

Preliminary communication

Investigations on organozinc compounds

XV★. Novel trinuclear phenylzinc- β -diketonate complexes

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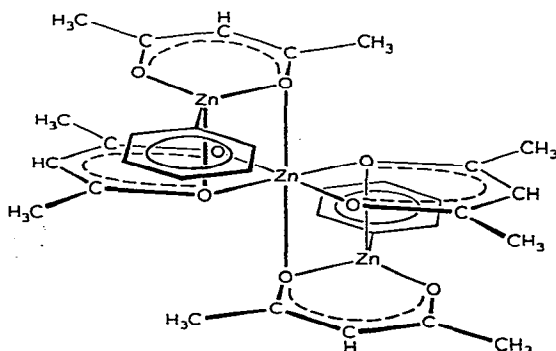
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Ethylzinc acetylacetonate (EtZnacac) is stable in boiling in which it occurs as a dissociating dimer². The corresponding phenylzinc compound PhZnacac slowly disproportionates under similar conditions into diphenylzinc and a trinuclear species with composition $(\text{PhZnacac})_2 \cdot \text{Zn}(\text{acac})_2$ (I); (yield 37%; m.p. 118°). The same compound was obtained in essentially quantitative yield (97%) by treating PhZnacac with $\text{Zn}(\text{acac})_2$ in a 2/1 molar ratio in benzene at room temperature. (I) is completely dissociated in boiling benzene, but has the correct molecular weight (found: 749; calcd.: 746.8) in freezing benzene. A microwave titration³ of (I) with *N,N,N',N'*-tetramethylethylenediamine (TMED) in benzene shows three equivalence points at a 1/1, 1/2 and 1/3 molar ratio. According to the IR and PMR spectrum the solution at the 1/3 equivalence point contains $\text{Zn}(\text{acac})_2 \cdot \text{TMED}$ and $\text{PhZnacac} \cdot \text{TMED}$ in a 1/2 ratio. Attempted isolation of the latter complex results in the isolation of $(\text{PhZnacac})_2 \cdot \text{TMED}$ (II); (m.p. 116°) in which TMED acts as a bridging ligand (*cf.* ref. 2).

The NMR spectrum of (I), taken at room temperature in boiling benzene, shows only a single set of acetylacetonate absorptions (δ (Me) 1.78 ppm, δ (H) 5.03 ppm; intensity ratio Ph/Me/H 10/24/4). However, cooling down to -70° in toluene-*d*₈ results in a broadening and splitting of both the γ -H and -Me signals into doublets of unequal intensity (δ (H) 4.71 and 4.82 ppm; δ (Me) 1.67 and 1.80 ppm (shoulder)). Apparently, at room temperature a relatively fast exchange of acetylacetonate ligands takes place. According to the IR spectrum only chelated acetylacetonate ligands are present (ν (C=O) 1579 cm⁻¹ and ν (C=C) 1521 cm⁻¹).

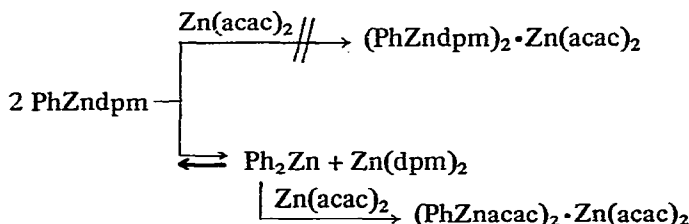
We propose for (I) a structure with one hexacoordinate central zinc atom and two tetracoordinate terminal zinc atoms. One of the various possible configurations is shown in Fig. 1. This structure is related to that reported by Bennett *et al.*⁴ for solid trimeric $\text{Zn}(\text{acac})_2$.

★For part XIV see ref. 1.



Attempts to synthesize similar species derived from pivaloylacetone (pac) and dipivaloylmethane (dpm) revealed that only in the case of the pac derivative can a stable trinuclear compound be isolated. PhZnpac (III); (m.p. 101°) is stable towards disproportionation. However, $(\text{PhZnpac})_2 \cdot \text{Zn}(\text{pac})_2$ (IV); (m.p. 121°) was obtained by the 2/1 reaction of PhZnpac and $\text{Zn}(\text{pac})_2$ (V); (m.p. 160°). The NMR spectrum of (IV) in benzene again shows only one set of β -diketonate signals (δ (H) 5.45 ppm, sharp; δ (Me) 1.91 ppm; δ (t-Bu) 1.08 ppm) and also the IR spectrum shows only chelating pac ligands (ν (C=C) 1510 cm^{-1} and ν (C=O) 1560 cm^{-1}).

The mixed compound $(\text{PhZnpac})_2 \cdot \text{Zn}(\text{acac})_2$ (VI); (m.p. 110°) has been obtained by the 2/1 reaction of PhZnpac with $\text{Zn}(\text{acac})_2$. PhZndpm (VII); (m.p. 141°) does not interact with $\text{Zn}(\text{dpm})_2$. When PhZndpm was reacted with $\text{Zn}(\text{acac})_2$, the only reaction products were $(\text{PhZnacac})_2 \cdot \text{Zn}(\text{acac})_2$ (I) and $\text{Zn}(\text{dpm})_2$ (VIII); (m.p. 142°), indicating that PhZndpm does disproportionate, but that a trinuclear compound cannot form:



(IV) and (VI) titrate with TMED in a similar way as (I), *e.g.* both react successively with 3 moles of TMED. The NMR spectrum of (VI) shows sharp signals of both the pac and acac ligands (δ (H(acac)) 5.04 ppm; δ (H(pac)) 5.44 ppm; δ (Me(acac)) 1.75 ppm; δ (Me(pac)) 1.84 ppm; δ (t-Bu(pac)) 1.07 ppm) with the correct intensity ratio. Molecular weight determinations of (IV) and (VI) show that even at 5° in benzene dissociation occurs ((IV): found: 502; calcd.: 915.1 at 1.0 wt.-%; (VI): found: 690; calcd.: 830.9 at 1.1 wt.-%).

For (IV) and (VI) we propose a structure similar to that of (I), with the acac ligands in (VI) being attached to the central zinc atom. The failure to obtain $(\text{PhZndpm})_2 \cdot \text{Zn}(\text{dpm})_2$ and even $(\text{PhZndpm})_2 \cdot \text{Zn}(\text{acac})_2$ contrasts with the accessibility of $(\text{PhZnpac})_2 \cdot \text{Zn}(\text{pac})_2$ and $(\text{PhZnpac})_2 \cdot \text{Zn}(\text{acac})_2$. Apparently, in trinuclear species of this type, β -diketonate ligands with two t-Bu groups cannot be sterically accommodated.

Satisfactory analytical data have been obtained for all new compounds. Further work on this new type of organozinc complexes is in progress.

ACKNOWLEDGEMENT

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