[7] IR: $\tilde{\nu}=790, 730, 690$ cm^{-1}; MS: m/z 158 ($M^{\oplus}$, 10%), 104 ($M^{\oplus}-C_4H_6$, 100%); ^{1}H-NMR (360 MHz, CDCl$_3$): $\delta=7.20$ (2H, dd, $^4J=1.0$, $^5J=0.9$ Hz, H^8, H^9), 7.07 (2H, dd, $^4J=1.0$, $^5J=0.9$ Hz, H^{11}, H^{12}), 4.68 (2H, XX' of AA'BB'XX', $^3J=12.2$, $^3J=11.9$, $^3J\approx5$, $^4J=-0.8$, $^4J\approx-1$ Hz, H^3, H^4), 2.79 (2H, ddd, $^2J=12.0$, $^3J=3.5$, $^3J=3.5$ Hz, H^1, H^6), 2.26 (2H, ddd, $^2J=12.0$, $^3J=12.0$, $^3J=3.0$ Hz, H$^{1'}$, H$^{6'}$), 1.88 (2H, m, H$^{2'}$, H$^{5'}$), 1.01 (2H, m, H^2, H^5). Upon irradiation at $\delta=4.68$, the multiplets at 1.88 and 1.01 changed into ddd with $^2J=12.0$, $^3J=3.5$, $^3J=3.0$ Hz and $^2J=12.0$, $^3J=12.0$, $^3J=3.5$ Hz, respectively. ^{13}C-NMR (CDCl$_3$): $\delta=142.9$ (s), 136.0 (d), 132.1 (d), 132.0 (d), 35.8 (t), 34.2 (t).

[8] [6]Paracyclophane: UV (hexane): $\lambda_{max}=299$ ($\varepsilon=460$), 251 (6500), and 214 (17000) nm.

[Cp(CO)$_2$Mo{NR*[Rh(norbornadiene)]-CH(pyridyl)}], a Rhodium Complex with an Asymmetric Molybdenum Atom in the Chelate Skeleton**

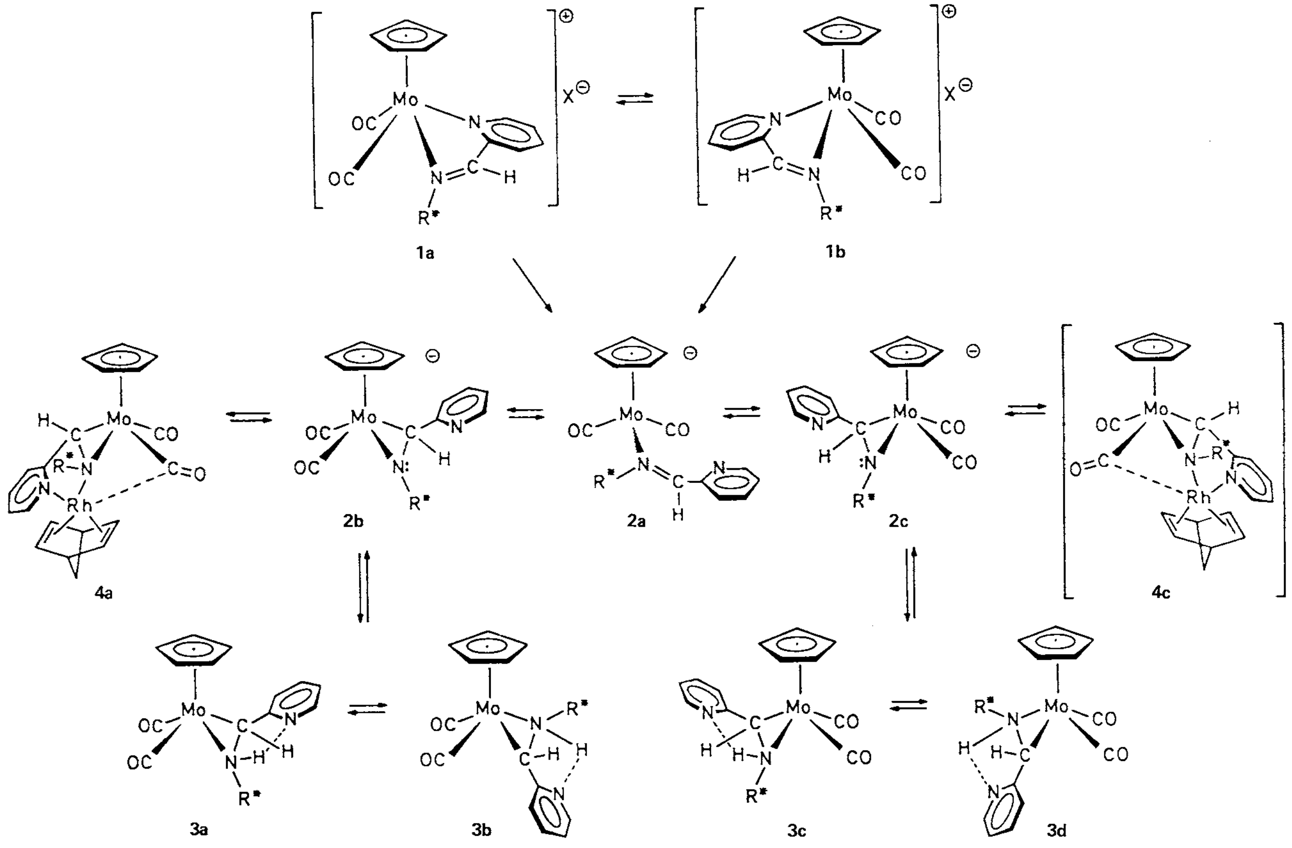
By *Henri Brunner,* Joachim Wachter,*
Johann Schmidbauer, George M. Sheldrick, and
Peter G. Jones

