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Highly Restricted Dimensionality in Cesium Aryl Phosphides

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The molecular structures of four different crown ether adducts of CsP(H)^{t}Bu$_3$Mes and CsP(H)Dmp (^{t}Bu$_3$Mes = 2,4,6-tri-*tert*-butylphenyl; Dmp = 2,6-dimesitylphenyl) are reported featuring monomeric or triple-decker-type structures in the solid state. The crown ether adducts **1**, **2**, and **4** are prepared in good yields using different stoichiometries CsP(H)R/18-crown-6 followed by crystallization of the corresponding cesium phosphide derivative from toluene at −30 °C. **1** crystallizes from toluene as the crown ether adduct [CsP(H)^{t}Bu$_3$Mes](18-crown-6)·0.5toluene (**1**·0.5toluene) in the monoclinic space group $P2_1/c$. Crystal data for **1**·0.5toluene at 243 K: $a = 22.919(4)$ Å; $b = 17.184(3)$ Å; $c = 21.307(6)$ Å; $\beta = 113.79(2)°$; $V = 7697(4)$ Å^3; $Z = 8$; $D_{calcd} = 1.247$ g/cm^3; R1 = 4.89%. **2** crystallizes from toluene in the presence of excess crown ether as the adduct [CsP(H)Dmp](18-crown-6) (**2**) in the orthorhombic space group $P2_12_12_1$. Crystal data for **2** at 173 K: $a = 13.8223(2)$ Å; $b = 14.6926(2)$ Å; $c = 18.6259(2)$ Å; $V = 3782.60(8)$ Å^3; $Z = 4$; $D_{calcd} = 1.304$ g cm^{-3}; R1 = 3.97%. Using deuterated benzene instead of toluene as the recrystallization solvent, **2** crystallizes as the benzene solvate [CsP(H)Dmp]-(18-crown-6)(η^2-C$_6$D$_6$)·benzene (**3**·benzene) in the orthorhombic space group *Pccn* (No. 56). Crystal data for **3** at 173 K: $a = 20.1567(4)$ Å; $b = 25.8617(5)$ Å; $c = 17.3173(4)$ Å; $V = 9027.3(5)$ Å^3; $Z = 8$; $D_{calcd} = 1.340$ g cm^{-3}; R1 = 9.34%. **4** crystallizes from toluene using a 2:1 stoichiometry [CsP(H)Dmp:18-crown-6] as the crown ether adduct [CsP(H)Dmp]$_2$(18-crown-6)·toluene (**4**·toluene) in the triclinic space group $P\bar{1}$. Crystal data for **4**·toluene at 198 K: $a = 11.2885(2)$ Å; $b = 11.6675(2)$ Å; $c = 14.5247(2)$ Å; $\alpha = 66.5752(3)°$; $\beta = 71.1301(7)°$; $\gamma = 88.0975(8)°$; $V = 1650.96(6)$ Å^3; $Z = 1$, $D_{calcd} = 1.321$ g/cm^3, R1 = 4.29%. **1**·0.5toluene, **2**, and **3**·benzene represent first examples of monomeric cesium phosphide species, while the solid state structure of **4**·toluene features a triple-decker-type arrangement.

Introduction

The Cs$^+$ cation, having the largest radius of all nonradioactive elements in the periodic table and being (compared with smaller alkali metal cations) a less charge-localizing cation, is expected to accommodate more aggregated and/or polymeric arrangements in the solid state structures of its salts.

Our previous work[1,2] in the area of M−P chemistry has shown that alkali metal salts (M = K−Cs) of "supermesitylphosphane"[3,4] (=^{t}Bu$_3$MesPH$_2$) exhibit infinitely extended M−P ladder-type connectivities. Depending on the donor ligand employed in the crystallization process, different base adducts of CsP(H)^{t}Bu$_3$Mes showing a manifold of geometric variations of the polymeric Cs−P ladder framework were obtained. So far, all of the bases employed in the crystallization process did not result in cleavage of the polymeric ladder-type arrangements.

Continuing efforts produced crystal structures of the potassium, rubidium, and cesium derivatives[5−7] of 2,6-dimesitylphenylphosphane[8] (=DmpPH$_2$), which were found to adopt three differently aggregated structural types in the solid state.

