

IR. SPECTRA OF COMPLEXES OF n- AND s-BUTYLLITHIUM WITH ELECTRON DONORS

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(Received October 2nd, 1978)

Summary

Complexes of n- and s-butyllithium (BL) with THF, $(\text{CH}_3)_2\text{O}$ and $(\text{CH}_3)_3\text{N}$ have been investigated over a wide temperature range (+20 to -100°C). These electron donors (D) are much less actively complexed with s-BL than with n-BL. For both alkyllithium compounds the trend of D to complexation decreases in the following order: $\text{THF} > (\text{CH}_3)_2\text{O} > (\text{CH}_3)_3\text{N}$. Usually, for the n-BL/D systems several complexes coexist with different Li/D ratios. At low temperatures and at the n-BL/D ratio ≥ 4 , in addition to complexes with the limiting stoichiometry $(\text{n-BL})_4 \cdot 4\text{D}$, associates complexed with one D molecule and a hexamer n-BL are present. The bands of $\nu(\text{C-Li})$ stretching vibrations for s-BL complexes are not very characteristic and therefore only the average stoichiometry of the complex can be evaluated; the limiting stoichiometry detected was $(\text{s-BL})_4 \cdot 4\text{D}$. It is supposed that as the temperature decreases the inversion of the molecules of s-BL occurs during their interaction with excess ethers.

Many papers deal with the association of alkyllithium compounds and complexes with electron donors. Spectroscopic methods and methods based on the determination of colligative properties of particles [1] have been used. It has been shown that in hydrocarbon media n-butyllithium (n-BL) exists as hexamer (H) and s-butyllithium (s-BL) as tetramer (T) over a wide concentration range [2]. Isopropylolithium (i-PrLi) is transformed from T to H with increasing concentration (above 0.02 M) [2,3]. In electron donor media n-BL is dissociated to the tetrameric form [4]. The addition of electron donors to hydrocarbon solutions of n-BL is accompanied by stepwise solvation of n-BL with a simultaneous change in the degree of association [2,5,6]. However, the relationship between the structure of alkyllithium compounds and their tendency towards association and complexation has not been studied in detail. Studies of the complexation of branched alkyllithium compounds with electron donors are not numerous and are usually

carried out at temperatures close to room temperature [5], whereas many processes, including polymerization, are often studied at -70°C and at even lower temperatures.

Hence, we have studied in this work the IR spectra of the complexes of n-BL and s-BL with THF, $(\text{CH}_3)_2\text{O}$ and $(\text{CH}_3)_3\text{N}$ over the temperature range from 20° to -100°C . The selected electron donors have no rotational isomers and this facilitates the interpretation of IR spectra. A comparison of the complexing ability of n-BL, s-BL and i-PrL was made.

Results and discussion

The complexation of alkyllithium compounds with ethers and amines is exhibited in the IR spectra as the low-frequency displacement of three groups of bands: stretching symmetric ($\nu_s(\text{CO})$, $\nu_s(\text{CN})$) and asymmetric ($\nu_{as}(\text{CO})$, $\nu_{as}(\text{CN})$) vibrations of CO and CN groups, bending vibrations of CH ($\delta(\text{CH})$) and stretching vibrations of C—Li ($\nu(\text{CLi})$) (Table 1). It should be noted that the displacement of bands $\nu(\text{CO})$ and $\nu(\text{CN})$ to lower frequencies is only slightly dependent on the nature of the acceptor and the stoichiometry of the complex. Hence, the bands of complexed electron donors are not very sensitive to the manifestations of stepwise solvation [6]. However, quantitative measurements based on the determination of the intensities and half-widths of the bands make it possible to obtain data on the stoichiometry of the complexes and their energy characteristics. The bands of bending vibrations of C— $\text{CH}_2(\text{Li})$ in the region $800\text{--}1000\text{ cm}^{-1}$ are displaced towards low frequencies during complexation, but this displacement is usually small (Table 1). The bands of stretching vibrations $\nu(\text{CLi})$, that undergo a stepwise displacement to lower frequencies (n-BL complexes) with increasing concentration of D, are the most sensitive to complexation.

n-BL and s-BL exhibit two bands in the region of $\nu(\text{CLi})$ at 370 and 550 cm^{-1} for n-BL and 445 and 518 cm^{-1} for s-BL. The region of the IR spectrum below 400 cm^{-1} was not investigated. The band at 445 cm^{-1} strongly overlaps the i-octane band at 453 cm^{-1} . Hence, changes in the $\nu(\text{CLi})$ region related to complexation were considered mainly for the high-frequency vibrations of the $\nu(\text{CLi})$ bond in n- and s-BL.

