

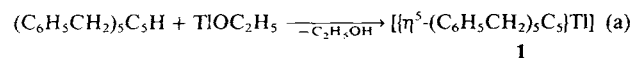
- [8] **3c**, <sup>1</sup>H-NMR ([D<sub>6</sub>]toluene, -80°C): δ(CH<sub>3</sub>) (ring) = 10.95 and 10.11 [2 × 6 H], δ(CH<sub>2</sub>) = 2.29 [2 H], δ(CH<sub>3</sub>) (C<sub>5</sub>H<sub>5</sub>) = 4.30 [3 H]; all signals are broadened, so <sup>2</sup>J(H,H)-couplings do not appear.
- [9] Summaries: a) W. A. Herrmann, *J. Organomet. Chem.* **300** (1986) 111; b) W. A. Herrmann, E. Herdtweck, M. Flöel, J. Kulpe, U. Küsthardt, J. Okuda, *Polyhedron* **6** (1987) 1165; c) J. Okuda, W. A. Herrmann, *J. Mol. Catal.* **41** (1987) 109.
- [10] W. A. Herrmann, J. K. Felixberger, E. Herdtweck, A. Schäfer, J. Okuda, *Angew. Chem.* **99** (1987) 466; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 466.
- [11] **3a**: Red platelets from *n*-hexane at -78°C; orthorhombic, space group *P*222<sub>1</sub> (No. 17), *Z* = 2, *a* = 674(1), *b* = 773(1), *c* = 1401(1) pm; *V* = 730 × 10<sup>6</sup> pm<sup>3</sup>; *T* = 173 K; *ρ*<sub>calc</sub> = 1.74 g·cm<sup>-3</sup>. Re occupies the special position 2c, giving rotational symmetric positions for the methyl groups and the C<sub>5</sub>Me<sub>5</sub> ligand. Superstructure reflections and doubling of an axis were not observed. 586 measured reflections, 482 independent reflections with *I* > 1σ(*I*); Enraf-Nonius CAD4, graphite monochromator, ω-scan, 2° < θ < 18°; *h* ± 5, *k* + 6, *l* + 12; *F*<sub>000</sub> = 372. Solution and refinement by Patterson and difference Fourier methods, anisotropic temperature factor for Re, common isotropic temperature factors for C(1...4) and C(11...15), individual isotropic temperature factors for methyl carbons C(21...25) at the ring ligands, anomalous dispersion taken into consideration, empirical absorption correction μ = 84.2 cm<sup>-1</sup>; *R* = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|: 0.040; *R*<sub>w</sub> = [Σ w(|*F*<sub>o</sub>| - |*F*<sub>c</sub>||)<sup>2</sup>/Σ w|*F*<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup>: 0.046. Number of parameters: 55. -Shift/error: < 0.00 in the last cycle of refinement; residual electron density: + 1.52 e/Å<sup>3</sup>. Hydrogen atoms were not considered.

### Pentabenzylcyclopentadienylthallium(I): Synthesis and Structure of a "Dimeric" Organothallium Compound with Tl-Tl Interaction\*\*

By Herbert Schumann,\* Christoph Janiak,  
Joachim Pickardt, and Ute Börner

Cyclopentadienylthallium is valued as a mild reagent for the synthesis of difficultly isolable cyclopentadienyl derivatives of main group elements, transition metals, and lanthanoids.<sup>[1,2]</sup> In fact, some organometallic compounds with substituted cyclopentadienyl ligands can only be obtained from the corresponding cyclopentadienylthallium(I) reagents.<sup>[3]</sup> The preparative potential of these reagents is, however, limited, owing to their very different stabilities and solubilities, which depend on the ring substituents and are, in turn, also influenced by the molecular and crystal structures of the compounds. So far, however, X-ray structure analyses have been carried out only on C<sub>5</sub>H<sub>5</sub>Tl<sup>[4]</sup> and (C<sub>5</sub>Me<sub>5</sub>)Tl;<sup>[5]</sup> both compounds have a polymeric structure of zig-zag chains.

