

Study of the Lithiated Phenylacetonitrile Monoanions and Dianions Formed According to the Lithiated Base Used (LHMDS, LDA, or *n*-BuLi). 1. Evidence of Heterodimer (“Quadac”) or Dianion Formation by Vibrational Spectroscopy

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Received July 25, 2002

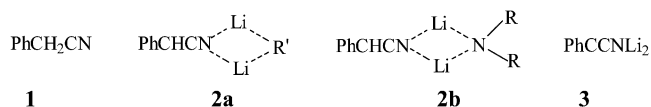
It is evidenced through vibrational spectroscopy that a heterodimer or “Quadac” is formed when an excess of base (LHMDS, LDA, or *n*-BuLi) is added to PhCH₂CN in THF, THF–hexane, or THF–toluene solution. The amount of heterodimer increases with the p*K*_{H_a} of the lithiated base. A dianionic species may be formed through decomposition of this heterodimer if the p*K*_{H_a} of the base is sufficiently high, as in the case of *n*-BuLi. With LDA, only a very small amount of dianion is observed, and with LHMDS, no dianion is detected. The predominant dianionic species observed are the linear and bridged separated ion pairs of the dilithiated dianion. The presence of the amine in the medium is of paramount importance. The PhCHCNLi monomer–dimer equilibrium is entropy driven toward the dimer solvated by the amine.

Introduction

gem-Dilithiated reagents prepared by metalation of compounds containing acidic hydrogens, as, for instance, alkyl, allyl, benzyl, phenyl sulfones and phenyl^{1,2} or trimethylsilyl acetonitriles,³ possess great synthetic potential.

Kaiser et al.⁴ have postulated the formation of a dianion (**3**) from PhCH₂CN (**1**) with an excess of *n*-butyllithium (*n*-BuLi), on the basis of deuteration and alkylation experiments. Later on, Crowley et al.⁵ investigated the reaction of PhCH₂CN with 2 equiv of lithium hexamethyldisilazide (LHMDS) by ¹³C NMR experiments and have not observed dianion formation. According to the base used, a sequential process involving a rapid intra-aggregate lithiation through a species called a heterodimer or quasi dianion complex “Quadac” (**2a** with R' = *n*-Bu, or **2b** with R = *i*-Pr or Me₃Si) rather than direct dianion (**3**) formation was proposed.

The structure of the heterodimer, in which lithium diisopropylamide (LDA) is the base, was established by Zarges et al. by X-ray crystal analysis.⁶ More recently,



the structure of the heterodimer, in which LHMDS is the base, was confirmed by ⁶Li/¹⁵N NMR solution study in TMEDA/toluene.⁷

We have been particularly interested in the elucidation of the structures of the lithiated species derived from PhCH₂CN under a slight excess of base in different media by IR, FT-Raman, and ¹³C NMR spectroscopies.⁸ We have thus shown that the 1,2- versus 1,4-regioselectivity of lithiated phenylacetonitrile toward α,β-unsaturated carbonyl compounds^{9,10} was related to the ion-pair monomer–dimer equilibrium.

In this paper, we present the IR, FT-Raman, and ¹³C NMR spectroscopic study of the species formed from PhCH₂CN with an excess (1–3 equiv) of different bases (LHMDS, LDA, and *n*-BuLi) in THF, THF–hexane, and THF–toluene (30/70 v/v) media. We have calculated the structures and the spectra¹¹ of most species by the B3-

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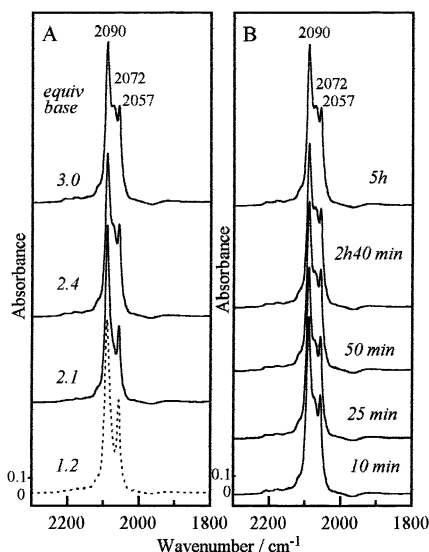


FIGURE 1. Evolution of the IR spectra of a 0.25 M solution of PhCH₂CN in THF in the $\nu(\text{CN})$ spectral region: (A) with increasing amounts of LHMDS (time, 10 min); (B) with time (LHMDS, 3 equiv).

LYP method,^{12,13} based on density functional theory (DFT). The calculated spectra have been compared to the experimental spectra of the mono- and dianionic species observed in the presence of *n*-BuLi.¹¹ This comparative study allows identification the species by their vibrational spectra. The influence of the secondary amine (*i*-Pr)₂NH or (Me₃Si)₂NH on the monomer–dimer equilibrium will be discussed. These results will be used in the second part of this paper to explain the nature of the products obtained by alkylation with benzyl chloride or by deuteration with DCl solution in D₂O (4 N) of the anions formed with different bases.

Besides the different monoanionic (monomers, dimers, heterodimer) and dianionic species, we have observed a THF cleavage reaction with *n*-BuLi leading to the formation of the acetaldehyde lithium enolate. The mechanism of this reaction and the structure of the species have been presented in another paper.¹⁴

Results and Discussion

(1) Vibrational Study of the Anionic Species Formed in Solution According to the Nature and the Concentration of the Base. (1.1) LHMDS. Figure 1A shows the evolution of the IR spectra of a 0.25 M solution of PhCH₂CN in THF in the $\nu(\text{CN})$ spectral range with increasing amounts of LHMDS added to the solution. With 1.2 equiv of LHMDS, the main IR bands observed at 2090 and 2057 cm⁻¹ are related to PhCHCNLi ion pair and to its dimer (PhCHCNLi)₂, respectively, as already described.^{8–10} When the base amount increases up to 3.0 equiv, only small changes are observed. The intensity of the bands at 2090 and 2057 cm⁻¹ slightly decreases, and a new band appears at 2072 cm⁻¹.

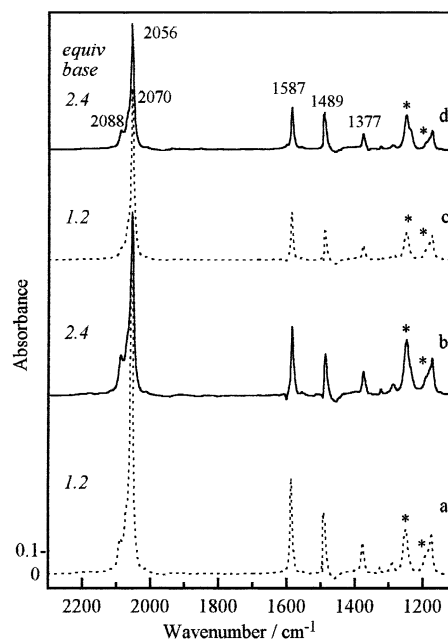


FIGURE 2. IR spectra of a solution of PhCH₂CN in THF–toluene solvent mixture (30/70 v/v) at two concentrations [(a) and (b) 0.25 M; (c) and (d) 0.12 M] and for two LHMDS amounts [(a) and (c) 1.2 equiv; (b) and (d) 2.4 equiv] (time, 10 min). The bands marked by a star are related to (Me₃Si)₂NH amine formed.

