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Dual Supermesityl Stabilization: A Room-Temperature-Stable 1,2,4-Triphosphole Radical, Sigmatropic Hydrogen Rearrangements, and Tetraphospholide Anion[‡]

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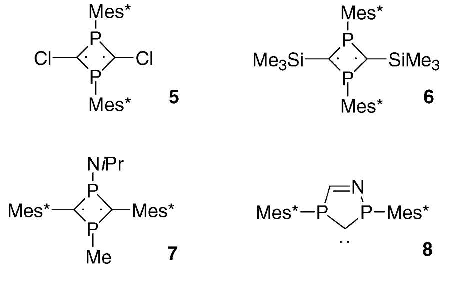
Cesium 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,4-triphospholide (**12**) and cesium 5-(2,4,6-tri-*tert*-butylphenyl)tetraphospholide (**13**) were synthesized and isolated with flat five-membered rings, which are an indication of the aromaticity in these anions. Compound **13** is the first example of a stable tetraphospholide anion, which is structurally characterized. Kinetic stabilization of the 1,2,4-triphospholide system by two supermesityl groups resulted in the detection of the room-temperature-stable radical **17** and the observation of a series of successive sigmatropic hydrogen shifts in the first stable 1*H*-1,2,4-triphosphole **14** with a P–H bond.

Introduction

In this report we describe the use of CsF in the formation of $P{=}C$ and $P{\equiv}C$ bonds by the hexamethyldisiloxane elimination route.[1] It has been shown that the reaction between simple tris(trimethylsilyl)phosphane (**2**), as a source of phosphorus, and 2,4,6-tri-*tert*-butylbenzoyl chloride (**3**) does not take place at room temperature. More active metal bis(trimethylsilyl)phosphides, e.g., lithium bis(trimethylsilyl)phosphide, are required for the reaction to take place.[2] Thus, it is an attractive possibility for cesium bis(trimethylsilyl)phosphide (**4**) to facilitate the introduction of not only one, but two supermesityl groups to the core of the molecules. The introduction of two supermesityl groups has been recently shown to stabilize such intriguing diradicals as **5**–**7** and the diphosphorus analogue **8** of a cyclic carbene (Scheme 1).[3–5]



Scheme 1.

Results and Discussion

Three-component reaction between tris(trimethylsilyl) phosphane (**2**), cesium fluoride (**1**) and 2,4,6-tri-*tert*-butylbenzoyl chloride (**3**) resulted in variable yields of six products (**4**, **9**–**13**), depending on the reaction time (Scheme 2). Shorter reaction times (up to 1 d in dioxane, at 90 °C) led predominantly to the first four products in Scheme 2. Longer reaction times (up to 5 d) led to the formation of cesium 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,4-triphospholide (**12**) and cesium 5-(2,4,6-tri-*tert*-butylphenyl)tetraphospholide (**13**). Continued heating of the reaction mixture (up to 10 d) favors the formation of **13**. Two-component reaction between tris(trimethylsilyl)phosphane (**2**) and cesium fluoride (**1**) (3 h in dioxane at 90 °C) led exclusively to the formation of cesium bis(trimethylsilyl)phosphide (**4**). Progress of the reactions can be accurately monitored by ^{31}P NMR spectroscopy, since the compounds of interest have distinctive chemical shifts: δ = –276.10 (**4**);[6] 33.2 (**10**);[7] 117.24 (**11**); 267.87 (d), 287.55 (t) (integral ratio 2:1; $^{3}J_{PP}$ = 36.7 Hz; **12**) ppm. The most deshielded resonances were observed for **13**. They represent an $AA'MM'$ spin system at δ = 341.60 ppm for the P_A and $P_{A'}$ atoms and at δ = 386.50 ppm for the P_M and $P_{M'}$ atoms. The simulated coupling constants are $^{1}J_{AA'}$ = –485.60 Hz, $^{3}J_{MM'}$ = 52.20 Hz, $^{1}J_{AM}$ = –486.80 Hz, $^{2}J_{AM'}$ = 2.00 Hz.

