Organometallics **1993**, *12*, 1193–1200

Cation-Induced Structural Alterations in the Organo Alkali Metal Derivatives of Triphenylmethane: Combined X-ray and NMR Study of the K–Cs Salts

Daniele Hoffmann,† Walter Bauer,† Paul von Ragué Schleyer,*,†
Ursula Pieper,‡ and Dietmar Stalke‡

Institute of Organic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, W-8520 Erlangen, Germany and the Institute of Inorganic Chemistry, Georg-August-Universität Göttingen, Tammanstrasse 4, W-3400 Göttingen, Germany

Received September 29, 1992

The set of alkali metal solid-state structures of $Ph_3CM{\cdot}nL$ [M = K, Rb, Cs; L = (ligands) PMDTA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine), THF (tetrahydrofuran)] provides instructive comparisons. $Ph_3CK{\cdot}THF{\cdot}PMDTA$ (**1**) crystallizes as a monomeric contact ion pair: the K^+ cation is symmetrically η^6-coordinated to one of the phenyl rings, but not to the deprotonated central carbon. Both $[Ph_3CRb{\cdot}PMDTA]_n$ (**2**) and $[Ph_3CCs{\cdot}PMDTA]_n$ (**3**) form one-dimensional polymers and eschew THF. The Rb cations in **2** bridge the triphenylmethyl moieties by η^6-coordination to separate phenyl rings. This gives rise to a zigzag chain. In **3**, each Cs cation also bridges two carbanions, but in a somewhat different fashion. While Cs^+ is located rather symmetrically (η^6) above the phenyl ring of one trityl moiety, a “propeller”-like coordination to a second trityl anion involves contacts with all three phenyl rings as well as with the deprotonated central carbon. The structure of **3** in THF-d_8 solution was elucidated by $^{133}Cs,^1H$ HOESY spectroscopy, which reveals agostic interactions between cesium and hydrogen. This provides strong evidence that **3** is a contact ion pair in this solvent with the cation located above the central carbon. The recently proposed MNDO K parameters err in predicting $Ph_3CK{\cdot}nL$ (**1**) to be “oversolvated”; K–C distances and nonbonded repulsion energies are overestimated.

Introduction

Due to extensive π-delocalization, the triphenylmethyl moiety can be stabilized as a carbonium ion, a radical, or a carbanion. We have employed the triphenylmethyl anion to investigate the corresponding organometallic compounds of the heavier alkali metals. These “carbanions” serve as nonnucleophilic deprotonating agents in organic synthesis.[1a–c] The Li–K salts have been investigated in solution previously.[2] Solid-state structures of Ph_3CM (where M = alkali or alkaline earth metal) have been reported for $Ph_3CLi{\cdot}TMEDA$,[3] $Ph_3CLi{\cdot}2Et_2O$,[4] $[Ph_3C^-][Li^+(12\text{-crown-}4)_2]$,[5] $Ph_3CNa{\cdot}TMEDA$,[6] and $Ph_3CMgBr{\cdot}2Et_2O$,[7] but not for the heavier alkali metals, K, Rb, and Cs. We present here the X-ray structures of $Ph_3CK{\cdot}THF{\cdot}PMDTA$ (**1**), $[Ph_3CRb{\cdot}PMDTA]_n$ (**2**), and $[Ph_3CCs{\cdot}PMDTA]_n$ (**3**) and discuss the differences along the alkali metal cation series, from Li^+ to Cs^+.[8]

The interaction between a metal cation and a π-delocalized carbanion depends on the sizes of both partner ions[9] as well as on whatever additional donor ligands may be present. While small cations like Li^+ are charge-localizing and usually interact with the centers of highest charge, multihapto bonding prevails with larger and less charge-localizing cations like K^+, Rb^+, and Cs^+.[8] This is exemplified by the differences in the structures of fluorenyllithium[10a] and fluorenylpotassium,[10b] which show η^3- and η^5-coordination, respectively. The potential energy surfaces of ion pairs involving delocalized carbanions, often quite flat,[11,12] level off with increasing metal to ring distance. Especially with Li^+, several different metal cation locations may be minima and may even compete in the same compound.[12b] In contrast, carbanionic moieties containing a heteroatom, e.g. the diphenylpyridylmethyl carbanion, have distinct minima for cation locations at the negatively charged heteroatoms.[13] As the bonding is almost exclusively ionic,[14a] locations of alkali metal cations above a π-delocalized carbanion can often be predicted by simple electrostatic point charge models.[14b] For a given anion (i.e. triphenylmethanide) and the same polar ligands, structural changes can be expected along the Li–Cs series due to increasing ionic radii (increasing

---

† Friedrich-Alexander-Universität Erlangen-Nürnberg.

‡ Georg-August-Universität Göttingen.

(1) (a) House, H. O.; Kramer, V. *J. Org. Chem.* 1963, *28*, 3362. (b) Anton, D. R.; Crabtree, R. H. *Tetrahedron Lett.* 1983, *24*, 2449. (c) Levine, R.; Baumgarten, E.; Hauser, C. R. *J. Am. Chem. Soc.* 1944, *66*, 1230.

(2) (a) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* 1963, *85*, 2328. (b) O'Brien, D. H.; Russel, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (c) Buncel, E.; Menon, B. *J. Org. Chem.* 1979, *44*, 317. (d) Takahashi, K.; Kondo, Y.; Asami, R. *Org. Magn. Reson.* 1974, *6*, 580.

(3) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* 1972, *94*, 7333.

(4) Bartlett, R. A.; Dias, H. v. R.; Power, P. P. *J. Organomet. Chem.* **1988**, *341*, 1.

(5) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174.

(6) Köster, H.; Weiss, E. *J. Organomet. Chem.* 1979, *168*, 273.

(7) Engelhardt, L. M.; Harvey, S.; Raston, C. L.; White, A. H. *J. Organomet. Chem.* 1988, *341*, 39.

(8) An extensive bibliography is given in: Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* 1987, *27*, 169.

(9) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1982, *104*, 4781.

(10) (a) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* 1972, *94*, 7339. (b) Zerger, R.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* 1974, *96*, 5441.

(11) (a) Schleyer, P. v. R. *Pure Appl. Chem.* 1983, *55*, 355. (b) Schleyer, P. v. R. *Pure Appl. Chem.* 1984, *56*, 151.

(12) (a) Streitwieser, A. *Acc. Chem. Res.* 1984, *17*, 353. (b) Boche, G.; Etzrod, H.; Massa, W.; Baum, G. *Angew. Chem.* 1985, *97*, 858; *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 863.

(13) Pieper, U.; Stalke, D. Following article in this issue.

(14) (a) Lambert, C.; Kaupp, M.; Schleyer, P. v. R. *Organometallics* **1993**, *12*, 853. (b) Bushby, R. J.; Steel, H. L. *J. Chem. Soc., Perkin Trans. 2* 1990, 1143, 1155, 1169.

0276-7333/93/2312-1193$04.00/0

M–C distances) as well as to the higher coordination numbers of the larger alkali metal cations.[15]

While organolithium compounds have been investigated thoroughly[16] because of fundamental importance in modern synthetic organic chemistry,[17] relatively little attention has been paid to the heavier alkali metal analogues.[8,18] The recent boom, especially the examination of organosodium[19] and to a lesser extent of organopotassium structures,[19a,20] may partly be attributed to interest in improved synthetic methods.[17a,b,21–23] Moreover, mixtures of organolithium compounds with potassium (or sodium) alkoxides–termed "super bases", "complex bases", or LICKOR-reagents—have become valuable synthetic reagents, as they are by far more reactive than the organolithium compounds.[22,23] Although the exact nature of the metalating species in such mixtures is still a mystery, the active agent may be the organo alkali metal compound of the heavier alkali metal[24] rather than a mixed organolithium/alcoholate aggregate.[25]

Results and Discussion

Crystals of **1**–**3** were obtained from "model super base" mixtures, i.e. from equimolar mixtures of Ph_3CLi and MO^tBu (M = K, Rb, Cs) in THF/toluene after adding an excess of PMDTA (eqs 1 and 2).

