

predominantly in the CC singly bonded and twisted diphenylcarbanion molecular halves and partly—owing to the sandwich complexation of Na₂—also in the “one-dimensional” bands, which are separated from each other by the alternately “left-right” arranged counteranions $^{\ominus}\text{Na}(\text{OR})_2$. The unexpected formation of this solid-state structure may be tentatively rationalized by the following literature observations: tetraphenylethylene radical anion M^{\ominus} , generated by single electron transfer, is of comparable structure to the sterically overcrowded neutral molecule $M^{[11a]}$ and, therefore, in ether solution only forms “solvent separated”, radical-ion pairs $(M^{\ominus}_{\text{sol}} \cdots \text{Na}^{\oplus}_{\text{sol}})^{[11a]}$ and thus preferentially disproportionates via $2 M^{\ominus} \rightarrow M + M^{2\ominus}$ to its dianion.^[11b] Owing to considerable structural changes, this can be stabilized as a contact ion pair $[M^{2\ominus}\text{Na}_n^{\oplus}]^{(2-n)\ominus}$ ($n \leq 2$), and presumably crystallizes under the reaction conditions chosen—like the dimer [fluorenone $^{\ominus}\text{Na}^{\oplus}$ -(DME)₂]₂^[11b]—in the band structure reported.

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- [1] a) H. Bock, K. Ruppert, K. Merzweiler, D. Fenske, H. Goesmann, *Angew. Chem.* 101 (1989) 1715, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1684; b) cf. also H. Bock, H.-F. Herrmann, D. Fenske, H. Goesmann, *ibid.* 100 (1988) 1125 and 27 (1988) 1067, and references cited therein.
- [2] Remark by J. D. Dunitz, ETH Zürich, on the occasion of a lecture at the Universität Frankfurt on January 9, 1989.
- [3] Cf. reviews on the structures of organolithium compounds (W. N. Setzer, P. von R. Schleyer, *Adv. Organomet. Chem.* 24 (1985) 353) as well as on organometallic derivatives of higher alkali metals (C. Schade, P. von R. Schleyer, *ibid.* 27 (1987) 169), and references cited therein.
- [4] K. Ruppert, *Diplomarbeit*, Universität Frankfurt 1989. Approximative geometry-optimized MNDO calculations neglecting the counteranions predict for the fictive ethylene dianion the following (gas-phase) data. $\Delta E_{\text{total}} \approx 10$ eV, $\omega = 90^\circ$, $d_{\text{CC}} \approx 140$ pm (for Li₂C₂H₄ cf. A. J. Kos, E. D. Jemmis, P. von R. Schleyer, R. Gleiter, U. Fischbach, J. A. Pople, *J. Am. Chem. Soc.* 103 (1981) 4996). For the tetraphenylethylene dianion, the calculations started from the crystal structure data (exception: hexagonal C₆ rings) and on partial MNDO optimization (keeping $d_{\text{CC}} = 150$ pm and $\omega = 56^\circ$ constant) the bond distances $d_{\text{C-phenyl}} \approx 145$ pm and twist angles $\omega(\text{phenyl}) \approx 35^\circ$ result. The MNDO charge distribution is: C1 = C2 = -0.29, C^{ortho}_{phenyl} = -0.13, C^{para}_{phenyl} = -0.21. Calculations with cation simulating “sparkles” do not converge, cf. [8].
- [5] Cf. [2]. Vacuum distillation of 70 mg (3 mmol) of Na in a Schlenk trap under Ar yields a sodium mirror, which reacts with 505 mg (1.5 mmol) tetraphenylethylene in 30 mL of water-free diethyl ether under Ar at room temperature within 24 h to a dark-red solution. ESR and UV/VIS spectra ($\nu_{\text{m}} = 21\,000$ cm⁻¹) do not provide evidence for the radical anion as an intermediate, which in its blue dimethoxyethane solution shows a characteristic absorption ($\nu_{\text{m}} = 15\,400$ cm⁻¹). The green, shiny metallic crystals precipitated are extremely air-sensitive and, therefore, have to be handled in a stream of N₂.
- [6] Crystal structure analysis of C₂₆H₂₀Na₂ · 2 O(C₂H₅)₂: space group P2₁/n, Z = 4, lattice constants (210 K): a = 997.8(5), b = 1545.4(9), c = 2025.1(10) pm, β = 100.59°(4), V = 3069.5 × 10⁶ pm³ · μ(MoKα) = 0.63 cm⁻¹, Siemens AED-2 diffractometer, 3° < 2θ < 52°, 6199 reflections, of which 2932 are independent with I > 2σ(I). Direct methods, Na, O, and C positions anisotropic, detected H positions isotropically refined; R = 0.099, R_w = 0.102. The unsatisfactory high R value is due to decomposition of the crystal in the X-ray beam; for the decomposition correction, an approximate linear relation has been assumed. Deviations in structural parameters (Figs. 1–3): ±1.5 pm and ±0.8°; angle sums of all six-membered rings 720 ± 0.5°. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-51466, the names of the authors and the literature citation.
- [7] A. Hoekstra, A. Vos, *Acta Crystallogr. B* 31 (1975) 1722. Selected structural parameters: C1–C2 136 pm, C3–C1–C2–C15 8.4°, C15–C2–C21 114.4°, C–C₆H₅ 150 pm, C1–C2–C₆H₅ 43–57°, angle sum of all six-membered rings 720°. Cf. also the structure of the dianion of bifluorene, prepared by deprotonation (M. Walczak, G. D. Stucky, *J. Organomet. Chem.* 97 (1975) 313), which possesses a CC bond distance elongated from 139 pm to 149 pm and a dihedral angle ω(C₂C–CC₂) = 48°. In the largely interaction-free dianion of tetracyanoethylene (D. A. Dixon, J. S. Miller, *J. Am.*

