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# DIRECT OBSERVATION OF METALATED *N,N*-DIMETHYLBENZYLAMINES BY FT NMR SPECTROSCOPY

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## Summary

Direct observation of the respective *ortho* and benzylic metalated *N,N*-dimethylbenzylamines by $^{13}$C and $^{1}$H FT NMR spectroscopy has been achieved. NMR assignments and the effect of temperature on the $^{13}$C resonances are reported. Evidence for an essentially trigonal benzylic carbon in $\alpha$-potassio-*N,N*-dimethylbenzylamine is presented.

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## Introduction

Some time ago it was reported that *N,N*-dimethylbenzylamine could be metalated in the *ortho* position with n-butyllithium in ether [1]. *ortho*-Lithiations of aromatic rings have since proven to be very useful in organic and organometallic syntheses [2—5]. *N,N*-Dimethylbenzylamine metalated at the benzylic carbon has been prepared and also found to have synthetic applications [6,7]. Evidence for *ortho* or benzylic metalation has rested primarily on the analysis of products obtained from the reaction of these intermediates with electrophiles. In addition, there are several aspects involving conformation, barriers to rotation, and cation—carbanion interactions which are of particular interest [8,9].

In this paper we wish to report the direct observation by $^{13}$C and $^{1}$H FT NMR spectroscopy of the respective *ortho* and benzylic metalated *N,N*-dimethylbenzylamines in THF [10].

## Results and discussion

*o-Lithio-N,N-dimethylbenzylamine.* The 22.6 MHz carbon-13 NMR spectra of *N,N*-dimethylbenzylamine and the *ortho*-lithiated derivative in THF are shown in Fig. 1; the chemical shifts are listed in Table 1. The assignments are based on chemical shifts and off-resonance spectra. Upon formation of the lithium salt the benzylic carbon resonance, which is a clean triplet in the off-resonance spec-

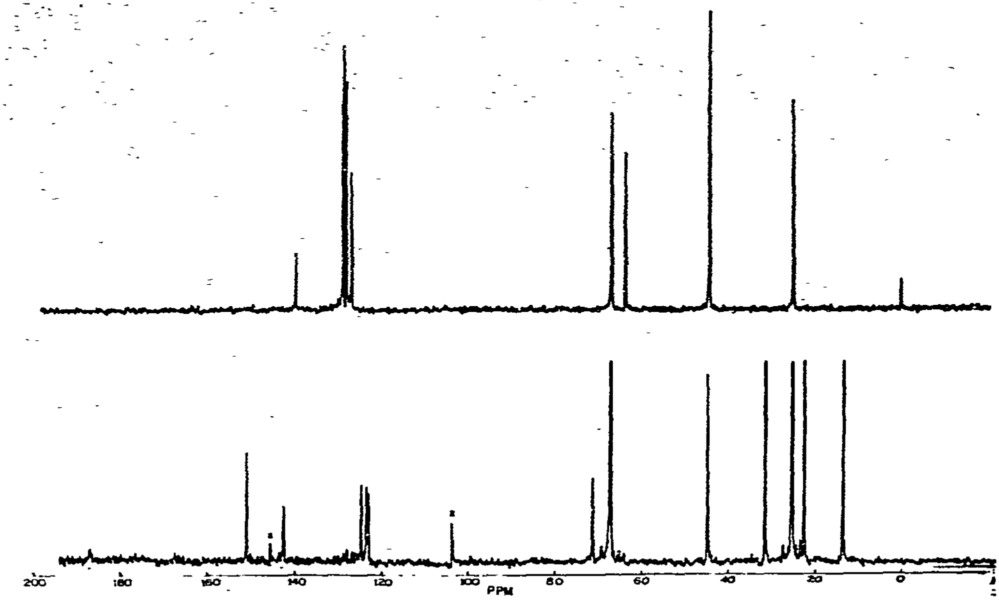
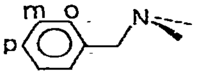
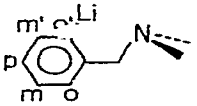
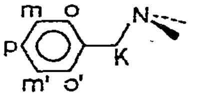
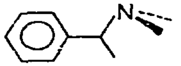
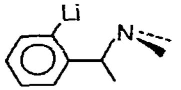
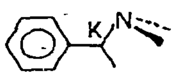


Fig. 1. Top. $^{13}$C NMR spectrum of *N,N*-dimethylbenzylamine in THF 50/50. Bottom. $^{13}$C NMR spectrum of *o*-lithio-*N,N*-dimethylbenzylamine in THF—residual hexane. X THF images (electronic artifacts due to the quadrature type of detection system used in the spectrometer).

