# 1,2,4-Diazaphospholide Complexes of Barium: Mechanism of Formation and Crystallographic Characterization[†]

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A number of barium 1,2,4-diazaphospholide (dp⁻) complexes have been prepared by protonolysis of barium bis[bis(trimethylsilyl)]amide (Ba[N(SiMe₃)₂]₂(THF)₂) and the corresponding 1,2,4-diazaphospholes. The bis(3,5-diphenyl-1,2,4-diazaphospholide)-tetrakis(tetrahydrofuran)barium [$\eta^2$(*N,N*)-3,5-Ph₂dp)₂Ba(THF)₄] (**1**) and bis(3,5-diphenyl-1,2,4-diazaphospholide)-tetrakis(dimethylsulfoxide)barium [$\eta^2$(*N,N*)-3,5-Ph₂dp)₂Ba(DMSO)₄] (**2**) were prepared by the reactions of Ba[N(SiMe₃)₂]₂(THF)₂ and 3,5-diphenyl-1,2,4-diazaphosphole (H[3,5-Ph₂dp]) in tetrahydrofuran (THF) or dimethylsulfoxide (DMSO), respectively, while the bis(3,5-disubstituted-1,2,4-diazaphospholide)-(18-crown-6) barium complexes [*trans*-$\eta^2$(*N,N*)-dp)₂Ba(18-crown-6)] (**3**), [*cis*-$\eta^2$(*N,N*)-*t*Bu₂dp)₂Ba(18-crown-6)] (**4**), [*trans*-$\eta^2$(*N,N*)-*t*Bu₂dp)₂Ba(18-crown-6)] (**5**), [*cis*-$\eta^2$(*N,N*)-Ph₂dp)₂Ba(18-crown-6)] (**6**), and [*trans*-$\eta^2$(*N,N*)-Ph₂dp)₂Ba(18-crown-6)] (**7**) were synthesized by the reaction of Ba[N(SiMe₃)₂]₂(THF)₂ and the corresponding 1,2,4-diazaphospholes in the presence of 18-crown-6 in THF or DMSO. Complexes **1**, **2**, **3**, **4**, and **7** have been structurally characterized. Complex **4** is the first structurally characterized barium complex in which the two organic ligands are located on the same side of 18-crown-6 (*cis* conformation). The ³¹P{¹H} NMR spectra suggested a partial dissociation of the barium 1,2,4-diazaphospholides **2**, **4**, and **7** into the corresponding ion associated complexes in solutions.

## Introduction

Interest in the organometallic chemistry of the heavy alkaline earth elements, calcium, strontium, and barium has been driven by their potential application in organic synthesis,[1a] anionic styrene polymerization,[1b] and thin films for solid-state devices.[1c,d] Although the low solubility in common organic solvents and marginal thermal stability of many calcium, strontium, and barium organometallic complexes have hindered their investigation, the use of sterically demanding ligands or multidentate Lewis bases for steric shielding of the metals is expected to promote encapsulation of the metal centers, resulting in stable, soluble, monomeric compounds; as the result, research into the organometallic chemistry of calcium, strontium, and barium has mainly focused on the identification of the sterically bulky ligands

and the accessible synthetic approaches which have made possible the isolation and detailed characterization of new ligand based compounds.[2] The successful synthesis of metallocenes [*trans*-(C₅ⁱPr₅)M(C₅ⁱPr₅)] (M = Ca, Sr, Ba),[3a] triple-decker sandwich alkaline-earth metal complexes [*trans*-(C₅HⁱPr₄)M(COT)M(C₅HⁱPr₄)] (M = Ca, Sr, Ba; COT = cyclooctatetraenyl),[3b,c] and monomeric barocene [*trans*-Ba(C₅H₅)₂(18-crown-6)][4] testified to the soundness of the

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synthetic method with bulky ligands. The recent application of the bulky stabilized calcium amide, benzylcalcium complexes to the catalytic heterofunctionalization or polymerization of substrates containing unsaturated carbon−carbon bonds has further verified the synthetic approach.[5−8]

The transamination of $M[N(SiMe_3)_2]_2(THF)_2$ (M = Ca, Sr, Ba)[9] is one of well-known methods for the synthesis of many organometallic complexes of heavy alkaline-earth metals, and generally allows the preparation of the corresponding product molecules in high yields and purity, employing a variety of ligand systems.[10,11] However, in the case of utilizing multidentate Lewis bases crown ethers, an unexpected reaction between bis(trimethylsilyl)amide of heavy alkaline-earth metals and the crown ethers occasionally occurred as it proceeded with elimination of the silylamine, $(Me_3Si)_2NH$, along with the formation of the ring-opened ether products.[9a,12] Ruhlandt-Senge and co-workers evidenced that a necessary requisite for a slightly lower acidity of the acid substrates than that of liberated $HN(SiMe_3)_2$, will promote the formation of a family of $\sigma$-bound organometallic complexes [trans-M(18-crown-6)(CCSiPh_3)_2] (M = Ca, Sr, Ba),[13a] charge-separated ion-associated species [Ba(CPh_3)_2-(18-crown-6)(hmpa)_2] (hmpa = hexamethylphosphoramide),[13b] and the semiseparated complex [Ba(18-crown-6)(hmpa)(SMes*)][SMes*] (Mes* = 2,4,6-$tBu_3C_6H_2$)[13c] without an ether-cleavage. The reactivity studies of crown ether cleavage chemistry have suggested a proton abstraction from the macrocycle by the silylamide anion, followed by C−O bond cleavage to give the vinyl ether,[9a,12] but little is known regarding the mechanism, and no direct evidence is available for the details about the formation of complexes [trans-M(18-crown-6)R_2]. To our surprise, monomeric complexes [cis-M(18-crown-6)R_2] (M = Ca, Sr, Ba; R = anionic organic group) have not yet appeared in the literature.

Recently we reported several novel ruthenium, samarium, and alkali metal derivatives[14−17] on the base of the sterically hindered 1,2,4-diazaphospholide ligands (dp[−]). The depro-

tonated 1H-1,2,4-diazaphosphole group[18] is a mixed nitrogen−phosphorus ($\sigma^2\lambda^3$) analogue of Cp[−] and may be viewed as the combination of phospholyl[19] and pyrazolato (pz)[20] ions. Since the $^{31}P$ NMR signals are very sensitive to the change in electronic environment around phosphorus nuclei, it seemed interesting to assess the potential of the corresponding heavy alkaline-earth metal complexes bearing 1,2,4-diazaphospholide ligands.[21] Herein, we reported the preparation of the first examples of 1,2,4-diazaphospholide derivatives of barium, as well as the possible mechanism of their formation.
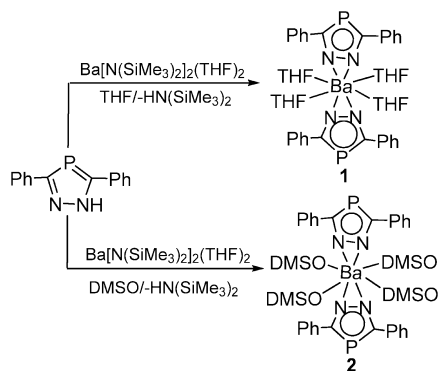
## Results and Discussion

**Syntheses.** The syntheses of barium 1,2,4-diazaphospholide complexes of types [$\eta^2$(N,N)-3,5-R_2dp)_2Ba(Sol)_x] (R = Ph; Sol = solvated tetrahydrofuran (THF) or dimethylsulfoxide (DMSO) molecules) and [$\eta^2$(N,N)-3,5-R_2dp)_2Ba(18-crown-6)] (R = H, Ph, tBu) provide a challenge by the transamination of $Ba[N(SiMe_3)_2]_2(THF)_2$ and 1,2,4-diazaphospholes since it is not clear what the acidity of 1,2,4-diazaphospholes is, and whether a reaction will occur in solution and by what mechanism the reaction will undergo in solution.