Our recent findings[2,6,9] suggest that aryl phosphide species containing Cs$^+$ centers, due to their large ionic radii, tend to crystallize in polymeric aggregates held together through multihapto interactions between the carbon atoms of aryl rings and the corresponding alkali metal atom.[10] Because of our interest in the structural details of cesium aryl phosphides, we wanted to find out whether the use of polyethers will moderate structure growth and how, in the absence of extended structures, the central coordination is affected. Crown ether ligands are known as selective complexing agents for alkali metal cations. The factors affecting the structures of such crown ether complexes are not readily comprehensible. Therefore, structural studies of such species are of particluar interest in this context.

We here report the synthesis and X-ray crystal structure of four novel crown ether adducts of cesium phosphide derivatives, namely, [CsP(H)^{t}Bu$_3$Mes](18-crown-6)·0.5toluene (**1**·0.5toluene), [CsP(H)Dmp](18-crown-6) (**2**), [CsP(H)Dmp](18-crown-6)(η^2-C$_6$D$_6$)·benzene (**3**·benzene), and [CsP(H)Dmp]$_2$(18-crown-6)·toluene (**4**·toluene), thereby demonstrating that both monomeric and triple-decker-type species of cesium aryl phosphides are accessible.

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Table 1. Crystallographic Data for [CsP(H)^{t}Bu$_3$Mes](18-crown-6)·0.5Toluene (**1**·0.5Toluene), [CsP(H)Dmp](18-crown-6) (**2**), [CsP(H)Dmp](18-crown-6)(η^2-C$_6$D$_6$)·Benzene (**3**·Benzene), and [CsP(H)Dmp]$_2$(18-crown-6)·Toluene (**4**·Toluene)[a]

complex	**1**·0.5toluene	**2**	**3**·benzene	**4**·toluene
formula	$C_{33.5}H_{58}CsO_6P$	$C_{36}H_{50}CsO_6P$	$C_{48}H_{50}CsD_{12}O_6P$	$C_{67}H_{84}Cs_2O_6P_2$
fw	720.68	742.64	910.93	1313.10
space group	$P2_1/c$	$P2_12_12_1$	*Pccn*	$P\bar{1}$
a, Å	22.919(4)	13.8223(2)	20.1567(4)	11.2885(2)
b, Å	17.184(3)	14.6926(2)	25.8617(5)	11.6675(2)
c, Å	21.307(6)	18.6259(2)	17.3173(4)	14.5247(2)
α, deg				66.5752(3)
β, deg	113.79(2)			71.1301(7)
γ, deg				88.0975(8)
V, Å^3	7679(4)	3782.60(8)	9027.3(5)	1650.96(6)
Z	8	4	8	1
D_{calcd}, g cm^{-3}	1.247	1.304	1.340	1.321
μ(Mo Kα), cm^{-1}	10.43	10.61	9.02	11.99
temp, K	243(2)	173(2)	173(2)	198(2)
R1, %	4.89	3.97	9.34	4.29
wR2, %	10.48	10.06	21.85	10.58

[a] The quantity minimized was $R(\mathrm{w}F^2) = \sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[(\mathrm{w}F_o{}^2)^2]^{1/2}$, $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk line double manifold, high-vacuum, and glovebox (M. Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained following typical laboratory procedures. ^{t}Bu$_3$MesPH$_2$ and DmpPH$_2$ were prepared according to the literature.[3,4,8] The synthesis and characterization data for both CsP(H)^{t}Bu$_3$Mes and CsP(H)Dmp were reported ealier.[2,6]