Usually, in enantioselective catalysis, optically active chelate ligands are employed which coordinate via P or N atoms.[1] In some of these ligands the P atoms are the chirality centers; mostly, however, the inducing chirality is located in the chelate skeleton, as a rule in the form of asymmetric C atoms, but occasionally also as axial and planar chiral moieties. We now report on nitrogen chelate ligands and their rhodium complexes, which, for the first time, contain chiral transition metal atoms besides asymmetric C and N atoms in the chelate skeleton.

Reaction of the molybdenum complex **1** with sodium amalgam (20°C, 2 h, tetrahydrofuran) leads to formation of the complex **3** in 46% yield; its formation in the reaction of **1** with LiCH$_3$ has already been reported.[2,3] **3** has four chirality centers. One of them is already contained in R* [(*R*)-1-phenylethyl], the other three, at the Mo, N and C atoms of the three-membered ring, are formed during the reaction. Thus, eight stereoisomers are possible, of which only four have been detected (by ^{1}H-NMR spectroscopy) and only two isolated in pure form.

Regardless of whether one starts from the pure diastereomers **1a** and **1b** or from a **1a/1b** mixture, the reaction always leads to a 55:45 mixture of two products having different ^{1}H-NMR spectra, which can be separated chromatographically. The first red zone obtained upon chromatography on Merck-Lobar columns[4] contains the complexes **3a/3b**, while the second red zone contains the complexes **3c/3d**.

The isomers **3a** and **3b** rapidly interconvert in solution at room temperature; this manifests itself in the breadth of the ^{1}H-NMR signals. The high-temperature limiting spectrum for the **3a/3b** mixture was observed at 100°C and the low-temperature limiting spectrum with separate signals for **3a** and **3b** in the intensity ratio 96:4 at −70°C.[5] The isomeric pair **3c/3d** behaves analogously (at −70°C 90:10).[5]



At −20°C, ether/pentane solutions of **3a/3b** and **3c/3d**, afforded single crystals of **3a** and **3c**, respectively, whose absolute configurations were determined by X-ray