When equimolar amounts of n-BL and s-BL are mixed in complexation, a broad band in the region of $\nu(\text{CLi})$ with a maximum at 533 cm^{-1} is observed. The mixed associate formed is relatively stable, as indicated by the unchanged $\nu(\text{CLi})$ band in the range from $+10$ to -100°C . If we compare the 533 cm^{-1} band to the position of $\nu(\text{CLi})$ band for the initial compounds (550 cm^{-1} for n-BL and 518 cm^{-1} for s-BL), it might be suggested that s-BL is a weaker Lewis acid. This fact may be explained by the positive induction effect of the CH_3 group in s-BL.

Our experimental data show that the complexation of n-BL and s-BL with electron donors proceed by different routes. Moreover, some peculiarities of complexation can be seen when the interactions of different alkyllithium compounds with ethers and $(\text{CH}_3)_3\text{N}$ are compared.

The consideration of complexation in the case of n-BL shows that when the donor is in excess or the temperature is low, a tetramer (T) of n-BL solvated by four electron donor (D) molecules, TD_4 , is the limiting structure [6–8] (Table 1). The intermediate complexes HD, TD, TD_2 and TD_3 appear as $\nu(\text{CLi})$ bands

displaced towards low frequencies. The assignment of the $\nu(\text{CLi})$ bands to each structure was made in experiments with the corresponding predetermined stoichiometry of n-BL and D from the $\nu(\text{CO})$ ($\nu(\text{CN})$) bands of free and bound D under conditions of the predominant formation of complexes of only one type (see also [6–8]). If several complexes are present in the system the $\nu(\text{CLi})$ bands are markedly superimposed. However, it is possible to distinguish clearly the corresponding bands for TD_2 and TD_4 complexes at 530 and 504 cm^{-1} , respectively.

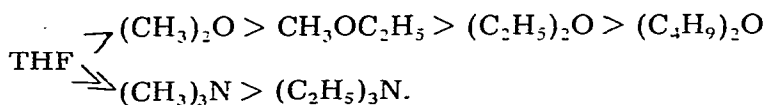
In contrast, the $\nu(\text{CLi})$ bands of s-BL complexes are not very sensitive to changes in the stoichiometry of the complexes (Table 1). The maximum amount of D molecules capable of interacting with the associate of s-BL was unknown. To determine the structure of the complexes, data on the intensity of the $\nu_{\text{as}}(\text{CO})$ ($\nu(\text{CN})$) bands of D were used. Since at lower temperatures or with excess of D equimolar amounts of s-BL and D are complexed, we concluded that the limiting complex is TD_4 , just as in the case of n-BL. It is of interest to note that the two last molecules of $(\text{CH}_3)_3\text{N}$ are complexed only within a narrow temperature range, from -70 to -100°C . The TD_4 complex is formed under much milder conditions when THF and $(\text{CH}_3)_2\text{O}$ are used.

When the third and the fourth D molecules are bonded to n-BL and s-BL tetramer, a slight ($2\text{--}3 \text{ cm}^{-1}$) high frequency displacement of the ν_{as} band of bonded D is observed. This shows that the coordination bond $\text{Li}\cdots\text{D}$ is slightly weakened. When the last and the penultimate molecules are complexed, the D bands become much broader. This indicates that complexes of various types coexist, since for a single structure the bands of the bound donor become narrower with decreasing temperature, due to the decreased rotational mobility of the molecules in the complex [8].

A comparison of $\nu_{\text{as}}(\text{CO})$ ($\nu_{\text{as}}(\text{CN})$) of the bound and free D in complexation with n- and s-BL under identical conditions, shows that the complexing ability of s-BL with the selected donors is much lower than that of n-BL. For example, at n-BL/D 2:1 and 0°C no free D remains, whereas at s-BL/D 4:1 the IR spectrum exhibits bands due to free $(\text{CH}_3)_3\text{N}$ and $(\text{CH}_3)_2\text{O}$. This may be interpreted as due to different accessibility of the lithium atom in these alkyllithium compounds. It is possible that different maximum values of the low frequency displacement $\Delta\nu(\text{CLi})$ in the formation of TD_4 (46 cm^{-1} for n-BL and 13 cm^{-1} for s-BL) are related precisely to the nature of the alkyl radical. It should be noted however, that the initiation rate for non-polar monomers in hydrocarbon media is much higher for s- than for n-BL [9].