**Preparation of Complex [$\eta^2$(N,N)-3, 5-Ph_2dp)_2Ba-(THF)_4], 1.** Given the N−H acidity of 1,2,4-diazaphospholes (H[3,5-R_2dp]),[16,18] though the exact values of their p$K_a$ are unknown,[22] the transamination route seemed feasible for the corresponding 1,2,4-diazaphospholide complexes of heavy alkaline-earth metals, where the hydrogen atoms on the N atoms of 1,2,4-diazaphospholes may act as the acid substrates. As expected, complex [$\eta^2$(N,N)-3,5-Ph_2dp)_2Ba-(THF)_4] (1) is readily accessible by the reaction of $Ba[N(SiMe_3)_2]_2(THF)_2$[23] and H[3,5-Ph_2dp] in THF at room temperature (Scheme 1), suggesting that the p$K_a$ of H[3,5-Ph_2dp] is higher than 25.8, that is, the p$K_a$ of $HN(Me_3Si)_2$.[24] Complex 1 crystallized from hot THF is soluble in THF and DMSO, but only sparingly soluble in toluene and n-hexane.

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**Scheme 1.** Preparation of Complexes **1** and **2**



**Scheme 2.** Preparation of Complex **3**



lographic analysis has unambiguously confirmed the ratio of DMSO molecules to 1,2,4-diazaphospholide ligands in **2**.

$$[\eta^2(N,N)\text{-}3,5\text{-}Ph_2dp)_2Ba(DMSO)_4] \xrightleftharpoons{DMSO}$$

**2**

$$[\eta^2(N,N)\text{-}3,5\text{-}Ph_2dp)Ba(DMSO)_4]^+[(3,5\text{-}Ph_2dp)]^- \quad (1)$$

The NMR data supported the existence of the coordinated THF molecules found in the crystalline form (in DMSO-$d_6$, 23 °C). In the $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 23 °C) spectrum, only one sharp resonance was observed at $\delta = 72.27$ ppm, indicating the solid state structure was maintained in the solution.

**Preparation of Complex [$\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba-(DMSO)$_4$], 2.** By slightly altering the reaction conditions, such as the use of DMSO as solvent, we were able to cleanly prepare in good yields and purity complex [$\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba(DMSO)$_4$] (**2**) (Scheme 1). Complex **2** shows similar physical properties to those of **1**. In the $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 23 °C) spectrum, however, two resonances were observed at $\delta = 71.94$ (br, strong) ppm and at $\delta = 34.46$ (s, weak) ppm (cf. 74.3 (s) ppm for H[3,5-Ph$_2$dp] in CDCl$_3$,[18a] 74.05(s) ppm in DMSO-$d_6$[25]). The $^1H$ NMR (DMSO-$d_6$, 23 °C) spectrum discounts the existence of H[3,5-Ph$_2$dp] in the solution because no N—H resonances were observed in the range of 9−12 ppm of the spectrum. The observed two resonances in the $^{31}P\{^1H\}$ NMR spectrum likely suggested a dissociation of **2** in the solution into an ion associated complex $\{[\eta^2(N,N)\text{-}3,5\text{-}Ph_2dp)Ba(DMSO)_4]^+[(3,5\text{-}Ph_2dp)]^-\}$ (eq 1). The broad resonance is tentatively assigned to the dp$^-$ ligands in **2** and in the cationic ion [$\eta^2(N,N)$-3,5-Ph$_2$dp)Ba(DMSO)$_4$]$^+$ where a dynamic process is probably involved.[25] The significant upfield shift resonance at 34.46 (s) ppm preliminarily implies [(3,5-Ph$_2$dp)]$^-$ species in the solution.[18a] The existence of the electrophilic species [$\eta^2(N,N)$-3,5-Ph$_2$dp)Ba(DMSO)$_4$]$^+$ seems important to understand the catalytic behavior of some recently prepared organometallic complexes of heavy alkaline earth elements.[5,26] Attempts to isolate the corresponding barium derivatives bearing the bulky 3,5-di-*tert*-butyl-1,2,4-diazaphospholide [3,5-*t*Bu$_2$dp]$^-$ and to fully characterize the reaction products by NMR spectroscopy proved difficult because of the complex mixture of products and the inability to obtain the crystals from the solution in good quality. The $^1H$ NMR data were obtained from solution of the complex in DMSO-$d_6$ at 23 °C, negating determination of the ratio of DMSO to 1,2,4-diazaphospholide ligands. Nevertheless, the X-ray diffraction crystal-
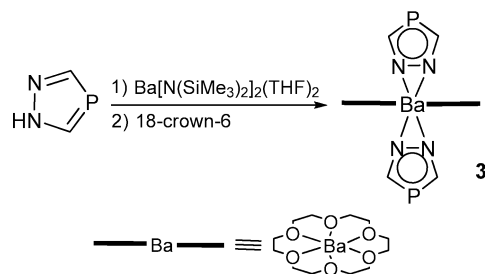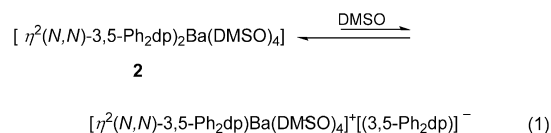
**Preparation of Complex [$\eta^2(N,N)$-dp)$_2$Ba(18-crown-6)], 3.** Similarly, the reaction of Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$[23] and the less bulky 1,2,4-diazaphosphole H[dp] was carried out. The resulting complex, however, demonstrated very limited solubility, even in THF and DMSO. This obviously reflects the propensity of polymeric array in the solid state because of the small ligand, the high electropositive character, and the large ionic radius of barium. To resolve the problem of the limited solubility of barium 1,2,4-diazaphospholide [Badp$_2$] and of the inability to obtain the crystals from solution, we utilized the multidentate Lewis bases crown ethers to shield the barium ion. By a two-step synthetic approach, *trans*-bis(1,2,4-diazaphospholide)-(18-crown-6)-barium complex [*trans*-$\eta^2(N,N)$-dp)$_2$Ba(18-crown-6)] (**3**) was successfully isolated as colorless crystals in good yields, which presents fair solubility in most common organic solvents (Scheme 2). The isolation of **3** suggests a higher p$K$a value of H[dp] than that of HN(Me$_3$Si)$_2$.[24] In comparison to **1** and **2**, compound **3** has even higher thermal stability (>340 °C decomposed). The NMR data (DMSO-$d_6$, 23 °C) supported 18-crown-6 and dp$^-$ ligands of **3**. In the $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 23 °C) spectrum, only one sharp resonance was observed at $\delta = 73.08$ (s) ppm for the dp$^-$ ligands, indicating the molecule composition of **3** in the solution (cf.$^{31}P$ NMR $\delta = 82.8$ (s) ppm (t, $^1J_{CP} = 44.1$ Hz) for H[dp] in CDCl$_3$).[18a,25] This is probably the result of the less steric bulkiness of the dp$^-$ anion.

