Dilithium Diphenylmethanediide; Generation, Redox Relationship with Lithium Chlorodiphenylmethanide, Implication with Regard to Aggregation

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Dilithium diphenylmethanediide, Ph_2CLi_2, prepared by reaction of dichlorodiphenylmethane with lithium *p,p'*-di-*tert*-butylbiphenyl, reacts with organic halides and carbonyl compounds to give lithium chlorodiphenylmethanide, Ph_2CLiCl, as a major product and is assumed to exist in two different states of aggregation.

Our simple method, exhaustive reduction of R_2CHHal_2 by lithium *p,p'*-di-*tert*-butylbiphenyl[1] (LiDBB) [*ca.* 0.45 mol dm^{-3}, tetrahydrofuran (THF), molar ratio of R_2CHal_2 and LiDBB 1:4.5, −95 °C],[2] shows promise as a general route, *via* the carbenoids $R_2CLiHal$, to geminal dilithium compounds, R_2CLi_2, a class of organolithiums whose chemistry and properties are largely unknown, owing to its limited accessibility in the past.[3,4] It was of interest to discover whether Ph_2CLi_2, the first representative of a potentially π-delocalised *gem*-dilithium compound, could be obtained in this way and what its reactivity would be.

When Ph_2CCl_2 in THF was added to LiDBB under the above conditions in an ESR tube the intensity of the ESR spectrum of LiDBB decreased steadily until, after approximately 20 minutes, only the ESR spectrum of a small amount of lithium tetraphenylethene[5] could be recorded. In a separate experiment deuteriolysis at this stage (C_2H_5OD, −95 °C) and removal of *p,p'*-di-*tert*-butylbiphenyl by precipitation by methanol gave (GC–MS): Ph_2CD_2 (92%), Ph_2CDCl (1%), $Ph_2C{=}CPh_2$ (1%) and $Ph_2DC{-}CDPh_2$ (6%). From the complete consumption of the LiDBB before deuteriolysis, we conclude that Ph_2CD_2 is derived from species that contain the

Table 1 Composition (%) of the product mixtures that were recovered after treatment of the solution obtained from Ph_2CCl_2 with 4.5 equiv. LiDBB with RHal (1 equiv.) and subsequent deuteriolysis

Entry	RHal	T/°C	Ph_2CD_2	Ph_2CDH	Ph_2CDCl	$(Ph_2C)_2$	$(Ph_2DC)_2$	Ph_2CDR
1	Bu^nBr	−85	18	—	64	1	14	—
2	Bu^nCl	−80	17	2	63	1	17	—
3	Bu^tCl	−85	31	13	28	5	18	5
4	1,2-$C_2H_4Cl_2$	−90	1	8	71	1	19	—
5	PhBr	−80	4	4	46	1	20	25
6	PhCl	−80	17	8	16	10	18	28

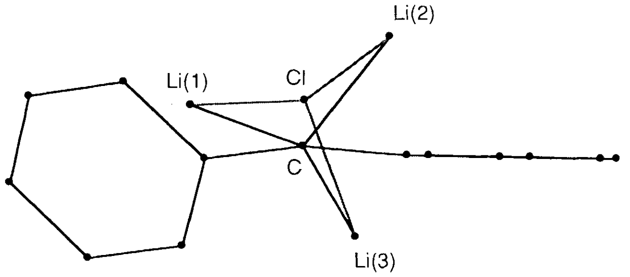
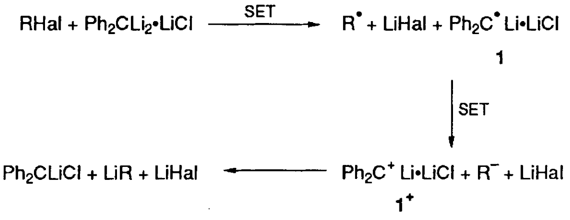


Fig. 1 MNDO-structure of $Ph_2CLi_2{\cdot}LiCl$. In keeping with the strong preference of lithium for tetrahedral coordination, in THF Li(1)–Li(3) would each bind two molecules of this solvent.

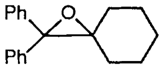
moiety Ph_2CLi_2. If, under the same conditions, Ph_2CBr_2 instead of Ph_2CCl_2 was reacted with LiDBB, Ph_2CD_2 (4–8%) and $Ph_2DC{-}CDPh_2$ (88–96%) were obtained. Possibly, unlike Ph_2CLiCl, the intermediate carbenoid Ph_2CLiBr undergoes self-condensation to $Ph_2C{=}CPh_2$ (which with LiDBB gives $Ph_2LiC{-}CLiPh_2$) faster than it is reduced by LiDBB to Ph_2CLi_2.

Treatment of the solutions containing Ph_2CLi_2 with MeI and EtI, respectively (molar ratio 1 : 4, −95 °C), gave only low yields of the dialkylated products Ph_2CMe_2 (33%) and Ph_2CEt_2 (20%), respectively. Major products were $Ph_2C{=}CH_2$ (67%) and $Ph_2C{=}CHMe$ (80%). It was assumed that they are formed by alkylation of a carbenoid $Ph_2CLiHal$ (Hal = Cl or I), followed by loss of H–Hal during work-up. In order to test this assumption, the solutions containing Ph_2CLi_2 were reacted with organohalogen compounds in the molar ratio 1 : 1 and subsequently deuteriolysed. The results are given in Table 1.