This indicates the formation of a new species. Figure 1B shows the evolution with time of the spectra of PhCH₂CN in THF in the $\nu(\text{CN})$ range for 3.0 equiv of LHMDS added to the solution. The appearance of the new band within 10 min indicates that the formation of the related species is rather fast. To favor the formation of this new species, we have used a less dissociating media such as a THF–toluene solvent mixture (30/70 v/v). Figure 2 shows the IR spectra of PhCH₂CN for two different concentrations (0.25 and 0.12 M) in this solvent mixture. With 1.2 equiv of LHMDS, only a small amount of PhCHCNLi still remains, while (PhCHCNLi)₂ is predominant, with the two coupled antisymmetric and symmetric $\nu(\text{CN})$ modes at 2056 and 2070 cm⁻¹ (shoulder), respectively. With 2.4 equiv of LHMDS, the intensity of the dimer band at 2056 cm⁻¹ decreases, while a band about 2070 cm⁻¹ related to the new species appears. No great change is observed in the spectral region of the benzenic skeleton (Figure 2). We noticed the appearance of a shoulder on the low wavenumber side of the (Me₃Si)₂NH amine at 1250 cm⁻¹, this shoulder being assigned to the excess of LHMDS (Figure 2b,d). As shown by the X-ray structure of the heterodimer formed with LDA,⁶ or by the calculated structure of the (PhCHCNLi, CH₃-Li) heterodimer¹¹ (Figure 3A), the structure of the anion in this new entity is very close to that of (PhCHCNLi)₂ or of the linear PhCHCNLi observed in [PhCHCNLi, 12-crown-4].^{9,10,15} The only difference expected in the spectrum of the new species with respect to that of (PhCHCNLi)₂ is the presence of only one $\nu(\text{CN})$ mode. Thus, the band appearing at 2072 cm⁻¹ in THF solution (Figure 1) is assigned to the $\nu(\text{CN})$ vibration of the (PhCHCNLi,

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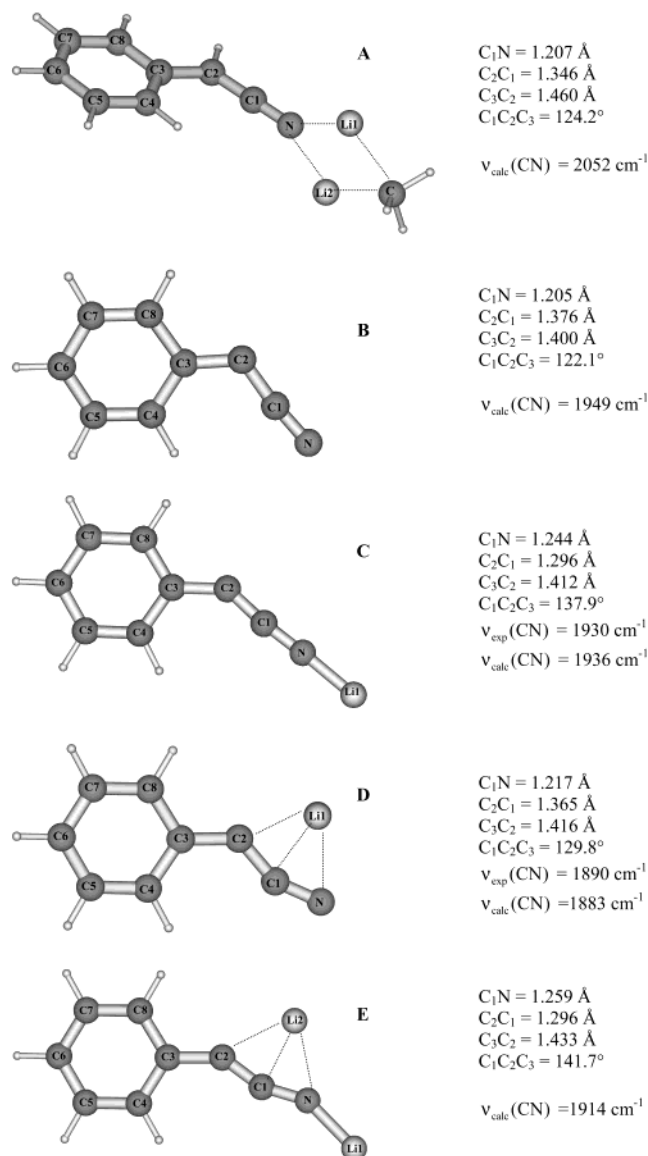


FIGURE 3. Calculated structures of $(\text{PhCHCNLi}, \text{CH}_3\text{Li})$ heterodimer (A), $(\text{PhCCN})^{2-}$ (B), linear $(\text{PhCCNLi})^-$ (C), bridged $(\text{PhCCNLi})^-$ (D), and PhCCNLi_2 (E) by the B3-LYP/DFT method using the 6-31+G* basis set (see ref 11). The hydrogen atoms are numbered as the carbon atoms to which they are bound. $\nu_{\text{exp}}(\text{CN})$ and $\nu_{\text{calc}}(\text{CN})$ are the experimental and calculated wavenumbers of the CN bond stretching, respectively.

LHMDS) heterodimer, taking into account the smaller basicity of LHMDS compared to that of CH_3Li . In the THF–toluene solvent mixture, the intensity of the $(\text{PhCHCNLi})_2$ band at 2056 cm^{-1} appreciably decreases and that of the PhCHCNLi band at 2088 cm^{-1} slightly increases on going from 1.2 to 2.4 equiv of LHMDS (Figure 2).

Under the addition of an excess of LHMDS, equilibria [2] and [3] (Scheme 1) appear. The formation of the heterodimer (equilibrium [3], Scheme 1), evidenced by the shoulder around 2072 cm^{-1} , leads to the decrease of the total PhCHCNLi and $(\text{PhCHCNLi})_2$ concentration. This shifts equilibrium [1] (Scheme 1) to the left, which decreases the dimer concentration at the benefit of the monomer concentration. This variation is observed in