We have now been able for the first time to obtain a cyclopentadienylthallium(I) compound in dimeric form in the solid state, namely pentabenzylcyclopentadienylthallium(I) (**1**). Compound **1** is formed in two, reversibly interconvertible, air- and light-stable modifications upon addition of thallium ethoxide to pentabenzylcyclopentadiene in hexane<sup>[6]</sup> [Eq. (a)].



The rapidly crystallizing needles exhibit a chain structure,<sup>[8]</sup> whereas the slowly crystallizing, thermodynamically

more stable parallelepipeds exhibit a new type of structure (Fig. 1). According to an X-ray structure analysis<sup>[9]</sup> the two halves of the quasi-dimeric molecule are coupled to each other via a symmetry center between the two Tl atoms. The distance between the two Tl atoms is 3.632 Å, which is far too large for a conventional bonding. However, as in [In<sub>6</sub>(C<sub>5</sub>Me<sub>5</sub>)<sub>6</sub>],<sup>[10]</sup> a bonding interaction is also essential in **1** in order to counteract an electronic repulsion of the [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>5</sub>C<sub>5</sub>]Tl dipole terminals. A comparison with the interactions in d<sup>10</sup>-d<sup>10</sup> transition metal complexes such as Cu<sup>I</sup>-Cu<sup>I</sup><sup>[11]</sup> and Au<sup>I</sup>-Au<sup>I</sup> complexes,<sup>[12]</sup> which had been interpreted theoretically in terms of an s + p<sub>z</sub> + d<sub>z<sup>2</sup></sub> "mixing",<sup>[13]</sup> was called for.

The angle of 131.8° at the thallium (ring center-Tl1-Tl1\*) is somewhat smaller than the Cp-Tl-Cp angle (Cp = C<sub>5</sub>H<sub>5</sub> or C<sub>5</sub>Me<sub>5</sub>) in the polymeric compounds (C<sub>5</sub>H<sub>5</sub>)Tl (137°)<sup>[4]</sup> and (C<sub>5</sub>Me<sub>5</sub>)Tl (145°, mean value).<sup>[5]</sup> The C-Tl distances in **1** (Tl1-ring center 2.490 Å) are smaller than the distances in (C<sub>5</sub>H<sub>5</sub>)Tl (3.19 Å) and (C<sub>5</sub>Me<sub>5</sub>)Tl (2.71 Å), indicating an increased covalent character of the Cp-Tl bond in **1**. Remarkably, three of the five benzyl groups of a cyclopentadienyl ring in **1** are oriented toward the thallium atoms. The extrapolated surfaces of the total of six phenyl groups in a "dimeric" unit form a parallelepiped which envelops the two thallium atoms (Fig. 1, bottom). The smallest phenyl carbon-thallium distances are