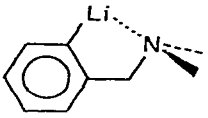
TABLE 1

$^{13}$C CHEMICAL SHIFTS FOR *N,N*-DIMETHYLBENZYLAMINES AND METALATED SPECIES ON THE TMS SCALE [a]

| Compound | N—$CH_3$ | Bz—C | *p*-C | *o*-C<br>*o'*-C | *m*-C<br>*m'*-C | *ipso*-C | C—$CH_3$ |
|---|---|---|---|---|---|---|---|
|  | 44.7 | 63.9 | 126.5 | 127.8 [c] | 128.4 [c] | 139.4 | |
|  | 44.8 | 71.2 | 124.3 [c] | 122.6 [c]<br>137.2 | 123.1 [c]<br>142.2 | 150.8 | |
|  | 45.1 [b] | 93.0 | 91.6 | 99.6 [c]<br>108.2 [c] | 128.0 [d]<br>130.4 [d] | 138.6 | |
|  | 42.8 | 65.6 | 126.3 | 126.9 [c] | 127.8 [c] | 144.8 | 20.2 |
|  | 42.5 | 71.1 | 122.8 [c] | 122.6 [c]<br>185.8 | 122.6 [c]<br>142.2 | 157.2 | 17.3 |
|  | 41.7 | 90.2 | 88.8 | 102.4 [c]<br>104.6 [c] | 129.1 [d]<br>129.5 [d] | 134.7 | 6.5 |

[a] Referenced to external TMS. [b] All peaks were referenced to the downfield resonance of solvent THF at 66.8 ppm. Ambient temperature. [c] Assignment may be interchanged. [d] Assignment may be interchanged.

trum, is shifted 7.3 ppm downfield while the *N*-methyls give rise to a single line which is shifted only 0.1 ppm downfield. The resonance attributable to the carbon atom bearing the lone pair of electrons is located 59 ppm downfield from the corresponding carbon resonance in *N*,*N*-dimethylbenzylamine. The carbon atoms adjacent to the anionic carbon are shifted downfield by 11—14 ppm. The remaining ring carbons are shifted upfield by 2—5 ppm. These results are explicable in terms of structure I. The downfield shifts of the anionic ring carbon and the carbon atoms adjacent to it most likely result from variation in the average excitation energy in the paramagnetic screening term [11]. The origin of the downfield shift of the benzylic carbon is unclear. The $^{13}C$ shifts and assignments for α,*N*,*N*-trimethylbenzylamine and its *ortho*-lithiated derivative are also given in Table 1. The benzylic carbon resonance in this derivative is a doublet in the off-resonance spectrum.



(I)

The 90 MHz proton spectrum of *o*-lithio-*N*,*N*-dimethylbenzylamine in THF-$d_8$ is shown in Fig. 2. The assignments and chemical shifts are given in Table 2. The farthest downfield resonance is due to the proton on the carbon atom *ortho* to the anionic carbon, a result which is consistent with the $^{13}C$ spectrum described above but appears to be somewhat different from the previously reported 60 MHz proton shifts in DMSO-$d_6$ [12].

*α-Potassio-N,N-dimethylbenzylamine.* The α-potassio species was obtained from the reaction of *N*,*N*-dimethylbenzylamine with potassium *t*-butoxide and

