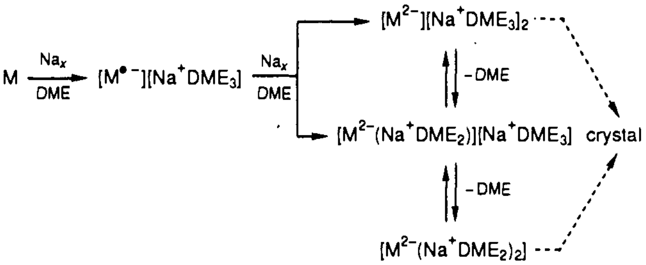
η^2-coordination by the DME chelate oxygen centers. In the crystal, however, the lattice packing cannot be neglected: supporting MNDO calculations for both the solvent-shared and solvent-separated ion tripels based on their structural data and using the sodium parameters[3b] yield approximate enthalpies 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 $[\mathrm{Na^+DME_3}]$, 123 and 31 cal K^{-1} mol^{-1}). The charges for the solvent-separated and solvent-shared dianions $\mathrm{M^{2-}}$ 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, $[\mathrm{M^{2-}K^+OR_2)_2]_\infty}$,[3c] and $[\mathrm{M^{\bullet-}}]\cdot[\mathrm{Li^+DME_3}]$,[5a] or other sodium (partly contact) ion multiples such as $[\mathrm{fluorenone^{\bullet-}(Na^+DME_2)}]_2$,[1h] $[\mathrm{tetraphenylbutatriene^{\bullet-}}]\cdot[\mathrm{Na^+DME_3}]$,[2b] $[\mathrm{terphenyl^{\bullet-}}]\cdot[\mathrm{Na^+DME_3}]$,[5b] or $[\mathrm{9,10\text{-}diphenylanthracene^{\bullet-}}]\cdot[\mathrm{Na^+(THF)_6}]$,[5c] which allow the following generalizations[2b] of countercation solvation. The smaller the cation $\mathrm{Me^+}$, 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 $\mathrm{K^+}$ and the monomeric 3-fold(!) DME-solvated $\mathrm{Li^+}$ salts of the anionic tetraphenylbutadiene species quoted above[3c,5a] with the two structurally different $\mathrm{Na^+}$ ion tripels, $[\mathrm{M^{2-}(Na^+DME_2)_2}]$ and $[\mathrm{M^{2-}}][\mathrm{Na^+DME_3}]_2$, reported here in between. As demonstrated by the dimeric fluorenone radical anion contact ion pair,[1h] preferred $\mathrm{Me^+}$ 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]

Acknowledgment. The research project Structures of Charge-Perturbed and Sterically Overcrowded Molecules is supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Chemistry, and the Humboldt Foundation (Z.H.).

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 $\mathrm{Cp^*M(PR_3)S_2IrCp^*}$ (**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 $\mathrm{(Cp^*{}_2MIrS_2)_2}$ (**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 $\mathrm{Cp^*IrS_2MCp^*}$ in the cubane-forming reaction.

Treatment of $\mathrm{Cp^*Ir(PMe_3)SH(Cl)}$ (**4**) with lithium hexamethyldisilazane at -78 °C resulted in the formation of $\mathrm{Cp^*Ir(PMe_3)S_2IrCp^*}$ (**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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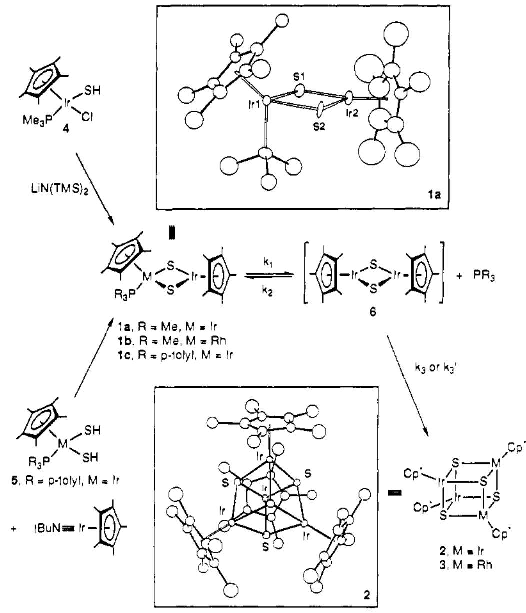
(15) Compounds **1a–c** are stable when the coordination sphere of only one metal is occupied by phosphine; all attempts to attach a second phosphine moiety to these molecules gave only starting material.

Scheme I



of Cp*Ir(P(p-tolyl)$_3$)S$_2$IrCp* (**1b**) and Cp*Rh(PMe$_3$)S$_2$IrCp* (**1c**). Treatment of Cp*Ir≡N-*t*-Bu[16] with Cp*Ir(P(p-tolyl)$_3$)(SH)$_2$ (**5**) resulted in the expulsion of *tert*-butylamine and the formation of **1b** in 94% yield. Likewise, when Cp*IrN-*t*-Bu was treated with Cp*Rh(PMe$_3$)(SH)$_2$,[17] **1c** was obtained in 93% yield. These reactions are summarized in Scheme I.