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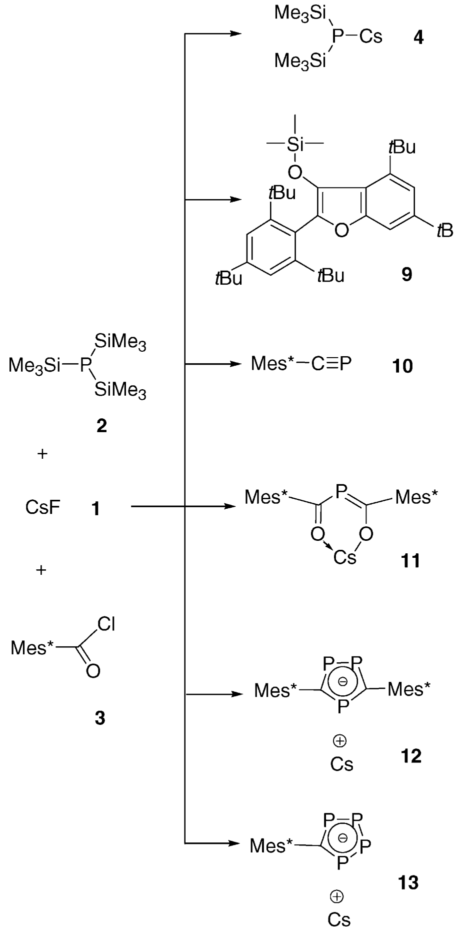


Scheme 2. Three-component reaction between tris(trimethylsilyl)phosphane (**2**), cesium fluoride (**1**) and 2,4,6-tri-*tert*-butylbenzoyl chloride (**3**). Coordinated solvents are omitted for clarity. Mes* = supermesityl (2,4,6-tri-*tert*-butylphenyl).

The formation of the three products **4**, **10** and **11** is expected on the basis of mechanistic studies between lithium bis(trimethylsilyl)phosphide and 2,4,6-tri-*tert*-butylbenzoyl chloride[7] and tris(trimethylsilyl)phosphane and cesium *tert*-butoxide.[6] The formation of the second three products **9**, **12** and **13** is new and specific to the use of CsF.

The cesium atom is octahedral in **12** (four η^1-coordination bonds to dioxane and one η^2-coordination bond to P=P) and in **13** (three η^1-coordination bonds to dioxane and three η^2-coordination bonds to P=P). The cesium atoms in **12** and in **13** have the potential ability to coordinate to the five-membered rings by an η^5-coordination mode. However, combinations of η^2-coordination bonds to P=P and η^1-coordination bonds to oxygen atoms prevail over a possible η^5-coordination mode. Theoretical calculations show that η^2-coordination is energetically only 1.4 times lower than η^5-coordination in the Cp^-Li^+ system.[8] Favorable coordination of the cesium cation with the oxygen atoms of dioxane also contributes to the overall preference for η^2- and η^1-coordinations over possible η^5-coordination in **12** and **13**. The cesium cation has a clear tendency to form infinite chains (e.g., in **12**; Figure 1) or a three-dimensional network (e.g., in **13**; Figure 2) in the solid state. Use of large alkali cations (cesium in our case) leads to increased coordination numbers and the ability to form coordination polymers (two- or three-dimensional) in the solid state. The distances between the cesium and phosphorus atoms are in the range of 3.60–4.24 Å, which are consistent with η^1- and η^2-coordinations, and are within such distances reported in the Cambridge Structural Database. The longest Cs–P distance of 4.24 Å is an η^2-coordination bond; therefore, the actual Cs–P bond should be shorter and should be pointed to the center of the P=P bond. The bond lengths between the cesium and oxygen atoms are in the range of 2.91–3.24 Å, which are the normal values in the Cambridge Structural Database, with 3.21 Å as a median for Cs–O bonds.

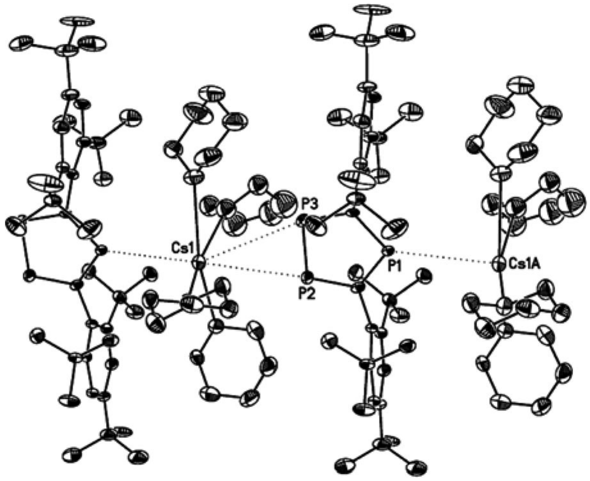


Figure 1. Packing diagram of **12**. Compound **12** forms infinite chains with four dioxane molecules bonded to each cesium atom. Thermal ellipsoids are drawn at the 50% probability level.[18]