**Preparation of Complexes [*cis*-$\eta^2(N,N)$-3,5-*t*Bu$_2$dp)$_2$Ba(18-crown-6)], 4 and [*trans*-$\eta^2(N,N)$-3, 5-*t*Bu$_2$dp)$_2$Ba(18-crown-6)], 5.** To explore the coordination variability of 1,2,4-diazaphospholide ligands with barium, the reaction of the bulky 3,5-di-*tert*-butyl-1,2,4-diazaphosphole H[3,5-*t*Bu$_2$dp] and Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ was carried out in the presence of 18-crown-6. In a fashion similar to the preparation of **3**, complex [*cis*-$\eta^2(N,N)$-3,5-*t*Bu$_2$dp)$_2$Ba(18-crown-6)] (**4**) was obtained as a group of colorless crystals from a mixed solvent of THF and *n*-hexane. Complex **4** is soluble in THF and DMSO and has high thermal stability (decomposed above 340 °C). The $^1H$ NMR data

(25) The $^1H$ NMR spectra of complexes **1**, **2**, **3**, **4**, **6**, and **7**, the $^{31}P$ NMR spectra of complexes **2**, **4**, **7**, and of 1,2,4-diazaphospholes in DMSO-$d_6$ are contained in the Supporting Information.

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**Scheme 3.** Preparation of Complexes **4** and **5**



**Scheme 4.** Preparation of Complexes **6** and **7**
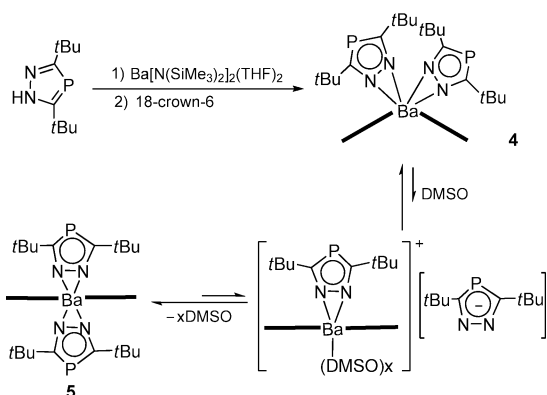


(DMSO-$d_6$, 23 °C) supported one 18-crown-6 and two dp$^-$ ligands. **4** is a remarkable monomeric species in which the two dp$^-$ ligands are arranged in a *cis*-conformation (vide infra, Scheme 3). In the $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C) spectrum, two sets of resonances are observed at $\delta = 59.44$ (very br.) and 38.22 (s) ppm (cf. $^{31}$P NMR $\delta = 65.4$ (s) ppm for H[3,5-tBu$_2$dp] in CDCl$_3$,[18a] 64.55(s) ppm in DMSO-$d_6$[25]). This is similar to that observed in the $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C) spectrum for **2**, suggesting the partial dissociation of **4** in solution into the ion associated complex {[$\eta^2(N,N)$-3,5-tBu$_2$dp)Ba(18-crown-6)(DMSO)$_x$]$^+$[(3,5-tBu$_2$dp)]$^-$}. The very broad resonance is assigned to the 1,2,4-diazaphospholide ligands with $\eta^2(N,N)$ coordination in **4** and in the cationic species [$\eta^2(N,N)$-3,5-tBu$_2$dp)Ba(18-crown-6)(DMSO)$_x$]$^+$ (overlapped). The upfield shift resonance at 38.22 (s) ppm relative to that of the neutral ligand H[3,5-tBu$_2$dp] ($\delta = 65.4$ (s) ppm in CDCl$_3$) is presumably attributed to [3,5-tBu$_2$dp]$^-$ ion in solution. After refluxing complex **4** in THF for 2 days, a pale yellowish solid was obtained from the solution at room temperature. The $^1$H and $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C) spectrum evidenced the formation of compound **5** in *trans*-conformation by the isomerization of **4** (one new broad resonance at about 65 ppm appeared). Unfortunately, the attempt to isolate the pure complex **5** has not been successful so far.

**Preparation of Complexes [*cis-$\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba(18-crown-6)], 6** and **[*trans-$\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba(18-crown-6)], 7.** To gain more insight into the dissociation behavior of the barium 1,2,4-diazaphospholide complexes in DMSO, the reaction of **1** and stoichiometric amount of 18-crown-6 was carried out and subsequently resulted in a compound (**6**) in 69% isolated yield as a group of colorless needles. In the $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C) spectrum, only one resonance was observed at $\delta = 70.18$ (s) ppm for **6** (cf. 74.3 ppm for H[3,5-Ph$_2$dp] in CDCl$_3$[18a]), indicating $\eta^2(N,N)$-3,5-Ph$_2$dp ligand in solution (Scheme 4). We did observe a weak single resonance at $\delta = 34.20$(w) ppm from the solution of **6**, likely because of a very slow isomerization and the very low concentration of the ion associated complex as soon as the sample was dissolved into DMSO-$d_6$ for the measurement. When this DMSO-$d_6$ solution was kept for 2 days, a new resonance was observed at 34.32(s). Unfortunately, we were unable to
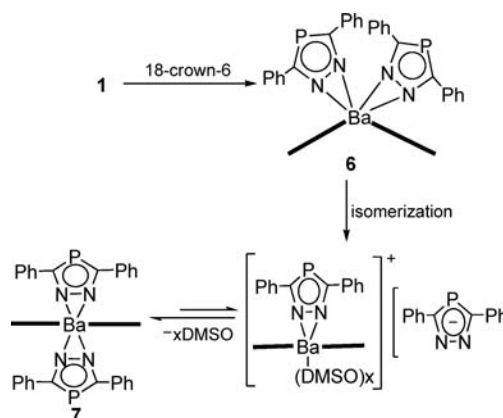
obtain the single crystals of **6** suitable for X-ray diffraction analysis. In a mixed solvent of THF and *n*-hexane, however, colorless complex **6** slowly converted into a group of yellow blocks (complex **7**) with significant color change (Scheme 4). In the $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C) spectrum, a resonance 34.37(s) ppm was observed at next to $\delta = 70.26$ (br.) ppm for **7**. This is clearly assigned to the [3,5-Ph$_2$dp]$^-$ anion in DMSO-$d_6$ as a result of the partial dissociation of **7**.[25]

**Single Crystal and Molecular Structures.** Ball and stick diagrams of the molecular structures of **1**–**4** and **7** are shown in Figure 1–5. Selected bond lengths (Å), the crystallographic data, and the selected dihedral angles of complexes are given in Tables 1–3, respectively.