These transmetalation reactions are exothermic due to the formation of the strong Li–O bond.[24,26] Even when an excess of MO^tBu was employed, crystallization yielded **1**–**3** exclusively. No mixed aggregate could be isolated, although ab initio calculations indicate that these should be possible.[27]

$$Ph_3CH + {}^nBuLi \underset{-20\,^\circ C}{\overset{THF}{\rightarrow}} Ph_3CLi + BuH \quad (1)$$

$$Ph_3CLi + MO^tBu \overset{THF}{\rightarrow} Ph_3CM + LiO^tBu \underset{+toluene}{\overset{3\text{-}7\ \text{equiv of PMDTA}}{\rightarrow}} [Ph_3CM{\cdot}L]_n \quad (2)$$

M = K, Rb, Cs; L = ligand (PMDTA, THF);
n = aggregation number

X-ray Structure of $Ph_3CK{\cdot}THF{\cdot}PMDTA$ (1). The molecular structure of **1** (Figure 1) can be described as a contact ion pair consisting of the triphenylmethyl carbanion and a potassium cation coordinated to one THF and one PMDTA ligand. Table I gives geometrical information and Table II contains fractional coordinates and isotropic displacement parameters.

The K^+ cation is located nearly symmetrically above one phenyl ring with six K–C contacts ranging from 314.2(5) to 325.3(4) pm and a K^+ to ring center distance of 287.1 pm. The coordiation sphere is completed by three K–N contacts [280.8(4)–288.1(3) pm] to the chelating triamine and by a further K–O interaction [272.1(4) pm] to THF. Unlike $Ph_3CLi{\cdot}TMEDA$,[3] $Ph_3CLi{\cdot}2Et_2O$,[4] and $Ph_3CNa{\cdot}TMEDA$, where the cations interact with the central carbon (which bears the highest charge) no such interaction is present in **1**. The "softer", i.e. more polarizable, K^+ cation favors interaction with a more charge-delocalized anionic moiety, essentially a single phenyl ring. This gives rise to the η^6-coordination of the cation. The result is the shortening of the C(1)–C(2) bond in **1** [143.5(5) pm], which is more pronounced than that in the corresponding Li and Na compounds (see Table III, which compares the most important geometrical features of the trityl alkali metal structures and Figure 2, which shows their superposition). The C(1) atom in **1** is essentially in plane with C(2), C(8), and C(14), the angles around C(1) deviating only slightly from 120° (Table I). The pyramidalization at the central carbon vanishes, as the cation is changed from Li^+ to Na^+ or K^+ [C(1) is 12, 0.39, and 1.0 pm out of the C(2)C(8)C(14) plane, respectively], reflecting "more ionic geometries" for the Na and K compound. Steric constraints prevent the phenyl rings in **1** from being coplanar, and a propeller arrangement results. The torsional angles of the rings with respect to the C(2)C(8)C(14) plane are 17.7, 31.1, and 40.2°, the smallest angle involves the phenyl ring to which the cation is coordinated. That the smaller twist angle corresponds to increased π-electron-delocalization also is suggested by the shorter C(1)C(2) bond length. The overlap in π-systems is a $\cos^2\theta$ function (θ = torsional angle between π-planes).[28] Thus, π-delocalization between the C(2)-C(8)C(14) plane and the phenyl rings is still effective, although the phenyl rings are twisted with respect to this central plane. For the 17.7° twist angle the overlap would still amount to ca. 90%, and even for the 40.2° twist angle ca. 58% of the overlap can be expected to remain. That

---

(15) (a) Truter, M. R. *Struct. Bonding* **1973**, *16*, 71. (b) Poonia, N. S.; Bajaj, A. *Chem. Rev.* **1979**, *79*, 389.

(16) (a) Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, U. K., 1974. (c) Schlosser, M. *Structure and Reactivity of Polar Organometallics*; Springer Verlag: Berlin, 1973.

(17) (a) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry I*; Springer: Berlin, 1987. (b) Brandsma, L. *Preparative Polar Organometallic Chemistry II*; Springer: Berlin, 1990. (c) Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988.

(18) (a) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217. (b) Williard, P. G. In *Comprehensive Organic Synthesis*; Fleming, I., Trost, B. M., Eds.; Pergamon Press: Oxford, U.K., 1971; Vol. 1, p 1.

(19) (a) Bock, H.; Ruppert, K.; Näther, C.; Havlas, Z.; Herrmann, H.-F.; Arad, C.; Göbel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B.; *Angew. Chem.* **1992**, *104*, 564; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550 and references therein. (b) Schümann, U.; Behrens, U.; Weiss, E. *Angew. Chem.* **1989**, *101*, 481; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 476. (c) Weiss, E.; Corbelin, S.; Cockroft, J. K.; Fitch, A. N. *Angew. Chem.* **1990**, *102*, 728; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 650. (d) Schade, C.; Schleyer, P. v. R.; Gregory, P.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1988**, *341*, 19. (e) Schade, C.; Schleyer, P. v. R.; Dietrich, H.; Mahdi, W. *J. Am. Chem. Soc.* **1986**, *108*, 2482. (f) Gregory, K.; Bremer, M.; Bauer, W.; Schleyer, P. v. R.; Lorenzen, N. P.; Kopf, J.; Weiss, E. *Organometallics* **1990**, *9*, 1485. (g) Corbelin, S.; Lorenzen, N. P.; Kopf, J.; Weiss, E. *Chem. Ber.* **1991**, *124*, 2417. (h) Corbelin, S.; Kopf, J.; Lorenzen, N. P.; Weiss, E. *Angew. Chem.* **1991**, *103*, 875; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 825.

(20) (a) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11. (b) Lorberth, J.; Shin, S.-H.; Wocadlo, S.; Massa, W. *Angew. Chem.* **1989**, *101*, 793; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735. (c) Gregory, K.; Bremer, M.; Schleyer, P. v. R. *Angew. Chem.* **1989**, *101*, 1261; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224.

(21) (a) Pi, R.; Bauer, W.; Brix, B.; Schade, C.; Schleyer, P. v. R. *J. Organomet. Chem.* **1986**, *306*, C1. (b) Schade, C.; Bauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *295*, C25.

(22) (a) Lochmann, L.; Popisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, *257*. (b) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1987**, *326*, 1. (c) Lochmann, L.; Lim, D. *J. Organomet. Chem.* **1971**, *28*, 153. (d) Lochmann, L.; Petranek, J. *Tetrahedron Lett.* **1991**, *32*, 1483. (e) Lochmann, L. *J. Organomet. Chem.* **1989**, *376*, 1.

(23) (a) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. (b) Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741. (c) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674. (d) Stähle, M.; Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1977**, *60*, 1730. (e) Schlosser, M.; Lehmann, R. *Tetrahedron Lett.* **1984**, *25*, 745.

(24) Bauer, W.; Lochmann, L. *J. Am. Chem. Soc.* **1992**, *114*, 7482.

(25) Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627.

(26) Hommes, N. J. R. v. E., Schleyer, P. v. R. Unpublished results.

(27) Harder, S.; Kremer, T.; Schleyer, P. v. R. To be published.

(28) Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. L. *J. Comput. Chem.* **1987**, *8*, 581.

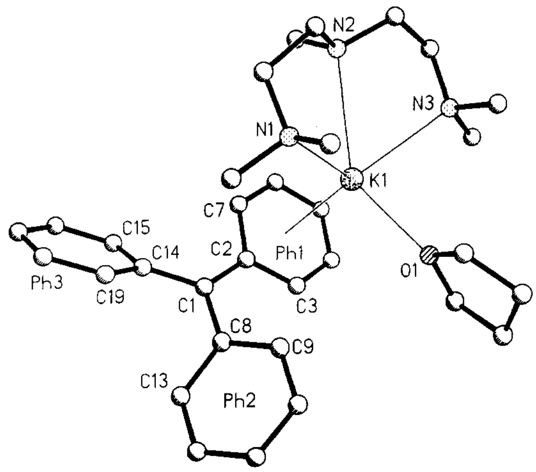

Figure 1. Molecular structure of $Ph_3CK\cdot THF\cdot PMDTA$ (1).