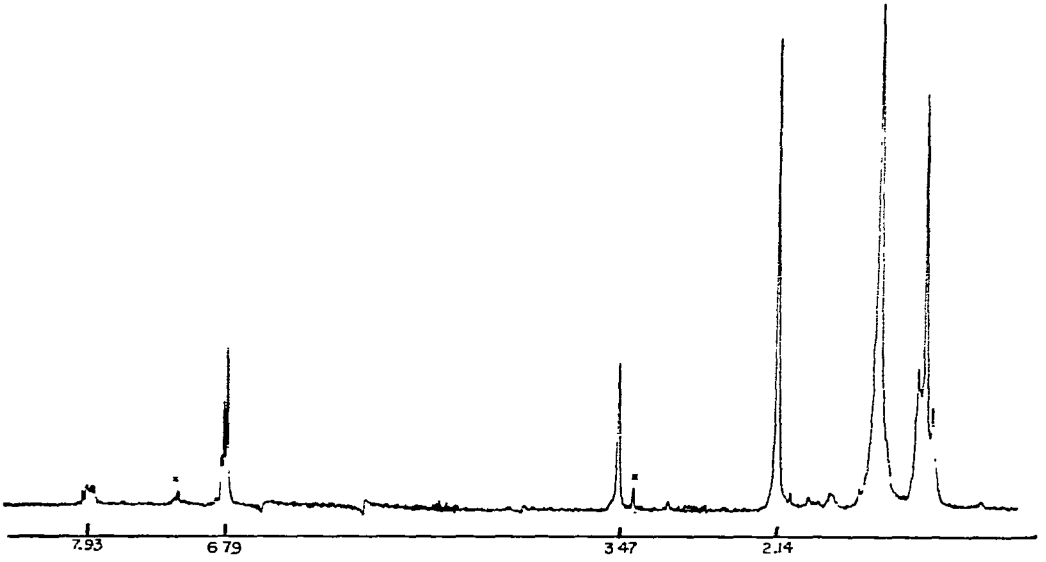
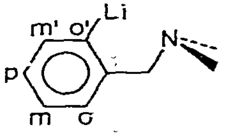


Fig. 2. PMR spectrum of *o*-lithio-*N*,*N*-dimethylbenzylamine in THF-$d_8$—residual hexane. X Unreacted *N*,*N*-dimethylbenzylamine.

TABLE 2

$^1$H CHEMICAL SHIFTS ($\delta$, ppm) FOR *o*-LITHIO-*N*,*N*-DIMETHYLBENZYLAMINE

| | N—$CH_3$ | $CH_2$ | *o*-H, *m*-H, *p*-H | *m'*-H |
|---|---|---|---|---|
|  | 2.14 [a] | 3.47 | 6.79 | 7.93 |

[a] Referenced to methylene protons of hexane (solvent is $THF\text{-}d_8$ with residual hexane) at 1.27 ppm.

n-butyllithium [13,14]. Kronzer and Sandel have shown that there is some lithium contamination of the potassium salt using this procedure but that the effect of the lithium impurity on the PMR spectrum of delocalized carbanions is negligible [14]. In the present case, several independent preparations of the benzylpotassium derivative yielded the same $^{13}$C NMR spectrum; a typical example is shown in Fig. 3. The chemical shifts are given in Table 1. The assignment of the spectrum was based on chemical shifts, off-resonance spectra, and selective proton decoupling. The benzylic carbon was an unambiguous doublet in the off-resonance spectrum. The benzylic carbon resonance of the $\alpha$-potassio derivative of $\alpha$,*N*,*N*-trimethylbenzylamine was a singlet in the off-resonance spectrum. The chemical shifts for the proton decoupled $^{13}$C NMR spectrum of this $\alpha$-potassio salt are given in Table 1.

The 90 MHz proton spectrum of $\alpha$-potassio-*N*,*N*-dimethylbenzylamine is shown in Fig. 4 with chemical shifts listed in Table 3. There is a rather good correlation of this spectrum with the $^{13}$C NMR spectrum. The *meta* protons are farthest downfield and the *ortho* and *para* protons have been shifted upfield.