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crystallography[6,7] (Fig. 1 and 2). In both compounds, the substituents Cp on Mo, H on N, and pyridyl on C are located on the same side of the three-membered ring; the NH proton forms a hydrogen bridge to the pyridine N. The configurations of the chirality centers in the three-membered ring are $S_{Mo}S_NS_C$ in **3a** and $R_{Mo}R_NR_C$ in **3c**.[11]

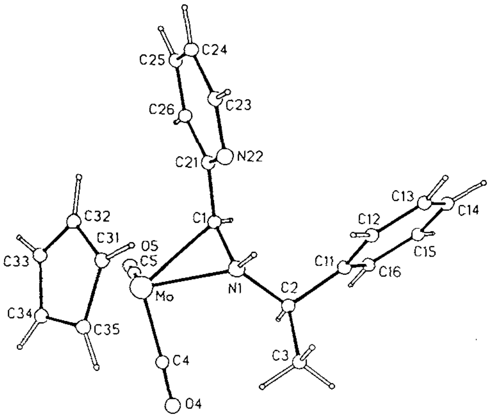

Fig. 1. Structure of **3a** in the crystal. Selected bond lengths [Å] and angles [°]: Mo-N1 2.174(4), Mo-C1 2.210(4), C1-N1 1.414(5), Mo-C4 1.921(5), Mo-C5 1.939(5), C4-O4 1.170(6), C5-O5 1.141(6), Mo-Cp 2.318-2.383, C1-C21 1.472(6), N1-C2 1.491(5), C2-C3 1.519(6), C2-C11 1.516(5), C-C(phenyl and pyridyl) 1.368-1.373, C-N22 1.339(6) and 1.340(6); N1-Mo-C1 37.6(2), Mo-N1-C1 72.6(3), Mo-C1-N1 69.8(3), N1-Mo-C5 107.4(2), N1-Mo-C4 90.7(2), C1-Mo-C4 110.9(2), C4-Mo-C5 77.3(3), C1-Mo-C5 81.1(3), Mo-N1-C2 126.2(3), Mo-C1-C21 116.3(3). Only one of two independent, very similar molecules is shown; in the second molecule the C11-C16 ring is rotated through ca. 30° compared to that in the first molecule.

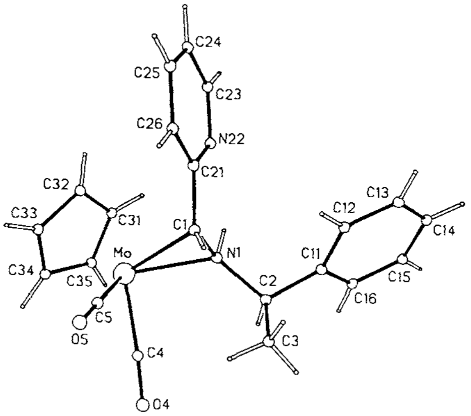

Fig. 2. Structure of **3c** in the crystal. Selected bond lengths [Å] and angles [°]: Mo-N1 2.172(3), Mo-C1 2.213(3), C1-N1 1.421(4), Mo-C4 1.938(4), Mo-C5 1.942(4), C4-O4 1.159(4), C5-O5 1.152(4), Mo-Cp 2.318-2.378, C1-C21 1.483(4), N1-C2 1.499(4), C2-C3 1.522(4), C2-C11 1.514(4), C-C (phenyl and pyridyl) 1.382-1.400, C21-N22 1.333(5), C23-N22 1.350(5); N1-Mo-C1 37.8(2), Mo-N1-C1 72.7(2), Mo-C1-N1 69.5(2), N1-Mo-C5 108.7(2), N1-Mo-C4 90.9(2), C1-Mo-C4 111.7(2), C4-Mo-C5 78.6(2), C1-Mo-C5 82.0(2), Mo-N1-C2 128.9(2), Mo-C1-C21 115.9(2).