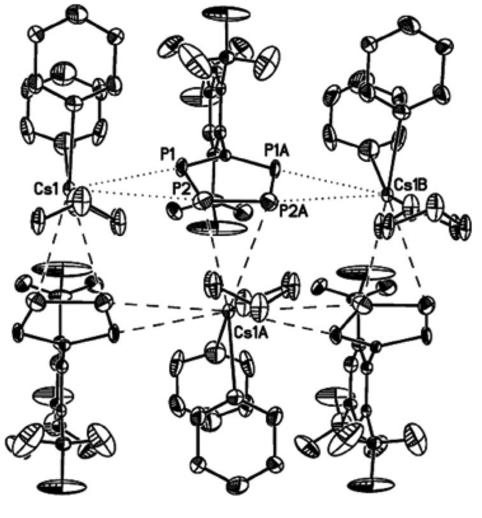


Figure 2. Packing diagram of **13**. Compound **13** forms a three-dimensional network that joins above and below the plane of the page through dioxane molecules. Each cesium atom is bonded to three dioxane molecules. Thermal ellipsoids are drawn at the 50% probability level.[18]

The five-membered rings in **12** and in **13** are perfectly flat, and there is averaging of bond lengths within the five-membered rings, which is an indication of the aromaticity in these triphospholide and tetraphospholide anions.[9] Compound **13** is the first example of a tetraphospholide anion that is structurally characterized. Sodium tetraphospholide was observed in the reaction mixture, but never was isolated.[10] The ability to isolate **12** and **13** comes from a combination of factors such as the ability of the large cesium cation to disperse its positive charge and thus to stabilize the unusual anions, a presence of sterically hindered supermesityl groups, and a good crystallinity of these species. To quantify which factor is more important is somewhat difficult.

The room-temperature ^{31}P NMR spectrum of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-1,2,4-triphosphole (**14**) shows only one broad signal at $\delta = 314.21$ ppm (Figure 3A). A series of successive [1,5]-sigmatropic hydrogen shifts between P-1 and P-2 is occurring so quickly that only the P-4 signal is manifested in the ^{31}P NMR spectrum. Slowing down the exchange by cooling to –80 °C produces the expected spectrum for **14** containing three chemical shifts: a singlet at $\delta = 310.22$ ppm (P-4), a doublet at $\delta = 299.20$ ppm ($^{1}J_{PP} = 405.9$ Hz, P-2), and a doublet at $\delta = 76.40$ ppm (P-1) with the same coupling constant (Figure 3B). The hydrogen atom is located at the phosphorus atom in 1-position of the ring. The most shielded signal (P-1) shows an additional splitting from the hydrogen atom in the ^{31}P NMR spectrum with a coupling constant of $^{1}J_{PP} = 128.2$ Hz. There are no studies on the hydrogen sigmatropic rearrangements for triphosphole systems in the literature to date. Although suprafacial [1,5]-sigmatropic shifts of a triphenylstannyl group are reported in the triphosphole system.[11]

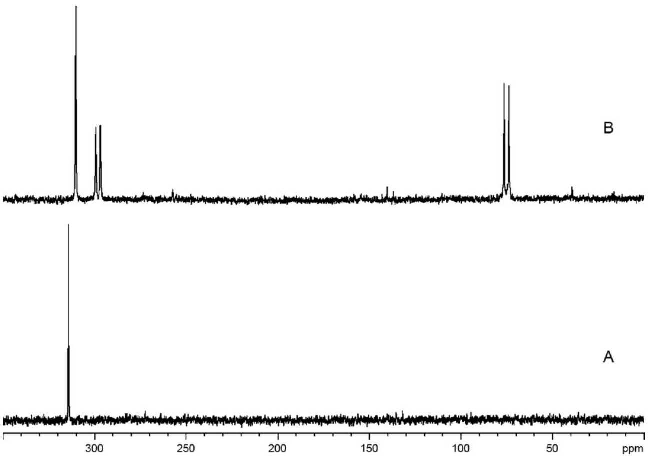


Figure 3. ^{31}P NMR spectra of **14**: (A) at 30 °C; (B) at –80 °C.