**[$\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba(THF)$_4$], 1.** The barium atom is eight-coordinate with a distorted octahedral geometry, assuming that the centers of N–N bonds of the 3,5-Ph$_2$dp ligands are treated as monodentate donors (Figure 1). The high coordination number can be accommodated by the larger size of barium ion radius. The molecule shows a *transoid* orientation of two $\eta^2$-3,5-Ph$_2$dp ligands with four THF donors in equatorial positions. The core planes (*NNCPC*) of two 3,5-Ph$_2$dp ligands are almost normal as shown in Table 3 (the dihedral angle of the two heterocyclic planes (*NNCPC*) is 86.6(2)°). The heterocyclic plane of 3,5-Ph$_2$dp ligand and the phenyl rings are nearly coplanar with
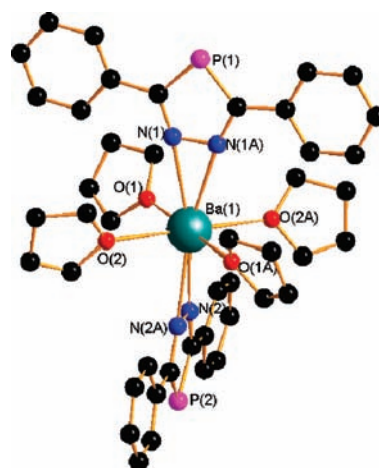


**Figure 1.** Ball and stick representation of complex **1**. Hydrogen atoms are omitted for clarity.
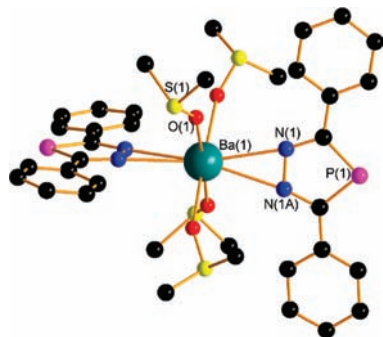
**Figure 2.** Ball and stick representation of complex **2**. Hydrogen atoms are omitted for clarity. The 50/50 disorder of the DMSO is simplified to show one orientation.
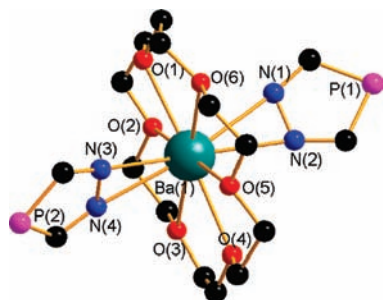


**Figure 3.** Ball and stick representation of complex **3**. Hydrogen atoms are omitted for clarity.
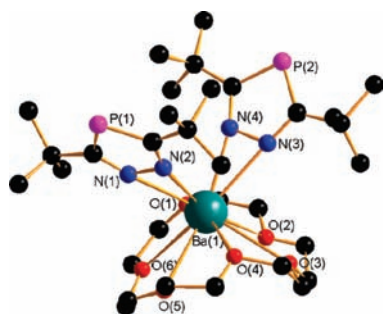


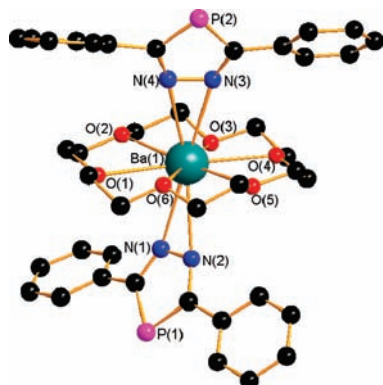**Figure 4.** Ball and stick representation of complex **4**. Hydrogen atoms are omitted for clarity.



**Figure 5.** Ball and stick representation of complex **7**. Hydrogen atoms are omitted for clarity.

average dihedral angle of 4.0(2)° (4.7(2)°, 4.7(2)°, 3.2(2)°, and 3.2(2)°). The structure feature observed in **1** is somewhat similar to that of the barium pyrazolato complex [Ba(Ph$_2$pz)$_2$(thf)$_4$] (monoclinic, space group $P2_1/c$),[27] probably reflecting some relevance of the 1,2,4-diazaphospholides to the pyrazolato ligands because of the diagonal relationship

between carbon and phosphorus.[14] The distances of Ba–N (2.797(4), 2.809(4) Å) fall in the expected range and are substantially comparable to those found in the complex [Ba(Ph$_2$pz)$_2$(thf)$_4$] (Ba–N 2.736(5)–2.813(5)Å).[27]

**[$\eta^2(N,N)$-3, 5-Ph$_2$dp)$_2$Ba(DMSO)$_4$], 2.** The geometry of central metal ion is similar to that found in **1** with DMSO in place of THF (Figure 2). The heterocyclic plane of 3,5-Ph$_2$dp ligand and the phenyl rings are nearly coplanar with average dihedral angle of 6.0° (Table 3), which is slightly larger than that found in **1**. Consistent with this observation is the longer Ba–N bond length (2.837(5) Å) in **2** than that found in **1**.

**[$trans$-$\eta^2(N,N)$-dp)$_2$Ba(18-crown-6)], 3.** Complex 3 contains two $\eta^2(N,N)$-dp and one $\eta^6$-18-crown-6 ligands (Figure 3). The barium ion is 10 coordinate with 4 nitrogen atoms of dp ligands and 6 oxygen atoms of the crown ether. The coordination sphere about the barium takes up a slightly distorted pseudo-dodecahedron geometry with the crown ether occupying the equatorial plane, assuming that the centers of the N–N bonds of the dp ligands are treated as monodentate donors. The hexadentate crown ether ligands show only minor variations within the ranges of the various Ba–O contacts, which are commensurate with previously reported barium structures containing 18-crown-6 ligands.[28] In **3**, the BaN$_2$ plane and dp ligand core are nearly coplanar (the angle between least-squares planes: 174.6(5)°, 177.3(5)°, respectively). The bond lengths of Ba–N (Ba–N1 2.828(9) Å, Ba–N2 2.767(10) Å, Table 1) in **3** suggest perfect $\eta^2$-interaction with the barium.

**[$cis$-$\eta^2(N,N)$-3,5-$t$Bu$_2$dp)$_2$Ba(18-crown-6)], 4.** Complex **4** contains two $\eta^2(N,N)$-3,5-$t$Bu$_2$dp and one $\eta^6$-18-crown-6 ligands, which crystallizes as a monomeric species (Figure 4, Table 2). However, the structure of **4** adopts a very irregular geometry with the quite folded crown ether macrocycle and two $\eta^2(N,N)$-3,5-$t$Bu$_2$dp ligands on the same side of the crown ether (in a $cis$-conformation). This is quite different from the $trans$-conformation found in **3**, as well as from the exclusive $trans$-conformations found in other barium complexes bearing 18-crown-6 ligands.[29] It is, to the best of our knowledge, the first example of monomeric barium complex that the organic ligands are completely located on the same side of the crown ether.

**[$trans$-$\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba(18-crown-6)], 7.** Complex **7** contains two $\eta^2(N,N)$-3,5-Ph$_2$dp and one $\eta^6$-18-crown-6 ligands (Figure 5). The dihedral angle of 64.3(1)° between the core of 3,5-Ph$_2$dp ligand and the best plane of the 18-crown-6 is smaller than the corresponding value in **3** (Table 3). The dihedral angles between the 3,5-Ph$_2$dp heterocyclic planes (NNP) and the corresponding phenyl planes (41.36°, 24.78°, 48.20°, and 28.35° as shown in Table 3) are substantially larger than those found in **1** or **2**. All these

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(28) (a) Dyer, R. B.; Metcalf, D. H.; Gbirardelli, R. G.; Palmer, R. A.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 3621. (b) Norman, J. A. T.; Pez, G. P. *Chem. Commun.* **1991**, 971. (c) Bremer, M.; Noth, H.; Schmidt, M. *Chem. Ber.* **1995**, *128*, 455. (d) Wojtczak, W. A.; Hampden-Smith, M. J.; Duesler, E. N. *Inorg. Chem.* **1998**, *37*, 1781.
(29) Alexander, J. S.; Ruhlandt-Senge, K. *Chem.—Eur. J.* **2004**, *10*, 1274.
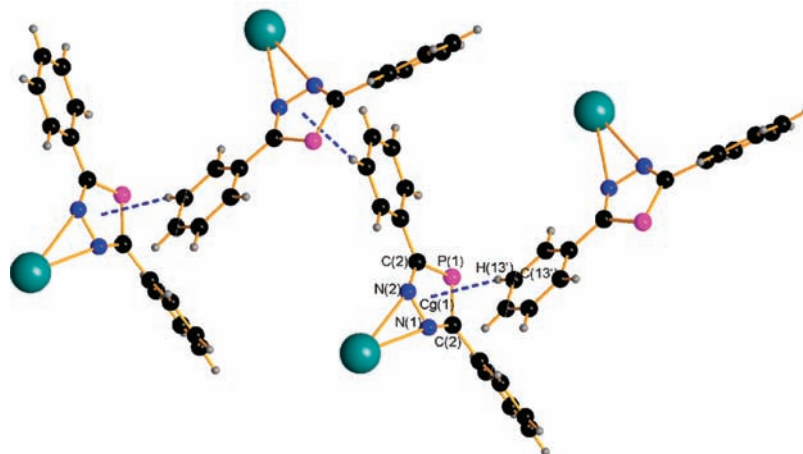
**Figure 6.** Intermolecular C−H···π interactions in complex **7** (the moiety of 18-crown-6 and partial 1,2,4-diazapspholide ligands are omitted for clarity), which are indicated by dashed lines. Cg(1) is the centroid of the N1, N2, C1, C2, and P1 ring. The weak interactions of the geometry (H(13′)···Cg(1) 2.707 Å, C(13′)···Cg(1) 3.579(8) Å, C(13′)−H(13′)−Cg(1) 156.4(5)°).

**Table 1.** Selected Bond Lengths (Å)

|  | **1** | **2** | **3** | **4** | **7** |
|---|---|---|---|---|---|
| Ba(1)−N(1) | 2.809(4) | 2.837(5) | 2.828(9) | 2.834(6) | 2.899(5) |
| Ba(1)−N(2) | 2.797(4) |  | 2.767(10) | 2.716(6) | 2.889(5) |
| Ba(1)−N(3) [or N(1A)] | 2.809(4) | 2.837(5) | 2.807(10) | 2.806(6) | 2.843(6) |
| Ba(1)−N(4) [or N(2A)] | 2.797(4) |  | 2.805(11) | 2.717(6) | 2.881(5) |

structural differences should be attributed to the intermolecular hydrogen bond-like interactions between the hydrogen atoms of phenyl rings of 3,5-ph₂dp ligands as shown in Figure 6. The distance (2.707 Å) between the hydrogen atom (H13′) of phenyl rings and the centroid (Cg(1)) of heterocycle of 3,5-ph₂dp ligand in **7** is significantly shorter than that reported by Reger for the complex [Ag₃{μ-CH₂[CH(pz)₂]₂}₂](NO₃)₃(CH₃CN)₂ (distance of H···centroid of the pz ring, 3.00 Å),[30a] and is comparable with the value (H···Cp$_c$ 2.71 Å) in [Cp₂Na]⁻[Ph₄P]⁺ observed by Harder,[30b] indicating the existence of the strong intermolecular C−H···π contacts responsible for the conformation of polymer in **7**. The bond lengths of Ba−N (Ba−N1 2.899(5) Å, Ba−N2 2.889(5) Å) in **7** suggest perfect η²-interaction with the barium ion, which are slightly longer than those (Ba−N1 2.828(9) Å, Ba−N2 2.767(10) Å) found in **3**, which apparently resulted from the bulky and electronic nature of phenyl rings.

**Possible Mechanism of the Formation for Complexes 2, 3, 4, 5, 6, and 7.** Brandley et al. previously reported that the reaction of Ba[N(SiMe₃)₂]₂(THF)₂ and 18-crown-6 was unable to lead to the expected species **8** and **9** instead of a ring-opened ether product **11** with elimination of silylamine, (Me₃Si)₂NH (Scheme 5)[9a] and its structure was confirmed by Ruhlandt-Senge and co-workers.[12] The formation of **11** was postulated to occur via *cis*-conformation intermediates of **8** and **10**. A ring-opened ether is suggested because of the strong basicity of the amide ligand.[9a] In the case of utilizing a weaker base relative to that of amide ligand, it will lead to the complexes [*trans*-M(18-crown-6)R₂] (M = Ca, Sr, Ba) without a cleavage of 18-crown-6 ligand. However, because the complexes as intermediates with *cis*-conformation similar to **8** and **10** outlined in Scheme 5 have not yet been structurally evidenced, the conversion via an

isomerization between *cis*- and *trans*- heavy alkaline-earth element complexes is still a question for debate.

In the course of preparing 1,2,4-diazaphospholide complexes of barium, we found that the complexes dissociate in the presence of the strong donors on the basis of ³¹P{¹H} NMR spectra. The successful isolation of **4** provides the first example of heavy alkaline earth complex in a *cis*-conformation. On the basis of our work, as well as others,[12,13] we suggest a possible mechanism of the formation of complexes **2**−**7** outlined in Scheme 6.

(1) The reaction of barium bis(trimethylsilyl)amide and 1,2,4-diazaphosphole gives the solvated complex **I**. In the case of the use of DMSO as solvent, the dissociated ion pair **Ia** forms as the semi-separated ion triples in the solution as indicated by the ³¹P NMR spectrum;

(2) The reaction of **I** and 18-crown-6 initially affords the complex of barium 1,2,4-diazaphospholide bearing 18-crown-6 ligand (**II**) in a cis-conformation, for example, complex **4**;

(3) Complex **II** dissociates into the dissociated ion pair **III** as indicated by the ³¹P NMR spectra;

(4) The complex **IV** forms by a formal rearrangement of **II** via an intermediate of the dissociated ion pair **III**.

## Conclusions

This work has demonstrated that several barium 1,2,4-diazapspholide compounds were prepared by the transamination of Ba[N(SiMe₃)₂]₂(THF)₂ and 1,2,4-diazaphospholes at room temperature. A few of the complexes undergo a dissociation in the solution on the basis of ³¹P{H} NMR spectra. For the barium 1,2,4-diazpspholides bearing 18-crown-6 ligand, the complexes likely proceed by a *cis/trans* conformation conversion in the solution spontaneously. An important *cis*-intermediate **4** has been successfully isolated and fully characterized for the first time. Our results in this paper likely provided a support for the *cis/trans* conformation conversion of the barium 1,2,4-diazaphospholide complexes

(30) (a) Reger, D. L.; Gardinier, J. R.; Semeniuc, R. F.; Simth, M. D. *Dalton Trans.* **2003**, 1712. (b) Harder, S. *Chem.—Eur. J.* **1999**, *5*, 1852.

