Remarkable Transformation of 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene into the 2,4,5-Tri-*tert*-butyl-1,3-diphosphacyclopentadienide Anion

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*Summary: In an unprecedented reaction, the reduction of 2,4,6-tri-tert-butyl-1,3,5-triphosphabenzene over a potassium mirror in toluene resulted in the abstraction of P^{3-} and generation of the 2,4,5-tri-tert-butyl-1,3-diphosphacyclopentadienide anion, $P_2C_3Bu^t{}_3{}^-$ (**3**). The potassium salt of this anion was characterized by an X-ray crystallographic study.*

There is considerable current interest in the synthesis and ligating properties of compounds containing P−C multiple bonds,[1−4] and very recently[5,6] synthetic routes have been developed for 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) (Figure 1), whose structure and PE spectrum have also been reported.[7]

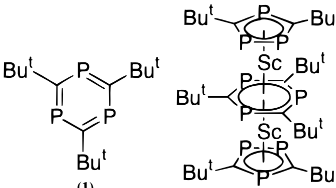

Figure 1. $P_3C_3Bu^t{}_3$ (**1**) and $[Sc_2(\eta^5\text{-}P_3C_2Bu^t{}_2)_2\ (\eta^6\text{-}P_3C_3Bu^t{}_3)]$ (**2**).

We recently described the first structurally characterized η^6-ligated complex of **1** in the triple-decker sandwich compound $[Sc_2(\eta^5\text{-}P_3C_2Bu^t{}_2)_2\ (\eta^6\text{-}P_3C_3Bu^t{}_3)]$ (**2**),[8] and Binger and co-workers have reported the complexes $ML_n(\eta^6\text{-}P_3C_3Bu^t{}_3)]$ (ML_n = $Mo(CO)_3$,$W(CO)_3$, $Mn(\eta^5\text{-}C_5H_5)$, Ru(COD)),[9] whose structures have been proposed on the basis of NMR spectroscopic studies.

In attempting to extend the range of transition-metal complexes of this novel triphosphabenzene ring system via synthesis of the corresponding $P_3C_3Bu^t{}_3$ radical anion, we reacted a THF solution of **1** with a potassium mirror at −78 °C. The solution immediately turned green and on warming to room temperature became red. The $^{31}P\{^1H\}$ NMR spectrum of the red solution showed that all the triphosphabenzene had been consumed and unexpectedly exhibited the characteristic singlet (δ_P 180 ppm) of the known 2,4,5-tri-*tert*-butyl-1,3-diphosphacyclopentadienide anion, $P_2C_3Bu^t{}_3{}^-$,[10] indicating the unprecedented reaction shown in Figure 2.

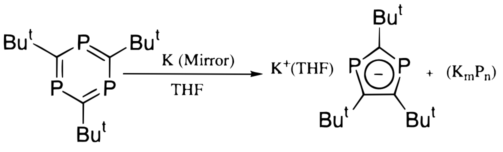

Figure 2. Formation of $[K^+(THF)\{P_2C_3Bu^t{}_3{}^-\}]$ (**3**).

Concentration of the reaction mixture, filtration, and addition of hexanes yielded $[K(THF)][P_2C_3Bu^t{}_3]$ (**3**) as an off-white powder (40% yield).[21] Evidence for the formation of the phosphide anion P^{3-}, among the other products, came from observation of the $^{31}P\{^1H\}$ resonance of the $P(SiMe_3)_2$ anion (δ_P −296 ppm),[11] formed by treatment of the solution mixture with Me_3SiCl.

Confirmation of the formation of **3** came from a single-crystal X-ray diffraction study of the air-sensitive white crystals, which were grown from a saturated THF solution at 4 °C, and the molecular structure is shown in Figure 3.[22] This is the first reported structural characterization of any 1,3-diphosphacyclopentadienide anion, although in unpublished work[12,13] we have determined the structures of both the corresponding lithium and potassium salts of the 1,2,4-triphosphacyclopentadienide anion $P_3C_2Bu^t{}_2{}^-$.

The structure of **3** consists of chains of alternating K(THF) cations and $P_2C_3Bu^t{}_3$ anions, the alkali metal interacting in an η^5-bonding mode with the rings. Particularly noteworthy are the short P−C bond distances in the ring (average 1.753(5) Å) and the C(2)−C(3) distance (1.416(6) Å), both indicative of significant

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(1) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, U.K., 1998; pp 366, and references therein.