[CsP(H)^{t}Bu$_3$Mes](18-crown-6) (1). Recrystallization of CsP(H)^{t}Bu$_3$Mes (237 mg, 0.58 mmol) from toluene/18-crown-6, followed by removal of solvent and drying of the crystals under vacuum, gave complex **1** as a bright yellow powder (196 mg, 50%). **1** is well soluble in toluene, but insoluble in aliphatic hydrocarbons. Anal. Calcd for $C_{30}H_{54}CsO_6P$: C, 53.41; H, 8.07. Found: C, 53.04; H, 7.82. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 1.49 (s, 9H, *p*-^{t}Bu), 2.19 (s, 18H, *o*-^{t}Bu), 3.31 (s, 24H, O−CH$_2$), 3.83 (d, $^1J_{P-H}$ = 160 Hz, 1H, P−H), 7.31 (s, 2H). ^{31}P NMR (C$_6$D$_6$, 161.9 MHz, 25 °C): δ −65.7 (d, $^1J_{P-H}$ = 160 Hz). ^{13}C NMR (C$_6$D$_6$, 100.4 MHz, 25 °C): δ 31.3, 31.4, 32.2, 34.1 (CH$_3$−*C*), 38.5 (CH$_3$−*C*), 70.1 (O−CH$_2$), 119.6 (*meta*-C), 133.8 (*para*-C), 145.2 (d, $^2J_{C-P}$ = 7 Hz, *ortho*-C), 162.5 (d, $^1J_{C-P}$ = 82 Hz, *ipso*-C). IR (Nujol): 2259 s, 1970 w, 1749 w, 1586 m, 1298 w, 1275 s, 1245 s, 1208 w, 1183 m, 1155 m, 1109 s, 1032 m, 956 s, 863 m, 839 s, 770 w, 743 m, 732 s, 695 m, 625 w, 595 m, 528 w, 521 w, 498 w, 486 w, 440 w cm^{-1}.

[CsP(H)Dmp](18-crown-6) (2). Recrystallization of CsP(H)Dmp (250 mg, 0.52 mmol) from toluene in the presence of excess 18-crown-6 gave, after removal of solvent and drying of the crystals under vacuum, the complex **2** as a yellow-orange powder (194 mg, 50%). **2** is soluble in toluene, but insoluble in aliphatic hydrocarbons. Due to the limited solubility of **2** in aromatic solvents, only an incomplete set of signals was obtained from the ^{13}C NMR spectrum in C$_6$D$_6$ at room temperature. Anal. Calcd for $C_{36}H_{50}CsO_6P$: C, 58.20; H, 6.79. Found: C, 57.94; H, 6.52. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 2.29 (s, 6H, *p*-CH$_3$), 2.72 (d, $^1J_{P-H}$ = 169 Hz, 1H, P−H), 2.74 (s, 12H, *o*-CH$_3$), 2.98 (s, 24H, O−CH$_2$), 7.01 (m, 3H), 7.02 (m, 4H). ^{31}P NMR (C$_6$D$_6$, 161.9 MHz, 25 °C): δ −100.0 (d, $^1J_{P-H}$ = 169 Hz. IR (Nujol): 2257 s, 1970 w, 1606 w, 1566 m, 1248 s, 1105 s, 952 s, 837 m, 776 m, 721 s, 590 m, 549 w, 523 w, 455 m cm^{-1}.

[CsP(H)Dmp]$_2$(18-crown-6) (4). Recrystallization of CsP(H)Dmp (300 mg, 0.63 mmol) from toluene in the presence of 1/2 equiv of 18-crown-6 (83 mg, 0.31 mmol) and removal of solvent followed by drying of the crystals under vacuum gave complex **4** as a yellow powder (191 mg, 50%). **4** is soluble in toluene, but insoluble in aliphatic hydrocarbons. Due to the limited solubility of **4** in aromatic solvents, only an incomplete set of signals was obtained from the ^{13}C NMR spectrum in C$_6$D$_6$ at room temperature. Anal. Calcd for $C_{60}H_{76}Cs_2O_6P_2$: C, 59.00; H, 6.28. Found: C, 58.84; H, 6.13. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 2.29 (s, 12H, *p*-CH$_3$), 2.69 (d, $^1J_{P-H}$ = 169 Hz, 2H, P−H), 2.74 (s, 24H, *o*-CH$_3$), 3.22 (s, 24H, O−CH$_2$), 7.01 (m, 6H), 7.02 (m, 8H). ^{31}P NMR (C$_6$D$_6$, 161.9 MHz, 25 °C): δ −99.5 (d, $^1J_{P-H}$ = 169 Hz). IR (Nujol): 2252 s, 1965 w, 1609 w, 1566 m, 1249 s, 1110 s, 950 s, 839 m, 774 m, 720 s, 590 m, 547 w, 522 w, 455 m cm^{-1}.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for Complexes 1·0.5Toluene, 2, 3·Benzene, and 4·Toluene. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction were selected and mounted in nitrogen-flushed, thin-walled glass capillaries. Graphite-monochromated Mo Kα radiation was used (λ = 0.710 73 Å). The data were collected on a Siemens P4 diffractometer (**1**·0.5toluene) and on a Siemens P4 diffractometer equipped with a SMART CCD detector (**2**−**4**), respectively.