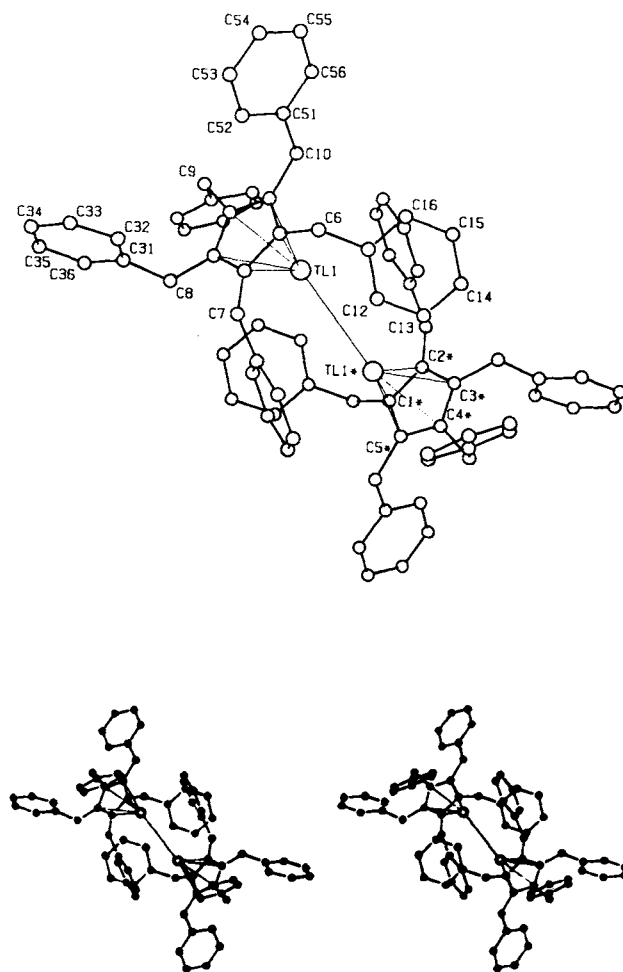


Fig. 1. Top: crystal structure of **1**. Selected bond lengths [Å] and angles [°]: Tl1-C1 2.753(6), Tl1-C2 2.808(7), Tl1-C3 2.816(6), Tl1-C4 2.749(7), Tl1-C5 2.704(6), Tl1-ring center 2.490, Tl1-Tl1\* 3.632, ring center-Tl1-Tl1\* 131.82. — Bottom: Stereodiagram of the structure of **1**.

[\*] Prof. Dr. H. Schumann, Dr. C. Janiak, Prof. Dr. J. Pickardt, U. Börner  
Institut für Anorganische und Analytische Chemie  
der Technischen Universität Berlin  
Strasse des 17. Juni 135, D-1000 Berlin 12

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those of the *meta*-C atoms to the other thallium of the quasi-dimeric unit (Tl1\* -C13 3.495 Å; Tl1\* C23 3.410 Å). A comparable protective shield arrangement of the benzyl groups was also found by us in the air-stable complexes decabenzyl-germanocene, -stannocene, and -plumbocene.<sup>[14]</sup>

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CAS Registry numbers:

1, 109531-29-5; (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H, 67209-29-4; TiOC<sub>2</sub>H<sub>5</sub>, 20398-06-5; Tl, 7440-28-0.

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[6] Procedure: A solution of thallium ethoxide (0.68 g, 2.70 mmol) in hexane (1 mL) was added dropwise within 15 min at room temperature to a stirred solution of pentabenzylcyclopentadiene [7] (1.40 g, 2.70 mmol) in hexane (40 mL). The solution turned yellow and a fine precipitate separated out. After a further 10 minutes' stirring the solution was allowed to stand before decanting off the clear yellow solution. After careful evaporation of the solution and cooling with ice, 0.95 g (49%) of needle-like crystals separated out. After careful evaporation of the mother liquor and subsequent storage, 0.51 g (26%) of large, yellow, parallelepipedal crystals separated out. These are also obtainable on slow recrystallization of the needles from toluene/hexane. Both modifications darken at 60°C, and soften at 80°C; the needles melt at 133–136°C, the parallelepipeds at 137–140°C. Characterization by complete elemental analysis, IR, Raman, and mass spectra. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 25°C): δ = 3.93 (d, 10H, CH<sub>2</sub>, <sup>3</sup>J(TlH) = 10.7 Hz), 7.19 (m, 25H, C<sub>6</sub>H<sub>5</sub>).  
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[9] 1: monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.288(3), *b* = 15.858(4), *c* = 18.890(6) Å, β = 91.23(3)°, *V* = 3081.1 Å<sup>3</sup>, *Z* = 4, MoK<sub>α</sub> radiation, ω/2θ scans, data reduction with Lorentz and polarization corrections, no absorption correction. The structure was solved by Patterson methods. 7415 independent reflections, 4473 with intensities *I* ≥ 2σ(*I*) used for the structure determination. *R* = 0.0386, *R*<sub>w</sub> = 0.0350. Further details of the structure determination are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52453, the names of the authors, and the journal citation.  
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## Substituted α-Pyrones as Starting Compounds for the Synthesis of 4,4-Disubstituted 1,4-Dihydropyridines