Thus, the following picture emerges: In the reduction of **1**, the cation accepts two electrons. The anionic intermediate **2a** is formed in which the Mo-N(pyridyl) bond is broken. The chirality of the Mo atom disappears, and **1a** and **1b**, despite the contrary Mo configurations, give the same products. In the reaction **2a** → **2b** + **2c** the σ-bonded imine ligand becomes π-bonded and thereby the configuration at the C atom of the three-membered ring is established (S_C in **2b** and R_C in **2c**). The placement of the proton on **2b** and **2c** on the pyridine side via a preformed H bridge explains the *cis* orientation of the substituents H and pyridyl in **3a** and **3c**; there is no experimental evidence for a *trans* orientation. The isomer **3b**, which constitutes about 4% of the mixture with **3a** ($S_{Mo}S_NS_C$), is assigned opposite Mo configuration ($R_{Mo}S_NS_C$) whereby rapid isomerization **3a** ⇄ **3b** might arise by intramolecular rotation of the immonium ligand,[8] comparable with the rotation of an olefin in a π-complex. Correspondingly, **3c** and **3d** can be assigned the configurations $R_{Mo}R_NR_C$ and $S_{Mo}R_NR_C$, respectively. **3a** and **3c**, with *cis* oriented Cp, H, pyridyl substituents on the MoNC three-membered ring, are thermodynamically more stable than **3b** and **3d**.

Reaction of **3a**/**3b** with $[Rd(nbd)Cl]_2$ (nbd = norbornadiene) afforded the complex **4**, which after chromatography was isolated as a reddish-brown powder in 61% yield.[9] The same product is formed on using **3c**/**3d** as starting material. Crystallization from ether/pentane at −20°C furnished single crystals of **4a**, whose absolute configuration was determined by X-ray crystallography.[6,7] In **4a** the chelate ring formed via the two N atoms and the Rh atom lies on the side of the MoNC three-membered ring opposite to the cyclopentadienyl ring. This is surprising, since the substituents Cp, H and pyridyl are located on the same side of the MoNC three-membered ring in the complexes **3a** and **3c**. The reason for the chelate ring in **4a**, in contrast to the N-H-N hydrogen bridge in **3a** and **3c**, preferring that side of the three-membered ring with the CO ligands, may be sought in the formation of a bond between the Rh atom and C10 of the CO group C10-O10 (Fig. 3). This CO group (Mo-C10-O10 166.9°) deviates from linearity; the Rh-C10 distance (2.821 Å), however, points to only a weak interaction of the Rh atom with the C atom. The formation of this CO bridge is unusual, because semibridging CO groups normally only occur when metal-metal bonds are present.

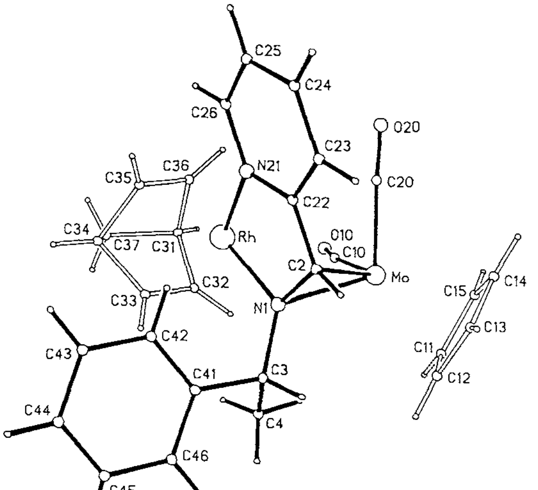

Fig. 3. Structure of **4a** in the crystal. Selected bond lengths [Å] and angles [°]: Mo-N1 2.221(5), Mo-C2 2.241(6), N1-C2 1.401(7), Mo-C10 1.966(6), Mo-C20 1.939(8), C10-O10 1.143(7), C20-O20 1.151(10), Mo-Cp 2.327-2.388, C2-C22 1.419(7), N1-C3 1.491(8), C22-N21 1.346(7), C26-N21 1.345(7), