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Tetraphenylbutadiene Disodium Dimethoxyethane: Solvent-Shared and Solvent-Separated Ion Tripels within a Single Crystal

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Redox reactions in solution proceed via a multidimensional network of electron transfer and contact ion formation as well as aggregation and solvation equilibria.[1] Single crystals grown, for instance, from aprotic solutions of phenyl-substituted unsaturated hydrocarbons such as ethylene, allene, or butadiene after reduction at a sodium metal mirror[2,3] not only yield anionic intermediates exhibiting severely distorted molecular skeletons and novel structural facets such as inter- and intramolecular dibenzene sodium sandwiches[3] but also provide some insight into their rather complex formation and crystallization.[2b,3] We report on the isolation and low-temperature X-ray structure determination of dark violet crystals (Figure 1)[4] unexpectedly containing the tetraphenylbutadiene dianion M^{2-} in a stoichiometric 1:1 ratio both as a solvent-shared contact ion tripel, $[M^{2-}(Na^+DME_2)_2]$, and as a solvent-separated ion tripel, $[M^{2-}][Na^+DME_3]_2$. The following structural observations (Figure 1) are emphasized.

Lattice Packing. Viewed in the *x*-direction (Figure 1A), *yz*-layers are recognized in which each the ellipsoidal (long axis ≈ 1200 pm, short axis ≈ 700 pm), solvent-separated ion tripels and the circular (average diameter ≈ 700 pm), solvent-shared contact ion tripels are arranged in *y*-horizontal strings. With respect to diagonal axes, perpendicular to each other and inclined by 35° and 55° toward the *z*-direction, both alternate chessboardlike, obviously resulting in an advantageous, rather dense packing.

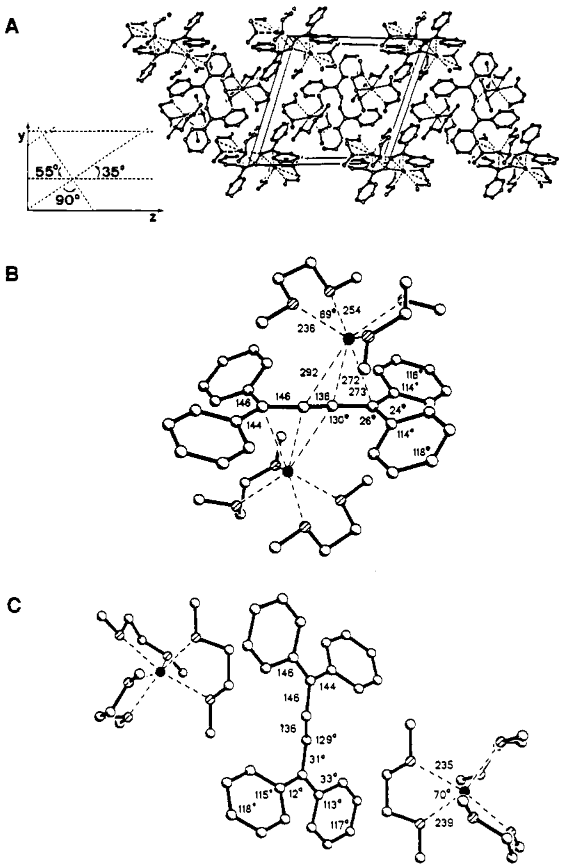

Figure 1. Single crystal structure of tetraphenylbutadiene disodium dimethoxyethane (DME).[4] (A) lattice in *x*-direction with unit cell, exhibiting horizontally alternating layers of $[M^{2-}(Na^+DME_2)_2]$ and $[M^{2-}][Na^+DME_3]_2$ and, diagonally with inclination angles of 35° and 55° toward the *z*-axis, two strings of alternating solvent-shared and solvent-separated ion tripels perpendicular to each other; (B) solvent-shared tetraphenylbutadiene disodium tetrakis(dimethoxyethane); (C) solvent-separated tetraphenylbutadiene dianion with (two) sodium tris(dimethoxyethane) countercations (●, Na; ▨, O; all distances in picometers and all angles in degrees; see text).