(2) Nixon, J. F. *Coord. Chem. Rev.* **1995**, *145,* 201.

(3) Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327.

(4) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; pp 496, and references therein.

(5) Binger, P.; Leininger, S.; Stannek, J.; Gabor, B.; Mynott, R.; Bruckmann, J.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 2227.

(6) Tabellion, F.; Nachbauer, A.; Leininger, S.; Peters, C.; Regitz, M.; Preuss, F. *Angew. Chem., Int. Ed.* **1998**, *37,* 1233.

(7) Gleiter, R.; Lange, H.; Binger, P.; Stannek, J.; Kruger, C.; Bruckmann, J.; Zenneck, U.; Kummer, S. *Eur. J. Inorg. Chem.* **1998**, 1619.

(8) Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P.; Nixon, J. F. *J. Am. Chem. Soc.* **1996**, *118,* 7630.

(9) Binger, P.; Stutzmann, S.; Stannek, J.; Gabor, B.; Mynott, R. *Eur. J. Inorg. Chem.* **1999**, 83.

(10) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem Commun.* **1987**, 1146.

(11) Uhlig, F.; Gremler, S.; Dargatz, M.; Scheer, M.; Herrmann, E. *Z. Anorg. Allg. Chem.* **1991**, *606*, 105.

(12) Caliman, V.; Jones, C.; Hitchcock, P. B.; Nixon, J. F. Unpublished results. Caliman, V. D. Phil. Thesis, Sussex University, 1994.

(13) Cloke, F. G. N.; Clentsmith, G. K. B.; Hitchcock, P. B.; Nixon, J. F. Unpublished results.

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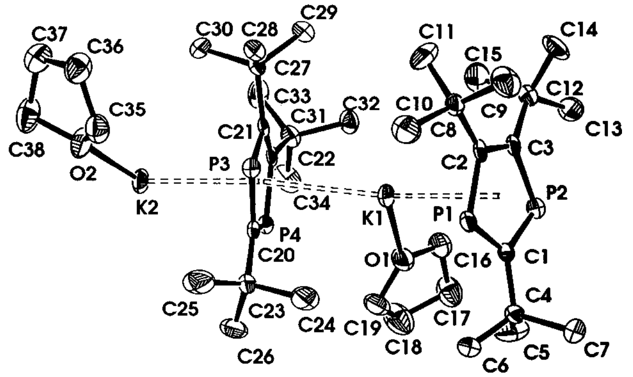

Figure 3. Molecular structure of $[(K^+(THF))\{P_2C_3Bu^t{}_3{}^-\}]_n$ (**3**). Selected distances (Å) and angles (deg): K(1)−O(1) = 2.691(4), K(1)−M(1) = 3.063(4), K(1)−M(2) = 3.054(4), P(1)−C(1) = 1.719(5), P(1)−C(2) = 1.775(5), P(2)−C(1) = 1.740(5), P(2)−C(3) = 1.777(5); M(2)−K(1)−M(1) = 154.6(2), C(1)−P(1)−C(2) = 97.6(2), C(1)−P(2)−C(3) = 97.2(2), P(1)−C(1)−P(2) = 115.2(3). Displacement elipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. M(1) and M(2) are the ring centroids.

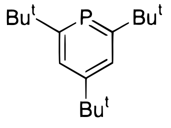

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Figure 4. $PC_5H_2Bu^t{}_3$ (**4**).

electron delocalization. Mathey et al.[14] observed a similar C−C distance in the tetraphenyltetraphosphafulvene dianion (a C_2-C_2' dimer of the 4,5-diphenyl-1,3-diphosphacyclopentadienide anion). The P−C bond distances are in excellent agreement with the calculated value for $P_2C_3H_3^-$ (1.750 Å), and the marginally longer C(2)−C(2) distance ($(C-C)_{calcd}$ = 1.387 Å) may be due to steric repusion of the Bu^t groups in **3**.[15]

Several years ago, Dimroth et al.[16] reported that the reduction of a THF solution of 2,4,6-triphenylphosphabenzene with a potassium mirror yields a green solution that showed a doublet pattern in its EPR spectrum, which was assigned to the mono radical anion (a_P = 32.4 G). They also provided evidence for the addition of two further electrons to afford radical di- and trianions. We find that, even with extended periods of exposure of the 2,4,6-tri-*tert*-butylphosphabenzene ring (**4**; Figure 4) to excess potassium in THF, the resulting dark black solution only exhibits a doublet in the EPR spectrum (a_P = 25.3 G), which we assign to the $PC_5H_2Bu^t{}_3$ mono radical anion.