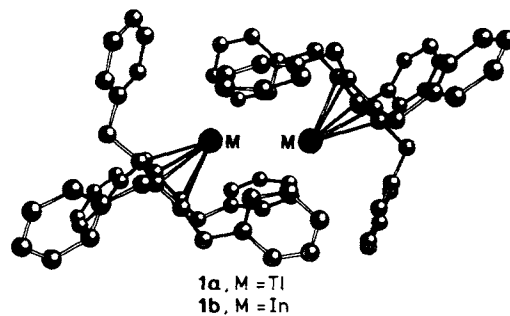
Chem. Soc. 109 (1987) 3656) a central CC bond distance of 149 pm and a dihedral angle of 87° are observed. After submission of this publication, the crystal structure of tetrakis(trimethylsilyl)ethylenedilithium was published (A. Sekiguchi, T. Nakanishi, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* 111 (1989) 3748); the dihedral angle (ω = 34°) is only slightly increased relative to that (ω = 34°) of the sterically overcrowded parent molecule.

- [8] Cf. M. A. Fox, D. Shultz, *J. Org. Chem.* 53 (1988) 4386, and references cited therein. The MO calculations, according to which a planar dianion should be about 40 kJ mol⁻¹ more stable than the one exhibiting orthogonal (H₅C₆)₂C molecular halves, neglect the effect of the counteranions (cf. also [2]); cf. also *J. Am. Chem. Soc.* 111 (1989) 6311.
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- [11] Cf. [8] and references cited therein, especially a) R. C. Roberts, M. Szwarcz, *J. Am. Chem. Soc.* 87 (1965) 5542; b) J. F. Garst, *ibid.* 93 (1972) 6312 and references cited therein.