Table I. Selected Bond Lengths (pm) and Angles (deg) of $Ph_3CK\cdot THF\cdot PMDTA$ (1)

K(1)–O(1)	272.1(4)	K(1)–N(3)	280.8(4)
K(1)–N(1)	281.9(3)	K(1)–N(2)	288.1(3)
K(1)–C(7)	314.2(5)	K(1)–C(3)	317.0(4)
K(1)–C(2)	318.6(4)	K(1)–C(6)	320.0(5)
K(1)–C(4)	321.0(4)	K(1)–C(5)	325.3(4)
C(1)–C(2)	143.5(5)	C(1)–C(14)	146.0(6)
C(1)–C(8)	147.5(6)	C(2)–C(3)	142.7(6)
C(2)–C(7)	143.1(6)	C(3)–C(4)	138.1(6)
C(4)–C(5)	138.7(6)	C(5)–C(6)	138.5(6)
C(6)–C(7)	138.0(6)	C(8)–C(9)	140.3(7)
C(8)–C(13)	141.7(5)	C(9)–C(10)	137.4(7)
C(10)–C(11)	138.4(6)	C(11)–C(12)	137.4(7)
C(12)–C(13)	138.4(7)	C(14)–C(15)	139.8(6)
C(14)–C(19)	142.5(5)	C(15)–C(16)	138.3(6)
C(16)–C(17)	138.1(6)	C(17)–C(18)	137.7(7)
C(18)–C(19)	138.4(6)		
O(1)–K(1)–N(3)	90.78(12)	O(1)–K(1)–N(1)	93.60(11)
N(3)–K(1)–N(1)	115.31(10)	O(1)–K(1)–N(2)	130.79(12)
N(3)–K(1)–N(2)	64.75(10)	N(1)–K(1)–N(2)	64.45(10)
C(2)–C(1)–C(14)	122.36(39)	C(2)–C(1)–C(8)	119.49(39)
C(14)–C(1)–C(8)	118.15(34)	C(3)–C(2)–C(7)	113.49(32)
C(3)–C(2)–C(1)	123.35(36)	C(7)–C(2)–C(1)	123.16(36)
C(4)–C(3)–C(2)	122.57(40)	C(3)–C(4)–C(5)	122.18(41)
C(6)–C(5)–C(4)	116.99(35)	C(7)–C(6)–C(5)	121.94(41)
C(6)–C(7)–C(2)	122.80(38)	C(9)–C(8)–C(13)	115.60(40)
C(9)–C(8)–C(1)	123.53(35)	C(13)–C(8)–C(1)	120.87(45)
C(10)–C(9)–C(8)	122.28(40)	C(9)–C(10)–C(11)	120.91(55)
C(12)–C(11)–C(10)	118.58(46)	C(11)–C(12)–C(13)	121.15(41)
C(12)–C(13)–C(8)	121.45(50)	C(15)–C(14)–C(19)	114.55(39)
C(15)–C(14)–C(1)	124.37(35)	C(19)–C(14)–C(1)	121.06(43)
C(16)–C(15)–C(14)	123.41(39)	C(17)–C(16)–C(15)	120.58(51)
C(18)–C(17)–C(16)	118.08(44)	C(17)–C(18)–C(19)	121.75(39)
C(18)–C(19)–C(14)	121.63(47)		

delocalization has a pronounced influence on the bond lengths in π-conjugated carbanions has been demonstrated both in the allyl[29] and the benzyl carbanions.[30]

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) of $Ph_3CK\cdot THF\cdot PMDTA$ (1)

	x	*y*	*z*	*U*(eq)[a]
K(1)	2472.7(5)	1797.6(8)	9565.4(6)	32.4(5)
C(1)	2554(2)	−1117(4)	11168(3)	26(2)
C(2)	2513(2)	299(4)	11176(3)	26(2)
C(3)	1798(2)	1015(4)	11014(3)	30(2)
C(4)	1770(3)	2377(4)	11049(3)	33(3)
C(5)	2438(3)	3146(4)	11243(3)	36(3)
C(6)	3144(3)	2488(4)	11397(3)	34(3)
C(7)	3187(2)	1129(4)	11357(3)	28(2)
C(8)	1859(2)	−1885(4)	10773(3)	27(2)
C(9)	1356(3)	−1524(4)	10046(3)	31(2)
C(10)	702(3)	−2243(4)	9699(3)	41(3)
C(11)	521(3)	−3386(4)	10048(4)	43(3)
C(12)	1007(3)	−3786(4)	10752(3)	37(2)
C(13)	1662(2)	−3062(4)	11114(3)	32(2)
C(14)	3260(2)	−1839(4)	11555(3)	24(2)
C(15)	3803(2)	−1410(4)	12236(3)	31(2)
C(16)	4462(3)	−2121(4)	12601(3)	37(3)
C(17)	4610(3)	−3331(4)	12305(3)	35(2)
C(18)	4088(3)	−3799(4)	11638(3)	37(3)
C(19)	3432(2)	−3088(4)	11265(3)	29(2)
N(1)	3329(2)	−136(3)	8990(2)	48(2)
N(2)	3916(2)	2688(3)	9279(3)	43(2)
N(3)	2417(2)	4295(3)	8854(2)	39(2)
C(20)	3358(4)	−1325(5)	9470(4)	62(3)
C(21)	2917(3)	−498(6)	8194(3)	63(3)
C(22)	4149(3)	263(5)	9147(5)	50(2)
C(23)	4219(5)	1646(6)	8834(5)	46(3)
C(24)	4419(3)	2984(5)	10048(3)	59(3)
C(25)	3788(3)	3889(4)	8795(3)	44(2)
C(26)	3212(2)	4844(4)	9007(3)	41(2)
C(27)	1927(3)	5180(4)	9181(3)	48(2)
C(28)	2069(3)	4116(5)	8012(3)	52(3)
O(1)	1101(2)	1112(4)	8543(3)	57(2)
C(29)	909(4)	664(7)	7749(4)	71(3)
C(30)	89(4)	997(10)	7412(5)	105(4)
C(31)	−234(4)	1158(10)	8074(5)	110(4)
C(32)	406(3)	1497(6)	8746(4)	66(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The phenyl rings display a considerable angle contraction at the ipso position [C(3)C(2)C(7) = 113.49(32)°, C(9)C(8)C(13) = 115.60(40)°, and C(15)C(14)C(19) = 114.55(39)°] and a slighter contraction at the para position. This quinonoid distortion is most pronounced in the phenyl ring to which the cation coordinates. Such ring deformation is a common feature in PhX compounds when X is an electropositive element or an electron-donating group (i.e. CH_2^-)[31] and has been observed in several PhLi[32] and PhNa structures[33] as well as in several benzylic-type organo alkali metal compounds.[19a,e,h,34] Both σ- and π-delocalization effects are responsible.[35]

A η^6-coordination for potassium is also found in alkali metal graphite intercalates (K–C: 305 pm).[36] In $KOsH_3(PMe_2Ph)_3$[37] and $K_2[(Ph_3P)_2(Ph_2PC_6H_4)RuH_2]_2\cdot C_{10}H_8\cdot Et_2O$,[38] the K^+ is encapsulated by two phenyl substituents of the phosphine ligands, but quite unsymmetrically. Wide K–C distance ranges (312–360 and 297–361 pm, respectively) result. Several other η^6-K^+–benzene coordinations in lattices are known.[39] The reduction of tetraphenylbutadiene with potassium yields a dianion triple salt, where the cations also interact with phenyl rings, but in a η^5-fashion (K–C: 302–312 pm).[19a] That 1

---

(29) Hommes, N. J. R. v. E.; Bühl, M.; Schleyer, P. v. R.; Wu, Y.-D. *J. Organomet. Chem.* **1991**, *409*, 307.

(30) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942.

(31) (a) Dunitz, J. D.; Wallis, J. D. *Helv. Chim. Acta* **1984**, *67*, 1374. (b) Domenicano, A.; Murray-Rust, P.; Vaciago, A. *Acta Crystallogr.* **1983**, *B39*, 457 and references therein.

(32) (a) Maetzke, T.; Seebach, D. *Helv. Chim. Acta* **1989**, *72*, 624. (b) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320. (c) Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3157. (d) Seebach, D.; Maetzke, T. *Helv. Chim. Acta* **1989**, *72*, 624. (e) Stalke, D.; Whitmire, K. *J. Chem. Soc., Chem. Commun.* **1990**, 833. (f) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. v. R. *Organometallics* **1992**, *11*, 2623.

(33) Schümann, U.; Behrens, U.; Weiss, E. *Angew. Chem.* **1989**, *101*, 481; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 476.

(34) Hoffmann, D.; Schleyer, P. v. R. To be published.

(35) Hommes, N. J. R. v. E., Schleyer, P. v. R. To be published.

(36) (a) Rüdorff, W. *Adv. Inorg. Radiochem.* **1959**, *1*, 223. (b) Solin, S. A. *Adv. Chem. Phys.* **1982**, *49*, 455. (c) Levy, F. *Intercalated Layered Materials*; Reidel: Dordrecht, The Netherlands, 1979.

(37) Huffman, J. C.; Green, M. A.; Kaiser, S. L.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 5111.

(38) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528.

Table III. Comparison of Geometrical Features of $Ph_3CM{\cdot}nL$ (Distances in Picometers, Angles in Degrees)

	$Ph_3C^-Li^+$		$Ph_3C^-Na^+$	Ph_3C^-	$Ph_3C^-K^+$ (**1**)	$Ph_3C^-Rb^+$ (**2**)	$Ph_3C^-Cs^+$ (**3**)
donor	TMEDA	$2Et_2O$	TMEDA	$[Li(12\text{-crown-}4)_2]^+$	PMDTA/THF	PMDTA	PMDTA
C(1)–C(2)	148.8(19)	148.4(9)	147.0(3)	145.9(4)	143.5(5)	144.2(4)	143.8(5)
δ^a	44.8	35.5	28.3	30.3	17.7	28.2	23.6
C(1)–C(8)	146.2(13)	147.6(9)	146.7(3)	145.1(5)	147.5(6)	146.3(6)	146.3(5)
ϵ^b	30.6	31.9	34.7	21.3	40.2	39.2	34.7
C(1)–C(14)	144.8(9)	145.0(10)	144.5(2)	145.0(4)	146.0(6)		146.8(5)
ϕ^c	19.7	24.8	27.6	42.0	31.1		37.7
C(1) out of plane	12	12	0.39	planar	1.0(4)	planar	0.7(4)
metal–C(1) distance	222.7(8)	230.6(14)	264.3(3)		404.8(4)	453.5(2)	334.8(4) 462.1(4)
shortest dist to phenyl ring					287.0(2)	317.3(1)	332.0(2)
dist to ring center					287.1	319.0	333.3
lit.	3	4	6	5	this work	this work	this work

[a] δ: angle between the C(1)–C(2)–C(8)–C(14) plane and the Ph(1) plane. [b] ϵ: angle between the C(1)–C(2)–C(8)–C(14) plane and the Ph(2) plane. [c] ϕ: angle between the C(1)–C(2)–C(8)–C(14) plane and the Ph_3 plane.

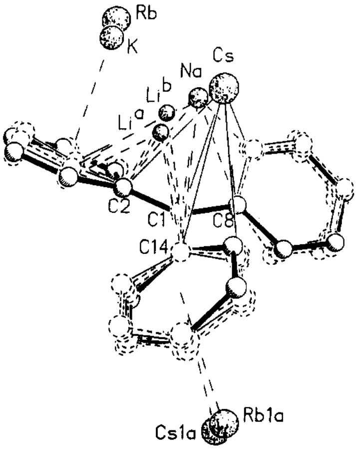

Figure 2. Superposition of the trityl alkali metal structures, which illustrates the locations of the alkali metal cations. Li^a corresponds to $Ph_3CLi{\cdot}TMEDA$; Li^b, to $Ph_3CLi{\cdot}2Et_2O$.

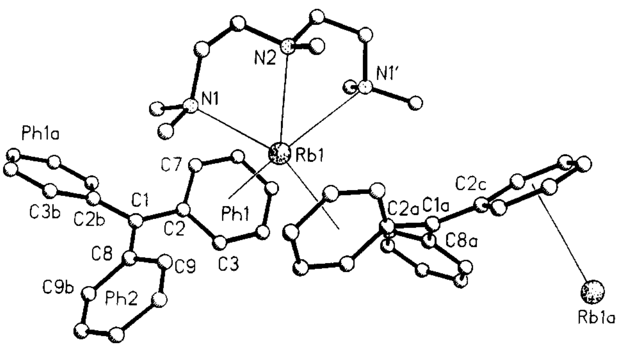

Figure 3. Molecular structure of $[Ph_3CRb{\cdot}PMDTA]_n$ (**2**).

crystallizes as a monomer may be attributed to the high steric requirements of the propeller-like Ph_3C^- moiety. In contrast, the K^+ ions both in $[Ph_2CHK{\cdot}PMDTA]_n$ and in $[PhCH_2K{\cdot}PMDTA]_n$ do not coordinate to THF, but instead to another carbanion and polymeric chains result.[34,40]

Table IV. Selected Bond Lengths (pm) and Angles (deg) of $[Ph_3CRb{\cdot}PMDTA]_n$

Rb(1)–N(2)	296.4(7)	Rb(1)–N(1)	313.2(11)
Rb(1)–N(1′)	317.3(9)	Rb(1)–C(2)	364.3(3)
Rb(1)–C(3)	354.0(3)	Rb(1)–C(4)	341.9(4)
Rb(1)–C(5)	335.1(4)	Rb(1)–C(6)	340.5(4)
Rb(1)–C(7)	352.4(3)	C(1)–C(2)	144.2(4)
C(1)–C(8)	146.3(6)	C(2)–C(3)	141.6(4)
C(2)–C(7)	142.5(5)	C(3)–C(4)	138.1(5)
C(4)–C(5)	139.7(5)	C(5)–C(6)	137.8(5)
C(6)–C(7)	138.5(5)	C(8)–C(9)	141.3(4)
C(9)–C(10)	138.2(5)	C(10)–C(11)	137.9(4)

N(2)–Rb(1)–N(1)	59.69(15)	N(2)–Rb(1)–N(1′)	59.76(16)
C(2)–C(1)–C(2b)	121.61(37)	C(2)–C(1)–C(8)	119.20(18)
C(3)–C(2)–C(7)	114.20(29)	C(3)–C(2)–C(1)	122.56(28)
C(4)–C(3)–C(2)	123.16(33)	C(3)–C(4)–C(5)	120.60(32)
C(6)–C(5)–C(4)	118.27(30)	C(5)–C(6)–C(7)	121.29(31)
C(9)–C(8)–C(9A)	114.78(39)	C(9)–C(8)–C(1)	122.61(19)
C(10)–C(9)–C(8)	122.33(30)	C(11)–C(10)–C(9)	121.18(31)
C(10)–C(11)–C(10A)	118.19(40)		

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) of $[Ph_3CRb{\cdot}PMDTA]_n$

	x	*y*	*z*	$U(eq)^a$
Rb(1)	−2381.5(4)	−2381.5(4)	0	27.5(2)
C(1)	0	−903(4)	1667	23(2)
C(2)	299(4)	−1473(4)	1159.7(12)	22(2)
C(3)	1234(4)	−447(4)	732.0(12)	26(2)
C(4)	1545(4)	−976(4)	247.1(13)	29(2)
C(5)	918(4)	−2592(4)	152.8(13)	32(2)
C(6)	0(4)	−3635(4)	557.6(13)	30(2)
C(7)	−321(4)	−3109(4)	1043.3(13)	25(2)
C(8)	0	596(4)	1667	21(2)
C(9)	−650(5)	1050(4)	1232.7(12)	29(2)
C(10)	−648(4)	2466(4)	1235.4(13)	29(2)
C(11)	0	3516(4)	1667	27(3)
N(2)	−5605(8)	−5157(8)	−101(2)	61(3)
C(16)	−6420(9)	−4498(10)	−412(3)	63(4)
N(1)	−4905(10)	−3114(9)	918(4)	56(4)
C(12)	−4089(10)	−3537(13)	1332(4)	59(3)
C(13)	−5160(13)	−1860(10)	1124(4)	68(6)
C(14)	−6444(8)	−4529(11)	787(3)	58(3)
C(15)	−6345(12)	−5719(10)	438(4)	62(5)
N(1′)	−3177(9)	−4882(10)	−955(3)	50(4)
C(12′)	−2741(14)	−4301(11)	−1523(3)	72(6)
C(13′)	−2205(11)	−5550(12)	−786(4)	61(4)
C(14′)	−4863(9)	−6104(11)	−940(3)	65(3)
C(15′)	−5634(12)	−6467(10)	−398(4)	66(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-ray Structure of $[Ph_3CRb{\cdot}PMDTA]_n$ (2). Unlike **1**, **2** crystallizes in a polymeric zigzag arrangement (Figure 3). Table IV gives geometrical information, and Table V, fractional coordinates and isotropic displacement parameters. Each rubidium cation bridges two trityl moieties by η^6-interactions with two phenyl rings. The coordination sphere is completed by a PMDTA ligand [Rb–N: 296.4(7)–317.3(9) pm].

---

(39) (a) Atwood, J. L.; Hrncir, D. C.; Priester, R. D.; Rogers, R. D. *Organometallics* **1983**, *2*, 985. (b) Atwood, J. L.; Hrncir, D. C.; Rogers, R. D. *J. Inclusion Phenom.* **1983**, *1*, 199. (c) Atwood, J. L.; Crissinger, K. D.; Rogers, R. D. *J. Organomet. Chem.* **1978**, *155*, 1. (d) Atwood, J. L. *J. Inclusion Phenom.* **1985**, *3*, 113. (e) Atwood, J. L. *Recent Dev. Sep. Sci.* **1977**, *3*, 195.

(40) Hoffmann, D.; Schleyer, P. v. R. To be published.

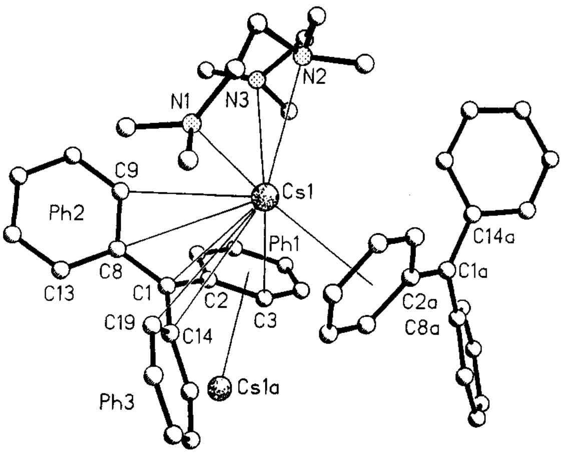

Figure 4. Molecular structure of $[Ph_3CCs{\cdot}PMDTA]_n$ (3).

The Rb–C distances range between 335.1(4) and 364.3(3) pm with a ring center–Rb distance of 319.0 pm. The cation location above the phenyl ring is slightly unsymmetrical and the cation is tilted toward the para and meta positions. There are two 2-fold axes of symmetry, one through C(1), C(8), and C(11) and one through Rb(1) and the center of the PMDTA molecule. The former results in the equivalence of two phenyl rings of the trityl moiety. The "inner" core of the carbanion is planar and no metal–C(1) interaction is present. The phenyl rings describe torsional angles of 28.2° (twice) and 39.2° with regard to the central C(1)C(2)C(8)C(14) plane. As with K^+ the Rb cation coordinates to the phenyl ring with the smallest twist angle, inducing the greatest π-electron-delocalization. The phenyl ring deformation [C(3)C(2)C(7) = 114.20(29)° and C(9)C(8)C(9a) = 114.78(39)°] is comparable to that in 1.

In contrast to 1, 2 crystallizes without coordinating the solvent THF. Instead, Rb^+ interacts with a second trityl moiety. This results in the formation of a polymeric chain and an overall coordination number of 15 for the larger Rb^+ cation. Coordination to a second PMDTA molecule would probably be unfeasible sterically. The larger Rb^+–phenyl ring distance allows the interaction with another carbanion. This situation probably would be unfavorable in 1 due to the steric hindrance of the bulky triphenylmethyl groups.

Very few organorubidium compounds are known.[8,41] Structures with π-delocalized carbanions include $Rb_2COT{\cdot}$diglyme (Rb–C: 310–343 pm)[42] and *N*-rubidiocarbazole·PMDTA[43] (Rb–C: 342–368 pm). A η^6-coordination is also found in graphite intercalates, where the Rb–C distances (Rb–C: 316 and 336 pm) were approximated from the layer separations.[36] Ab initio calculations on unsolvated allylrubidium predict distances of 302.5 and 305.2 pm for the bridged form.[29] Upon solvation these would be expected to lengthen by approximately 20 pm[8] and thus agree well with the experimental values.

X-ray Structure of $[Ph_3CCs{\cdot}PMDTA]_n$ (3). Like 2, 3 crystallizes as a polymer. The Cs cation also bridges different trityl moieties, but in a quite unexpected fashion (Figure 4). The coordination sphere is completed by one PMDTA ligand. Selected bond lengths and bond angles are given in Table VI. Table VII contains fractional coordinates and isotropic displacement parameters; Table VIII summarizes the crystallographic data for 1–3.

Table VI. Selected Bond Lengths (pm) and Angles (deg) of $[Ph_3CCs{\cdot}PMDTA]_n$ (3)

Cs(1)–N(3)	332.5(14)	Cs(1)–N(1)	316.0(17)
Cs(1)–C(2)	344.5(4)	Cs(1)–N(2)	330.1(4)
Cs(1)–C(8)	382.0(4)	Cs(1)–C(1)	334.8(4)
Cs(1)–C(14)	370.9(4)	Cs(1)–C(3)	343.4(4)
Cs(1)–C(2a)	375.1(4)	Cs(1)–C(9)	378.6(5)
Cs(1)–C(4a)	353.3(4)	Cs(1)–C(19)	378.5(4)
Cs(1)–C(6a)	357.4(4)	Cs(1)–C(3a)	362.2(4)
C(1)–C(2)	143.8(5)	Cs(1)–C(5a)	350.7(4)
C(1)–C(14)	146.8(5)	Cs(1)–C(7a)	369.3(4)
C(2)–C(7)	142.4(5)	C(1)–C(8)	146.3(6)
C(4)–C(5)	139.5(6)	C(2)–C(3)	142.4(6)
C(6)–C(7)	138.2(6)	C(3)–C(4)	138.1(6)
C(8)–C(13)	140.9(6)	C(5)–C(6)	138.1(6)
C(10)–C(11)	136.2(10)	C(8)–C(9)	139.4(6)
C(12)–C(13)	137.8(7)	C(9)–C(10)	139.0(7)
C(14)–C(19)	141.1(6)	C(11)–C(12)	136.8(10)
C(16)–C(17)	137.6(6)	C(14)–C(15)	140.9(6)
C(18)–C(19)	137.9(6)	C(15)–C(16)	138.0(6)
		C(17)–C(18)	138.3(7)

N(1)–Cs(1)–N(3)	87.87(29)	N(3)–Cs(1)–N(2)	56.47(18)
N(1)–Cs(1)–N(2)	54.69(20)	C(1)–Cs(1)–C(3)	43.52(9)
C(1)–Cs(1)–C(2)	24.38(9)	C(3)–Cs(1)–C(2)	23.90(9)
C(2)–C(1)–C(8)	121.65(34)	C(2)–C(1)–C(14)	121.36(33)
C(8)–C(1)–C(14)	116.99(34)	C(3)–C(2)–C(7)	113.95(35)
C(3)–C(2)–C(1)	123.05(35)	C(7)–C(2)–C(1)	122.98(35)
C(4)–C(3)–C(2)	123.37(38)	C(3)–C(4)–C(5)	120.34(40)
C(6)–C(5)–C(4)	118.35(38)	C(7)–C(6)–C(5)	121.48(39)
C(6)–C(7)–C(2)	122.50(38)	C(9)–C(8)–C(13)	115.71(41)
C(9)–C(8)–C(1)	123.68(41)	C(13)–C(8)–C(1)	120.57(39)
C(10)–C(9)–C(8)	121.80(54)	C(11)–C(10)–C(9)	120.98(59)
C(10)–C(11)–C(12)	118.64(53)	C(11)–C(12)–C(13)	121.43(62)
C(12)–C(13)–C(8)	121.42(55)	C(15)–C(14)–C(19)	115.01(35)
C(15)–C(14)–C(1)	123.34(35)	C(19)–C(14)–C(1)	121.64(35)
C(16)–C(15)–C(14)	122.37(38)	C(17)–C(16)–C(15)	120.64(39)
C(16)–C(17)–C(18)	119.15(40)	C(19)–C(18)–C(17)	120.19(43)
C(18)–C(19)–C(14)	122.64(40)		

The chelating triamine ligand is coordinated rather unsymmetrically [Cs–N: 316.0(17)–330.1(4) pm]. Usually the weakest interaction of the cation is to the central nitrogen of PMDTA. Instead, there are *two* long Cs–N distances in 3; the longest involves one of the terminal nitrogens.