The systematic absences in the diffraction data are uniquely consistent for the reported space groups for **1**·0.5toluene, **2**, and **3**·benzene, and no evidence of symmetry higher than triclinic was observed in the diffraction data of **4**·toluene. *E* statistics and the presence of an inversion center suggested the centrosymmetric space group option, $P\bar{1}$, for **4**·toluene. Solution in the respective space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. No additional absorption corrections were applied to **1**·0.5toluene because there was less than 10% variation in the integrated Ψ-scan intensity data. Corrections were applied to the data of **2**, **3**·benzene, and **4**·toluene using SADABS. There are two independent, but chemically similar, cesium complexes and one toluene molecule in the asymmetric unit of **1**·0.5toluene. The absolute configuration of the structure of **2**, in the solid state, was determined (Flack = 0.03(2)). There are two half-molecules of deuterated benzene (recrystallization solvent) each on a 2-fold rotation axis in **3**·benzene. The cesium dimer in **4**·toluene lies on an inversion center, and half a molecule of toluene is disordered over an inversion center. The carbon atoms of the crown ether on Cs(2) in **1**·0.5toluene were refined isotropically to preserve a reasonable data:parameter ratio. The carbon atoms of the solvent molecules, deuterated benzene in **3**·benzene and toluene in **4**·toluene, were refined isotropically, and the hydrogen/deuterium atoms were ignored. The carbon atoms C(12), C(13), and C(14) of one *tert*-butyl group of **1**·0.5toluene are positionally disordered, but the alternative positions for all three carbon atoms could not be resolved; therefore the disordered positions could not be modeled and the thermal parameters are high. All other non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the phosphorus atoms of **1**·0.5toluene were not located from the difference map, while those of **2** and **3**·benzene were located; the P−H distance for **1**·0.5toluene was fixed to an average distance of 1.40 Å and for **2** and **3**·benzene was allowed to refine. The hydrogen atom on the phosphorus atom of **4**·toluene could not be located from the

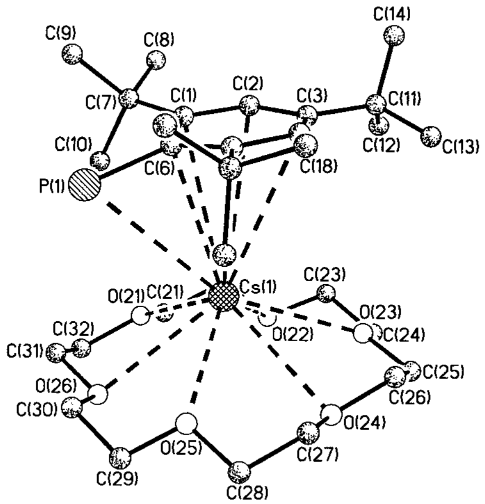

Figure 1. Molecular structure of [CsP(H)^{t}Bu$_3$Mes](18-crown-6)·0.5toluene (**1**·0.5toluene). Only one of the two independent molecules is presented, showing the π coordination of the aromatic ring to the cesium cation. Hydrogen atoms as well as the cocrystallized toluene molecule in the crystal lattice are omitted for clarity.

difference map and was ignored. All other hydrogen atoms were treated as idealized contributions.

All software sources of the scattering factors are contained in either the SHELXTL (5.03) or the SHELXTL (5.1) program libraries (G. M. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

[CsP(H)^{t}Bu$_3$Mes](18-crown-6)·0.5Toluene (1·0.5Toluene). Crystallization of CsP(H)^{t}Bu$_3$Mes from toluene in the presence of 18-crown-6 gives bright yellow crystals of the monomeric crown ether adduct **1**·0.5toluene. The composition of **1**·0.5toluene was determined crystallographically. The cesium cation is encapsulated by a crown ether molecule and a supermesityl ring via an approximate η^6-π interaction, thereby yielding a distorted sandwich-type arrangement (Figure 1). **1**·0.5toluene represents a first example of a monomeric cesium phosphide derivative.

Two independent molecules are present in the asymmetric unit of **1**·0.5toluene. The presence of multiple independent molecules offers an opportunity to evaluate the extent to which structural parameters are influenced by crystal packing forces. For **1**·0.5toluene, there are large differences in the Cs−P distances (3.847(2) Å [Cs(1)] and 4.069(3) Å [Cs(2)]) and other parameters involving Cs (see Table 2). These differences underscore the extreme stereochemical flexibility associated with a large, diffuse and spherically distributed charge, and clearly caution against seeking explanations for these differences in purely chemical terms.

The Cs−P distances in both independent molecules of **1**·0.5toluene compare well with the longer ones of the interatomic separations in previously characterized base adducts of CsP(H)^{t}Bu$_3$Mes exhibiting polymeric ladder-type structures,[2] but they are longer than the corresponding distances in other molecular Cs−P species.[11,12] The phenyl rings of the supermesityl ligand in both independent molecules of **1**·0.5toluene are slightly distorted. The deviation from planarity is greatest at the *ipso* carbon atoms C(6) and C(46), respectively. C(6) is 0.15 Å out of the plane formed by C(1) to C(5), and C(46) is 0.10 Å below the corresponding plane defined by C(41) to C(45), respectively. Additionally, C(6) and C(46) show the shortest distances to the cesium atoms at 3.411(6) Å [Cs(1)] and 3.405(6) Å [Cs(2)]. The average Cs···C(phenyl) distances are 3.73 Å [Cs(1)] and 3.60 Å [Cs(2)], respectively.

The shortest nonbonding Cs···C(crown ether) distances for both independent molecules of **1**·0.5toluene are 3.767(6) Å [Cs(1)···C(30)] and 3.697(6) Å [Cs(2)···C(61)], respectively. It is noteworthy that these interatomic separations are not much longer than the observed Cs···C(phenyl) distances. Additionally, there are two Cs···C(methyl) distances in **1**·0.5toluene shorter than 4 Å, namely, Cs(1)···C(17) [3.895(8) Å] and Cs(2)···C(50) [3.923(8) Å].

The approximate angle between the planes of the phenyl ring from the supermesityl group and the oxygen atoms of the crown ether ligand is 1.9° (3.8° for the other independent molecule) with a phenyl ring(centroid)−Cs−crown(centroid) angle of 167.6° and a P−Cs−crown(centroid) angle of 139.7° for Cs(1) (the corresponding angles are 171.6° and 137.1° for Cs(2)). The middle of the mean plane defined by the *six oxygen atoms* of the crown ether ligand is meant by the term “crown(centroid)”. Cs(1) is 1.51 Å above the plane defined by oxygen atoms O(21)−O(26), while Cs(2) is 1.58 Å above the corresponding plane defined by atoms O(61)−O(66). These values are in the typical range for the relatively large cesium cation coordinated to an 18-crown-6 ligand.[13,14] The Cs−O interatomic separations (Table 2) range from 3.048(5) to 3.448(11) Å and match the values for standard interatomic separations observed in other Cs/18-crown-6 systems.

The Cs(1)−P(1)−C(6) angle of 62.4(2)° [Cs(2)−P(2)−C(46) = 56.0(2)°] is found to be quite small and differs significantly from the corresponding angles in previously reported polymeric base adducts of CsP(H)^{t}Bu$_3$Mes. For example, the corresponding Cs−P−C angle is 139.6(2)° in [CsP(H)^{t}Bu$_3$Mes]$_x$.[2] The observation of significantly smaller Cs−P−C angles in both independent molecules of **1**·0.5toluene can be rationalized in terms of different coordination modes of the supermesityl ring in both systems.

[CsP(H)Dmp](18-crown-6) (2), [CsP(H)Dmp](18-crown-6)(η^2-C$_6$D$_6$)·Benzene (3·Benzene), and [CsP(H)Dmp]$_2$(18-crown-6)·Toluene (4·Toluene). Crystallization of CsP(H)Dmp from toluene or deuterated benzene in the presence of 18-crown-6 produces three different types of crystals, depending both on the stoichiometry [CsP(H)Dmp:18-crown-6] and the aromatic solvent employed in the crystallization process. Using an excess of crown ether ligand, formation of orange **2** (from toluene) and yellow **3**·benzene (from benzene), respectively, is observed, while a 2:1 ratio [CsP(H)Dmp:18-crown-6] yields yellow crystals of **4**·toluene. The composition of complexes **2**, **3**·benzene, and **4**·toluene was determined crystallographically. Crystals of **3**·benzene were found to desolvate upon exposure to vacuum, yielding **2**.