Tl^I–Tl^I Interactions in the Molecular State— an MO Analysis**

By Christoph Janiak and Roald Hoffmann*

Are direct bonds possible between Tl^I or In^I atoms? The question is raised by the pentabenzylcyclopentadienylthallium dimer, [(PhCH₂)₅C₅Tl]₂ (**1a**)^[1] and its isostructural indium analogue (**1b**),^[2] both synthesized by Schumann and co-workers.^[3]



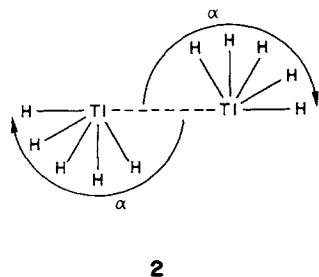
Both centrosymmetric dimers feature a relatively covalent metal–cyclopentadienyl interaction, a metal–metal contact of 363 pm and a Cp'(centroid)–M–M angle of 131.8° (**1a**) or 136.5° (**1b**).^[1, 2] Unambiguous Tl^I–Tl^I or In^I–In^I bonds are not yet known in molecular complexes, as they are, for example, for the related Ge^{II} or Sn^{II} in [(Me₃Si)₂CH]₂M₂.^[4] To us a Tl⋯Tl contact only about 20 pm longer than in Tl metal,^[5] occurring in the absence of bridging, is definitely suggestive of direct metal–metal bonding. A few bridged complexes with similar length Tl⋯Tl contacts are also

[*] Prof. R. Hoffmann, Dr. C. Janiak
Department of Chemistry and Materials Science Center
Cornell University, Ithaca, NY 14853 (USA)

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known.^[6] However, the apparent consensus and a brief theoretical study^[7] interpret these as resulting from the bridging coordination. A short Tl–Tl bond (284 pm), albeit between Tl^{II} centers, has recently been found in Tl_{0.8}Sn_{0.6}Mo₇O₁₁.^[8]

An analysis of a model C₅H₅Tl dimer led us to focus on the significant role of the L–Tl–Tl angle (L = ligand). The gist of what we observe is retained as we simplify the C₅H₅ ligand to OCH₃,^[6e] Te,^[6f] and H. So in the sequel we focus on the simplest model, namely, HTITlH (**2**), shown in



Scheme 1. Definition of the angle α in HTITlH (**2**).

Scheme 1 with the important H–Tl–Tl angle α . Figure 1 shows a plot of the calculated overlap population as a function of α .^[9]

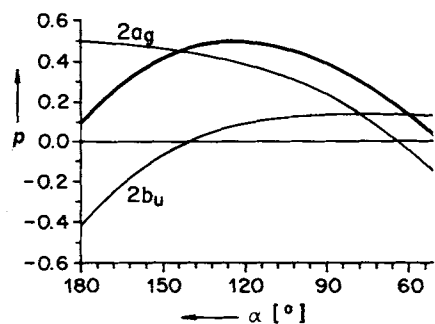


Fig. 1. Dependence of overlap population p on H–Tl–Tl angle α with Tl–Tl = 370 pm and Tl–H = 190 pm. Bold curve: total overlap populations. $\alpha = 180^\circ$ corresponds to linear H₂Tl₂.

The surprising result is that the overlap population between the Tl atoms in **2** shows a dramatic increase, upon bending, to a substantial maximum at a H–Tl–Tl angle of around 120° , followed by an eventual decline towards the bridging geometry. For the more realistic Cp ligand, the Tl–Tl overlap populations at $\alpha = 180^\circ$, 131.6° , 120° , and 90° are 0.177, 0.347, 0.367, and 0.296, respectively (Tl–Tl = 370, Tl–Cp(centroid) = 249 pm).

Both the magnitude and the range of variation are extraordinary. The question raised in the beginning is answered with a definite yes: There is a Tl^I–Tl^I bond in these compounds, at least for a bent geometry.

