** behaves as a chelate toward Na3 and binds Na2 through the phosphorus atom P3. The coordination spheres of cations Na1 and Na3 are completed in each case by the coordination of one molecule of DME. Note that the coordination of one lone pair of atom O4 helps to maintain the rigidity of the edifice. In the polymeric arrangement (see Figure 2), it becomes evident that the environment of the dianionic units **3** and cations Na1 and Na3 is roughly equivalent, cation Na2 acting as a link between the different subunits. The metric parameters within each dianionic subunit are typical. The P–C bond lengths are normal relative to those of classical phosphines (between 1.817(4) and 1.827(4) Å), and as expected, the C=C double bond character is maintained (for example, *d*(C1–C2) = 1.385(5) Å).

To test the ability of **3** to act as ligand for platinum, we reacted it with the [Pt(COD)Cl$_2$] precursor complex. Various experiments were carried out by modifying the nature of the solvent and the cation (Na or Li). In all cases, the reaction proceeds cleanly at −80 °C in THF or DME as solvent to yield complex **4M$_2$** (M = Na or Li) which in both cases appears as a singlet in ^{31}P NMR spectroscopy with characteristic Pt satellites [δ(**4Li$_2$**, THF) = 67.1 ppm with ^1J(Pt–P) = 957 Hz, and δ(**4Na$_2$**, DME) = 69.2 ppm with ^1J(Pt–P) = 943 Hz]. Despite many efforts, we were not able to grow crystals of the dilithium salt of the **4Li$_2$** complex. Fortunately, addition of cryptofix (2.2.1) allowed us to grow single crystals of complex **4[Li(2.2.1)]$_2$** (Scheme 2) which was isolated as a highly oxygen and moisture sensitive compound. Complex **4[Li(2.2.1)]$_2$** was characterized by ^{31}P and ^{1}H NMR spectroscopy (carried out on crystals used for the X-ray study) and elemental analysis. Unfortunately, its low solubility in THF precluded the recording of the ^{13}C NMR spectrum. An ORTEP view of one molecule of **4[Li(2.2.1)]$_2$** is presented in Figure 3, and the most significant bond lengths and angles are listed in the corresponding legend. Crystal data and structural refinement details are listed in Table 2.

As can be seen, the overall geometry around platinum is square planar (internal P–Pt–P angles, 86.26(4)° and 86.57(4)°; external, 94.17(4)° and 93.02(4)°), and only one diastereomer, (1-*R*, 2-*S*, 3-*R*, 4-*S*), is obtained. Indeed, for **4[Li(2.2.1)]$_2$**, four other possible diastereomers could have been obtained, (1-*R*, 2-*S*, 3-*S*, 4-*R*), (1-*R*, 2-*R*, 3-*S*, 4-*S*), and (1-*R*, 2-*S*, 3-*S*, 4-*S*), which are probably highly disfavored