The first stable P–H triphosphole **14** was shown to have a fruitful reactivity. It can be converted back to the cesium salt **12** by reaction with metallic cesium at room temperature. Exposure of this P–H compound to air for 24 h led to the formation of the P–P dimer **15** of 1*H*-1,2,4-triphosphole (Figure 4 and Scheme 3) and a small amount of 2,4,6-tri-*tert*-butylbenzoic acid (**16**). Compound **15** is the first example of a 2,2′,4,4′-tetraphospha-1,1′-biphospholyl ring system. Coupling reactions of the sterically less hindered *t*Bu systems gave only organophosphorus cage compounds with the general formula $P_6C_4tBu_4$.[12] The structure of **15** was investigated by X-ray analysis (Figure 4). The two triphosphole rings are not parallel to each other and are not π-stacked. They are connected by a P–P bond (2.17 Å), which is the longest P–P bond in this compound. The P–P bond length inside the triphosphole ring is 2.12 Å. The P=C bond lengths in the ring are within the normal range (between 1.72 and 1.78 Å). Characterization of **15** in solution by ^{31}P

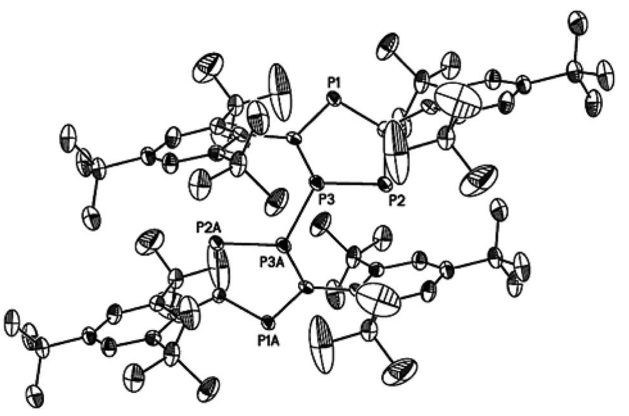
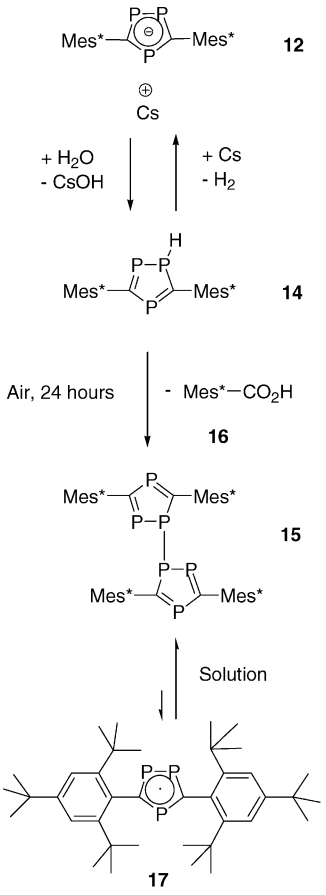


Figure 4. ORTEP drawing of **15**. Thermal ellipsoids are drawn at the 50% probability level.[18]



Scheme 3.

NMR spectroscopy was not possible; no ^{31}P NMR resonance at all was detected in the region between δ = 1000 and –700 ppm in [D$_8$]toluene. It was discovered that dimer **15** underwent P–P dissociation, forming the persistent free radical species **17** (Scheme 3). It is theorized that the presence of **17** effected paramagnetic broadening of the NMR signals, rendering them undetectable; P–P dissociations in related *t*Bu cage structures have been observed upon irradiation with UV light or daylight.[12]