How can there be a bond between two filled s² subshells, which is the way one might think of Tl^I or In^I? The answer is “it is a consequence of efficient mixing of formally vacant np orbitals, that is, hybridization”. In the case at hand, a calculation on 120° -bent HTITlH, using only a Tl 6s basis (i.e., no 6p orbitals) yields a Tl–Tl overlap population of -0.026 (compare the $+0.490$ from Fig. 1 for the case where both s and p orbitals on Tl are included). Changing an initial

repulsion of closed subshells into an attraction, by inclusion of unfilled orbitals, is a general phenomenon. It can also be seen in d¹⁰-d¹⁰ systems, such as Cu^I-Cu^I,^[13] Pt⁰-Pt⁰,^[14] and Au^I-Au^I,^[15] whose bonding interactions are based on a d–s–p mixing. Relativistic effects may be important in the bonding of some of these systems as well as in the thallium dimer.^[16]

For LTITl the relevant mixing is sp. In a sense this is no surprise—Tl is a main-group element. Perhaps it is worthwhile to draw an analogy with the “isoelectronic” HCCH²⁺. One would not doubt for a moment the necessity of sp hybridization or the presence of a C–C bond in this acetylene dication. But that just raises the further question: Why is LTITl bent? The acetylene analogy is not immediately helpful in this matter. There is also the remarkable sensitivity of the Tl–Tl bonding to the H–Tl–Tl angle displayed in Figure 1. We approach these questions by a decomposition of the total overlap population versus angle function (see Fig. 1) into its major components from the HOMO (2b_u) and the orbital below the HOMO (2a_g). From the slope of the curves, it is obvious that from 180° to 120° the 2b_u orbital dominates the changes in the overlap population, while from 120° to 60° the 2a_g orbital is the governing factor.

The origins of the bending can be traced with the help of a Walsh diagram for the relevant orbitals in **2** (Fig. 2). From

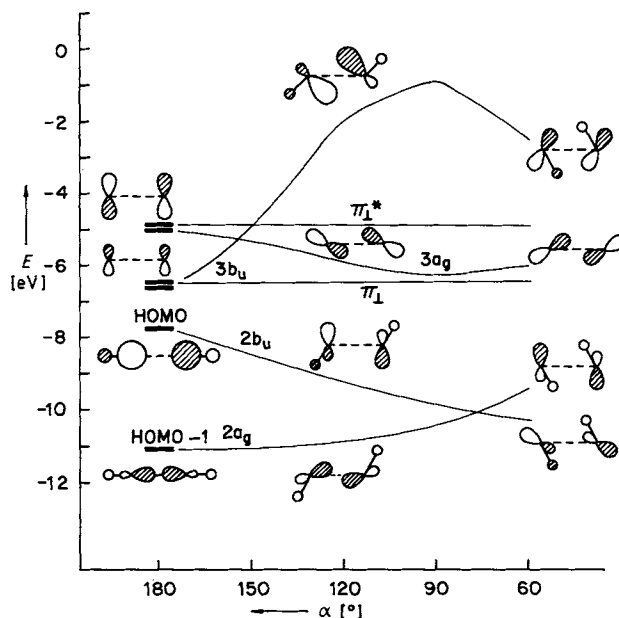
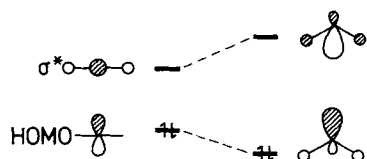


Fig. 2. Partial Walsh diagram for the bending in **2** with Tl–Tl = 370 pm and Tl–H = 190 pm. Symmetry labels are for point group C_{2h}; orbital drawings are schematic π_1 , π_1^* : π sets perpendicular to the plane of the molecule.

the orbital sketches, it may be seen that the stabilization and change in character of 2b_u results from strong mixing with the empty 3b_u orbital—pushing both levels apart. The lowest energy for **2** is calculated around 105° .

What happens in the *trans* bending of HTITlH is closely related to the critical orbital interactions in the pyramidalization of AH₃ systems (e.g., NH₃, CH₃⁺, PR₃) and the bending of AH₂ molecules (e.g., H₂O, H₂S).^[17] The orbitals guiding these deformations are sketched for AH₂ in Scheme 2.