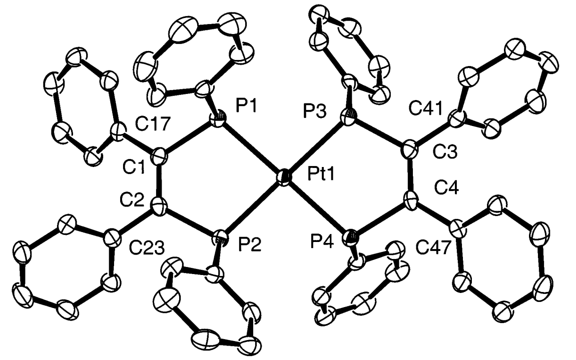


Figure 3. ORTEP drawing of complex **4[Li(2.2.1)]$_2$**. Ellipsoids are scaled to enclose 50% of the electron density. The two [Li(2.2.1)] units and hydrogen atoms are omitted for clarity. Important bond distances [Å] and angles [deg]: P1−C1, 1.862(5); P1−C5, 1.839(5); P2−C2, 1.826(5); P2−C11, 1.840(5); P3−C3, 1.807(5); P3−C29, 1.833(5); P4−C4, 1.858(4); P4−C35, 1.846(4); Pt1−P1, 2.347(1); Pt1−P2, 2.315(1); Pt1−P3, 2.319(1); Pt1−P4, 2.349(1); P2−Pt1−P3, 178.71(5); P2−Pt1−P1, 86.26(4); P3−Pt1−P1, 94.17(4); P2−Pt1−P4, 93.02(4); P3−Pt1−P4, 86.57(4); P1−Pt1−P4, 178.76(4); C5−P1−C1, 100.1(2); C5−P1−Pt1, 106.9(1); C1−P1−Pt1, 105.3(2); C2−P2−C11, 104.0(2); C2−P2−Pt1, 107.9(2); C11−P2−Pt1, 113.2(2), C3−P3−C29, 103.7(2); C3−P3−Pt1, 107.6(2).

Table 2. Crystal Data and Structural Refinement Details for Structures of Complexes **4[Li(2.2.1)]$_2$** and **4[Na(DME,Et$_2$O)]$_2$**

	4[Li(2.2.1)]$_2$	**4[Na(DME,Et$_2$O)]$_2$**
emp formula	$C_{88}H_{112}Li_2N_4O_{12}P_4Pt$	$C_{68}H_{80}Na_2O_6P_4Pt\cdot 1/2Et_2O$
fw	1750.67	1395.33
temp, K	150.0(1)	150.0(1)
λ, Å	0.71069	Mo Kα
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$C2/c$
a, Å	12.6947(2)	17.832(5)
b, Å	17.2161(3)	17.818(5)
c, Å	37.8877(5)	23.651(5)
β, deg	90.0000(1)	90.010(5)
V, Å^3	8280.5(2)	109.550(5)
Z	4	4
D_{calcd}, g/cm^3	1.404	1.309
μ, cm^{-1}	1.835	2.132
h,k,l ranges	−16−16; −22−22; −49−49	−23−23; −21−23; −23−30
cryst size, mm^3	0.15 × 0.06 × 0.06	0.20 × 0.16 × 0.13
cryst color and habit	red needle	deep red plate
$2\theta_{max}$, deg	27.50	27.48
no. reflns measured	17543	17725
no. indep reflns	17543	8120
no. reflns used	15305	6789
R1[a] $[I > 2\sigma(I)]$	0.0431	0.0317
wR2[b] $[I > 2\sigma(I)]$	0.0866	0.0693
Flack param	0.005(4)	not applicable
GOF on F^2		1.020
largest diff peak, e Å^{-3}	1.233(0.094)/ −0.563(0.094)	1.380 (0.081) / −0.602 (0.081)

[a] $R1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

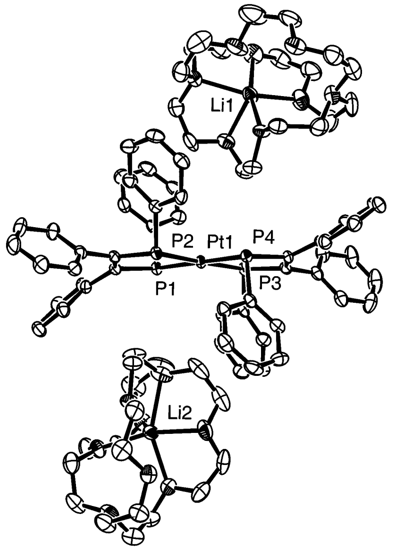
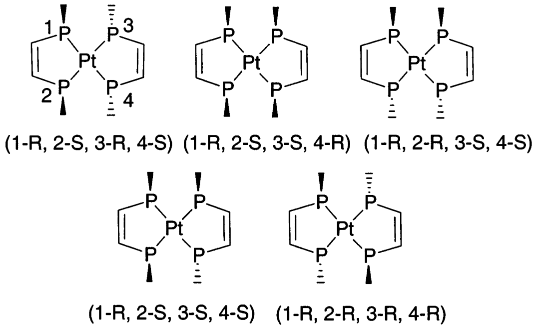


Figure 4. Complete view of **4[Li(2.2.1)]$_2$** in order to emphasize the particular spatial arrangement of the complex and the two countercations.