**Table 2.** Crystal and Data Collection Parameters of Complexes **1**, **2**, **3**, **4**, and **7**

| | 1 | 2 | 3 | 4 | 7 |
|---|---|---|---|---|---|
| formula | $C_{44}H_{52}BaN_4O_4P_2$ | $C_{36}H_{44}BaN_4O_4P_2S_4$ | $C_{16}H_{28}BaN_4O_6P_2$ | $C_{32}H_{60}BaN_4O_6P_2$ | $C_{40}H_{44}BaN_4O_6P_2$ |
| fw | 900.18 | 924.27 | 571.70 | 769.12 | 876.07 |
| cryst. size (mm) | $0.12 \times 0.10 \times 0.12$ | $0.20 \times 0.12 \times 0.05$ | $0.15 \times 0.15 \times 0.12$ | $0.15 \times 0.15 \times 0.12$ | $0.15 \times 0.12 \times 0.04$ |
| cryst. syst. | monoclinic | tetragonal | triclinic | monoclinic | monoclinic |
| space group | $C2/c$ | $I4_1/a$ | $P\bar{1}$ | $P2_1$ | $P2_1/n$ |
| $a$ (Å) | 20.256(10) | 15.236(4) | 9.980(7) | 10.203(3) | 10.809(4) |
| $b$ (Å) | 19.749(10) | 15.236(4) | 10.186(7) | 16.122(5) | 10.871(4) |
| $c$ (Å) | 14.175(7) | 18.958(8) | 13.325(9) | 13.078(4) | 34.470(12) |
| $\beta$ (deg) | 126.997(5) | 90.00 | 73.752(7) | 110.688(4) | 95.712(5) |
| $V$ (Å$^3$) | 4529(4) | 4401(2) | 1227.5(14) | 2012.5(11) | 4030(2) |
| $Z$ | 4 | 4 | 2 | 2 | 4 |
| $D_c$ (g cm$^{-3}$) | 1.320 | 1.395 | 1.547 | 1.314 | 1.444 |
| $\mu$ (mm$^{-1}$) | 0.991 | 1.204 | 1.783 | 1.108 | 1.115 |
| $F$ (000) | 1848 | 1880 | 572 | 828 | 1784 |
| $T$ (K) | 293.2 | 293.2 | 293.2 | 293.2 | 293.2 |
| $\theta$ range (deg) | 1.63−26.01 | 1.71−26.01 | 1.62−25.00 | 1.66−27.02 | 1.97−25.01 |
| reflns measured | 10071 | 8994 | 4983 | 9756 | 12943 |
| unique reflns | 4447 | 2158 | 4185 | 6249 | 6812 |
| $\theta_{max}$ (deg) | 26.01 | 26.00 | 25.00 | 27.02 | 25.01 |
| $R_{int}$ | 0.0447 | 0.0660 | 0.0590 | 0.0311 | 0.0531 |
| Max and min Transmn | 0.9074 and 0.8904 | 0.9422 and 0.7947 | 0.8145 and 0.7758 | 0.8785 and 0.8514 | 0.9568 and 0.8506 |
| R1, wR2 [I > 2σ(I)]$^a$ | 0.0499, 0.1544 | 0.0528, 0.1418 | 0.0697, 0.2207 | 0.0501, 0.1187 | 0.0567, 0.1438 |
| R1, wR2 (all data)$^b$ | 0.0784, 0.1647 | 0.0756, 0.1550 | 0.07626, 0.2247 | 0.0595, 0.1272 | 0.0749, 0.1540 |
| GOF | 1.035 | 0.962 | 1.092 | 1.069 | 1.071 |
| $\Delta\rho$(max) (e Å$^{-3}$) | 0.785 | 0.418 | 1.859 | 0.918 | 1.650 |
| $\Delta\rho$(min) (e Å$^{-3}$) | −0.318 | −0.583 | −1.204 | −0.390 | −2.839 |

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

**Table 3.** Selected Dihedral Angles of Complexes **1**, **2**, **3**, **4**, and **7**



| | 1 | 2 | 3 | 4 | 7 |
|---|---|---|---|---|---|
| A−B (deg) | 179.5(3) | 180.0(3) | 177.3(5) | 173.6(3) | 162.3(2) |
| A′−B′ (deg) | 179.6(4) | 180.0(0) | 174.6(5) | 178.2(4) | 160.1(2) |
| A−E (deg) | 90.0(1) | 90.0(8) | 84.0(3) | | 64.3(1) |
| A−A′ (deg) | 86.6(2) | 90.0(4) | 63.6(4) | 68.8(2) | 73.8(2) |
| A−C (deg) | 3.2(2) | 6.1(2) | | | 28.4(2) |
| A−C′ (deg) | 3.2(2) | 6.1(2) | | | 48.2(2) |
| A−D (deg) | 4.7(2) | 6.0(0) | | | 14.6(3) |
| A′−D′ (deg) | 4.7(2) | 5.9(1) | | | 42.2(3) |

$^a$ Dihedral angles between the mean planes A and A′/B/B′/C/C′/D/D′/E.

bearing a crown ether ligand. The dissociation of barium 1,2,4-diazaphospholides suggests that the σ-bound barium 1,2,4-diazaphospholide complexes are to a certain extent ionic. The $^{31}$P NMR signals of the corresponding barium 1,2,4-diazaphospholides are quite sensitive to the change in electronic environments around phosphorus nuclei, and the frameworks of 1,2,4-diazaphospholides therefore render a useful tool to probe the behaviors of the corresponding metal complexes in solutions. The exploration of other alkaline-earth metal complexes containing 1,2,4-diazaphospholide ligands are in progress.

## Experimental Section

All manipulations were carried out in a nitrogen atmosphere under anaerobic conditions using standard Schlenk, vacuum line, and glovebox techniques. The solvents were thoroughly dried, deoxygenated, and distilled in a nitrogen atmosphere prior to use. DMSO-$d_6$ was degassed and dried over molecular sieves for 24 h before use. The $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra were recorded with a Bruker DRX-400 or JEOL ECA-400 spectrometer. IR measurements were carried out on a NICOLET 360 FT-IR spectrometer from Nujol mulls prepared in a dry box. Decomposition points were measured in sealed nitrogen-filled capillaries without temperature correction with a Reichert-Jung apparatus type 302102. Reliable elemental analyses could not be obtained, even when a glovebox handling was attempted, likely because of the high moisture and oxygen sensitivity of all compounds reported. This is a well-known problem in alkaline-earth-metal chemistry.[1d] Therefore, the analysis is limited to NMR and IR spectroscopic investigations, supplemented by single-crystal X-ray diffraction studies in the cased of **1**, **2**, **3**, **4**, and **7**. Barium (99.7%) was purchased from Aldrich. Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$[23] and 1,2,4-diazaphospholes[18a] were prepared according to the literatures. 18-