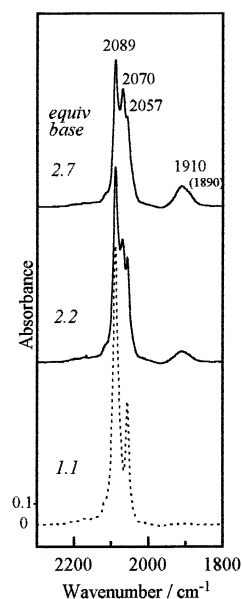


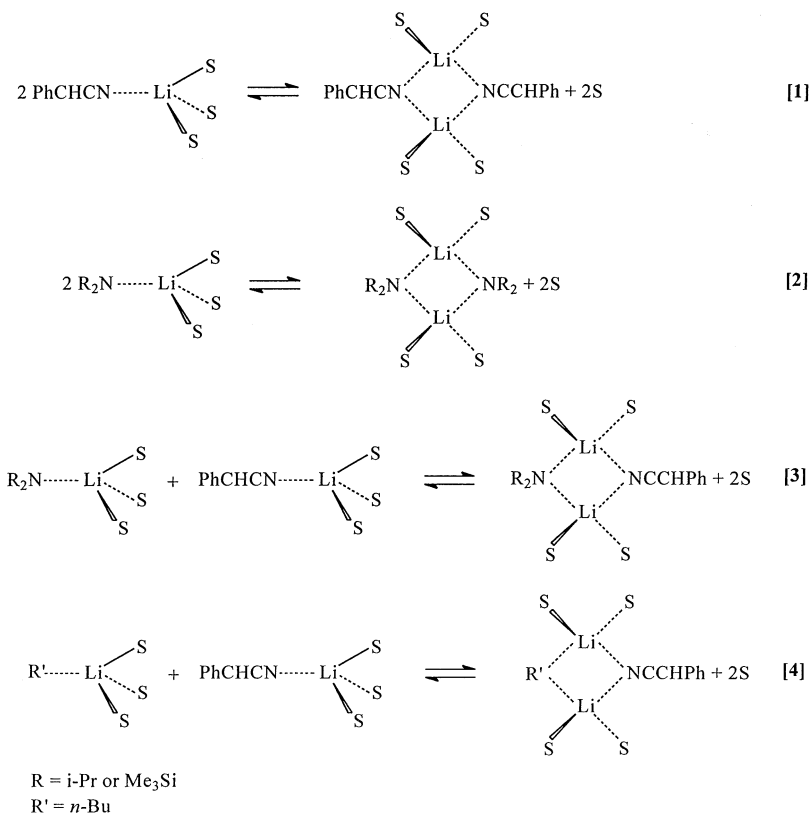
FIGURE 4. Evolution of the IR spectra of a 0.25 M solution of PhCH_2CN in THF in the $\nu(\text{CN})$ spectral region with increasing amounts of LDA (time, 2 h).

THF–toluene medium, but not in neat THF, due to the solvation by the conjugate acid formed, as will be seen further.

(1.2) LDA. Figure 4 shows the evolution of the IR spectra of a 0.25 M solution of PhCH_2CN in THF in the $\nu(\text{CN})$ spectral range with increasing amounts of LDA added to the solution. With 1.1 equiv of LDA, PhCHCNLi (at 2089 cm^{-1}) predominates over $(\text{PhCHCNLi})_2$ (at 2057 cm^{-1}). With an excess of LDA, the intensity of the bands of PhCHCNLi and $(\text{PhCHCNLi})_2$ strongly decreases and a band at 2070 cm^{-1} related to a $(\text{PhCHCNLi}, \text{LDA})$ heterodimer appears (equilibrium [3], Scheme 1). Despite the large decrease of PhCHCNLi and $(\text{PhCHCNLi})_2$ bands with LDA, the variation of the intensity ratio of the two bands indicates that equilibrium [1] (Scheme 1) is shifted to the right because of solvation of the species by the amine, as will be seen later on. On the other hand, with LDA, a small band around 1910 cm^{-1} appears. As for LHMDS, the heterodimer formation is fast and the equilibrium seems to be reached within 30 min. With 2.7 equiv of LDA, the heterodimer formation increases at the expense of equilibrium [1] (Scheme 1) and a shoulder around 1890 cm^{-1} appears on the low wavenumber side of the band at 1910 cm^{-1} . As will be seen below, these bands are related to a small amount of dianionic species.

(1.3) *n*-BuLi. Figure 5 shows the evolution of the IR spectra of a 0.25 M solution of PhCH_2CN in THF–hexane solvent mixtures with increasing amounts of *n*-BuLi added to the solution. With 1.1 equiv of *n*-BuLi, PhCHCNLi and $(\text{PhCHCNLi})_2$ are formed. The equilibrium between both species is shifted toward the dimer when compared to the equilibrium observed with 1.1 equiv of LHMDS (Figure 1A) or LDA (Figure 4) in THF. This is due both to the lowering of the dielectric constant of the THF–hexane medium (82/18 v/v) with respect to that of THF and to the decrease of the THF content (solvation). With an excess of *n*-BuLi (2.2–2.7 equiv), several new bands appear. The band at 2071 cm^{-1} is related to the $(\text{PhCHCNLi}, n\text{-BuLi})$ heterodimer (equilibrium [4], Scheme

SCHEME 1



1). But the most noticeable fact is the appearance in the $\nu(\text{CN})$ region of two strong bands at 1930 and 1890 cm^{-1} , the intensity of which increases with the excess of base added. Simultaneously, the intensity of the monoanionic species bands decreases, thus showing that the formation of the dianionic species is irreversible. In the benzenic skeleton region, two groups of bands are observed. First, bands appear in correlation with the disappearance of bands related to the benzenic skeleton modes of PhCHCNLi , $(\text{PhCHCNLi}, n\text{-BuLi})$ heterodimer, and $(\text{PhCHCNLi})_2$. For instance, the bands appearing at 1576 and 1481 cm^{-1} correspond, respectively, to the bands at 1585 cm^{-1} (mode 8a) and 1488 cm^{-1} (mode 19a), the intensity of which decreases. These benzenic skeleton bands, slightly shifted, and the strong bands at 1930 and 1890 cm^{-1} correspond well to the vibrational modes expected for a dianion (Figure 3), as previously shown by the calculations.¹¹ Second, three bands at 1608, 1314, and 1215 cm^{-1} (marked by an asterisk in Figure 5), the intensities of which do not correlate with the disappearance of the bands of the monoanionic species, are related to the most intense bands of the acetaldehyde lithium enolate formed by reaction of $n\text{-BuLi}$ in excess with THF. They correspond to the $\nu(\text{CC})$, $\beta(\text{CH})$, and $\nu(\text{CO})$ vibrational modes of this enolate anion, as has been shown recently.¹⁴

Figure 6 shows the evolution with time of the IR spectra of a 0.25 M solution of PhCH_2CN in THF–hexane solvent mixture (65/35 v/v) with 2.2 equiv of $n\text{-BuLi}$. The intensity of the $\nu(\text{CN})$ bands of PhCHCNLi at 2089 cm^{-1} and $(\text{PhCHCNLi})_2$ at 2057 cm^{-1} no longer varies after 20 min. This indicates that the formation of the $(\text{PhCHCNLi}, n\text{-BuLi})$ heterodimer (equilibrium [4], Scheme 1) is fast. The intensity of the heterodimer band located at

2068 cm^{-1} in this solvent mixture decreases at least during 70 min, while those of the dianion bands at 1930 and 1890 cm^{-1} slightly increase. The intensity decrease of the heterodimer band indicates that this species is in the way of the dianion formation, as will be confirmed further.