The high proportion of Ph_2CDCl in four of the six product mixtures indicates that some Ph_2CLi_2-containing species is oxidized to give Ph_2CLiCl when treated with organohalogen compounds. Most interestingly, the chlorocarbenoid is also formed upon treatment of the Ph_2CLi_2-system with n-butyl bromide and bromobenzene (entries 1 and 5).[†] From this we conclude that chlorine in Ph_2CLiCl stems from the Ph_2CLi_2-containing species oxidized by RHal, and chlorine–lithium exchange of Ph_2CLi_2 with some RCl reagent cannot be the (sole) source of Ph_2CLiCl. The simplest species in our system that on electron-loss could yield Ph_2CLiCl is a 1 : 1 complex of Ph_2CLi_2 and LiCl. Fig. 1 shows the structure calculated by MNDO.



Scheme 1 SET = single electron transfer



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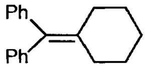

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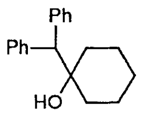

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The μ_3-bonding of both chlorine and methanediide carbon conforms to known structures of mixed aggregates $(4-n)$ $LiR{\cdot}n$LiHal.[6] A very similar structure [Li(3) is absent and the system adopts C_2-symmetry] was calculated for the potential intermediate in the $Ph_2CLi_2{\cdot}LiCl/Ph_2CLiCl$ redox system, **1**, formed by SET from $Ph_2CLi_2{\cdot}LiCl$ to RHal (Scheme 1). After a second SET, from **1**, it is apparently easier for $\mathbf{1}^+$ to form Ph_2CLiCl by capture of its own Cl^-, which in **1** is located at a calculated distance of about 3.6 Å from the methide carbon atom, than to bind the more distant R^- or Hal^-.[7] Capture of $R^{\cdot}(R^-)$ by $\mathbf{1}(\mathbf{1}^+)$ could explain the final products Ph_2CDR (entries 3, 5 and 6), while Ph_2CDH could be derived from $H(H^-)$-transfer from $R^{\cdot}(R^-)$ or solvent to **1** ($\mathbf{1}^+$).[‡]

The fact that with all halides of Table 1 a similar percentage (±18%) of $Ph_2DC{-}CDPh_2$ is obtained, lets us speculate that besides the mixed complex involving LiCl, about 20% of the Ph_2CLi_2 units are present as (an aggregate containing) $(Ph_2CLi_2)_2$.[§] Conceivably, after its formation by loss of e^- with Li^+ from $(Ph_2CLi_2)_2$, a unit $Ph_2CLi_2{\cdot}Ph_2CLi^{\cdot}$ might undergo faster a second such step, concurrent with association to $Ph_2LiC{-}CLiPh_2$, than recombine with $R^{\cdot}$. The latter process, however, must prevail in the reactions with excess of MeI and EtI.[8]

If the solutions formed from Ph_2CCl_2 and LiDBB are reacted (−95 °C) with benzaldehyde (3 equiv.), the Ph_2CLi_2 units undergo both oxidation to Ph_2CLiCl and addition to the carbonyl group to form $Ph_2LiC{-}CPhHOLi$. The latter eliminates Li_2O forming $Ph_2C{=}CHPh$ (62% of the product

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[†] Ph_2CLiBr, if formed by bromine–lithium exchange, might have eluded deuteriolysis by very fast further reaction (*vide supra*). However, a corresponding increase of the percentage of $Ph_2C{=}CPh_2$ was not observed (Table 1). The reaction between Ph_2CBr_2 and LiDBB (*vide supra*) was not influenced by the presence of an excess of LiCl. This excludes formation of Ph_2CLiCl from Ph_2CLiBr by fast halide exchange with the excess of LiCl generated during formation of Ph_2CLi_2 in the experiments of entries 1 and 5 of Table 1.

[‡] Writing DBB instead of $R^{\cdot}$ and Hal (RHal = 2 DBB), respectively, and reading Scheme 1 in the reverse direction would give the probable mode of formation of $Ph_2CLi_2{\cdot}LiCl$ from Ph_2CLiCl and 2 LiDBB.

[§] We propose two different species, each yielding its own typical product, because it seems unlikely to us that upon reaction with a series of halides differing in their nature as widely as those of Table 1, any single species would partition into derivatives of diphenylmethane and $Ph_2LiC{-}CLiPh_2$ in a, practically, unchanging ratio.

mixture), while Ph_2CLiCl reacts with a molecule of benzaldehyde to give triphenyloxirane (33%).[9] In addition, $Ph_2C{=}CPh_2$ (6%) was found. The composition of the product mixture obtained with cyclohexanone (2.4 equiv.) indicates the following reactions of the ketone with Ph_2CLi_2: formation of Ph_2CLiCl (→ 65% **2**); addition to the carbonyl group followed by elimination of Li_2O (→ 11% **3**); protonation of Ph_2CLi_2 to give Ph_2CLiH, which adds to the carbonyl group (→ 24% **4**).

In summary: (*i*) THF solutions containing Ph_2CLi_2 are easily obtained by LiDBB-reduction of Ph_2CCl_2. The behaviour of Ph_2CBr_2 shows that for exhaustive LiDBB-reduction of R_2CHal_2 a minimum lifetime of the intermediate lithium halocarbenoid is required, *i.e.* reduction of lithium halocarbenoids by LiDBB has a substantial activation barrier. (*ii*) While the corresponding monolithium compound, Ph_2CHLi, is present as ion-pair(s) in THF and undergoes S_N2-reactions with alkyl halides,[10] Ph_2CLi_2, owing to the doubling of charges, appears to be aggregated and, if reacted with electrophiles, prefers electron-transfer followed by intra-aggregate reaction. Electron-transfer reactions have also been reported for $(H_2CLi_2)_x$.[3] In the present case SET from $Ph_2CLi_2{\cdot}LiCl$ to give Ph_2CLiCl represents the first example of a novel, oxidative route to carbenoids $R_2CLiHal$.

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