Heating the PM$_3$-substituted diiridium complex **1a** to 150 °C in toluene resulted in the loss of phosphine and the slow formation of a new complex, the iridium–sulfur cubane cluster (Cp*IrS)$_4$ (**2**). The reaction was 44% complete in 8 h, after which time little additional conversion was observed (probably due to inhibition from released phosphine; see below). Candy-apple-red X-ray quality crystals were obtained directly from the reaction mixture upon cooling to room temperature. An ORTEP diagram of this complex is shown in Scheme I (iridium–sulfur distance = 2.372 (3) Å). Heating **1c** in benzene resulted in loss of triarylphosphine at substantially lower temperatures (reaction complete in 8 h at 77 °C) and once again gave cubane **2**. Heating the mixed-metal dinuclear complex **1b** to 90 °C in benzene provided only the dirhodium–diiridium sulfur cluster (Cp*IrS)$_2$(Cp*RhS)$_2$ (**3**). The structure of compound **3** was deduced from ^{1}H and ^{13}C{^{1}H} NMR spectra, mass spectral data, elemental analysis, and an X-ray structure which, although disordered as to the positions of the rhodium and iridium atoms, did confirm the cubane-like structure.

Possible mechanisms for the formation of the cubanes include the production of a "monomeric" intermediate (Cp*IrS) which undergoes self-assembly to produce the cluster. This possibility can be eliminated by the fact that thermolysis of Ir/Rh complex **1b** leads only to cubane **3**; no RhIr$_3$S$_4$, Rh$_3$IrS$_4$, Rh$_4$S$_4$, or Ir$_4$S$_4$ clusters are observed. The rate of disappearance of **1a** is also found to be strongly dependent on the concentration of PMe$_3$: addition of 1 equiv of PMe$_3$ results in complete inhibition of the reaction at 150 °C. Thus we conclude that the initial step in the cubane assembly reaction involves reversible dissociation of phosphine from the dinuclear starting material (steps k_1 and k_2 illustrated in Scheme I) to give coordinatively unsaturated intermediate **6**.

Two other important mechanistic alternatives can be distinguished kinetically. It is possible (a) that intermediate **6** dimerizes (with rate constant k_3) to give the cubane or (b) that it attacks a molecule of starting material (rate constant k_3') to give cubane with loss of a second phosphine. Application of the steady-state approximation to these mechanisms gives quite complicated equations, especially in the case of mechanism a where the intermediate goes on to product in a bimolecular step.[18] Instead of attempting a full analytical solution of the kinetics, we derived the simpler rate laws for limiting cases at low and high [PR$_3$]. At low [PR$_3$], it is likely that k_3 or k_3' in Scheme I would be faster than k_2[PR$_3$]. With this assumption, both mechanisms predict a rate law that is first order in starting complex **1** and zero order in phosphine. However, at high [PR$_3$] rapid reversibility of step 1 should hold (i.e., $k_2[\mathrm{PR}_3] \gg k_3$ or k_3'), and in this case the two mechanisms are distinguishable: a leads to rate law 1 and b leads to rate law 2.

$$\text{rate} = \frac{k_3 k_1^2 [\mathbf{1}]^2}{k_2^2 [\mathrm{PR}_3]^2} \tag{1}$$

$$\text{rate} = \frac{k_1 k_3' [\mathbf{1}]^2}{k_2 [\mathrm{PR}_3]} \tag{2}$$

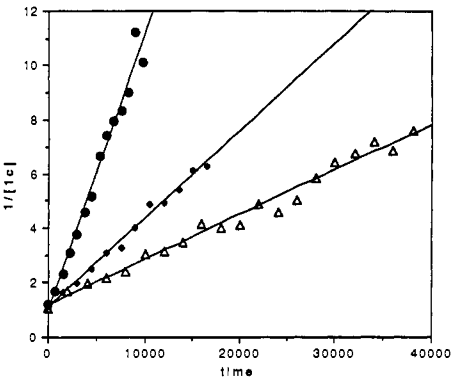


Figure 1. Dependence of k_{obsd} on the concentration of added P(p-tolyl)$_3$ in the thermolysis of **1c** (7.2 × 10^{-3} M) at 98 °C: ●, [P(p-tolyl)$_3$] = 0.129 M, k_{obsd} = 1.0 × 10^{-3} M^{-1} s^{-1}; ◆, [P(p-tolyl)$_3$] = 0.240 M, k_{obsd} = 3.2 × 10^{-4} M^{-1} s^{-1}; △, [P(p-tolyl)$_3$] = 0.298 M, k_{obsd} = 1.7 × 10^{-4} M^{-1} s^{-1}. The standard deviation of the slopes of the lines is ≤3.2%.

Monitoring the triarylphosphine-substituted complex **1c** at 77 °C by ^{1}H NMR spectrometry in the absence of added phosphine led to a reaction that was cleanly first order in starting material (e.g., k_{obsd} = 3.0 × 10^{-5} s^{-1}). However, when a high (flooding) concentration of P(p-tolyl)$_3$ was used at 98 °C, the rate law changed to become cleanly second order in **1c**. Repeating the reaction at different excess concentrations of phosphine demonstrated that the rate was *inversely dependent on the square of the concentration* of added phosphine (Figure 1) as predicted by mechanism a.

In summary, we have identified a system in which both homo- and heteronuclear bridging sulfur dimers can be prepared, and these can be converted cleanly to cubane complexes. Our mechanistic studies provide strong evidence that the cubane assembly takes place by direct dimerization of coordinatively unsaturated dimeric species. We hope that this work will stimulate similar mechanistic studies of other important cluster-forming reactions.

Acknowledgment. We are grateful for support of this work from the National Science Foundation (Grant No. CHE-9113261). We also acknowledge a gift of iridium chloride from the Johnson-Matthey-Aesar/Alfa metal loan program.

Supplementary Material Available: Listing of spectroscopic and analytical data for complexes **1a–5** and X-ray diffraction data, including ORTEP diagrams, crystal and data collection parameters, positional and anisotropic thermal parameters, and intermolecular distances and angles, for **1a**, **2**, and **3** (18 pages). Provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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