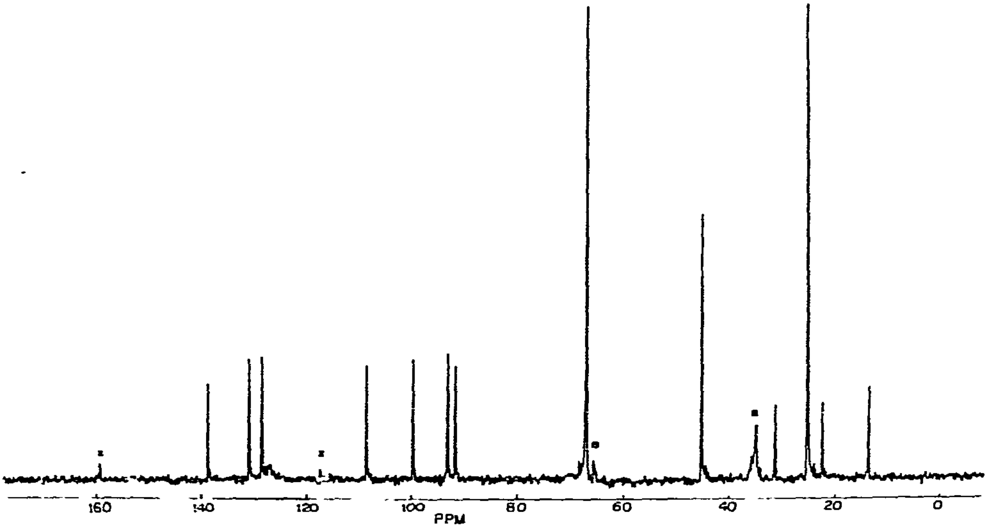


Fig. 3. $^{13}$C NMR spectrum of $\alpha$-potassio-*N*,*N*-dimethylbenzylamine in THF—residual hexane. X THF images. ■ Lithium t-butoxide.

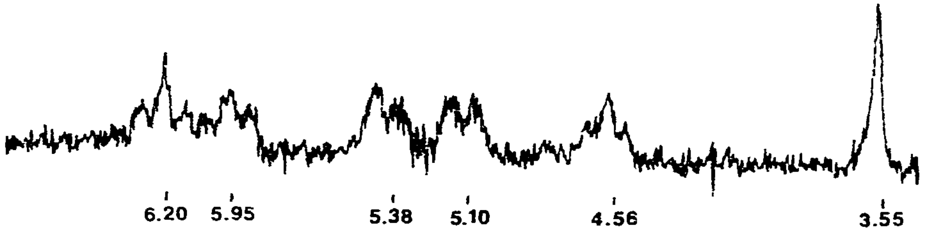
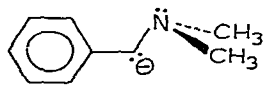


Fig. 4. PMR spectrum of α-potassio-*N*,*N*-dimethylbenzylamine in THF-$d_8$—residual hexane.

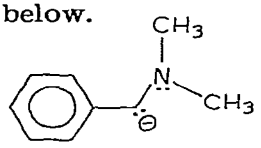
The benzylic proton is shifted downfield slightly. This assignment is consistent with the proton spectrum reported for benzylpotassium in THF [8].

The effect of temperature on the $^{13}$C resonances of α-potassio-*N*,*N*-dimethylbenzylamine is shown in Fig. 5. The two pairs of resonances corresponding to the two *ortho* and two *meta* carbons are observed at all temperatures measured (205 to 328 K). The benzylic carbon resonance has a significant temperature coefficient which suggests the possible involvement of contact ion pairs [15]. Aggregation of the organometallic also seems possible at the concentrations employed in the NMR studies (1—3 *M*) although in donor solvents such as THF such effects should be minimal. Changes in the state of aggregation are not expected to substantially alter the $^{13}$C NMR spectrum or to account for the unique temperature dependence of the benzylic carbon resonance [16]. $^1J(^{13}\text{C—}^1\text{H})$ for the benzylic carbon and its proton is 162 Hz, a value obtained from the completely coupled spectrum. This result and the observation of two upfield *ortho* carbon resonances (109.6 and 100.8 ppm), an upfield *para* carbon (92.8 ppm) and two *meta* resonances (131.7 and 129.2 ppm) clearly indicate that the benzylic carbon is essentially trigonal and that considerable negative charge has been delocalized into the phenyl ring [17].

We have carried out CNDO/2 MO calculations on the benzylic anion derived from *N*,*N*-dimethylbenzylamine for the purpose of obtaining further insight into the structure of this species [18,19]. The two limiting conformations (IIa and IIb) considered are shown below.