However, the series of relative abilities of the investigated D for complexation with n-BL and s-BLi are identical: $\text{THF} > (\text{CH}_3)_2\text{O} \gg (\text{CH}_3)_3\text{N}$.

For both alkyllithium compounds the most stable complexes are those with THF due to both the good electron donor properties of THF ($I = 9.49 \text{ eV}$ [10]) and the steric accessibility of the oxygen atom which is the centre of interaction. The significance of the steric factor in the donor structure can be seen if complexes with n-BL are taken as an example (see also [7,8]):



In contrast to the complexes of s-BL with TMA, complexes of the former with

TABLE 1
 SOME FREQUENCIES OF THE VIBRATIONS (cm^{-1}) OF ALKYL LITHIUM COMPOUNDS AND DONORS IN THE FREE AND BONDED STATE
 (H-hexamer, T-tetramer, D-electron donor)

Com- pound	$\nu(\text{C}(6)\text{Li})$ (free)		$\nu(\text{C}(7)\text{Li})$ (free)		$\nu(\text{C}(7)\text{Li})$ (complex)				$\delta(\text{C}(6)\text{H}(\text{Li}))$		$\nu_{\text{as}}(\text{Co}(\text{CN}))$		$\nu_3(\text{Co}(\text{CN}))$	
	H	T	H	T	HD ₁ , TD ₁	TD ₂	TD ₃	TD ₄	Free	Com- plex ^a	Free	Com- plex ^a	Free	Com- plex ^a
n-C ₄ H ₉			550		547-535	536- 530	525- 520	504	967	967	1074	1054	912	880
s-C ₄ H ₉	530	518				518-505; 475			942	938	1096	1087	924	920
	475	445				440-430			867	860				
i-C ₃ H ₇	558	480	508	480	475-465				1060	1058	1043	1026	828	822
	470	>400	417	>400	>400				835	828				

^a Frequencies correspond to the stoichiometry of TD₁ or TD₂

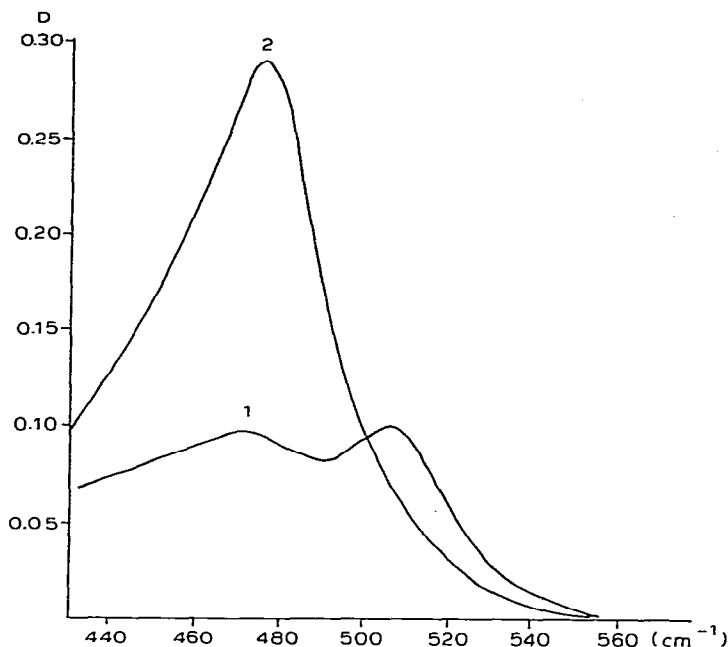


Fig. 1. $\nu(\text{CLi})$ of the system s-BL/THF 1/1.55, 1) -26°C , 2) -53°C . $[\text{s-BL}]$ 0.36 mol l^{-1} , layer thickness 115μ .