The ESR spectrum of **17** in [D$_8$]toluene at 298 K is shown in Figure 5a. The primary feature is a broad 1:3:3:1 quartet with a hyperfine coupling of approximately 19 G and an isotropic g_e of 2.002. The hyperfine coupling pattern is consistent with the resonance structure of **17**, in which an unpaired electron in a π-orbital interacts almost equally with the three spin 1/2 ^{31}P nuclei. Neither the magnitude of the hyperfine coupling constant nor the isotropic *g* factor is consistent with an unpaired electron localized on a single phosphorus atom.[13] Both the *g* factor and the hyperfine coupling constant are comparable to the somewhat similar 1,3-diphosphacyclobuten-4-yl radical synthesized by Ito et al.[14] In that case, unlike **17**, the magnitudes of the ^{31}P hyperfine coupling constants were different, suggesting partial localization of the unpaired electron on the cyclobutene ring. Another comparable radical, the diphosphaallyl species described by Canac et al.,[15] showed an allyl hyperfine coupling of 9.4 G and an isotropic *g* of 2.0048. In contrast to our system, the diphosphaallyl species identified as an intermediate in the formation of hexaphosphapentaprismane by Al-Ktaifani et al.[16] showed a much higher g_e (2.013) and allyl ^{31}P hyperfine coupling constants of 80–84 G. The dissimilarity of the ESR signal attributed to **17** to any of these previously reported species supports the conclusion that the unpaired electron in **17** is fully delocalized over the cyclopentadienyl ring.[17]

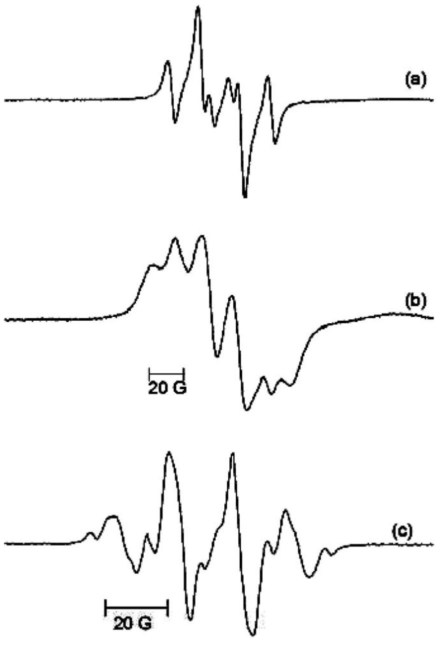


Figure 5. ESR spectra of **17**: (a) in [D$_8$]toluene at 298 K; (b) in [D$_8$]toluene at 185 K; (c) in [D$_8$]tetrahydrofuran 18 h after addition of TEMPO at room temperature; (a) and (b) are on the same horizontal scale.

The minor species detected in the ESR spectrum has not been identified. Attributed to it are two resonances of equal amplitude, the separation of which is strongly temperature-dependent. At 298 K, the two resonances are separated by 13 G. This separation increases with decreasing temperature; at the lowest temperature studied, 185 K, the separation is approximately 83 G (Figure 5b). The analyte was still fully soluble at 185 K by visual inspection. The nature of this apparent kinetic effect is unclear.

A solution of the unpurified product mixture containing **17** in [D$_8$]tetrahydrofuran evidenced many persistent free radical species by ESR spectroscopy, perhaps attributable to supermesityl-centered free radicals. Since **17** was believed to be the sterically most hindered of all of the radical species, 2,2,6,6-tetramethyl-4-oxopiperidinoxy free radical (TEMPO) was added to the product solution at ambient temperature under nitrogen in an attempt to quench the less hindered free radical species, and leave **17** as the remaining persistent radical; 18 h after addition of TEMPO, a simplified ESR spectrum was obtained (Figure 5c), in which a quartet described in the experiments above was observed as the dominant signal.

Conclusions

We presented here a new approach for generating P=C and P≡C bonds in a condensation reaction between silylphosphanes and aroyl chloride in the presence of CsF. A combination of factors such as the ability of the large cesium cation to disperse its positive charge and thus to stabilize the unusual anions, a presence of sterically hindered supermesityl groups, and a good crystallinity led to the isolation of cesium 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,4-triphospholide (**12**) and cesium 5-(2,4,6-tri-*tert*-butylphenyl)-tetraphospholide (**13**). Kinetic stabilization of the 1,2,4-triphospholide system by two supermesityl groups resulted in detection of the room-temperature-stable radical **17** and the observation of a series of successive sigmatropic hydrogen shifts in **14**. The reactivity of **13**, mechanistic studies and use of **12** and **13** in homogeneous catalysis will be further investigated and reported in due time.

Supporting Information (see footnote on the first page of this article): ESR experimental details, synthesis of **4**, **9**, **11**, **12**, **13**, **14** and **15**.

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[18] CCDC-681038, -681039, -681040, -681041, -681042, -681043, -681044 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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