Dianion Molecular Structure. The CC chain bond lengths in tetraphenylbutadiene (M) of 136, 144, and 136 pm[2b,3c] are reversed on its 2-fold reduction to generate the dianion M^{2-} to 146, 136, and 146 pm, providing via C═C double-bond shift a maximum separation of the negative charges. These are delocalized predominantly in the diphenylcarbon molecular subunits as substantiated by shortened $C\text{–}C_{phenyl}$ bonds (cf.[3c] 149 in M vs 145 pm in M^{2-}), equal twisting of the phenyl rings (cf.[3c] 18° and 70° in M vs $\overline{25°}$ in M^{2-}), and decreased phenyl ipso angles due to the adjacent carbanionic centers (cf.[2b,3c] 118° in M vs 114° in M^{2-}).

Structural Differences between Solvent-Shared and Solvent-Separated Contact Ion Tripels. The dianion M^{2-} in $[M^{2-}(Na^+DME_2)_2]$, which has been separately grown pure in single crystals and structurally characterized,[2b,3c] does not exhibit significant differences from the one in $[M^{2-}][Na^+DME_3]_2$ other than slightly altered phenyl twisting angles (Figure 1B,C: $\Delta w < 14°$). In contrast, the Na^+ coordination number is reduced from seven to six, replacing three Na···C contacts of 272, 273, and 292 pm length by two Na···O ones of 235–239 pm length and shortening two other ones to the DME ligands by about 17 pm (Figure 1B,C).

The different Na^+ countercation solvation in the two ion tripels, which crystallize together in a stoichiometric 1:1 ratio under the very same conditions, would—if both were also present in solution[1d]—demonstrate that the η^3-coordination to the hydrocarbon dianion skeleton must be approximately equivalent to the

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(4) Tetraphenylbutadiene reduction: A sodium metal mirror is generated by vacuum distillation of 150 mg of Na (6.5 mmol) in a carefully dried Schlenk trap, and under Ar, 10 mL of absolute dimethoxyethane and 300 mg (0.8 mmol) of 1,1,4,4-tetraphenyl-1,3-butadiene are added. After 3 days, all sodium has vanished, and from the resulting violet blue solution, after adding an *n*-hexane layer, almost black air- and moisture-sensitive crystals have grown. Crystal structure: $[(H_5C_6)_2CHC{=}CHC(C_6H_5)_2]Na_4(H_3COCH_2\text{-}H_2COCH_3)_{10}$ (MW: 764.95 + 945.19); $a = 1232.8$ (6), $b = 1497.7$ (7), $c = 1585.9$ (8) pm; $\alpha = 98.29$ (3), $\beta = 111.08$ (4), $\gamma = 109.52$ (4)°, $V = 2455.92 \times 10^6$ pm³ (150 K); $Z = 2$, $\rho_{ber} = 1.156$ g cm^{-3}, μ(Mo Kα) = 71.07 cm^{-1}; triclinic, space group $P\bar{1}$; Siemens AED II four-circle diffractometer, 9021 measured reflexes within $3° < 2\theta < 48°$, of which are 5953 independent with $I > 1\sigma(I)$. Structure solution by direct methods (SHELXTL-PLUS), $R = 0.043$, $R_w = 0.036$, $w = 1/\sigma^2(F) + 0.0002\,F^2$, ext 0.0013 (1) C, O, Na atoms anisotropically, H isotropically refined, GOF = 1.4715, rest electron density +0.22/−0.18 e Å^{-3}. The molecules are located around crystallographic inversion centers.

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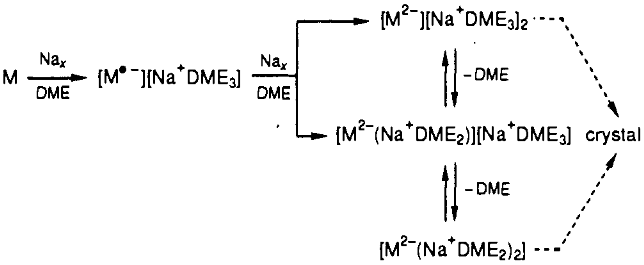
η^2-coordination by the DME chelate oxygen centers. In the crystal, however, the lattice packing cannot be neglected: supporting MNDO calculations for both the solvent-shared and solvent-separated ion tripels based on their structural data and using the sodium parameters[3b] yield approximate enthalpies of formation of 1010 and 2130 kJ mol^{-1} which, after adding the values of two DME molecules (−390 kJ mol^{-1}) for an isodesmic estimate, still differ by about 340 kJ mol^{-1}. As concerns estimates of entropy contributions, the translational one is calculated to be negligible, whereas the vibrational and rotational ones, due to the many degrees of freedom, might be substantial (calculated for [Na$^+$DME$_3$], 123 and 31 cal K^{-1} mol^{-1}). The charges for the solvent-separated and solvent-shared dianions M^{2-} are approximated to be −1.99 and −1.50.