The controlling orbital (HOMO for both AH₃ and AH₂) is a lone pair centered on the A atom. This level decreases in



Scheme 2. The orbitals involved in bending of AH_2 molecules. Left: linear AH_2 . Right: bent AH_2 .

energy with bending, mixing in more s character and a hydrogen contribution from an empty $A-H$ σ^* orbital above, to give a stabilized filled orbital with $A-H$ nonbonding character and an empty level which is destabilized and strongly $A-H$ antibonding. The lone pair occupies a pure p orbital in the planar AH_3 or linear AH_2 geometry. The closer the higher σ^* combination to the p orbital, the stronger is the tendency to bend. Essentially the same thing happens in $HTlTIH$. The only difference is that in the Tl case the upper orbital ($3b_u$) is of Tl p character, whereas in AH_3 and AH_2 it is the lower orbital. This can be traced to the long $Tl-Tl$ separation. As soon as bending and therefore mixing begins, this distinction becomes unimportant. The $2b_u$ and $3b_u$ orbitals in **2** are close to each other in energy, which they are not in the isoelectronic $HCCH^{2+}$.

While the $2b_u$ mixes very strongly with the $3b_u$ combination in the 180° to 120° range, thereby transforming its character from strongly antibonding to slightly bonding, the main $Tl-Tl$ bonding orbital, $2a_g$, shows only very small interactions with orbitals of the same symmetry in this region. The $2a_g$ orbital thus retains its strongly bonding character (see Fig. 1). From 120° on, the mixing of $2a_g$ with other levels, however, gets much stronger as appropriate symmetry combinations come closer in energy. Hence, the $2a_g$ $Tl-Tl$ overlap population drops rapidly to nonbonding as one approaches the bridging geometry. With the ligands in the bridging positions, both $2a_g$ and $2b_u$ can be considered as lone-pair combinations, with only a small overlap population between the thalliums. Another way of thinking about this mixing, governed by orbital level energies, is that it provides the opportunity for a stereochemically active lone pair.

To summarize: $HTlTIH$ and $CpTlTlCp$ want to bend at Tl as a result of a near resonance in the energy of the $2b_u$ (σ^*) and $3b_u$ (π) orbitals. The factors favoring pyramidalization are similar to those for EL_2, EL_3 (and L_2EEL_2), except that the driving force is stronger in $HTlTIH$. There definitely is Tl^I-Tl^I bonding in these structures. The bonding in the formally s^2-s^2 closed subshell interaction is due to the mixing of formally empty p levels into the filled s combinations. We are now analyzing the full range of Tl^I-Tl^I interactions in molecular and extended structures.

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TIH, 13763-69-4.

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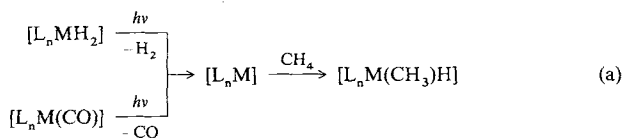
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Inter- and Intramolecular Photochemical C-H Activation in Matrices and in Solution with $(\eta^6\text{-Arene})(\text{carbonyl})\text{osmium Complexes}^{**}$

By Andrew McCamley, Robin N. Perutz,* Stefan Stahl, and Helmut Werner*

Dedicated to Professor Walter Strohmeier on the occasion of his 70th birthday

Matrix isolation has proved to be an effective means both for observing C-H activation of methane and for characterizing the coordinatively unsaturated complexes implicated in this process.^[1, 2] However, the identification of the (methyl)-hydride complexes resulting from insertion into methane [Eq. (a)] has rested so far on the observation of CO and



MH stretching vibrations in the IR spectrum (e.g., in the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})(\text{CH}_3)\text{H}]$ from $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})_2]$).^[11] Suitable precursors for such photochemi-

[*] Dr. R. N. Perutz, A. McCamley
Department of Chemistry, University of York
York YO1 5DD (UK)

Prof. Dr. H. Werner, Dipl.-Chem. S. Stahl
Institut für Anorganische Chemie der Universität Würzburg
Am Hubland, D-8700 Würzburg (FRG)

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