The molecular structure of the monomeric complex **2** (Figure 2) features a cesium atom which is encapsulated by a crown ether ligand and one mesityl ring from the Dmp ligand through a multihapto interaction with the carbon atoms of the phenyl ring with Cs···C(phenyl) distances ranging from 3.645(5) to 3.893(5) Å (average: 3.75 Å). The shortest nonbonding Cs···C(crown ether) distances are 3.718(8) Å [Cs(1)···C(34)] and 3.721(12) Å [Cs(1)···C(31)]. These numbers can actually be compared with the numbers found for the Cs···C(phenyl) distances in **2**.

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Table 2. Significant Interatomic Separations (Å) and Angles (deg) for Complexes **1**·0.5Toluene, **2**, **3**·Benzene, and **4**·Toluene[a]

	1·0.5toluene	**2**	**3**·benzene	**4**·toluene
M−P (Å)	3.847(2)/4.069(3)	3.6084(13)	3.715(3)	3.4196(9)
M···C(phenyl) (Å)	3.411(6) [C(6)]/3.405(6) [C(46)]	3.645(5) [C(17)]	3.705(9) [C(17)]	3.477(4) [C(17)]
	3.637(6) [C(5)]/3.494(7) [C(41)]	3.679(5) [C(18)]	3.777(9) [C(16)]	3.517(3) [C(18)]
	3.675(6) [C(1)]/3.605(7) [C(45)]	3.703(4) [C(19)]	3.904(17) [C(56)]	3.618(4) [C(16)]
	3.850(6) [C(4)]/3.644(6) [C(42)]	3.751(4) [C(16)]	4.064(13) [C(55)]	3.636(3) [C(19)]
	3.878(6) [C(2)]/3.721(7) [C(44)]	3.818(5) [C(20)]		3.771(3) [C(21)]
	3.952(6) [C(3)]/3.756(7) [C(43)]	3.893(5) [C(21)]		3.774(3) [C(20)]
M−O (Å)	3.048(5) [O(21)]/3.066(9) [O(64)]	3.081(5) [O(32)]	3.078(7) [O(36)]	3.198(2) [O(34)]
	3.127(5) [O(23)]/3.117(8) [O(66)]	3.108(6) [O(34)]	3.089(8) [O(32)]	3.286(2) [O(30)]
	3.127(5) [O(25)]/3.202(6) [O(65)]	3.177(5) [O(33)]	3.110(8) [O(34)]	3.341(2) [O(32A)]
	3.186(5) [O(26)]/3.252(10) [O(62)]	3.178(6) [O(36)]	3.146(9) [O(31)]	3.404(2) [O(32)]
	3.273(5) [O(22)]/3.268(9) [O(63)]	3.233(6) [O(35)]	3.236(9) [O(33)]	3.422(3) [O(30A)]
	3.299(5) [O(24)]/3.448(11) [O(61)]	3.300(7) [O(31)]	3.285(8) [O(35)]	3.565(2) [O(34A)]
M−P−C (deg)	62.4(2)/56.0(2)	126.37(15)	127.3(3)	126.43(10)

[a] Both independent molecules of complex **1**·0.5toluene are listed.

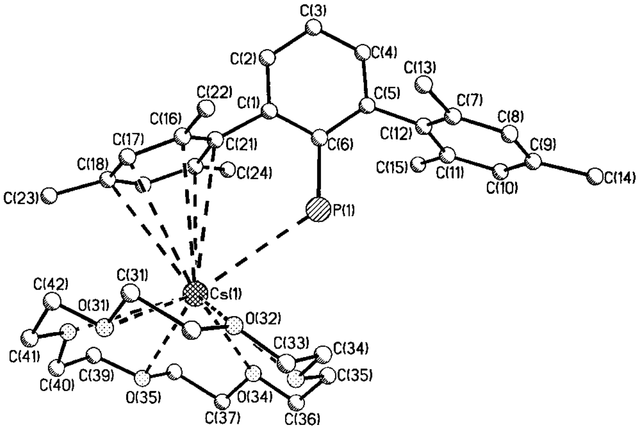

Figure 2. Molecular structure of [CsP(H)Dmp](18-crown-6) (**2**). Hydrogen atoms are omitted for clarity.