The Cs^+ interacts in a η^6-fashion with the phenyl ring of one carbanion [Cs–C: 350.7(4)–375.1(4)], with a Cs to ring center distance of 333.3 pm. The location is slightly unsymmetrical (29.4 pm off-center) with closer contacts to the meta and para positions of this ring. In contrast, the second triphenylmethyl moiety is coordinated in a propeller-like arrangement with three shorter and four longer distances [Cs–C: 334.8(4)–382.0(4) pm]. These involve the deprotonated C(1) atom, the ipso carbons of the three phenyl groups, and one ortho position of each ring. Interestingly, the shortest Cs–C distance is to C(1). The other two shorter contacts, to C(2) and C(3), result in one "stronger" benzylic interaction. Thus, there are two different cation locations in the polymer, as illustrated in Figure 4. Both locations involve principally the phenyl ring with the smallest torsional angle [23.6° with respect to the C(2)C(8)C(14) plane]. The propeller-like interaction (Cs(1) in Figure 5) resembles that for Na^+ in $Ph_3CNa{\cdot}$TMEDA.[6] Hard-sphere electrostatic calculations[14b] predict a very shallow energy surface for the trityl system. Several local minima are indicated for tritylcesium. In fact the coordination of Cs^+ to C(1) is the most favorable. However, all minima are very close in energy, and hence the cation adopts different positions in 3.

---

(41) Mooji, J. J.; Klaasen, A. A. K.; de Boer, E.; Degens, H. M. L.; van den Hark, T. E. M.; Noordik, J. H. *J. Am. Chem. Soc.* 1976, *98*, 6801.

(42) Noordik, J. H.; Degens, H. M. L.; Mooji, J. J. *Acta Crystallogr.* 1975, *B31*, 2144.

(43) Gregory, K. Ph.D. Thesis, Universität Erlangen-Nürnberg, 1991.

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) of $[Ph_3CCs{\cdot}PMDTA]_n$ (3)

	x	*y*	*z*	*U*(eq)[a]
Cs(1)	4004.1(2)	554.9(2)	2305.85(14)	35.4(2)
C(1)	3136(3)	−2411(4)	1730(2)	29(2)
C(2)	2994(3)	−2420(4)	2443(2)	27(2)
C(3)	2365(3)	−1539(4)	2636(2)	32(2)
C(4)	2250(3)	−1513(4)	3328(2)	38(2)
C(5)	2743(3)	−2397(5)	3876(2)	42(3)
C(6)	3354(3)	−3280(4)	3711(2)	38(2)
C(7)	3485(3)	−3292(4)	3024(2)	31(2)
C(8)	4010(3)	−2942(4)	1629(2)	36(2)
C(9)	4924(3)	−2841(4)	2158(3)	50(2)
C(10)	5744(4)	−3290(6)	2021(4)	71(3)
C(11)	5682(5)	−3873(7)	1365(5)	88(4)
C(12)	4793(5)	−4004(6)	837(4)	77(5)
C(13)	3971(4)	−3561(5)	959(3)	51(3)
C(14)	2401(3)	−1884(4)	1068(2)	29(2)
C(15)	1403(3)	−2044(4)	923(2)	35(2)
C(16)	725(3)	−1576(4)	286(2)	39(2)
C(17)	1006(3)	−911(5)	−237(2)	43(3)
C(18)	1978(4)	−721(4)	−118(3)	44(3)
C(19)	2655(3)	−1193(4)	518(2)	37(2)
N(2)	5884(3)	2517(4)	2872(2)	63(2)
C(24)	5415(4)	3718(5)	2937(3)	60(3)
N(1)	5385(10)	1260(9)	1388(8)	78(5)
N(3)	5963(8)	−90(8)	3745(9)	56(4)
C(20)	5686(9)	15(11)	1180(7)	75(7)
C(21)	4828(12)	1812(14)	685(8)	86(8)
C(22)	5892(7)	2576(10)	1628(5)	70(4)
C(23)	6494(6)	2564(14)	2373(5)	73(3)
C(25)	6488(8)	2295(10)	3666(5)	90(5)
C(26)	6307(10)	1273(9)	4020(6)	83(5)
C(27)	6458(8)	−1326(11)	3800(7)	67(4)
C(28)	5330(8)	−332(17)	4177(5)	68(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

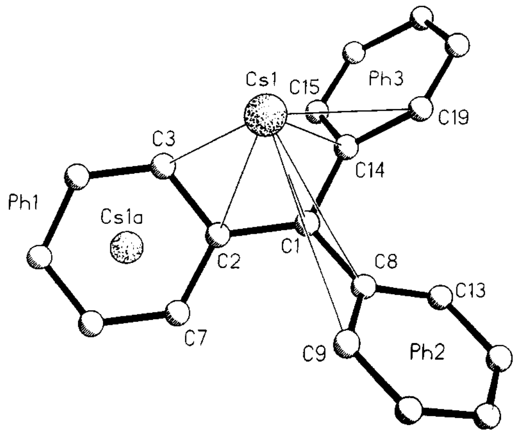

Figure 5. Projection of the molecular structure of 3 which illustrates the surrounding of the Cs cation.

Table VIII. Crystal Data for 1–3

	1	**2**	**3**
formula	$C_{32}H_{46}N_3OK$	$C_{28}H_{38}N_3Rb$	$C_{28}H_{38}N_3Cs$
fw	527.82	502.1	549.52
cryst size (mm)	0.4 × 0.5 × 0.6	0.3 × 0.5 × 0.7	0.5 × 0.5 × 0.5
space group	$P2_1/c$	$P3_121$	$P2_1/n$
a (pm)	1777.4(4)	976.7(2)	1466.8(2)
b (pm)	1012.2(2)	976.7(2)	1028.1(2)
c (pm)	1750.7(4)	2432.0(7)	1902.6(2)
α (deg)	90	90	90
β (deg)	104.79(3)	90	109.038(8)
γ (deg)	90	120	90
V (nm^3)	3.045	2.009	2.712
Z	4	3	4
ρ_c (Mg m^{-3})	1.151	1.245	1.346
μ (mm^{-1})	0.202	1.87	1.38
F(000)	1144	792	1128
2θ range (deg)	8–45	8–45	8–45
no. of reflns measd	2864	1783	4922
no. of unique reflns	2681	1727	3525
no. of restraints	255	203	511
R_w2 (all data)	0.139	0.0687	0.088
$R1$ ($F>4\sigma(F)$)	0.052	0.0284	0.033
*g*1	0.053	0.039	0.05
*g*2	5.20	1.44	4.50
refined param	353	206	380
highest diff peak (10^{-6} e pm^{-3})	0.41	0.23	0.68
abs corr		semiempirical	semiempirical

All other geometrical features of **3** are similar to those in **1** and **2**: the C(1)C(2) bond is shortened significantly [143.8(5) pm], and the ring deformation at the ipso and para positions is most pronounced in the phenyl ring with the smallest twist angle [e.g. C(3)C(2)C(7) = 113.95(35)°]. The triphenylmethyl moiety is essentially planar, with C(1) being 0.7(4) pm out of the plane defined by C(2)C(8)C(14). The angles around C(1) differ insignificantly from 120°.