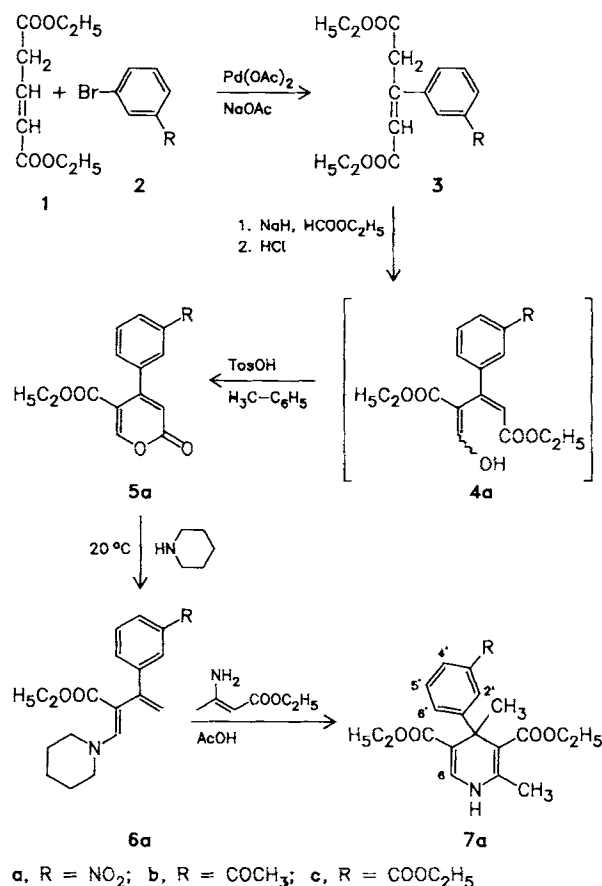
By Vratislav Kvita\* and Hans-Peter Sauter

Following the discovery that some 4-aryl-1,4-dihydropyridines are highly effective calcium antagonists,<sup>[1]</sup> numerous papers reporting the synthesis of derivatives of this

class of substances appeared in the literature over a relatively short period of time. However, the derivatizations were for a long time restricted to the phenyl group and to C-2 and C-3 of the 1,4-dihydropyridine ring. 4,4-Disubstituted 1,4-dihydropyridines were not obtainable via the methods being used at the time.

The first synthetic method affording access to 4,4-disubstituted 1,4-dihydropyridines was that reported by Goldmann,<sup>[2]</sup> but even this method is not generally applicable; for instance, compounds with the mostly desired 2- or 3-nitrophenyl groups on C-4 cannot be synthesized by this method.

Starting from the α-pyrone derivative we have now obtained, via a new synthetic strategy, a 4-methyl-4-(3-nitrophenyl)-1,4-dihydropyridine which combines all the structural moieties which have previously proven to be advantageous.



The diethyl 3-(3-nitrophenyl)-2-pentenedicarboxylate **3a** was prepared from diethyl glutaconate **1** and 1-bromo-3-nitrobenzene **2a** by a Heck reaction.<sup>[3]</sup> It was then formylated to **4a** and cyclized in toluene in the presence of a catalytic amount of toluenesulfonic acid to give the diethyl 4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5a**, which was allowed to react with piperidine at room temperature to furnish, via cleavage of CO<sub>2</sub>, ethyl 3-(3-nitrophenyl)-2-piperidinomethylene-3-buten-2-ylidene-1,4-dicarboxylate **6a**.<sup>[4]</sup> This was then cyclized with ethyl 3-aminocrotonate to diethyl 2,4-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **7a**. Also 3-Bromoacetophenone **2b** and ethyl 3-bromobenzoate **2c** react similarly to 1-bromo-3-nitrobenzene **2a**.

[\*] Dr. V. Kvita, H.-P. Sauter  
Zentrale Forschungslaboratorien und  
Zentrale Funktion Forschung Physik der Ciba-Geigy AG  
Rosental, CH-4002 Basel (Switzerland)