Scheme 3



because of the steric congestion between the phenyl groups, and (1-*R*, 2-*R*, 3-*R*, 4-*R*) in which the phenyl groups alternatively point above and below the PtP_4 plane of the complex (see Scheme 3). It is very likely that the energy difference between the diastereomer we obtained and (1-*R*, 2-*R*, 3-*R*, 4-*R*) is weak. It must be noted that other crystallization attempts, carried out under the same experimental conditions, yielded a similar result. A possible explanation would be that the packing forces in the crystal are minimized when the complex adopts such a configuration, the cavity formed by the two phenyl groups acting as an ideal host for the [Li(2.2.1)] units. Indeed, as can be seen in Figure 4, the structure of **4[Li(2.2.1)]$_2$** turns out to be very compact, and the electrostatic interaction between the complex and the two $[(2.2.1)Li]^+$ countercations is probably favored in this arrangement.

The examination of metric parameters reveals some distortions, and the P−Pt bond and P−C bond distances are not equivalent. Thus, P1−Pt1 (2.347(1) Å) and P4−Pt1 (2.349(1) Å) bond distances are slightly longer than P2−Pt1 (2.315(1) Å) and P3−Pt1 (2.319(1) Å), and conversely, P1−C1 (1.862(5) Å) and P4−C4 (1.858(4) Å) are longer than P2−C2 (1.826(5) Å) and P3−C3 (1.805(5) Å). This disymmetry is also apparent in the measure of the pyramidality of the phosphorus atoms (Σ of the bond angles at P atoms: 312.4° for P1, 311.6° for P4, 325.1° for P2, and 325.2° for P3). However, in both diphospholene subunits, the C−C bond lengths are equivalent (1.374(7) and 1.357(6) Å) and close to that recorded in the structure of dianion **3**. This observation tends to show that no delocalization occurs in the metallacycle and that the charges are mainly localized on the phosphorus atoms. According to the square planar geometry of the metal, complex **4[Li(2.2.1)]$_2$** can thus be regarded as the coordination of two dianions **2** onto a d^8 Pt^{2+} center.

We were able to grow crystals of the **4[Na(DME,Et$_2$O)]$_2$** complex using a mixture of DME and ether (Scheme 4). Like

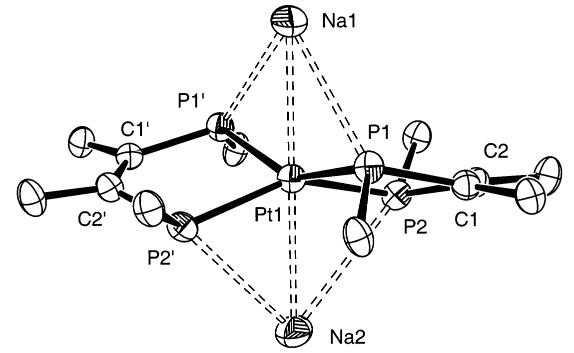
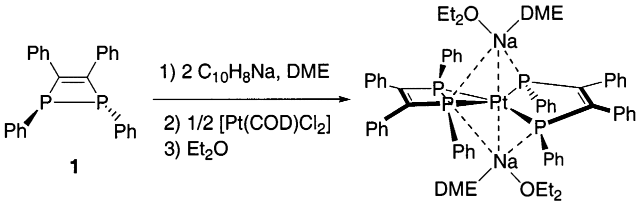


Figure 5. ORTEP drawing of a **4[Na(DME,Et$_2$O)]** $_2$ unit. Ellipsoids are scaled to enclose 50% of the electron density. Five carbon atoms of each phenyl group at phosphorus and carbon atoms and hydrogen atoms are omitted for clarity. Important bond distances [Å] and angles [deg]: P1−C1, 1.823(3); C1−C2, 1.363(4); C2−P2, 1.825(3); P1−Pt1, 2.304(1); P2−Pt1, 2.3041(8); P1′-Pt1, 2.303(1); P2′−Pt1, 2.3043(8); P1−Na1, 3.210(2); Na1−P1′, 3.211(2); P2−Na2, 3.223(2); P2′−Na2, 3.222(2); Pt1−Na1, 2.927(2); Pt1−Na2, 2.950(2). P1−Pt1−P1′, 149.34(4); P2−Pt−P2′, 149.05(4); P1−Pt1−P2, 85.11(3); P1′−Pt1−P2′, 85.10(3); P1−Pt−P2′, 103.09(3); P2−Pt1−P1′, 103.08(3); P1−Na1′−P1′, 87.57(6); P2−Na2′−P2′, 87.11(5); Pt1−P1−C1, 108.3(1); P1−C1−C2, 117.4(2); C1−C2−P2, 117.9(2); C2−P2−Pt1, 107.9(1).

Scheme 4



4 [Na(DME, Et$_2$O)]$_2$

its lithium counterpart, this complex is highly moisture and oxygen sensitive. An ORTEP view of one molecule of **4[Na(DME,Et$_2$O)]$_2$** is presented in Figure 5, and the most relevant bond distances and angles are listed in the corresponding legend. Crystal data and structural refinement details are listed in Table 2.

As can be seen, the structure of **4[Na(DME,Et$_2$O)]$_2$** is markedly different from that of **4[Li(2.2.1)]$_2$**. The most significant difference concerns the overall geometry around the platinum atom and the coordination of the two [Na(DME,Et$_2$O)] cations. If we do not take the two cations which are located on a C_2 axis into account, **4[Na(DME,Et$_2$O)]$_2$** can be described as a distorted square planar platinum complex (interplane angle between the two platinadiphospholene units = 35°). Another important difference between the two complexes concerns the configuration of the phosphorus atoms. Unlike the lithium complex, the diastereomer obtained here is (1-*S*, 2-*S*, 3-*S*, 4-*S*), and other crystallization attempts, carried out under the same experimental conditions, led to the same result. The preference for this diastereomer is obvious if we consider the overall geometry of the complex. Indeed, changing the configuration, for example at P1, would generate an important steric congestion with sodium cation Na1.

The examination of bond distances reveals that the two cations are weakly coordinated to the central platinum atom (d(Pt−Na) = 2.927(2) and 2.950(2) Å). Though there is no covalent bonding between P and Na atoms (∑ of the respective covalent radii = 2.60 Å), a weak interaction probably exists because P−Na bond distances are smaller than the sum of the van der Waals radii (4.07 Å). Thus, cation Na1 interacts with phosphorus atoms P1 (d(P1−Na1) = 3.210(2) Å) and P1′ (d(P1′−Na1) = 3.211(2) Å). Apart from the platinum−phosphorus bond distances (2.303(1)−2.3043(8) Å) which are slightly shorter than in **4[Li(2.2.1)]$_2$**, the metric parameters in each platinadiphospholene unit are quite similar to those recorded in dianion **3**. All the P atoms are pyramidal (∑ of angles at P$_1$ and P$_1$′= 329.5° and 330.1° for P2 and P2′). On the other hand, at 1.825(3) Å, the P−C bond distances are normal, and the short C−C connection (d(C1−C2) = 1.363(4) Å) is in good agreement with a double bond character.[10] According to this useful criterion, complex **4[Na(DME,Et$_2$O)]$_2$** is also best described by the coordination of two dianions **3** onto a d^8 Pt^{2+} center. It is interesting to compare these data with those of the neutral platinadiphospholene bis(triphenylphosphine) complex of general formula [Pt(P$_2$C$_2$Ph$_4$)(PPh$_3$)$_2$] which was structurally characterized by some of us in 1992.[5] This complex adopts a distorted tetrahedral geometry with an interplane angle (between the platinadiphospholene and the plane defined by the two phosphine ligands) of 57°. A comparison with the metric parameters of **4[Na(DME,Et$_2$O)]$_2$** indicates that this neutral complex seems to be closer to a platinum(0) species (see form III in Chart 1). Thus, at 1.799(6) and 1.797(6) Å, the two P−C bond lengths are slightly shorter, and conversely, a lengthening of the C−C connection (1.376(9) Å) and a shortening of the P−Pt bonds (2.282(1) and 2.288(2) Å) can also be noted. Besides, the two P atoms in this complex are also slightly more planar (∑ of angles at P atoms = 336° and 337°). In good agreement with these structural differences, the two P atoms also exhibit a greater s-character as shown by the larger ^1J(Pt−P) = 1512 Hz coupling constant.