Multihapto interactions of Cs again are found in graphite intercalates (Cs–C: 329 pm).[36] In *N*-cesiocarbazole·PMDTA[20c] there are two different dimers in the crystal structure exhibiting different cation locations. The range of Cs–C distances (323–375 pm) agrees quite well with those in **3**. However, the Cs–N contacts to the PMDTA ligand are shorter than in **3**, where a tighter interaction might be prevented due to steric interaction with the carbanions. Several other structures involve η^6-type coordinations of cesium to xylene[39d,44] or toluene[39d,e] on interstitial spaces. In $Cs[Al_7O_6Me_{16}]{\cdot}3C_6H_5Me$, the cation is encapsulated by as many as three toluene molecules and has 21 carbon contacts overall![39a] Ab initio calculations on unsolvated bridged allylcesium predict somewhat shorter (323 pm) Cs–C contacts, as expected.[29]

NMR Results for $[Ph_3CCs{\cdot}PMDTA]_n$ (3). UV investigations show Ph_3CLi to be a 39:1 SSIP/CIP mixture in THF at 25 °C.[2c] The SSIP:CIP ratio is reduced to 2:1 for Ph_3CK. NMR studies reveal that Ph_3CNa is a 1:10 SSIP/CIP mixture.[2b] Molecular weight determinations demonstrate Ph_3CNa to be monomeric in THF at 30 °C.[45] Likewise, **3** can be expected to be exclusively a monomeric CIP in THF.

The structure of **3** in THF-d_8 solution was investigated by means of the ^{133}Cs, ^1H HOESY method,[24,46] a valuable tool for revealing agostic interactions between cesium and hydrogen. The corresponding two-dimensional spectrum of **3** is shown in Figure 6. Two intense cross peaks are observed. One includes the ortho aromatic protons whereas the other involves the CH_3 groups of the triamine ligand. The extreme upfield shift of the ^{133}Cs signal (−64.0 ppm) may be attributed to the strong anisotropic environment of the trityl anion.[24] This indicates **3** to be a CIP under these conditions. As only a cross peak to the ortho protons is detected, the Cs^+ ion is probably attached to C(1) and experiences a similar propeller-like surrounding as in the crystal structure. Clearly, no η^6-coordination is present, since no cross peaks to the meta and para hydrogens are observed.

Ph_3CK Computations. Semiempirical MNDO calculations[47] are quite useful in predicting general structural

---

(44) (a) Rogers, R. D.; Atwood, J. L. *J. Cryst. Mol. Struct.* **1979**, *9*, 45. (b) Marsh, R. E. *J. Cryst. Mol. Struct.* **1980**, *10*, 163.

(45) Halaška, V.; Lochmann, L.; Lim, D. *Collect. Czech. Chem. Commun.* **1968**, *33*, 3245.

(46) Bauer, W. *Magn. Reson. Chem.* **1991**, *29*, 494.

(47) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

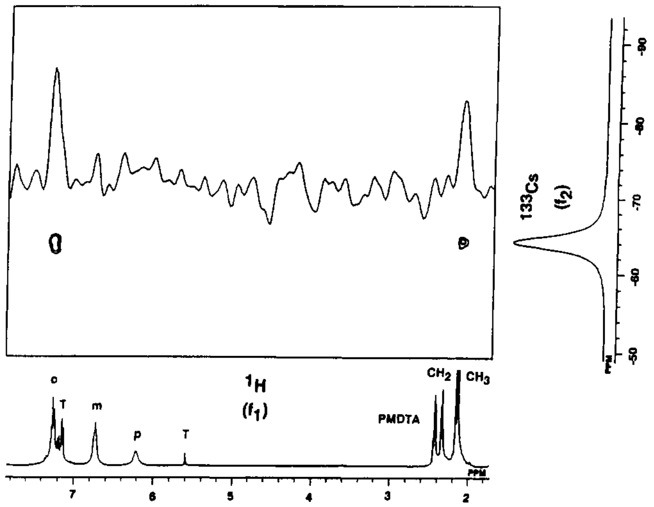

Figure 6. 2D ^{133}Cs, ^{1}H HOESY contour plot of 3 in THF-d_8 at +27 °C (saturated solution), mixing time 100 ms. Insert: f_1 trace of the ^{133}Cs signal. o, m, p = ortho, meta, and para hydrogens of the trityl anion; T = triphenylmethane resulting from hydrolysis.

Table IX. Heats of Formation ($\Delta H_f°$) and Solvation Enthalpies (ΔH_{solv}) in kcal/mol for $Ph_3CK{\cdot}L_n$ ($\Delta H_f°$ for PMDTA and THF: +15.6 and -59.3 kcal/mol)[47]

	Ph_3CK	$Ph_3CK{\cdot}PMDTA$	$Ph_3CK{\cdot}PMDTA{\cdot}THF$
$\Delta H_f°$	-64.4	-97.4	-150.3
ΔH_{solv}		-48.6	-42.2
hapticity	$2\eta^6$	η^6	η^6

features of organolithium compounds. We employed this method for 1 to test the MNDO potassium parameters, which were developed recently.[48] Ph_3CK, $Ph_3CK{\cdot}PMDTA$, and $Ph_3CK{\cdot}PMDTA{\cdot}THF$ were computed using several different starting geometries. All were optimized without symmetry constraints. Heats of formation, solvation energies, and hapticities are given in Table IX. The MNDO $\Delta H_f°$ values for PMDTA and THF were taken from the literature.[49]

In the parent species Ph_3CK, K^+ is sandwiched between two somewhat twisted phenyl rings due to the lack of additional polar ligands. Sandwiching is also known to occur in crystal structures, if polar ligands are missing.[50] Solvation of K^+ by PMDTA ($Ph_3CK{\cdot}PMDTA$) is exothermic by -48.6 kcal/mol and results in a η^6-coordination of the K^+ to one phenyl ring. However, attempts to provide additional solvation by a THF ligand (using several different starting geometries) usually led to extrusion of this second ligand, indicating that this cation was "oversolvated" by the THF. One local $Ph_3CK{\cdot}PMDTA{\cdot}THF$ minimum could be found with both PMDTA and THF coordinated. However, this species is 6.4 kcal/mol less stable than $Ph_3CK{\cdot}PMDTA$. Moreover, the THF in this $Ph_3CK{\cdot}PMDTA{\cdot}THF$ complex is only attached loosely (rather long K–O distance) and the contact between K^+ and the central nitrogen of PMDTA also is weak. When the X-ray structure was used as the starting geometry, optimization also resulted in extrusion of THF (similarly, we found THF coordination to be unfavorable in $Ph_2CHK{\cdot}THF{\cdot}PMDTA$ and in $PhCH_2K{\cdot}THF{\cdot}PMDTA$ according to the MNDO computations). Geometrical features are not discussed here. It suffices to mention that the provisional MNDO K parametrization[48] underestimates K–C distances (more than 60 pm too short) and K–N distances (about 15–20 pm too short). MNDO fails to reproduce the experimental potassium structure, as it overestimates the K–C interaction energies.

Conclusions

Multihapto interactions become more important in going along the alkali metal series from M = Li to M = Cs in $Ph_3CM{\cdot}nL$. Both the polar ligand and the carbanion compete for the cation. In 1, the "winner" is THF. This can be attributed to the high steric requirements of the triphenylmethyl moiety, which prevents the interaction with a second carbanion. For the heavier alkali metals, Rb and Cs, M–C distances are larger so that the coordination to a second carbanion is favored over the coordination to additional polar ligands, even though these are abundant in solution. Hence, one-dimensional polymers result.

Experimental Section

All manipulations were carried out under an argon atmosphere by using standard Schlenk as well as needle/septum techniques. All solvents were freshly distilled from Na/K alloy under argon. PMDTA was dried according to common procedures and distilled from Na/Pb alloy. KO^tBu was used without further purification as purchased from Aldrich. RbO^tBu and CsO^tBu were prepared by the reaction of the metals with ^tBuOH in THF. In the case of cesium the reaction was complete within 2 h; in the case of rubidium the reaction requires refluxing for 1 week. THF was removed in vacuo, and the products were dried at a high vacuum line for several hours. The white powders can be stored indefinitely under argon.

$Ph_3CK{\cdot}THF{\cdot}PMDTA$ (1). Triphenylmethane (1.059 g, 4.3 mmol) was dissolved in 5 mL of THF. At -20 °C 2.7 mL of ^{n}BuLi (1.6 M in hexane; 4.3 mmol) was added and the dark red solution was allowed to warm to room temperature. To this was added a solution of 0.504 g (4.5 mmol) of KO^tBu in 5 mL of THF. After 1 h nearly all of the THF was removed under reduced pressure and 25 mL of toluene as well as 4.8 mL (22.5 mmol) of PMDTA was added. The solution was cooled to -30 °C. After 1 week dark red crystals of X-ray quality had formed. Yield: 1.40 g (61%), first batch. Anal. Calcd for $C_{32}H_{46}N_3OK$: C, 72.82; H, 8.78; N, 7.96. Found: C, 72.88; H, 8.94; N, 8.01. ^{1}H NMR (400 MHz, THF-d_8), in ppm: δ 7.56 (6 H, d, J = 8.2 Hz, *o*-H), 6.63 (6 H, dd, J = 7.0, 8.2 Hz, *m*-H), 6.12 (3 H, t, J = 7.0 Hz, *p*-H); PMDTA signals at δ 2.41 and 2.31 (4 H, t, J = 6.7 Hz, N-CH_2), 2.21 (3 H, s, N-CH_3), 2.16 (12 H, s, N-CH_3). ^{13}C NMR (100 MHz, THF-d_8), in ppm: δ 148.70 (*ipso*-C), 129.28 (*m*-C), 123.53 (*o*-C), 114.49 (*p*-C), 88.71 (C(1)); PMDTA signals at δ 58.61 and 57.14 (CH_2), 46.07 (CH_3, terminal), 43.01 (CH_3, central).

$[Ph_3CRb{\cdot}PMDTA]_n$ (2). The reaction was carried out as described for 1, using 1.06 g (4.3 mmol) of Ph_3CH, 688 mg (4.3 mmol) of Rb^tOBu, 2.7 mL (4.3 mmol) of ^{n}BuLi (1.6 M solution in hexane), and 10 mL of THF. Addition of the Rb^tOBu solution to the Ph_3CLi solution caused a deepening of the red color and significant warming. After 1 h ca. three-fourths of the solvent was removed under reduced pressure and 30 mL of toluene was added, whereupon a red solid precipitated. This was dissolved by dropwise addition of 5 mL (23.4 mmol) of PMDTA under gentle heating. Cooling the dark red solution to room temperature afforded a microcrystalline precipitate. Crystals of X-ray quality were obtained from the filtrate after storing it at +4 °C for 2 days. Total yield: 2.026 g (93%). Anal. Calcd for $C_{28}H_{38}N_3Rb$: C, 66.98; H, 7.63; N, 8.37. Found: C, 67.02; H, 7.84; N, 8.43. ^{1}H

---

[48] Havlas, Z. Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, unpublished results.

[49] Kaufmann, E.; Gose, J.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 2577.

[50] (a) Schmidt, H.-J.; Rewicki, D. *Acta Crystallogr.* **1984**, *A40*, C-293. (b) Bladauski, D.; Dietrich, H.; Hecht, H.-J.; Rewicki, D. *Angew. Chem.* **1977**, *89*, 490; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 474.

NMR (400 MHz, THF-d_8), in ppm: δ 7.53 (6 H, d, J = 8.1 Hz, *o*-H), 6.64 (6 H, dd, J = 7.0, 8.1 Hz, *m*-H), 6.10 (3 H, t, J = 7.0 Hz, *p*-H); PMDTA signals at δ 2.40 and 2.30 (4 H, t, J = 6.3 Hz, N-CH_2), 2.17 (3 H, s, N-CH_3), 2.14 (12 H, s, N-CH_3). ^{13}C NMR (100 MHz, THF-d_8), in ppm: δ 148.77 (*ipso*-C), 128.96 (*m*-C), 123.56 (*o*-C), 114.44 (*p*-C), 88.51 (C(1)); PMDTA signals at δ 58.50 and 57.09 (CH_2), 45.98 (CH_3, terminal), 42.78 (CH_3, central).

It should be noted that crystallization of 1 and 2 is prevented if too much THF is present in the solutions.

[Ph$_3$CCs·PMDTA]$_n$ (3). At −20 °C 1.9 mL (3.1 mmol) of ^{n}BuLi (1.6 M solution in hexane) was added to a solution of 0.759 g (3.10 mmol) of Ph$_3$CH in 5 mL of THF. The reaction mixture warmed to room temperature, and a fine suspension of CsO^{t}Bu in 10 mL of THF was added (exothermic reaction). After 7 h most of the precipitate had dissolved and 10 mL (46.7 mmol) of PMDTA and 20 mL of toluene were added. The dark red solution was filtered and concentrated to ca. three-fourths of its original volume. Cooling it briefly to −80 °C and storing it at +4 °C for 2 weeks yielded red crystals suitable for X-ray analysis. Yield: 1.24 g (73%). Anal. Calcd for $C_{28}H_{38}N_3Cs$: C, 61.20; H, 6.97; N, 7.65. Found: C, 61.24; H, 7.19; N, 7.74. ^{1}H NMR (400 MHz, THF-d_8), in ppm: δ 7.23 (6 H, d, J = 8.5 Hz, *o*-H), 6.65 (6 H, dd, J = 7.0, 8.5 Hz, *m*-H), 6.11 (3 H, t, J = 7.0 Hz, *p*-H); PMDTA signals at δ 2.42 and 2.31 (4 H, t, J = 7.0 Hz, N-CH_2), 2.19 (3 H, s, N-CH_3), 2.15 (12 H, s, N-CH_3). ^{13}C NMR (100 MHz, THF-d_8), in ppm: δ 148.85 (*ipso*-C), 129.18 (*m*-C), 123.73 (*o*-C), 114.79 (*p*-C), 89.08 (C(1)); PMDTA signals at δ 58.79 and 57.75 (CH_2), 46.18 (CH_3, terminal), 43.22 (CH_3, central).

The ^{133}Cs,^{1}H HOESY spectrum[24] of 3 was recorded under the following conditions: saturated solution in THF-d_8; spectral widths 2500 Hz (f_2) and 2467 Hz (f_1); measuring temperature, +28 °C; mixing time, 100 ms; interpulse delay, 2.2 s; number of points in t_2, 256; number of increments in t_1: 64, zero filled to 256 complex data points in t_1; phase-sensitive pure absorption quadrature detection in f_1.

X-ray Measurements. The crystal data for the three structures 1–3 are presented in Table VIII. All data were collected at −120 °C on a Stoe-Siemens AED with Mo Kα (λ = 71.073 pm) radiation. The structures were solved by direct methods (1) or by the Patterson method (2 and 3) (SHELXS-92).[51] All non-hydrogen atoms were refined anisotropically (SHELXL-92).[52] For hydrogen atoms the riding model was used; refinement was on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o)^2 + (g1P)^2 + g2P$ with $P = (F_o + 2F_c^2)/3$.

All structures had disordered PMDTA molecules. In the refinement of the PMDTA ligands all 1–2 and 1–3 distances were restrained to be equal. Anisotropic refinement required the use of rigid bond restraints and weak ADP restraints. The latter render the corresponding U_{ij} components of neighboring atoms similar. The PMDTA molecule in 2 lies on a 2-fold axis. Because of this symmetry we refined one complete PMDTA with occupancies set to 0.5; the second position was generated by the 2-fold axis. That the absolute structure of 2 was correct was established by refining the Flack x-parameter[53] to −0.01(1).

The atomic coordinates and selected bond lengths and angles of structures 1–3 are found in Tables I, II, and IV–VII.

Acknowledgment. The authors gratefully acknowledge the support of this work by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. We are indebted to Chemetall GmbH (Frankfurt a. Main) for the generous gift of rubidium and cesium metal, and to the Riedel-de Haën AG (Seelze) for supplying the polyfluoropolyethers applied in crystal mounting. We especially thank Thomas Sahiri for his assistance in synthesizing 1–3.

Supplementary Material Available: Tables of crystal data, bond distances, bond angles, atomic coordinates, and anisotropic displacement parameters as well as ORTEP plots for 1–3 (30 pages). Ordering information is given on any current masthead page.

OM920597U

---

(51) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(52) Sheldrick, G. M. SHELXL-92, Göttingen, 1992.

(53) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.