Figure 7 shows the evolution of the Raman spectra of a 0.25 M solution of PhCH_2CN in THF–hexane solvent mixtures with increasing amounts of $n\text{-BuLi}$. Behaviors similar to those of the IR spectra are expected for the Raman spectra. Indeed, with 1.1 equiv of $n\text{-BuLi}$, the $\nu(\text{CN})$ band of PhCHCNLi at 2091 cm^{-1} and the symmetric $\nu(\text{CN})$ band of $(\text{PhCHCNLi})_2$ at 2070 cm^{-1} are observed. With an excess of $n\text{-BuLi}$, a broad $\nu(\text{CN})$ band at 1912 cm^{-1} appears, related to the dianionic species. It is similar to the band observed at 1910 cm^{-1} in the IR spectra with LDA in THF (Figure 4). Two shoulders around 1932 and 1890 cm^{-1} (Figure 7) correspond to the strong IR bands at 1930 and 1890 cm^{-1} (Figure 5). The benzenic skeleton modes are shifted similarly as in the IR spectra. The wavenumbers of the observed $\nu(\text{CN})$ new bands at 1912, 1890, and 1932 cm^{-1} are assigned to dianionic species. Indeed, they appear in the spectral range of the calculated $\nu(\text{CN})$ wavenumbers of the four dianionic entities: $(\text{PhCCN})^{2-}$ free dianion, $(\text{PhCCNLi})^-$ monolithiated linear and bridged ion pairs, and PhCCNLi_2 dilithiated species (1880–1950 cm^{-1})¹¹ (Figure 3B–E), in good agreement with the IR absorption reported for similar dianionic entities.^{4,16} As expected, the structure of the CCN group in these dianionic species is very close to that observed in ketene imine molecules

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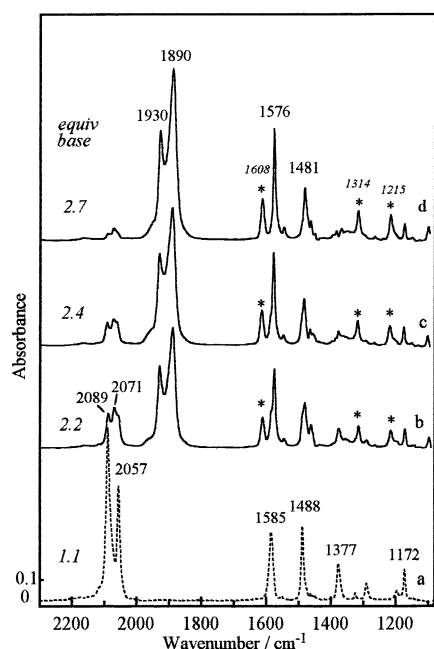


FIGURE 5. Evolution of the IR spectra of a 0.25 M solution of PhCH₂CN in THF–hexane solvent mixtures [(a) 82/18 v/v; (b) 65/35 v/v; (c) 62.5/37.5 v/v; (d) 57.5/42.5 v/v] with increasing amounts of *n*-BuLi (time, 1 h). The bands marked by a star are related to the acetaldehyde lithium enolate formed.

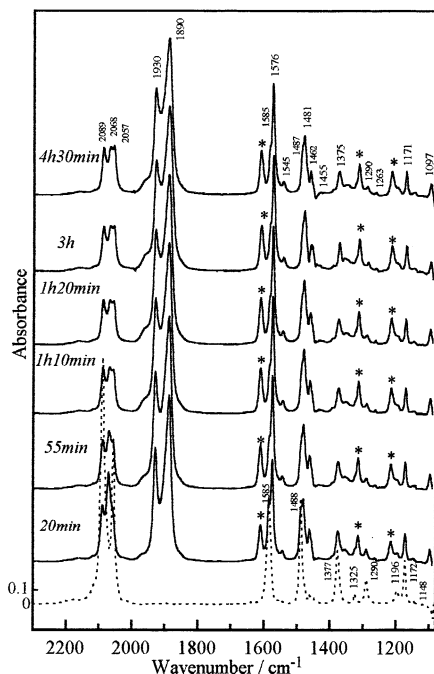


FIGURE 6. Evolution with time of the IR spectra of a 0.25 M solution of PhCH₂CN in THF–hexane solvent mixture (65/35 v/v) with 2.2 equiv of *n*-BuLi. The bands marked by a star are related to the acetaldehyde lithium enolate formed. The dotted spectrum corresponds to 1.1 equiv of *n*-BuLi.

such as *N*-*p*-tolyl-2,2-diphenylvinylideneamine.¹⁷ The $\nu(\text{CN})$ is observed around 2000 cm^{-1} in such ketene imine molecules.¹⁸ Furthermore, it was impossible to find overtones or harmonics that could explain the multiplicity

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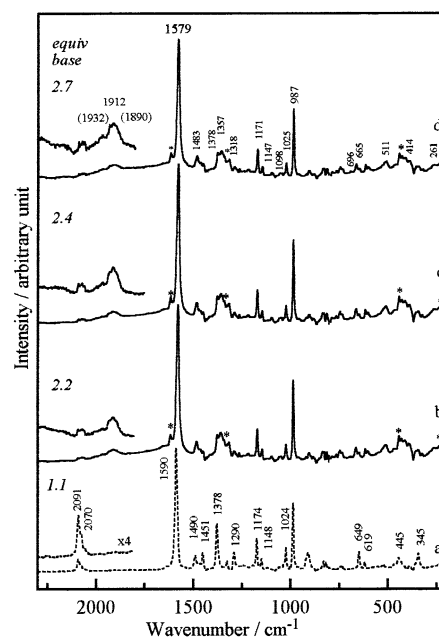


FIGURE 7. Evolution of the Raman spectra of a 0.25 M solution of PhCH₂CN in THF–hexane solvent mixtures [(a) 82/18 v/v; (b) 65/35 v/v; (c) 62.5/37.5 v/v; (d) 57.5/42.5 v/v] with increasing amounts of *n*-BuLi (time, 1 h). The bands marked by a star are related to the acetaldehyde lithium enolate formed.

of these bands by a Fermi resonance. Calculations indicate only one stable conformer for (PhCCN)²⁻ free dianion and PhCCNLi₂ dilithiated species, while two isomers are calculated for the (PhCCNLi)⁻ dianionic monolithiated species,¹⁹ as for the monoanionic PhCHCNLi. The IR band at 1910 cm^{-1} in THF with an excess of LDA is related to traces of dianions, probably as solvent-separated ion pairs (Figure 4). The wavenumbers of the other IR and Raman bands assigned to benzenic skeleton modes of the dianionic entities fit rather the calculated values rather well.¹¹ This is noticeable for the 8a and 19a $\nu(\text{CC})$ modes, which appreciably shift on going from the monoanionic to the dianionic species. Nevertheless, there is a discrepancy between the calculated $\nu(\text{C}_2\text{C}_3)$ mode and the observed one, which has been discussed.¹¹

The IR bands at 1930 and 1890 cm^{-1} in THF–hexane solvent mixtures with an excess of *n*-BuLi correspond to lithiated dianionic species (Figure 5). To assign these bands, we have tried to vary the dianion concentration on a range as large as possible. Figure 8 shows the evolution of the IR spectra of a solution of PhCH₂CN in THF–hexane solvent mixtures (65/35 to 91/9 v/v) with 2.2 equiv of *n*-BuLi for decreasing concentrations of PhCH₂CN from 0.25 to 0.06 M after 1 h of reaction. As expected, the dianion formation, proved by the intensity of the bands at 1930 and 1890 cm^{-1} after 1 h, depends on the initial concentration. For instance, it is more than twice as high for a 0.12 M initial total concentration than