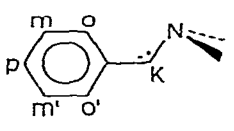
(IIa)



(IIb)

TABLE 3

$^1$H CHEMICAL SHIFTS (δ, ppm) FOR α-POTASSIO-*N*,*N*-DIMETHYLBENZYLAMINE

| | N—CH$_3$ | $\ddot{\text{C}}$H | *m*-H<br>*m'*-H | *o*-H<br>*o'*-H | *p*-H |
|---|---|---|---|---|---|
|  | 2.12 [a] | 3.55 | 6.20 [b]<br>5.95 [b] | 5.38 [c]<br>5.10 [c] | 4.56 |

[a] Referenced to methylene protons of hexane (solvent is THF-$d_8$ with residual hexane) at 1.24 ppm.
[b] Assignment may be interchanged. [c] Assignment may be interchanged.

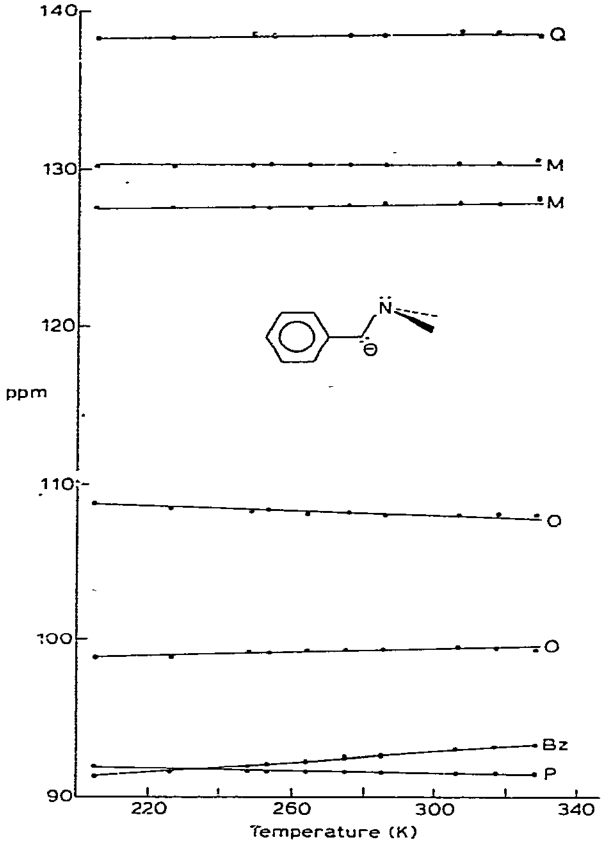
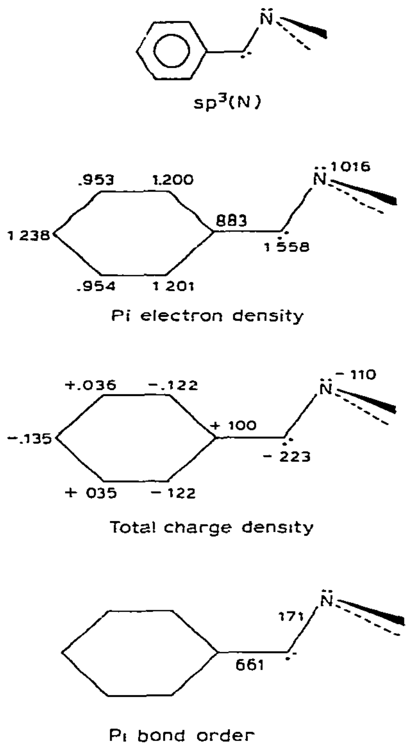


Fig. 5. Variation of $^{13}C$ NMR shifts with temperature for α-potassio-*N*,*N*-dimethylbenzylamine.

IIa ($sp^3$ nitrogen, total energy −84.7236 au) was found to be more stable than IIb ($sp^2$ nitrogen, total energy −84.6447 au). Charge densities and pertinent bond orders for IIa are shown in Fig. 6. The calculations indicate that the negative charge is distributed primarily on the *ortho*, *para*, and benzylic carbon atoms and that there is substantial π-bond character in the benzylic carbon—*ipso* carbon bond. The NMR data can be qualitatively rationalized in terms of these results. The *ortho* and *para* carbon resonances are shifted upfield due to the increase in electron density. The benzylic carbon undergoes a downfield shift caused by change of the hybridization from $sp^3$ to $sp^2$ which is partially offset by an upfield shift from the fractional negative charge present on that carbon [17]. The $-\ddot{\mathrm{C}}\mathrm{H}-\ddot{\mathrm{N}}=$ π-bond orders calculated for IIa and IIb are 0.171 and 0.116 respectively. The *N*-methyls give rise to a single resonance at all temperatures measured suggesting that the barrier to rotation about the $-\ddot{\mathrm{C}}\mathrm{H}-\ddot{\mathrm{N}}=$ bond must be very low. The barrier to rotation of the phenyl ring is, however, sufficiently high that proton abstraction (presumably from THF) by the anion was observed when measurement was attempted at approximately 350 K. This is in agreement with the substantial π-bond order of 0.661 calculated by the CNDO/2 method (Fig. 6).



Pi electron density

Total charge density

Pi bond order

Fig. 6. Summary of CNDO/2 MO calculations for the α-anion *N*,*N*-dimethylbenzylamine (with $sp^2$ hybridization for α-carbon and $sp^3$ hybridization for nitrogen).

## Experimental

### *General comments*

All glassware, syringe stopcocks, syringes, and needles were dried in a 110°C oven for several days before use. Reactions were carried out in an atmosphere of dry argon using syringes to transfer reagents. THF was dried over sodium metal and distilled under argon immediately before use. Mass spectra were recorded on a Hitachi RMU-6 single focusing spectrometer.

### *FT NMR measurements*

Proton and carbon FT NMR spectra were recorded on a Bruker WH-90DS equipped with a Nicolet 1180 16K computer and a Diablo disk drive. Broad band proton decoupled (5 Watts of power) $^{13}C$ spectra were recorded at 22.625 MHz with the instrument locked on the deuterium signals of either external $CDCl_3$ or internal THF-$d_8$. Generally 100 to 5000 pulses were obtained with a sweep width of 5000 Hz (1.22 Hz/pt) in the quadrature detection mode. A line broadening (LB) of 1.00 was employed. Pulse widths were 2—5 μs. Proton FT NMR spectra were obtained at 90 MHz in quadrature mode using a sweep width of 1000 Hz (0.244 Hz/pt), a pulse width of 3.0 and an LB of zero. The spectrometer was equipped with a Bruker B-ST 100/700 C variable temperature unit.

### *o-Lithio-N,N-dimethylbenzylamine*

To a room temperature sample of 5.0 g (37 mmol) of *N,N*-dimethylbenzylamine was added 37 mmol of n-butyllithium (2.4 *M* in hexane). The resulting slightly orange solution was allowed to stir overnight with precipitation of *o*-lithio-*N,N*-dimethylbenzylamine after 8—10 h. The heterogeneous reaction mixture was centrifuged to give a light orange colored pellet that was washed with 2 × 5 ml of dry hexane. Hexane was removed by syringe after centrifugation to give a white solid. The product was then dissolved in a minimum amount of dry THF to give a nearly saturated solution estimated to be about 2.5 *M* in lithium reagent. Transfer of a portion of this sample to an NMR tube was accomplished with a syringe flushed with argon.

Reaction of the *ortho*-metalated compound (prepared as above) with benzaldehyde gave 2-(dimethylaminomethyl)benzhydrol, m.p. 71.3—72.3°C (lit. [2]: 72.5—73°C). NMR (CDCl$_3$, JEOL C-60H): $\delta$(ppm) 2.1 (s, 6.1H, N(CH$_3$)$_2$), 3.1 (s, 1.9H, CH$_2$), 5.7 (s, 1H, CH), 7.1 (m, 10H, ArH + OH); IR (nujol, PE 237B): cm$^{-1}$ (848, 771, 752, 732, 712). Mass spectrum *m/e* 241 ($M^+$), 224 ($M^+ - 17$), 196 ($M^+ - 45$), 195 ($M^+ - 46$), 178 ($M^+ - 63$), 165 ($M^+ - 76$), 132 ($M^+ - 109$), 119 ($M^+ - 122$), 105 ($M^+ - 136$), 91 ($M^+ - 150$), 77 ($M^+ - 164$), 58 ($M^+ - 183$).

### *α-Potassio-N,N-dimethylbenzylamine*

Twice sublimed potassium t-butoxide, 0.95 g (8.5 mmol), was introduced into a small vessel and the solid surface wetted with 1.2 g (8.5 mmol) of *N,N*-dimethylbenzylamine. To this was added dropwise 3.5 ml (8.5 mmol) of 2.4 *M* n-butyllithium in hexane causing vigorous reaction and evolution of gas. The reaction mixture turned a dark red immediately and with stirring the reaction was completed in about 15 min with precipitation of α-potassio-*N,N*-dimethylbenzylamine and lithium t-butoxide. The mixture was centrifuged and the resulting pellet washed twice with 3 ml portions of dry hexane. Residual hexane was removed under reduced pressure. The red solid was cooled to —78°C and dissolved in a minimum amount of dry THF (—78°C) to give a dark red solution approximately 2.5 *M* in organopotassium reagent.

Reaction of the potassium derivative (prepared as above) with benzaldehyde yielded a mixture of the *threo* and *erythro* forms of 2-dimethylamino-1,2-diphenylethanol. NMR (DMSO-$d_6$, WH-90): $\delta$(ppm) 2.13 and 2.20 (s, 6.3H, N(CH$_3$)$_2$) 3.59 and 3.34 (d, 1.1H, CHN), 5.01 and 5.17 (d, 1H, CHO), 7.05—7.25 (M, 9.8H, PhH). Mass spectrum *m/e* 241 ($M^+$), 223 ($M^+ - 18$), 181 ($M^+ - 60$), 180 ($M^+ - 61$), 178 ($M^+ - 63$), 165 ($M^+ - 76$), 152 ($M^+ - 89$), 135 ($M^+ - 106$), 134 ($M^+ - 107$), 118 ($M^+ - 123$), 105 ($M^+ - 136$), 91 ($M^+ - 150$), 77 ($M^+ - 164$).

### *Preparation of d,l-α,N,N-trimethylbenzylamine*

To a 1 liter round bottom flask containing 126 g of formic acid (100 ml of 97—100%, 2.6 mol) cooled in a water bath was added 50 g of *d,l*-α-methylbenzylamine (0.41 mol) cautiously. The clear yellow solution was stirred and 97 g of 37% formaldehyde was added and the reaction mixture warmed in a water bath until the evolution of bubbles was evident. The bath was removed and bubbling continued for 5—10 min; the solution was then refluxed 18 h, using an efficient

60 cm condenser. The solution was cooled and 200 ml of 4 *N* HCl was added slowly. The volume of the solution was reduced at 55—65°C with a rotary evaporator. The greenish yellow residue was dissolved in 100 ml of water and then 120 ml of saturated NaOH solution was added cautiously. The aqueous phase was separated and the organic layer washed twice with 30 ml portions of the NaOH solution. The resulting yellow liquid was dried over $Na_2CO_3$. The yield of crude product was 53.6 g, 87%. Distillation from sodium metal was accomplished by floating a glass wool plug to prevent excessive foaming and frothing. A center cut, 85—86°C/3.5 mmHg (lit. [20] 92—95°C/30 mmHg) of *d,l-α,N,N*-trimethylbenzylamine was used for the preparation of the organometallic compounds. NMR: (neat, Jeol C-60H): $\delta$(ppm) 1.25 (d, 3.0H, C—$CH_3$), 2.08 (s, 5.6H, $N(CH_3)_2$), 3.08 (q, 1.0H, CH) 7.15 (m, 4.9H, Ph); see Table 1 for $^{13}C$ NMR shifts. Mass spectrum *m/e* 149 ($M^+$), 135 ($M^+ - 14$), 134 ($M^+ - 15$), 118 ($M^+ - 31$), 105 ($M^+ - 44$), 91 ($M^+ - 58$), 77 ($M^+ - 72$), 72 ($M^+ - 77$).

### *Molecular orbital calculations*

Charge densities, bond orders, and total energies were calculated by the CNDO/2 method [18,19]. Standard bond lengths and bond angles were employed since we were interested in observing trends in charge densities and bond orders. Hydrogens on methyl groups were staggered.

## Acknowledgement

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