There are numerous literature reports[2,3] on structures of related alkali organic compounds such as other tetraphenylbutadiene salts, [M^{2-}K$^+$OR$_2$)$_2$]$_\infty$,[3c] and [M$^{\bullet-}$]·[Li$^+$DME$_3$],[5a] or other sodium (partly contact) ion multiples such as [fluorenone$^{\bullet-}$(Na$^+$DME$_2$)]$_2$,[1h] [tetraphenylbutatriene$^{\bullet-}$]·[Na$^+$DME$_3$],[2b] [terphenyl$^{\bullet-}$]·[Na$^+$DME$_3$],[5b] or [9,10-diphenylanthracene$^{\bullet-}$]·[Na$^+$(THF)$_6$],[5c] which allow the following generalizations[2b] of countercation solvation. The smaller the cation Me$^+$, i.e., the larger its effective ionic charge $1/r_{\mathrm{Me}^+}$ and the stronger the partly chelating ether ligand complexation, the more likely the crystallization of solvent-separated complexes. This is exemplified especially by the polymeric diethyl ether singly solvated K$^+$ and the monomeric 3-fold(!) DME-solvated Li$^+$ salts of the anionic tetraphenylbutadiene species quoted above[3c,5a] with the two structurally different Na$^+$ ion tripels, [M^{2-}(Na$^+$DME$_2$)$_2$] and [M^{2-}][Na$^+$DME$_3$]$_2$, reported here in between. As demonstrated by the dimeric fluorenone radical anion contact ion pair,[1h] preferred Me$^+$ coordination numbers are of importance and can initiate aggregation.[1d]

All of the above details are summarized in a tentative simplified proposal for the formation and crystallization of the title ion tripels, which are not impeded by steric overcrowding[2b,3] in the hydrocarbon precursor M:



The stoichiometric 1:1 crystallization of both solvent-shared and -separated ion tripels is most likely due to their advantageous lattice packing (Figure 1A). If so, the structure reported adds an interesting facet to the presently intensely reinvestigated[6a,b] problem of crystallization as a model case for self-organization of molecular entities.[6]

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Supplementary Material Available: Tables of crystal data, atomic coordinates, isotropic and anisotropic displacement factors, bond lengths and angles, and torsion angles (15 pages). Ordering information is given on any current masthead page.

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Rational Synthesis of Organometallic Bridging Sulfur Dimers and Their Conversion into Homo- and Heterometallic Cubane Complexes. Evidence for a Mechanism Involving Dimerization of Doubly Unsaturated Dinuclear Intermediates

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Because of their presence in the active sites of both electron-transfer and nonredox enzymes and cofactors,[1-4] a large number of homometallic and mixed-metal tetranuclear sulfur-bridged cubane clusters have been synthesized.[5-9] However, few rational stepwise synthetic methods for the preparation of such clusters are available, and mechanistic studies of cubane assembly reactions are even more rare.[10-12] We report here (a) a systematic preparation of a group of bimetallic bridging sulfur complexes having the general structure Cp*M(PR$_3$)S$_2$IrCp* (**1a**, R = Me, M = Ir; **1b**, R = Me, M = Rh; **1c**, R = *p*-tolyl, M = Ir), (b) thermolysis of these materials to give cubane complexes (Cp*$_2$MIrS$_2$)$_2$ (**2**, M = Ir; **3**, M = Rh),[13] and (c) a mechanistic study of the cubane assembly reaction. Our observation that diiridium/dirhodium complex **3** is the only product obtained quantitatively from the thermolysis of **1b** provides evidence for an associative two-fragment mechanism for cubane formation rather than dissociation to monomeric units followed by reassembly into a tetramer. Kinetic studies also support this conclusion and provide evidence for the intermediacy of an unsaturated complex Cp*IrS$_2$MCp* in the cubane-forming reaction.

Treatment of Cp*Ir(PMe$_3$)SH(Cl) (**4**) with lithium hexamethyldisilazane at −78 °C resulted in the formation of Cp*Ir(PMe$_3$)S$_2$IrCp* (**1a**).[14] Single crystals suitable for an X-ray diffraction study of **1a** were obtained after recrystallization from diethyl ether at −40 °C; an ORTEP diagram of this compound is shown in Scheme I (Ir(1)–S(1) = 2.370 (4) Å; Ir(2)–S(1) = 2.273 (5) Å).[15] A different method was employed for the preparation

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