In the end, it is not easy to rationalize the difference observed between the two geometries of complexes **4**. One may argue that the energetic barrier between the square planar and the observed strongly distorted square planar geometry does not exclusively result from electronic effects. We propose that the energetic difference between the two geometries is sufficiently weak to be overcome by the four weak interactions between phosphorus atoms and sodium cations in **4[Na(DME,Et$_2$O)]$_2$**.

In conclusion, we have synthesized and structurally characterized the first homoleptic platinadiphospholene complexes. With the synthesis of complex **4[Na(DME,Et$_2$O)]$_2$**, we also showed that interactions between the metal, phosphorus, and the cations probably play an important role in defining the overall geometry. On the basis of structural data, it seems that both cryptated and uncryptated species have to be considered as platinum +2 complexes coordinated by two dianionic ligands (form **I** in Chart 2). Studies aimed

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(10) A shortening of the internal C−C bond of metalladiphospholene can be used as a criterion of electronic delocalization, see: Le Floch, P.; Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Inorg. Chem.* **1995**, *34*, 5070−5072.

at expanding the coordination chemistry of dianions **2** and **3** to other metallic centers are currently underway in our laboratories.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone, and dry CH_2Cl_2 and $CDCl_3$, from P_2O_5. CD_2Cl_2 was dried and stored, like $CDCl_3$, on 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. The following abbreviations are used: b; broad, s; singlet; d, doublet; t, triplet; m, multiplet; v, virtual. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyze du CNRS", at Gif sur Yvette, France.

Synthesis of Dianion 2. To a solution of tetraphenyldiphosphetene **1** (197 mg, 0.5 mmol) in 20 mL of THF were added 2 equiv of Li metal (7 mg, 1 mmol). The very dark red solution was stirred at room temperature for 2 h. The reaction was followed by ^{31}P NMR. The dianion formed was used in subsequent reactions without further purification. Alternatively, the dianion can also be obtained with equal purity through the reaction of **1** with 2 equiv of Li naphthalenide. ^{31}P (THF): δ 24.1 (s).

Synthesis of Dianion 3. In a glovebox, solid **1** (19.7 mg, 4.92 $\times$ 10^{-5} mol) was added to a DME solution of Na naphthalenide (2 mL, 5 $\times$ 10^{-5} mol/mL, 10^{-4} mol). After 10 min stirring at room temperature, a ^{31}P NMR spectrum of the red solution showed the presence of the dianion. The solution was then evaporated under vacuum. Once dry, the solid was kept under vacuum for several hours to allow for the sublimation of most of the naphthalene. In the glovebox, the solid was dissolved in a 1:1 mixture of DME and Et_2O, and the solution was placed in a tube which was subsequently sealed. Dark red crystals formed within a few days at room temperature. As seen in the X-ray structure analysis, the crystals also contained one molecule of naphthalene. Alternatively, last traces of naphthalene were removed by extraction with dry hexanes to yield pure dianion. Yield: 90%, 30.0 mg, 4.5 $\times$ 10^{-5} mol. ^{31}P (THF-*d*^{8}): δ −2.7 (s). ^{13}C (THF-*d*^{8}): δ 117.0−128.3 (CH of Ph), 131.7 (vt, AXX′, $\sum J$(C−P) = 19.9, Cα of P−Ph), 132.8−140.0 (CH of Ph), 147.7 (s, Cα of Ph), 156.6 (vt, AXX′, $\sum J$(C−P) = 27.7, =C−Ph).

