the higher $\nu$(Fe$^{II}$–imidazole) frequency for HRP indicates stronger imidazole ligation.[19,20] For the oxy complexes, $\nu$(Fe$^{II}$–imidazole) is also higher for HRP than for myoglobin but its $\nu$(Fe–$O_2$)[8c] is lower. A similar inverse relationship between $\nu$(Fe$^{II}$–CO) and trans ligand strength has been reported for monomeric insect hemoglobins[18a] and heme model compounds.[18b]

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## 3-Lithio-1,5-dimethoxypentane. Prognostication, Preparation, and Some Properties of a Dimeric Alkyllithium

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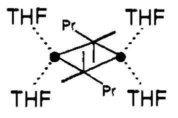
Tetracoordination of lithium is an important principle of organolithium aggregation and complexation.[1] Accordingly, the dimer of *n*-BuLi, recently shown to be present in THF solutions, was assigned a structure of type I, in which two molecules of THF are coordinated to each lithium atom.[2,3] Due to its ephemerality,[3,4] chances for isolation of I are dim. However, closer scrutiny of its properties would seem desirable. Many reactions of tetrameric alkyllithiums in ether solvents involve deaggregated species as the reactive intermediates.[5] In view of the advantages gained by coordinating the required alkoxy groups *intramolecularly*, we expected the dimer of 3-lithio-1,5-dimethoxypentane (II) to be stable in hydrocarbon solutions and amenable to the usual methods of examination.[6]

After treating *tert*-butyl(1,5-dimethoxy-3-pentyl)mercury with 1 equiv of *t*-BuLi in pentane at −15 °C and removing volatile materials (pentane, $(t\text{-Bu})_2Hg$, etc.) by bulb-to-bulb distillation (20 °C, $10^{-5}$ torr), we extracted II from the residue with pentane and purified it by sublimation (20 °C, $10^{-5}$ torr) to give colorless crystals melting around 30 °C. Reaction with $C_2H_5OD$ gave 1,5-dimethoxypentane-*3-d*$_1$. The degree of association of II was found to be 2 (isothermal distillation, 0.004–0.02 M pentane, 28.4 °C).[7,8]

The $^1H$ and $^{13}C$ NMR spectra of $(II)_2$ at ambient and low temperature are given in Table I. At −110 °C the signals of $H_b$ and $H_{b'}$ are extremely broad. During these temperature variations the signal of $H_c$ remains essentially unchanged. At 71 °C (solvent $C_6D_6$) all proton signals are broadened, that of $H_c$ approximating the shape of a quintet. The $^7Li$ NMR spectrum consisted of a singlet at 1.34 ($\Delta\nu_{1/2}$ = 4.6 Hz, $C_6D_6$, 20 °C) or 1.40 ppm ($\Delta\nu_{1/2}$ = 14 Hz, cyclopentane, −100 °C).[9]

The 1:1 pairs of similar signals in the low-temperature $^1H$ and $^{13}C$ NMR spectra of $(II)_2$ suggest that in the predominating species the $CH_2CH_2OMe$ moieties are present in two different environments. These are averaged by transpositions of chelate rings that are fast on the NMR time scales above ca. −100 °C. Structure III [$\rightleftharpoons$ III′ (mirror image)] fits the NMR data. It contains two types of $CH_2CH_2OMe$ groups, while the presence of only one type of $H_c$ and lithium atom, respectively, is in accord with the observation of a single signal for $H_c$ and one (though broadened at −100 °C) $^7Li$ resonance at all temperatures studied. However, stereoisomers with two types of lithium atoms [e.g., IV ($\rightleftharpoons$ IV′)] with equal or only slightly different chemical shifts cannot be excluded. The remaining possible structures for $(II)_2$ with fully coordinated lithium atoms, V–VIII, are not in agreement with the −90 °C $^1H$ NMR data.