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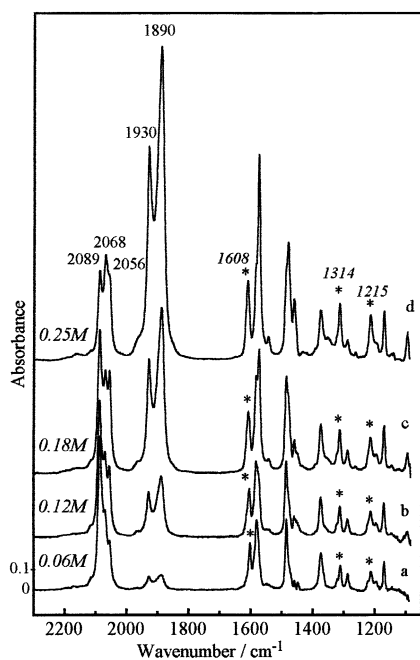


FIGURE 8. Evolution of the IR spectra of a solution of $\text{PhCH}_2\text{-CN}$ at different concentrations [(a) 0.06M; (b) 0.12 M; (c) 0.18 M; (d) 0.25 M] with 2.2 equiv of $n\text{-BuLi}$ in THF–hexane solvent mixture [(a) 91/9 v/v; (b) 82/18 v/v; (c) 75/25 v/v; (d) 65/35 v/v] (time, 1 h).

for a 0.06 M initial concentration. This indicates that the reactive species is probably the heterodimer. Indeed, the intensity of the monoanionic species bands at 2089, 2068, and 2056 cm^{-1} shows that the equilibria of Scheme 1 are strongly shifted toward the heterodimer formation as the initial total concentration increases. Thus, after 1 h of reaction, the predominant monoanionic species is the monomer for 0.06 M, while it is the heterodimer at 0.25 M. For the dianionic species, both the decrease of the THF proportion in the solvent mixture and the concentration effect increase the association of the species, as observed for the monoanionic species. The relative intensity variation of the two bands at 1930 and 1890 cm^{-1} is small and is consequently in favor of their assignment to an equilibrium between the two isomers found for $(\text{PhCCNLi})^-$ (Figure 3C,D) or the corresponding solvent-separated ion pairs $(\text{PhCCNLi})^-/\text{Li}^+$. On going from 0.06 to 0.25 M, the small intensity increase of the 1890 cm^{-1} band relative to the 1930 cm^{-1} band is due to the lowering of the THF content in the solvent mixture. The 1930 cm^{-1} component is thus assigned to the linear trisolvated ion pair (Figure 3C), and the 1890 cm^{-1} component is attributed to the bridged disolvated ion pair (Figure 3D), in excellent agreement with their calculated wavenumbers in the absence of solvent. We may not exclude the appearance of a small amount of higher aggregates such as PhCCNLi_2 , the absorption of which being calculated under these two bands at 1914 cm^{-1} (Figure 3E).

Figure 9 shows the evolution with time of the IR spectra of a 0.25 M solution of PhCD_2CN in THF–hexane solvent mixture (65/35 v/v) with $n\text{-BuLi}$. As illustrated in Figure 9, the second proton abstraction reaction shows a strong isotopic kinetic effect. With 1.1 equiv of $n\text{-BuLi}$, the species mainly formed is PhCDCNLi . On going from PhCHCNLi to PhCDCNLi , the $\nu(\text{C}_2\text{C}_3)$ mode is shifted

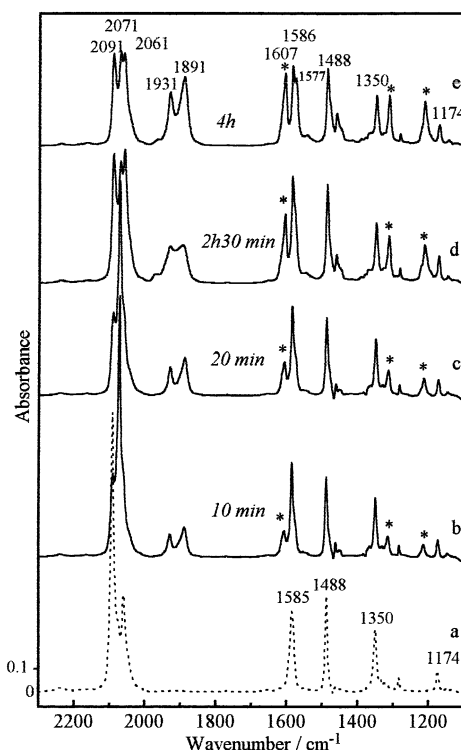


FIGURE 9. Evolution with time of the IR spectra of a 0.25 M solution of PhCD_2CN in THF–hexane solvent mixture (65/35 v/v) with 2.2 equiv of $n\text{-BuLi}$. The dotted spectrum corresponds to 1.1 equiv of $n\text{-BuLi}$. The bands marked by a star are related to the acetaldehyde lithium enolate formed.

from 1377 to 1350 cm^{-1} , in good agreement with the calculated shift from 1352 to 1335 cm^{-1} for the pyramidal PhCHCNLi .¹¹ With 2.2 equiv of $n\text{-BuLi}$, after 10 min, the predominant formation of the heterodimer (PhCDCNLi , $n\text{-BuLi}$) characterized by the strong 2071 cm^{-1} band is observed. This confirms that with $n\text{-BuLi}$ the equilibria of Scheme 1 are strongly shifted toward the heterodimer, which is much more stable than the dimer. The intensity of this band decreases much more slowly with time than that of the corresponding hydrogenated species (see spectrum at 20 min in Figure 6). This indicates that the dianion formation is much slower from the $(\text{PhCDCNLi}$, $n\text{-BuLi}$) heterodimer, which is the reactive species. As the kinetics is much slower, the reaction of $n\text{-BuLi}$ involved in this heterodimer with THF leads to a larger amount of enolate, as indicated by the large intensity increase of the $\nu(\text{CC})$ band at 1607 cm^{-1} (Figure 9). Under these conditions, only a part of the $(\text{PhCDCNLi}$, $n\text{-BuLi}$) heterodimer contributes to the dianion formation. After reaction of its $n\text{-BuLi}$ with the solvent to form $(\text{PhCDCNLi}$, $\text{CH}_2\text{CHOLi})$ heterodimer, this last one partly dissociates to form again PhCDCNLi and $(\text{PhCDCNLi})_2$, as shown by the increase of their $\nu(\text{CN})$ bands at 2091 and 2061 cm^{-1} , respectively, between 10 min and 4 h (Figure 9).

(2) ^{13}C NMR Spectroscopic Study of the Anionic Species Formed from PhCH_2CN in Different Solutions according to the Nature and the Concentration of the Base. In Table 1, the ^{13}C chemical shifts observed according to the nature of the solvent (THF, THF–toluene, or THF–hexane) and of the base used (LHMDS, LDA, or $n\text{-BuLi}$) are reported. As seen by IR

TABLE 1. ^{13}C Chemical Shifts of Anionic Species Derived from PhCH_2CN in Function of the Nature of the Solvent and of the Base Used

solvent (v/v)	base (equiv)	chemical shifts $\delta^{a,b}$						species c,d
		C ₁	C ₂	C ₃	C ₇ ,C ₅	C ₄ ,C ₈	C ₆	
THF	LHMDS (1.2–3.0)	144.4	31.9	149.5	127.8	118.2	112.1	mono, M
THF–toluene (30/70)	LHMDS (1.2–3.0)	150.0	32.0	148.0		119.2	114.3	mono, D
THF	LDA (1.1–3.0)	143.9 ^e	32.0	149.4	127.9	118.4	112.4	mono, M
THF–toluene (30/70)	LDA (1.1–2.2)	150.5	32.0	148.1		119.4	114.5	mono, D
THF–hexane (82/18)	<i>n</i> -BuLi (1.1)	145.4	31.8	149.2	127.8	118.3	112.4	mono, M
THF–hexane (65/35)	<i>n</i> -BuLi (2.2)		31.9	149.0	127.8	118.6	112.9	mono, M
		155.7	41.9 ^f		127.1;127.5	-	113.6	di
THF–hexane (58/42)	<i>n</i> -BuLi (2.7)	155.5	41.9 ^f		127.3;127.6	118.8	114.1	di

^a δ are reported in ppm from TMS at 20 °C. The PhCH_2CN concentration is 0.25 M. ^b With LHMDS and LDA, δ values not significantly varying from 1.1 to 3.0 equiv, a mean value is observed. ^c mono, monoanionic species; di, dianionic species. ^d M (monomer) and D (dimer) represent the predominant species in the medium. ^e Between 1.1 and 3.0 equiv of LDA, the C₁ signal is not observed at 20 °C; the δ value at 0 °C for 2.2 equiv of base is reported. ^f Partly masked by a peak of *n*-BuLi/hexane solution.

TABLE 2. Properties of the Lithiated Bases and Their Conjugate Acids

	conjugate acid		lithiated base		
	ΔG_{acid}^a (kcal mol ⁻¹)	$\text{p}K_{\text{a}}^a$	$\text{p}K_{\text{H}_a}^b$ (THF)	$\text{p}K_{\text{H}_a}^b$ (DMSO)	agg state ^c
<i>n</i> -BuH	407.1	686.2	<i>n</i> -BuLi ^d		<i>T</i> , D
(<i>i</i> -Pr) ₂ NH	382.8	645.2	LDA	35.7	D
(Me ₃ Si) ₂ NH	349.0	588.2	LHMDS	25.8	<i>D</i> , M
PhCH ₂ CN			PhCHCNLi	18.6 ^e	D, M

^a Gas-phase acidity of the R'H or R₂NH conjugate acid or gas-phase basicity of the corresponding anionic base expressed as ΔG_{acid} or $\text{p}K_{\text{a}}$, respectively. ^b $\text{p}K_{\text{H}_a}$ of the lithiated base in THF or in DMSO. ^c Aggregation state in THF: M, monomer; D, dimer; T, tetramer. The predominant species is in italics. ^d $\text{p}K_{\text{H}_a}$ of *n*-BuLi in benzene is 44 (see ref 45). ^e See ref 46. ^f See ref 47.

vibrational study, very similar results are found for LHMDS and LDA: with LHMDS, the dianion does not form, and with LDA, only traces are observed. The species in equilibrium are PhCHCNLi, (PhCHCNLi)₂, and (PhCHCNLi, NR₂Li) heterodimers. Their relative proportions depend on the solvent and on the quantity of base used. We have previously shown that in THF the major species is PhCHCNLi, while in THF–toluene (30/70 v/v) (PhCHCNLi)₂ is predominant.⁸ In ^{13}C NMR spectra, a mean δ value was observed for monoanionic species. This allows us to estimate a monomer and dimer chemical shift difference of 6 ppm for C₁.⁸ The very small chemical shift differences observed when the base concentration increases from 1.1 to 3.0 equiv whatever the solvent (Table 1) are related to the fast Li cation exchange between species. It is thus impossible to distinguish PhCHCNLi or (PhCHCNLi)₂ from the heterodimer in THF. The largest chemical shift difference, previously noticed,⁸ observed for C₁ ($\Delta\delta \sim 6$ ppm) on going from THF to THF–toluene solvent mixture is also related to the predominance of either monomers or dimers in these media, respectively.

The addition of 2.2 equiv of *n*-BuLi in THF leads to the formation of dianionic species and a small amount of monoanionic species (Figure 5), which give rise to two different sets of signals. Only the dianionic entities are observed with 2.7 equiv of *n*-BuLi. The dianionic species are then characterized by a $\Delta\delta$ C₁ of 10.1 ppm compared to PhCHCNLi with 1.1 equiv of *n*-BuLi and a strong $\Delta\delta$ C₂ of 10.1 ppm. The observation of two signals for the aromatic meta carbons C₅ and C₇, although predicted almost equivalent by the calculations,¹¹ seems to indicate a higher rotation barrier of the phenyl group in the dianionic species. These results may be compared to those of Bestmann et al.,²⁰ who have been able to deprotonate the cyanomethylenetriphenylphosphorane into a dian-

ionic species containing a C₂C₁N moiety as in our case. The chemical shift of the cyanomethylenetriphenylphosphorane C₂ is observed at -2.7 ppm,²¹ while the C₂ of the dianionic species appears at 6.6 ppm.²⁰ The $\Delta\delta$ C₂ of 9.3 ppm thus observed compares well with the $\Delta\delta$ C₂ of 10.1 ppm observed in our case.

In all the ^{13}C NMR spectra of solutions containing 2.2–2.7 equiv of *n*-BuLi, two signals at about 158.5 and 83.0 ppm due to the formation of the acetaldehyde lithium enolate are observed.¹⁴

(3) Structure and Stability of the Species (Dimers, Heterodimers) Formed in the Presence of the Various Lithiated Bases. (3.1) Structure and Stability of the Species Formed according to the $\text{p}K_{\text{H}_a}$ of the Lithiated Bases. We have reported in Table 2 the properties of the lithiated bases R'Li or R₂NLi used and those of the corresponding conjugate acids R'H or R₂NH. The gas-phase acidities (or anion proton affinities) of the parent acids R'H or R₂NH measured by their free energies²² are in the inverse order of the R' or R₂N group polarizability: *n*-Bu < (*i*-Pr)₂N < (Me₃Si)₂N < PhCH₂CN. The basicity of the lithiated ion pair R'Li or R₂NLi ($\text{p}K_{\text{H}_a}$ measured in THF or DMSO²³) thus decreases with the R' or R₂N group polarizability. This polarizability favors the charge delocalization in the anion and hence decreases the neat charge on the negative carbon center bonded to the Li⁺ cation, leading to a less stable and less polar ion pair. The stability of this ion pair naturally follows that of its dimer in THF. The more the ion pair is polar, the more the dimer formation through dipole–

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TABLE 3. Comparison of the X-ray Structures of the LDA and PhCHCNLi Dimers with That of the (PhCHCNLi, LDA) Heterodimer

dimer or heterodimer	bond lengths (Å)				bond angle (deg)
	LiN	C ₁ N	C ₁ C ₂	C ₂ C ₃	
[LDA, THF] ₂ ^a	2.00(5)				
[PhCHCNLi, TMEDA] ₂ , C ₆ H ₆ ^b	2.018	1.171	1.372	1.442	80.9
[(PhCHCNLi, LDA), (TMEDA) ₂] ^c					
LDA	2.025 ^d				82.7
PhCHCNLi	2.092 ^d	1.173	1.383	1.430	80.0