A distorted sandwich-type arrangement is found with an approximate angle of 27.4° between the planes of the phenyl ring and the six oxygen atoms of the 18-crown-6 ligand, a mesityl ring(centroid)−Cs(1)−crown(centroid) angle of 155.1°, and a P(1)−Cs(1)−crown(centroid) angle of 135.1°. The Cs−P distance of 3.6084(13) Å is shorter than the corresponding distance in both independent molecules of **1**·0.5toluene, and the Cs(1)−P(1)−C(6) angle of 126.37(15) is about twice the values found for **1**·0.5toluene. Atom Cs(1) is 1.48 Å above the plane defined by the six oxygen atoms of the crown ether ligand, and the average Cs−O distance (3.18 Å) can be compared with those in **1**·0.5toluene.

The molecular structure of **3**·benzene (Figure 3) shows a heavily distorted sandwich-type arrangement of the mesityl and the crown ether ligand, similar to the structural motif found in complex **2**. In contrast to complex **2**, coordination of a benzene molecule is seen in **3**·benzene, which is bonded in an η^2 fashion to the metal center, forming a dihedral angle of 115.7° between the Cs(1)−C(55)−C(56) triangle and the plane defined by the six carbon atoms of the benzene ring. As a result of additional coordination of a solvent benzene molecule, an η^2 bonding mode of the mesityl ligand is found in **3**·benzene, as opposed to an η^6-coordinated mesityl ligand in the case of **2**. The Cs−P distance of 3.715(3) Å in **3**·benzene is approximately $^1/_{10}$ Å longer than the corresponding value in **2**. On the other hand, the average Cs−O distance of 3.16 Å is slightly shorter than the average distance found in **2** (3.18 Å), with atom Cs(1) residing 1.49 Å above the plane defined by the six oxygen atoms of the crown ether ligand. The Cs···C(phenyl) distances of 3.705(9) Å [C(17)] and 3.777(9) Å [C(16)] are clearly shorter than the Cs···C(benzene) separations of 3.904(7) Å [C(56)] and 4.062(13) Å [C(55)], and the shortest Cs···C(crown ether) distances are 3.704(12) Å [C(31)] and 3.711(12) Å [C(38)]. The Cs−P−C angle of 127.3(3)°, the P(1)−Cs(1)−crown(centroid) angle of 144.0°, and the mesityl ring(centroid)−Cs(1)−crown(centroid) angle of 149.0° can be compared with the corresponding numbers in **2**. A detailed comparison of further bonding parameters can be derived from Table 2.

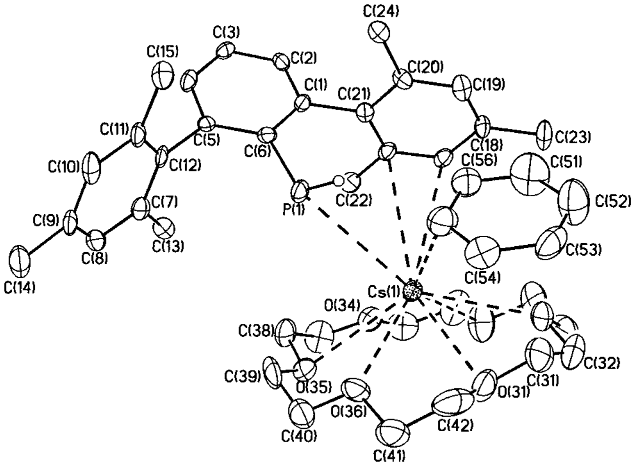

Figure 3. Molecular structure of [CsP(H)Dmp](18-crown-6)(η^2-C_6D_6)·benzene (**3**·benzene). Hydrogen atoms as well as the two cocrystallized half-molecules of benzene in the crystal lattice are omitted for clarity.

Different from the solid state structures of monomeric **1**·0.5toluene, **2**, and **3**·benzene, the molecular structure of centrosymmetric $[CsP(H)Dmp]_2$(18-crown-6)·toluene (**4**·toluene) consists of two CsP(H)Dmp moieties, coordinating to both sides of a crown ether ligand, thereby forming a distorted triple-decker-type arrangement (Figure 4). Atoms Cs(1) and Cs(1A), respectively, are "sandwiched" between the crown ether ligand and one mesityl ring, exhibiting an intramolecular η^6-π interaction with the mesityl ring with Cs···C(phenyl) distances ranging from 3.477(4) to 3.774(3) Å (average: 3.63 Å) and resulting in complete encapsulation of the two cesium atoms by two mesityl rings, two phosphorus atoms, and one 18-crown-6 ligand. Other than in complex **2**, the shortest Cs···C(crown ether) distances in **4**·toluene [Cs(1)···C(34) = 3.830(6) Å and Cs(1)···C(33) = 3.906(6) Å] are clearly longer than the observed Cs···C(phenyl) separations, which can be explained in terms of a sterically more crowded situation around the crown ether ligand in the case of complex **4**·toluene.

The Cs−P interatomic separation of 3.4196(9) Å in **4**·toluene is significantly shorter than the corresponding distance in **2**, while the Cs(1)−P(1)−C(6) angle of 126.43(10)° matches the

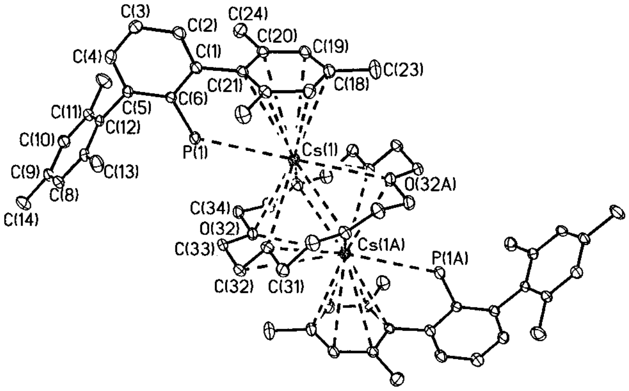

Figure 4. Molecular structure of $[CsP(H)Dmp]_2$(18-crown-6)·toluene (**4**·toluene). Hydrogen atoms as well as the cocrystallized toluene molecule in the crystal lattice are omitted for clarity.

value found for **2**. The deviation from ideal triple-decker geometry in the distorted "club sandwich"[14] structure of **4**·toluene is most readily seen by inspecting the mesityl ring-(centroid)−Cs(1)−crown(centroid) angle, which is 153.4°, which is not very different from the corresponding value found for **2**. The approximate angle between the planes of the mesityl ring and the plane defined by the oxygen atoms of the crown ether ligand is 30.7°, and the P(1)−Cs(1)−crown(centroid) angle (130.3°) is only slightly smaller than the corresponding angle in **2**. Atom Cs(1) resides above the center of the corresponding crown ether cavity and is 1.93 Å above the plane defined by oxygen atoms of the crown ether ligand. The Cs−O distances in **4**·toluene (Table 2), ranging from 3.198(2) to 3.565(2) Å (average: 3.37 Å), are found to be longer than the corresponding distances in **1**·0.5toluene (average: 3.18 and 3.23 Å, respectively) and **2** (average: 3.18 Å). A comparison of further significant interatomic separations and angles of **1**·0.5toluene, **2**, **3**·benzene, and **4**·toluene can be derived from Table 2.

It is noteworthy that the solution ^{1}H NMR spectra of both **2** and **4** in benzene show the presence of only one set of mesityl rings, thereby indicating a solution structure different from the arrangement found in the solid state.

Conclusion

Our work provides insight into the solid state structures of 18-crown-6 adducts of four different arene soluble cesium phosphide derivatives. We can demonstrate that monomeric cesium aryl phosphide species are accessible by blocking further association/aggregation in the solid state using (a) bulky aryl substituents on phosphorus forming multihapto interactions between the metal and the aryl ring carbon atoms and (b) polyether ligands for saturating the remaining coordination sphere of the relatively large cesium. We are thereby able to limit nuclearity of the resulting complexes and moderate structure growth in the solid state. The lack of other examples of monomeric cesium phosphide derivatives precludes further comparison of the molecular structures of **1**·0.5toluene, **2**, **3**·benzene, and **4**·toluene with established compounds.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[CsP(H)^tBu_3Mes]$(18-crown-6)·0.5toluene (**1**·0.5toluene), [CsP(H)Dmp](18-crown-6) (**2**), [CsP(H)Dmp](18-crown-6)(η^2-C_6D_6)· benzene (**3**·benzene), and $[CsP(H)Dmp]_2$(18-crown-6)·toluene (**4**·toluene). This material is available free of charge via the Internet at http://pubs.acs.org.

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