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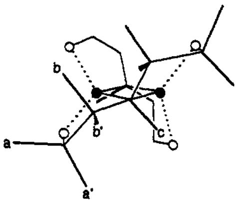

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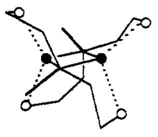

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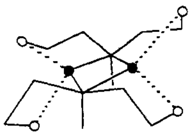

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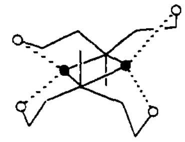

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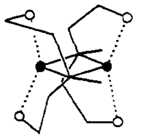

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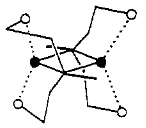
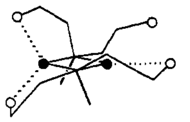


VIII



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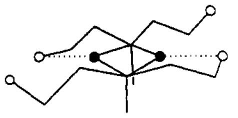

X

● = Li ○ = OMe

The coalescence temperature of the methoxy proton signals (−91 ± 2 °C) shows that $\Delta G^{\ddagger}$ for the chelate ring transpositions has a value of 9.3 ± 0.2 kcal/mol, which is lower than those ($\Delta G^{\ddagger}$ = 12–15 kcal/mol) found for similar transpositions ($CH_2OMe$,[10] $CH_2NMe_2$[6b]) in intramolecularly coordinated alkyllithium tetramers. We suppose that the breaking of Li–O coordinative bonds

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(1) (a) Crystal structures: Schleyer, P. v. R.; Setzer, W. *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Solution structures: Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664. Brown, T. L. *Pure Appl. Chem.* **1970**, *23*, 447. McKeever, L. D. *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 263 and references given in these papers.

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(8) The preparation of II and all operations involving II were carried out in evacuated sealed vessels by using the break-seal technique.

(9) Chemical shift of $^7Li$ relative to external 1 M dry LiBr in THF [$\delta$ (50% LiBr in $H_2O$) −1.04 and $\delta$ (2-lithiobutane in $C_6D_6$) 0.77. Not corrected for volume magnetic susceptibility.

(10) Klumpp, G. W.; Vos, M.; Dorlas, R.; de Kanter, F. J. J., unpublished results.

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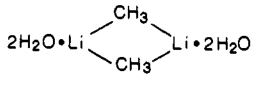
**Table I.** $^1H^a$ and $^{13}C^b$ NMR Spectra [$\delta$ ($Me_4Si$), ppm] of $(II)_2$

| temp, °C | $H_{a'}$ | $H_a$ | OMe | $H_b$ | $H_{b'}$ | $H_c$ | $C1(H_aH_{a'})$ | OMe | $C2(H_bH_{b'})$ | $C3(H_c)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 23 | 3.671<br>m$^c$ | 3.445<br>m$^c$ | 3.338<br>s | 2.202<br>m$^c$ | 1.860<br>m$^c$ | −1.055<br>tt$^c$ | 78.3<br>t, 139 Hz | 58.3<br>q, 139 Hz | 41.4<br>t, 118 Hz | 24.6<br>br s |
| −90 | 3.67<br>br m | 3.44<br>br m | 3.358 s<br>3.318 s<br>(1:1) | 2.22 br m<br>2.19 br m<br>(1:1) | 1.87 br m<br>1.84 br m<br>(1:1) | −1.055<br>tt$^c$ | | | | |
| −100 | | | | | | | 77.6 t<br>77.2 t<br>(1:1) | 57.4 q | 39.8 t | $d$ |

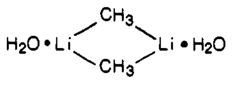
$^a$In $n$-$C_5D_{12}$. $^b$In $C_6D_6$ (23 °C) and cyclopentane (−100 °C). $^c$$J$(Hz): a′a, 7.8; a′b, 11.4; a′b′, 2.7; ab, 4.2; ab′, 3.2; bb′, 13.8; bc, 12.3; b′c, 5.3. $^d$Coincides with signal of cyclopentane ($\delta$ 25.3).

in rate-determining steps such as III → IX (→ V → IX′ → III′) or III → X (→ III′) is partially compensated by stronger bonding of the chelate moieties that remain attached to the tricoordinated lithium atom(s) in IX (X).[11]

Model MNDO calculations on XI and XII



XI



XII

indicate that 80% of the coordination energy of XI is retained in XII![12] Greater steric accessibility and neutralization of negative charge on carbon by two lithium cations (instead of three, in the case of tetramers) have been adduced as possible causes for the higher reactivity of organolithium dimers vs. tetramers.[2a] Greater ease of displacement of a solvating Lewis base by the reactant in the precoordination step of organolithium reactions[13] is now offered as an additional reason. The broadening in the proton spectrum at the lower temperature limit of −110 °C is tentatively ascribed to the loss of conformational mobility of the chelate rings. At 71 °C inversion of C3 ($H_c$ quintet) occurs with $\Delta G^* > 16$ kcal/mol (separate signals for $H_b$ and $H_{b'}$).

The effect on reactivity of lowering the degree of aggregation from 4 to 2 and doubling the number of solvating ether molecules was assessed for secondary alkyllithiums by comparing the reactivities of $(II)_2$ and tetrameric 3-lithio-1-methoxybutane $(XIII)_4$.[6a] In competition experiments involving benzaldehyde and a mixture in pentane of $(II)_2$ and $(XIII)_4$ (each in eightfold molar excess and each showing its own typical $^1H$ and $^7Li$ NMR signals), the ratio of the secondary alcohols formed provided values of $k_{(II)_2}:k_{(XIII)_4}$ of 3.0 (23 °C) and 7.5 [−17 °C, $\Delta\Delta H^* = 3.4$ kcal/mol, $\Delta\Delta S^* = 9.5$ cal/(mol K)]. In separate experiments at 26 °C terminated after 77 h by quenching with $ClSnMe_3$, $(II)_2$ and $(XIII)_4$ (0.224 mmol) dissolved in a mixture of 9.7 mL of pentane and 0.6 mL of toluene (5.6 mmol) gave $\alpha$-(trimethylstannyl)toluene in 11.4% and 3.9% yield, respectively. Relative reactivity data are available for two other alkyllithium dimers: at 50 °C, yields of benzyllithium from menthyllithium (dimer) and cyclohexyllithium (tetramer and/or hexamer) dissolved in toluene were 35% and 6.2%, respectively.[14] At −85 °C in THF, I reacts with benzaldehyde about 10 times faster than the tetramer.[15] Though the results of the present and the former studies are strikingly similar we refrain from generalizing, since the differences between the systems compared are still considerable.

**Acknowledgment.** We thank G. Schat for the association measurements.

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(11) Since no Li-O coordinative bond has to be broken, internal rotation in $(n\text{-}BuLi)_2$ (see ref 3) is presumed to be even faster than the processes operating on $(II)_2$.

(12) See also ref 1a, p 364. According to MNDO, synchronous exchange of the two Lewis base ligands at the same lithium atom is less favorable than processes leading to IX or X.

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## Slow Triplet Energy Transfer to Lower Excited States in Ruthenium(II) Acylpyridine Complexes

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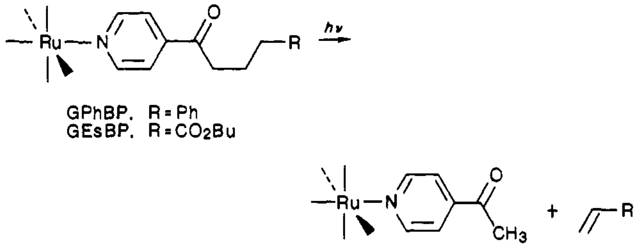
A few years ago we reported that locally excited acylpyridine (AP) triplets in $Ru^{II}(NH_3)_5AP$ complexes undergo relatively slow internal conversion (IL → MLCT) to the lower lying metal-to-ligand charge-transfer states.[1] At that time, we could merely place a maximum value of $10^8$ $s^{-1}$ on the rate constant $k_{ic}$ for such internal conversion. We now can report the actual value more precisely. We also find that internal quenching of triplet acylpyridines in $Ru^{II}(bpy)_2(AP)_2$ complexes by triplet energy transfer from acylpyridine to bipyridine is unexpectedly slow, unique behavior for two organic chromophores held so close together.



We have studied the reactivity of two 4-acylpyridines: $p$-($\gamma$-phenylbutyryl)pyridine (GPhBP) and $p$-($\gamma$-carbobutoxybutyryl)pyridine (GEsBP). As Table I shows, these two ketones undergo Norrish type II photoelimination[2] in identical quantum efficiency in acetonitrile. Stern–Volmer quenching studies, with ethyl sorbate as quencher, indicate that triplet GEsBP is only 6% as reactive as triplet GPhBP, as anticipated from earlier studies.[3] Likewise, the two hydrochloride salts react with the same quantum efficiency as each other and exhibit the same ratio of triplet reactivities. As is now well understood,[4] the observation of identical quantum yields but much different triplet lifetimes indicates that the triplets undergo no reaction except $\gamma$-hydrogen abstraction ($k_r = 1/\tau$) and that quantum yields are determined solely by later biradical partitioning.

The $Ru(NH_3)_5(AP)(BF_4)_2$[1] and $Ru(bpy)_2(AP)_2(BF_4)_2$[5] complexes were prepared as described in the literature. Irradiation at 313 nm of 0.004–0.04 M acetonitrile solutions did not cause

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