**Scheme 5.** Reaction of Ba[N(SiMe₃)₂]₂(THF)₂ with 18-crown-6
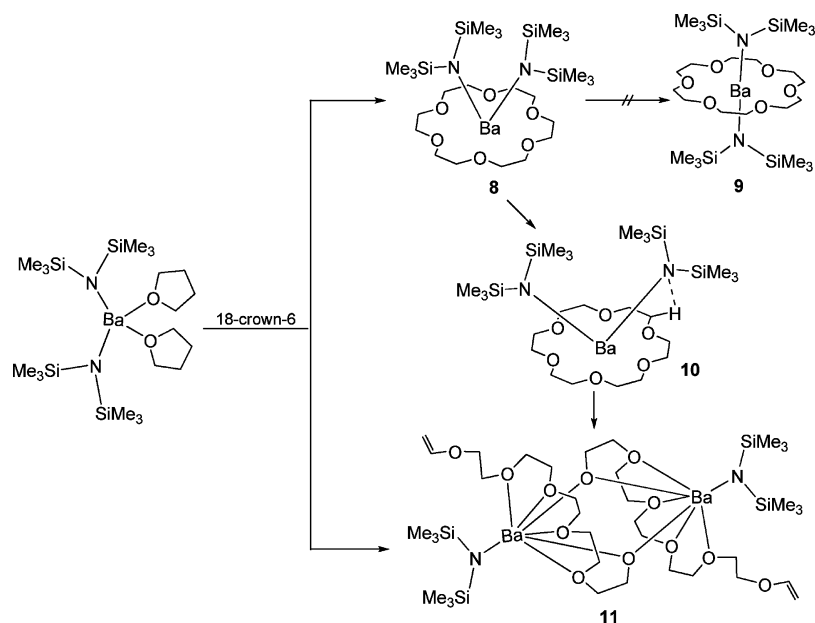


**Scheme 6.** Possible Mechanism of Formation for Complexes 2−7
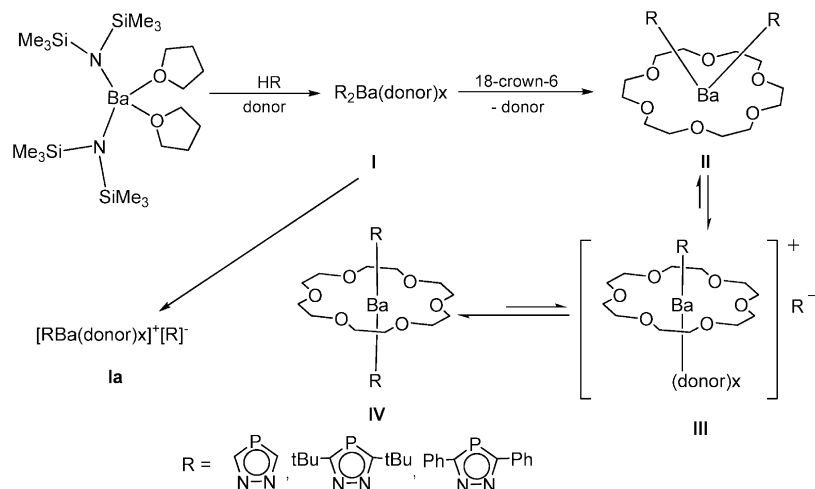


Crown-6 was dissolved in *n*-hexane, and the solution was dried over molecule sieves for several days. The dried 18-crown-6 solid was obtained from recrystallization in *n*-hexane prior to use.

**Synthesis of [η²(*N,N*)-3,5-Ph₂dp)₂Ba(THF)₄] (1).** To a Schlenk flask charged with H[3,5-Ph₂dp] (0.953 g, 4.0 mmol) and Ba[N(SiMe₃)₂]₂(THF)₂ (1.20 g, 2.0 mmol), THF (30 mL) was added by syringe and the reaction was allowed to stir for 5 h at room temperature. The solution was filtered through Celite, and the solvent of the filtrate was reduced under vacuum until lots of white solid precipitated. The system was warmed up and the clear solution slowly cooled down to room temperature to afford **1** as colorless crystals. The X-ray crystallographic analysis of this material revealed the complex [η²(*N,N*)-3,5-Ph₂dp)₂Ba(THF)₄], but the isolation by filtration and drying under vacuum gave [η²(*N,N*)-3,5-Ph₂dp)₂Ba(THF)₃] (1.24 g, 75%, based upon one THF molecule being removed upon drying) as a white semicrystalline solid. Mp: >135 °C, dec ¹H NMR (DMSO-*d₆*, 23 °C): $\delta$ = 1.76 (m, 12 H, THF), 3.60 (m, 12 H, THF), 7.13 (t, 4 H, Ph ring), 7.27 (t, 8 H, Ph ring) 7.98 (d, 8 H, Ph ring); ¹³C {¹H} NMR (DMSO-*d₆*, 23 °C): $\delta$ = 25.05, 66.94(s, C[THF]), 125.56, 125.59, 125.65 (s, C[ph]), 127.93 (s, C[ph]), 139.55, 139.78 (s, C[ph]), 176.31 (s, C[dp]) (d, $^1J_{CP}$ = 176 Hz, P*C*N); ³¹P{¹H} NMR (DMSO-*d₆*, 23 °C): 72.27

(s); IR (Nujol mull, cm⁻¹): $\tilde{v}$ = 3073 (w), 3048 (w), 3021 (w), 1958 (w), 1900 (w), 1834 (w), 1752 (w), 1680 (w), 1594 (s), 1574 (w), 1493 (vs), 1348 (m), 1315 (m), 1290 (w), 1256(m), 1246 (w), 1175 (w), 1069 (w), 1037 (vs), 1007 (m), 883 (s), 801 (m), 765 (m), 695 (vs), 664 (w), 613 (w).

**Synthesis of [(η²(*N,N*)-3,5-Ph₂dp)₂Ba(DMSO)₄] (2).** To a Schlenk flask charged with H[3,5-Ph₂dp] (0.476 g, 2.0 mmol) and Ba[N(SiMe₃)₂]₂(THF)₂ (0.602 g, 1.0 mmol), THF (20 mL) was added by syringe. The reaction was allowed to stir for 5 h at room temperature and then the solution was evaporated to dryness. The resulting residue was dissolved in DMSO (5 mL), and the solution was then filtered through Celite. The filtrate was layered with the mixture of toluene and hexane (50 mL, 1:1) to afford **2** as large yellow blocks at room temperature. Yield: 0.527 g (57% based on barium). Mp: 123−123 °C, dec Single crystals suitable for X-ray diffraction analysis were obtained from recrystallization at room temperature in the mixture of toluene, hexane, and DMSO. ¹H NMR (DMSO-*d₆*, 23 °C): $\delta$ = 7.09(t, 4 H, Ph ring) 7.24 (t, 8 H, Ph ring) 7.91 (d, 8 H, Ph ring); ¹³C {¹H} NMR (DMSO-*d₆*, 23 °C): $\delta$ = 126.14, 126.23 (s, C[ph]), 128.56 (s, C[ph]), 140.30, 140.53 (s, C[ph]), 177.45 (d, $^1J_{CP}$ = 224 Hz, P*C*N); ³¹P{¹H} NMR (DMSO-*d₆*, 23 °C): 71.94 (s), 34.46 (s); IR (Nujol mull, cm⁻¹): $\tilde{v}$ = 3056

(m), 3031 (m), 1941 (w), 1876 (w), 1785 (w), 1746 (w), 1665 (w), 1594 (m), 1578 (w), 1494 (s), 1399 (m), 1342 (m), 1312 (w), 1261 (m), 1218 (w), 1069 (w), 1028 (vs), 953 (m), 905 (w), 800 (m), 767 (vs), 698 (s), 687 (m), 611 (w).