Synthesis of Complex 4[Li(2.2.1)]$_2$. To a DME solution of Li naphthalenide (2 mL, 6.25 $\times$ 10^{-5} mol/mL, 1.25 $\times$ 10^{-4} mol) was added **1** (24.6 mg, 6.25 $\times$ 10^{-5} mol) under argon. After 10 min, the solution was checked by ^{31}P NMR. The solution was then cooled to −78 °C, and [Pt(COD)Cl_2] (11.7 mg, 3.125 $\times$ 10^{-5} mol) was added. The mixture was then warmed back to room temperature and brought back in the glovebox. Cryptand (2.2.1) (23 mg, 6.25 $\times$ 10^{-5} mol) was then added inducing a rapid precipitation of red microcrystals which precluded the recording of ^{13}C NMR spectra. However, ^{31}P NMR of the crude mixture revealed the formation of a single species. The microcrystals were collected on a fine frit. Yield: 84%, 46.0 mg, 2.6 $\times$ 10^{-5} mol. ^{31}P (THF): δ 67.1 (s, ^1J-(Pt−P) = 957 Hz). ^{1}H (THF-*d*^{8}): δ 6.98−7.50 (m, 40H, H of C_6H_5 groups). Anal. Calcd for $C_{88}H_{112}Li_2N_4O_{12}P_4Pt$: C, 60.37; H, 6.45. Found C, 60.80; H, 6.65.

Synthesis of Complex 4[Na(DME,Et$_2$O)]$_2$. Diphosphetene **1** (19.7 mg, 5 $\times$ 10^{-5} mol) was added to a DME solution of Na naphthalenide (2 mL, 5 $\times$ 10^{-5} mol/mL, 1 $\times$ 10^{-4} mol) under argon. After 10 min, the solution was checked by ^{31}P NMR. The solution was then cooled to −78 °C, and [Pt(COD)Cl_2] (8.6 mg, 2.5 $\times$ 10^{-5} mol) was added. The mixture was then warmed back to room temperature and brought back in the glovebox. The volume of solvent was reduced under vacuum, and the complex was characterized in a mixture of DME and THF-*d*^{8}. To obtain crystals, the solution was taken to dryness and the solid dissolved in a mixture of DME and Et_2O. The solution was then sealed, and crystals formed within days at room temperature. Yield: 80%, 27.9 mg, 2.0 $\times$ 10^{-5} mol.^{31}P (THF-*d*^{8}): δ 69.2 (s, ^1J(Pt−P) = 943 Hz). ^{13}C (THF-*d*^{8}): δ 59.5 (s, DME), 73.3 (s, DME), 124.0−132.3 (m, CH of Ph), 137.0 (m, Cα of Ph), 148.0 (vt, AXX′, $\sum J$(C−P) = 11.2, =C−Ph), 152.6 (m, Cα of P−Ph). Anal. Calcd for $C_{68}H_{80}Na_2O_6P_4$-Pt·$(C_4H_{10}O)_{0.5}$: C, 60.26; H, 6.14. Found: C, 59.95; H, 6.45.

X-ray Structural Determination. As described previously, dianion **3** and complexes **4[Li(2.2.1)]$_2$** and **4[Na(DME,Et$_2$O)]$_2$** were crystallized in sealed tubes. In each case, the tube was broken in the glovebox, and crystals were protected with paratone oil for handling and then submitted to X-ray diffraction analysis. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. Experimental details are described in Tables 1 and 2. The crystal structures were solved using SIR 97[11] and Shelxl-97.[12] ORTEP drawings were made using ORTEP III for Windows.[13]

Acknowledgment. The authors thank the CNRS and the Ecole Polytechnique for supporting this work.

Supporting Information Available: Listings of atomic coordinates, including H atoms and equivalent isotropic displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020103D

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