The cyclic voltammogram of the 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene ring **1** exhibits a quasi-reversible wave at −2.315 V (relative to Cp_2Fe^+/Cp_2Fe), which we attribute to the $P_3C_3Bu^t{}_3/P_3C_3Bu^t{}_3{}^-$ couple.[23]

Phosphacyclopentadienide anions, $C_nR_nP_{5-n}$ (n = 1−5), are known to be highly aromatic species, and recent theoretical studies[17−19] established that their aromaticity indices are all of magnitude comparable to that of the cyclopentadienide anion itself; furthermore, their aromatic stabilization energies are also very similar. The mechanism of the remarkable transformation of the neutral triphosphabenzene **1** to the anionic diphosphacyclopentadienide **3** is currently the subject of a detailed theoretical study,[20] but the driving force of the reaction presumably reflects both the substantial aromatic character of the five-membered anionic ring and the lattice energies of the two potassium salts.

The availability of the 2,4,5-tri-*tert*-butyl-1,3-diphosphacyclopentadienide anion **3** in a single step from the readily available triphosphabenzene **1** should enable us to study its reactions with transition-metal halides to afford novel metallocenes.

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Supporting Information Available: Tables of crystal data and structure solution and refinement details, atomic coordinates, and anisotropic thermal parameters for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1031.

[15] Dransfield, A.; Nyulaszi, L.; Schleyer, P. v. R. *Inorg. Chem.* **1998**, *37*, 4413.

[16] Dimroth, K.; Steuber, F. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 445.

[17] Malar, P. *J. Org. Chem.* **1992**, *57*, 3694.

[18] Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755.

[19] Hamilton, T. P.; Schaeffer, H. F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1989.

[20] Nyulaszi, L.; Nixon, J. F. Unpublished results.

[21] Experimental details for $[K(THF)_x(P_2C_3Bu^t{}_3)]$ (**3**). A THF solution (30 mL, −78 °C) of $P_3C_3Bu^t{}_3$ (0.200 g, 0.66 mmol) was stirred over a potassium mirror for 10 min. The reaction mixture was warmed to room temperature with stirring, and the resulting dark red solution was filtered through a sintered-glass frit. The filtrate was subsequently concentrated (10 mL), and hexanes (30 mL) were added slowly with stirring, yielding a flocculent off-white powder. Filtration via filter cannula, washing with hexanes, and drying in vacuo yielded **3** as a white powder (yield 0.110 g, 43%). The molar ratio (x) of coordinated THF, measured by ^{1}H NMR spectroscopy, varied with the length of drying times (x = 0−1). To obtain a satisfactory microanalysis, the TMEDA adduct $[K(TMEDA)(P_2C_3Bu^t{}_3)]$ was prepared through treatment of **3** with TMEDA. ^{1}H NMR data (d_5-pyridine, 295 K): δ 1.88 [s, 18H, $CC(CH_3)_3$], 1.92 [s, 9H, $PCC(CH_3)_3P$] ppm. $^{31}P\{^1H\}$ NMR data (d_5-pyridine, 295 K): δ 187.6 ppm. Anal. Found: C, 59.05; H, 9.78; N, 6.46. Calcd for $C_{21}H_{43}N_2P_2K$: C, 59.40; H, 10.21; N, 6.60.

[22] Crystal data for **3**: $C_{19}H_{35}KOP_2$, M_r = 380.51, monoclinic, space group $P2_1/c$ (No. 14), a = 9.533(5) Å, b = 19.775(8) Å, c = 23.497(9) Å, β = 99.72(5)°, U = 4366(3) Å^3, Z = 8, D_c = 1.16 Mg m^{-3}, crystal dimensions 0.2 × 0.1 × 0.1 mm, $F(000)$ = 1648, T = 173(2) K, Mo Kα radiation, λ = 0.7107(3) Å. Data were collected on an Enraf-Nonius CAD4 diffractometer. A total of 6055 independent reflections were measured; 4368 having $I > 2\sigma(I)$ were used in the calculations. The final indices ($I > 2\sigma(I)$) were R1 = 0.059 and wR2 = 0.145.

[23] Cyclic voltammetry was performed using an EG&G potentiostat. The single-compartment airtight cell comprised a Pt-disk working electrode, Pt-wire auxiliary electrode, and Ag wire pseudoreference and 0.1 Bu_4NPF_6 in THF as the electrolyte.