**Synthesis of [*trans*-($\eta^2(N,N)$-dp)$_2$Ba($\eta^6$-18-crown-6)] (3).** To a Schlenk flask charged with H[dp] (0.172 g, 2.0 mmol) and Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.602 g, 1.0 mmol) was added THF (20 mL) by syringe, and the reaction was allowed to stir for 5 h at room temperature. The solvent was removed under reduced pressure to leave a residue to which 18-crown-6 (0.264 g, 1.0 mmol) was added. The mixture was dissolved in DMSO (5 mL) and toluene (40 mL) was then layered. The clear solution was allowed to be undisturbed at room temperature for several weeks to afford **3** as colorless crystals. Yield: 0.212 g (37% based on barium after washing the crystals with toluene, and dried under vacuum). Mp: >340 °C, dec $^1$H NMR (DMSO-$d_6$, 23 °C): $\delta$ = 3.59 (s, 24H, C$H_2$), 8.46 (s, 2 H, dp), 8.59 (s, 2 H, dp); $^{13}$C {$^1$H} NMR (DMSO-$d_6$, 23 °C): $\delta$ = 158.65 (d, $^1J_{CP}$ = 200 Hz, P$C$N), 69.63(s, C[-OCH$_2$CH$_2$O-]); $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C): 73.08 (s); IR (Nujol mull, cm$^{-1}$): $\tilde{v}$ = 3036(m), 3021(m), 1621(w), 1347(s), 1315(w), 1285(m), 1261(w), 1264(m), 1092(vs), 984(m), 958(s), 810(w), 881(m), 828(s), 612(w).

**Synthesis of [*cis*-($\eta^2(N,N)$-3,5-*t*Bu$_2$dp)$_2$Ba($\eta^6$-18-crown-6)] (4).** To a Schlenk flask charged with H[3,5-*t*Bu$_2$dp] (0.397 g, 2.0 mmol) and Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.602 g, 1.0 mmol) was added THF (20 mL) by syringe, and the reaction was allowed to stir for 5 h at room temperature. After the solution was evaporated to dryness, 18-crown-6 (0.264 g, 1.0 mmol) was then added. The mixture was dissolved in THF (10 mL) to give a clear solution to which *n*-hexane (10 mL) was layered via syringe. The solution was undisturbed at room temperature for several weeks to afford **4** as colorless crystals. Yield: 0.423 g (55% based on barium). Mp: >340 °C, dec $^1$H NMR (DMSO-$d_6$, 23 °C): $\delta$ = 1.30 (s, 36 H, Me$_3$C), 3.56 (s, 24H, -OCH$_2$CH$_2$O-); $^{13}$C {$^1$H} NMR (DMSO-$d_6$, 23 °C): $\delta$ = 187.74 (d, $^1J_{CP}$ = 200 Hz, P$C$N), 70.30 (s, C[-OCH$_2$CH$_2$O-]), 35.82, 35.62, 33.64 (s, Me$_3$C); $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C): 59.44 (br.), 38.22 (s); IR (Nujol mull, cm$^{-1}$): $\tilde{v}$ = 1598(w), 1359(m), 1257(s), 1215(w), 1094(s), 1021(s), 945(m), 864(m), 710(s), 667(w).

**Synthesis of [*cis*-($\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba($\eta^6$-18-crown-6)] (6) and [*trans*-($\eta^2(N,N)$-3,5-Ph$_2$dp)$_2$Ba($\eta^6$-18-crown-6)](7).** To a Schlenk flask charged with complex **1** (0.828 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) was added THF (20 mL) by syringe, and the reaction was allowed to stir for 2 h at room temperature. To this clear solution, *n*-hexane (10 mL) was slowly added via syringe. The solution was allowed to be undisturbed at room temperature for a few days to afford **6** as tiny colorless needles (0.727 g, 83% based on barium). Complex **6** slowly isomerized into **7** as yellow blocks for several weeks at room temperature. Yield: 0.569 g (65% based on barium).

**6.** Mp: >330 °C, dec $^1$H NMR (DMSO-$d_6$, 23 °C): $\delta$ = 3.56 (s, 24 H, C$H_2$), 7.12 (t, 4 H, Ph ring), 7.27 (t, 8 H, Ph ring) 7.93 (d, 8 H, Ph ring); $^{13}$C {$^1$H} NMR (DMSO-$d_6$, 23 °C): $\delta$ = 70.25 (s, C[-OCH$_2$CH$_2$O-]), 126.06, 126.13, 126.23 (s, C[ph]), 128.55 (s, C[ph]), 140.49, 140.72 (s, C[ph]), 177.02 (d, $^1J_{CP}$ = 172 Hz, P$C$N);

$^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C): 70.18(s); IR (Nujol mull, cm$^{-1}$): $\tilde{v}$ = 3058 (m), 3022 (w), 1957 (w), 1885 (w), 1813 (w), 1757 (w), 1595 (m), 1492 (s), 1352 (s), 1286 (w), 1258 (m), 1098 (vs), 1024 (m), 963 (m), 914 (w), 874 (w), 801 (m), 762 (s), 732 (w), 696 (s).

**7.** Mp: >350 °C, dec its $^1$H NMR (DMSO-$d_6$, 23 °C) spectrum is close to that of **6**; $^{13}$C {$^1$H} NMR (DMSO-$d_6$, 23 °C): $\delta$ = 69.63 (s, C[-OCH$_2$CH$_2$O-]), 125.44, 125.51, 125.60 (s, C[ph]), 127.93 (s, C[ph]), 139.86, 140.09 (s, C[ph]), 176.40 (d, $^1J_{CP}$ = 172 Hz, P$C$N); $^{31}$P{$^1$H} NMR (DMSO-$d_6$, 23 °C): 70.26 (s), 34.37 (s); IR (Nujol mull, cm$^{-1}$): $\tilde{v}$ = 3021(m), 1957 (w), 1891 (w), 1815 (w), 1594 (m), 1493 (s), 1449 (s), 1438 (s), 1414 (w), 1247 (m), 1238 (m), 1092 (vs), 1005 (m), 960 (s), 909 (w), 780 (w), 772 (s), 764 (s), 703 (s), 687 (m), 652 (w), 612 (w).

**X-ray structure determinations.** Suitable single crystals were sealed under N$_2$ in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo-K$\alpha$ radiation, $\varphi$-$\omega$-scan technique, $\lambda$ = 0.71073 Å). The intensity data were integrated by means of the SAINT program.[31] SADABS[32] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against $F^2$ using all reflections with the aid of the SHELXTL package.[33] All non-hydrogen atoms in **1**, **3**, and **7** were refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program. Crystallographic parameters for compounds **1**, **2**, **3**, **4**, and **7** along with details of the data collection and refinement, are collected in Table 2. The DMSO bonded to the Ba atom of compound **2** are highly disordered, and the *t*Bu groups and 18-crown-6 in **4** are also found to be disordered. Thus, some atoms of **2** and **4** were modeled and refined isotropically.

**Supporting Information Available:** The X-ray crystallographic files for **1**, **2**, **3**, **4**, and **7** in CIF format, the $^1$H NMR spectra of complexes **1**, **2**, **3**, **4**, **6**, and **7**, the $^{31}$P NMR spectra of complexes **2**, **4**, **7**, and of 1,2,4-diazaphospholes in DMSO-$d_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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