^a See ref 48. ^b See ref 41. ^c See ref 6. ^d Average value of the two LiN lengths.

dipole interaction is favored. It is indeed well-known that *n*-BuLi exists in THF as a tetramer in equilibrium with a dimer^{24–26} that is at the origin of the THF cleavage.¹⁴ It has been shown by NMR that for LDA the dimer is the exclusive species in THF solution^{27–29} and that this dimer may undergo successive solvation without deaggregation.³⁰ Kimura and Brown³¹ have reported that LHMDS forms a dimer–monomer ion pair equilibrium in THF. This has been confirmed by solvation studies in THF–HMPA media.³² Our IR studies have proved that in THF the monomer–dimer equilibrium of lithiated phenylacetonitrile is strongly shifted toward the monomeric ion pair. The stability of the mixed dimeric aggregate formed by the association of PhCHCNLi with a lithiated base R¹Li (**2a**) or R₂NLi (**2b**) follows the same stability order as that of the lithiated base dimer. This is in agreement with the relative order of stability found by vibrational spectroscopy for the different heterodimers observed: (PhCHCNLi, *n*-BuLi) > (PhCHCNLi, LDA) > (PhCHCNLi, LHMDS).

It is further interesting to notice that the heterodimer structure is not a simple addition of the structures of the two entities involved in the dimers (Table 3). The X-ray structure shows indeed that the NLi distance increases, mainly for the PhCHCNLi part. This is probably due to the charge delocalization overall the anion into the PhCHCNLi part, due to the larger charge on the LDA nitrogen atom. This charge delocalization is confirmed by the C₂C₃ shortening of 0.01 Å, which explains the LiN lengthening of 0.07 Å in the mixed dimeric species, the CN bond length remaining about the same.

(3.2) Influence of the Solvation by the Amine on the Monomer–Dimer Equilibrium. In a previous paper,¹⁰ we had attempted to calculate the apparent equilibrium constant of the monomer–dimer equilibrium [1] (Scheme 1) for the lithiated phenylacetonitrile formed in THF with 1.2 equiv of LHMDS. We had observed a

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TABLE 4. Influence of the Presence of the Conjugate Acid of the Base Used on the Monomer–Dimer Equilibrium of PhCHCNLi Solution in Neat THF or THF–Hexane Mixture

entry	PhCH ₂ CN concentration/M	base used ^{a/} equiv	amine added ^{a,b/} equiv	A _D /A _M ^c
1	0.25	<i>n</i> -BuLi ^{d/} 1.1		0.27
2	0.25	LHMDS ^{e/} 1.2		0.38
3	0.25	<i>n</i> -BuLi ^{f/} 1.1		0.50
4	0.25	<i>n</i> -BuLi ^{f/} 1.1	(Me ₃ Si) ₂ NH/1	0.63
5	0.25	<i>n</i> -BuLi ^{f/} 1.1	(Me ₃ Si) ₂ NH/2	0.73
6	0.25	<i>n</i> -BuLi ^{f/} 1.1	(Me ₃ Si) ₂ NH/3	0.93
7	0.25	LDA ^{g/} 1.1		0.31
8	0.37	LDA ^{g/} 1.1		0.40
9	0.33	LDA ^{g/} 1.1	(<i>i</i> -Pr) ₂ NH/2	0.55

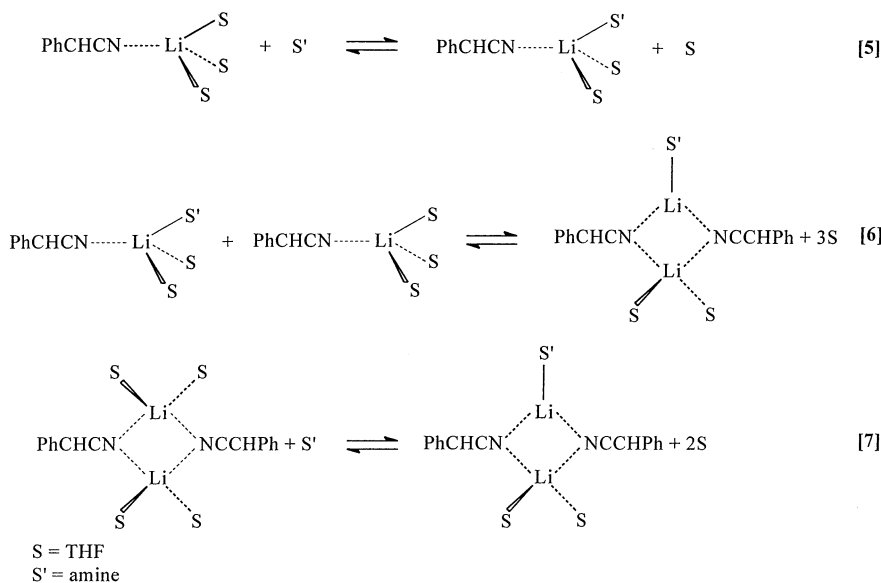
^a The amine or conjugate acid of the base is present at the same concentration in the medium. ^b The amine was added 10 min after formation of PhCHCNLi, and the anion concentration was kept constant. ^c Ratio of the IR integrated intensities of the PhCHCNLi band around 2090 cm⁻¹ (A_M) and of the (PhCHCNLi)₂ band around 2057 cm⁻¹ (A_D), after decomposition of the spectra into three components corresponding to the bands at 2090 and 2057 cm⁻¹, and to the symmetric mode of the dimer around 2070 cm⁻¹. ^d After evaporation of the solvents (hexane and THF) and their replacement by neat THF. ^e In neat THF. ^f In THF–hexane mixture (82/18 v/v).

strong increase of the apparent equilibrium constant with the decrease of the total concentration. We had explained this variation by the appearance of a new monomeric species when the lithiated phenylacetonitrile concentration decreases. We had then neglected the solvation of the anionic species formed by the (SiMe₃)₂NH amine present in the medium, though it is of paramount importance, as it will be seen below. To check the influence of the (SiMe₃)₂NH amine, we have measured the ratio A_D/A_M of the IR integrated intensity of the (PhCHCNLi)₂ band at 2057 cm⁻¹ (A_D) to that of the PhCHCNLi band at 2090 cm⁻¹ (A_M) for a 0.25 M PhCH₂CN solution in THF after addition of 1.1 equiv of *n*-BuLi (1.6 M in hexane) and evaporation of the solvents and their replacement by neat THF (entry 1, Table 4). The same result has been obtained when LHMDS is used instead of *n*-BuLi, after elimination of (SiMe₃)₂NH. When the amine formed in the medium is not eliminated (entry 2, Table 4), A_D/A_M strongly increases from 0.27 to 0.38, indicating a shift of the equilibrium toward the dimer formation. This is confirmed by the A_D/A_M increase from 0.50 to 0.93 when (Me₃Si)₂NH is added from 0 to 3 equiv to an anion formed with *n*-BuLi in a THF–hexane solvent (82/18 v/v) (entries 3–6, Table 4).