THF and $(\text{CH}_3)_2\text{O}$ exhibit a band at 475 cm^{-1} which dominates the spectrum when ethers are present in excess and the temperatures are low (Fig. 1). In contrast, when $(\text{CH}_3)_3\text{N}$ is present in excess this band is absent. It should be emphasized that when D is present in excess and the temperatures are relatively low, equimolar amounts of s-BL and each D can be complexed. Hence, the band at 475 cm^{-1} cannot be associated with the formation of TD_1 alone.

One can hardly suppose that during complexation the degree of association of alkyllithium can increase. On the other hand, it is also improbable that the band at 475 cm^{-1} , appearing at temperatures that do not exceed -15°C and increasing in intensity as the temperature decreases, is due to the formation of dimeric (monomeric?) complexes of s-BL with ester. Quantum chemical investigations show [11] that the associated forms are more advantageous than the monomeric forms. In the absence of D and with decreasing temperature the fraction of a more associated form can increase [3].

The quantum chemical investigations show that several alkyllithium conformations can coexist [12]. It is known that in complexes with alkyllithium compounds, ethers are mainly in *gauche*-conformations whereas in the free state the planar *trans*-conformation is preferred [13]. In other words, it can be assumed that when the temperature decreases the geometry of the molecules of s-BL in the associate can alter. Moreover, the degree of association of the associate bonded in the complex can remain unchanged.

An important point in the elucidation of the mechanism of complexation is the establishment of a relationship between the complexation and dissociation of the initial associates when they complex with D. At n-BL/D 2:1 for THF and

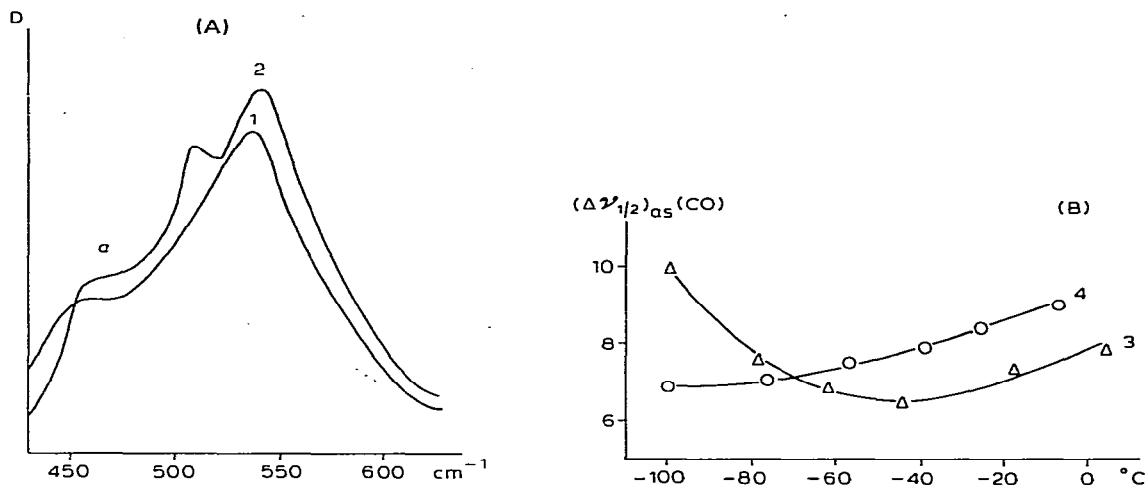


Fig. 2. (A) $\nu(\text{CLi})$ of *n*-BL in complex *n*-BL/ $(\text{CH}_3)_2\text{O}$ 2/1, 1 – 51°C 2 – 100°C. (B) Temperature dependence of the half-width $(\Delta\nu_{1/2})_{\text{as}}(\text{CO})$ for the systems *n*-BL/ $(\text{CH}_3)_2\text{O}$ 2/1 (curve 3) and *s*-BL/ $(\text{CH}_3)_2\text{O}$ ~2:1 (curve 4) [*n*-BL] = [*s*-BL] = 0.4 mol l⁻¹. *a* *i*-Octane.

$(\text{CH}_3)_2\text{O}$ at -30°C , all the donor is complexed and only the band at 530 cm^{-1} is observed in the region $\nu(\text{CLi})$ [6] (see Table 1). However, in the range from -50 to -100°C for THF and $(\text{CH}_3)_2\text{O}$, and from -70 to -100°C for $\text{CH}_3\text{OC}_2\text{H}_5$ and $(\text{CH}_3)_3\text{N}$, the situation in the region of $\nu(\text{CLi})$ is different. In the absence of free D the intensity of the band at 530 cm^{-1} decreases with decreasing temperature. At the same time two new bands appear with maxima at 504 and $535\text{--}538\text{ cm}^{-1}$ * (depending on D) [7,8] (Fig. 2a). It should be noted first of all that the most drastic changes are observed for the weakest of the donors investigated, $(\text{CH}_3)_3\text{N}$; for THF and $(\text{CH}_3)_2\text{O}$ the effect is somewhat less pronounced. This redistribution of bands suggests that disproportionation occurs according to eq. 1.



Nevertheless, since this redistribution of bands occurs with decreasing temperature, the question of the driving force of this process remains unresolved. On the other hand, the energy required for the degradation of TD_2 can be obtained by the formation of a more highly associated structure HD_1 (eq. 2).



In this case the appearance of broad bands at $535\text{--}542\text{ cm}^{-1}$, (depending on D) in the absence of disproportionation at temperatures not lower than -20°C for the systems with the *n*-BL/D 4/1, can be interpreted by the simultaneous formation of two structures: TD_1 and HD_1 . It is difficult to separate the two bands assigned to these structures. However, since the bands are displaced towards higher frequencies (up to 547 cm^{-1}) when the Li/D ratio increases from 2 to 6, it might be suggested that the band at the lower frequency can be assigned to TD_1

* In reference 8, p. 782, line 14 from below should read 537 cm^{-1} instead of 547 cm^{-1} . Curve 4 in Fig. 3 is correct.

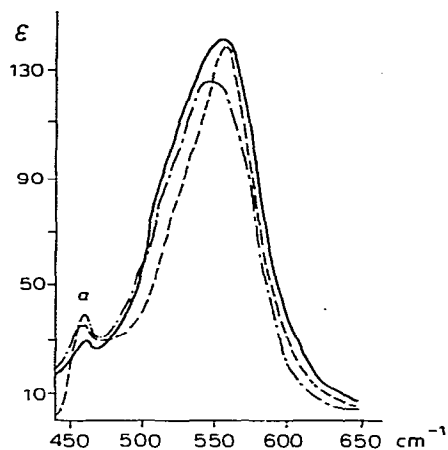


Fig. 3. $\nu(\text{CLi})$ (1) — — — n-BL [n-BL = 0.35 mol l^{-1} , -101°C]; (2) - · - · - n-BL/THF 3.9/1 ([n-BL] = 0.35 mol l^{-1} , -102°C); (3) — — — n-BL/THF 6/1 [n-BL] = 0.36 mol l^{-1} , -95°C). $\epsilon = D/cd$ where D is the optical density, c is the concentration of n-BL, d is the layer thickness (124μ). a i-Octane.

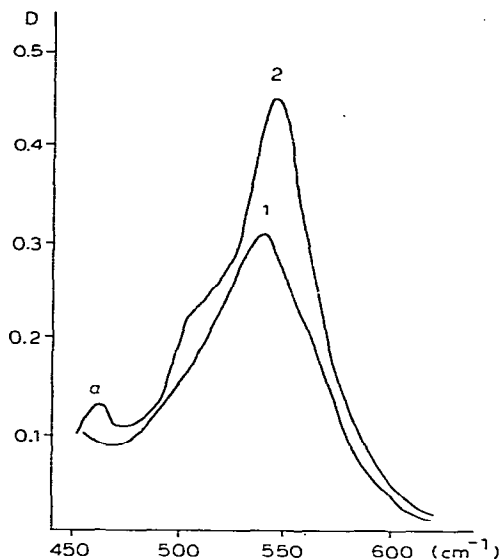
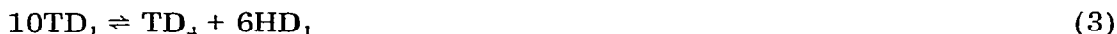


Fig. 4. $\nu(\text{CLi})$ of the system n-BL/TMA 5.63/1 (1) $+3^\circ\text{C}$; (2) -95°C . [n-BL] = 0.4 mol l^{-1} , layer thickness $100 \mu\text{m}$ a i-Octane.

and that at the higher frequency to HD_1 . At n-BL/D 4:1 the intensity of the band at 504 cm^{-1} appearing at low temperatures is greatly reduced. For THF it is indicated only as a small shoulder (Fig. 3, curve 2). It should be emphasized that the initial band at $535\text{--}542 \text{ cm}^{-1}$, (depending on D) corresponding to the predetermined stoichiometry 4 Li/1 D, becomes weaker as the temperature decreases. Simultaneously, two bands at lower (504 cm^{-1}) and higher (up to 547 cm^{-1}) frequencies appear. On the basis of these experiments the formation of the HD_1 structure (eq. 3) seems highly probable.



The disproportionation observed at n-BL/D $> 4/1$ was even more unexpected (Fig. 4, see also Fig. 3, curve 3). Irrespective of whether the TD_1 or HD_1 complex existed or not at relatively high temperatures, this disproportionation effect can be interpreted only by the assumption of the coexistence of TD_1 and the uncomplexed n-BD at low temperatures (eq. 4).



Another spectral effect related to disproportionation is the change in the band width of the bonded donor when the complex with n-BL is formed (Fig. 2, curve 3). The anomalous shape of the temperature dependence of the half-width of the $\nu_{\text{as}}(\text{CO})$ ($\nu_{\text{as}}(\text{CN})$) bands appears simultaneously with the appearance of the band at 504 cm^{-1} .

As was already mentioned, for s-BL the bands in the region of $\nu(\text{CLi})$ cannot be assigned to definite types of complex. Correspondingly, when this region is

considered it is impossible to draw any conclusions concerning the occurrence of disproportionation for complexes with s-BL. However, because the half-width of the $\nu_{as}(\text{CO})(\nu_{as}(\text{CN}))$ bands monotonically decreases with decreasing temperature (Fig. 2, curve 4), it might be suggested that for the complexes of s-BL, disproportionation either does not occur at all or occurs only to a slight extent.

Our interpretation of the above facts is based on the assumption of the coexistence of TD_1 and HD_1 , but this assumption was not proven. To elucidate this question, IR spectra of complexes of THF and n-BL were recorded over the temperature range from +20 to -100°C with a six- and four-fold excess of n-BL (Fig. 4). If the complex of HD_1 was not formed two bands in the region of $\nu(\text{CLi})$ could be expected for the initial stoichiometry 6n-BL : 1D; the band at 550 cm^{-1} due to the uncomplexed hexamer and the band due to the TD_1 complex. In this case, however, the broadest band is observed; its components may include $\nu(\text{CLi})$ of TD_1 , HD_1 and H. For n-BL/THF 3.9/1 the band of $\nu(\text{CLi})$ is narrower and displaced towards lower frequencies (535 cm^{-1}). In this case the main contribution is probably that of TD_1 but HD_1 , H and TD_2 can also be present in small amounts.

Experimental

IR spectra in the region $400\text{--}1300\text{ cm}^{-1}$ were recorded with a UR-20 spectrometer in sealed KBr cells $100\text{--}150\text{ }\mu$ thick. A cryostat with liquid nitrogen as cooling medium was used for thermostating to within $\pm 2^\circ\text{C}$. The temperature was measured with a differential thermocouple with one thermojunction placed in the cell window.

All operations with alkyllithium compounds, electron donors and their complexes were carried out in all-sealed systems under high vacuum ($10^{-5}\text{--}10^{-6}$ mmHg). Solutions were prepared in special double-chamber instruments. The upper chamber was closed with a self-sealing cap and the lower chamber was equipped with inlets to which ampules containing solutions of substances were sealed. After evacuation the upper chamber was filled with argon. Solutions of alkyllithium and the donor were mixed in the lower chamber at -78°C immediately prior to their introduction into the cell, after which the break-seal between the chambers was crushed. This procedure excluded the presence of traces of moisture and air-oxygen in the system. The appearance of lithium alkoxides was followed by monitoring the band at 615 cm^{-1} .

In the presence of an excess of ethers, in particular THF, s-BL and i-PrLi are unstable and react to form products absorbing at 550 cm^{-1} . At temperatures below -30°C the complexation is not accompanied by side reactions. n-BL is more stable to reactions with ethers. In contrast, the degradation of trimethylamine was not observed over the entire range of temperatures and ratios investigated.

Prior to use, purified donors and i-octane (2,2,4-trimethylpentane) were condensed from concentrated n-BL. Alkyllithium compounds were synthesized in pentane in all-sealed systems under high vacuum and the solvent subsequently replaced with i-octane.

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