Collum et al. have largely studied the solvation of LHMDS^{33–35} and LDA^{36–38} monomers and dimers by

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SCHEME 2



ethers and amines, using cosolvents such as pentane or toluene. They have shown that the base dimers of such hindered amines are usually disolvated, while the monomers are trisolvated rather than disolvated by ethers (mainly by THF³⁴). They have shown that with polydentate amines^{35,38} and even with TMEDA^{37,39} or DMEDA,⁴⁰ only one nitrogen is bound to each lithium atom in the dimer. On the contrary, with the less hindered lithiated phenylacetonitrile base, the two nitrogen atoms of one TMEDA are bound to each lithium in the dimer, as shown by Boche.⁴¹ We thus think that in THF, each lithium atom of the dimer is solvated by two THF molecules (equilibrium [1], Scheme 1). This has been confirmed by recent calculations, although a semiempirical method has been used for the geometry optimization.⁴² The monomer–dimer equilibrium in neat THF is thus entropy driven toward the dimer as usually observed for equilibria,³³ the enthalpy of which does not much depend on the solvent. When a hindered amine S' as (Me₃Si)₂NH or (*i*-Pr)₂NH is added to the medium, equilibria [5]–[7] (Scheme 2) take place. Two THF molecules are replaced by one S' amine molecule in the dimer and equilibria [6] and [7] are entropy driven toward the formation of the dimer solvated by the amine. Nevertheless, we may not exclude the formation of some amine triTHF tetrasolvated dimer or of some amine disolvated dimer over the THF tetrasolvated dimer. This replacement of two THF molecules by one amine molecule explains the large shift toward the dimer in the presence of (Me₃Si)₂NH (entries 1–2 and

3–6, Table 4) or the smaller one observed with (*i*-Pr)₂NH (entries 7–9, Table 4). Amine (*i*-Pr)₂NH has a more basic nitrogen atom than (Me₃Si)₂NH, but is a less hindering solvating agent,⁴³ and may partly lead to the formation of an amine triTHF tetrasolvated dimer. To confirm its solvating effect, we have added to a 0.37 M PhCH₂CN solution in the presence of 1.1 equiv of LDA (entry 8, Table 4), 2 equiv of (*i*-Pr)₂NH (entry 9, Table 4). Taking into account the small dilution effect by the amine added, the shift of A_D/A_M from 0.40 to 0.55 indicates a large shift of equilibria [6] and [7] (Scheme 2) toward the dimer solvated by the amine. To take into account the solvation by the amine S' conjointly with the dimerization,¹⁰ the measured dimerization equilibrium constant (K_{meas}) must be written as

$$K_{\text{meas}} = \{C_D[S]^2/C_M^2\}$$

where

$$C_D = [(\text{PhCHCNLi})_2, 4S] + [(\text{PhCHCNLi})_2, 2S, S']$$

and

$$C_M = [\text{PhCHCNLi}, 3S] + [\text{PhCHCNLi}, 2S, S']$$

It may be expressed as

$$K_{\text{meas}} = \{K_1(1 + K_7[S']/[S]^2)\} / \{(1 + K_5[S']/[S])\}^2$$

where K_1 , K_5 , and K_7 are the equilibrium constants of [1], [5], and [7] equilibria, respectively.

As $[S] \gg [S']$, K_{meas} becomes

$$K_{\text{meas}} \approx K_1(1 - 2K_5[S']/[S])$$

This explains the increase of the measured dimerization equilibrium constant,¹⁰ when the total PhCHCNLi

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concentration decreases, since the amine S' concentration also decreases.¹⁰

Conclusion

The formation of lithiated phenylacetonitrile from PhCH₂CN with LHMDS or LDA leads to the presence of the corresponding amine in the medium. The presence of the amine is of paramount importance, since it induces a shift of the monomer–dimer equilibrium of lithiated phenylacetonitrile toward the dimer, through a solvation entropic effect.

In the presence of an excess of base, a heterodimer is formed with the lithiated phenylacetonitrile. The quantity of this heterodimer increases with the p*K*_{H_a} of the lithiated base. This heterodimer is the reactive intermediate, which leads to the formation of a dianionic species. With LHMDS, no dianion is observed, because the p*K*_{H_a} of the base is too low to lead to a second proton abstraction inside the heterodimer. With LDA only a small amount of solvent-separated dianion ion pair is present. With *n*-BuLi the larger part of the heterodimer leads to lithiated dianions. A strong isotopic effect is observed for this second deprotonation, which is much slower for the deuterium abstraction and competes with the reaction between *n*-BuLi and the THF solvent. The absence of an appreciable concentration effect on the relative proportion of the two dianionic species observed at 1930 and 1890 cm⁻¹ and comparison with the calculations suggest that these species are the two isomers of (PhCCNLi)⁻//Li⁺, linear and bridged, respectively.

Experimental Section

Preparation of Anionic Solutions.^{8,9} THF was distilled under argon atmosphere from sodium/benzophenone immediately before use. Toluene was distilled over CaH₂. PhCH₂CN (Aldrich) was distilled prior to use. *n*-BuLi (1.6 M in hexane) was a fresh Aldrich commercial solution, checked against salt content.⁴⁴ The preparation of the solutions was performed under argon at 20 °C. To 10⁻³ mol of PhCH₂CN dissolved in the required amount of THF was added 1.1–2.7 equiv of *n*-BuLi.

The LHMDS and LDA solutions in THF were prepared from the corresponding amines, freshly distilled over CaH₂, and *n*-BuLi (1.6 M in hexane). The hexane and THF were evaporated under argon until a white powder was obtained. To 1.2–3.0 equiv of dry LHMDS or LDA dissolved in 4 mL of THF or THF–toluene solvent mixture (30/70 v/v) was added 10⁻³ mol of PhCH₂CN. In all cases, the solutions were stirred during 30 min for ¹³C NMR experiments and during various times for IR and Raman studies.

NMR Spectra. The ¹³C NMR spectra of anionic solutions were recorded on a Bruker AM 250 spectrometer operating at 62.9 MHz. A 10 mm tube filled with CD₂Cl₂ located outside the 8 mm tube containing the solution was used for ²H external lock.

IR Spectra. IR spectra were measured on a Perkin-Elmer 983 spectrometer. The spectral resolution was 3 cm⁻¹. Cells with CaF₂ windows were used, and their thickness was 0.0040 or 0.0052 cm for diluted solutions. The filling of the cells was performed under argon in a glovebag. Other windows such as KBr or CsI cannot be used because they react with the carbanions. The solvent bands were subtracted from the spectra.

Raman Spectra. Raman spectra were carried out on a Perkin-Elmer system 2000R NIR FT-Raman spectrometer equipped with a stabilized Nd:YAG laser emitting at 1064 nm. The spectral resolution was 4 cm⁻¹ in the 3600–200 cm⁻¹ range. To obtain a good signal-to-noise, about 50–100 scans were accumulated for each spectrum. More detailed experimental conditions have been described previously.^{9,10} The solvent bands were subtracted from the spectra. Because of the disorder in liquids and solutions, the broadening of the foot of the Rayleigh line prevents from properly observing low wavenumber modes with small diffusion cross sections, such as LiN modes. Their low diffusion cross section is related to their ionic character.

JO020492T

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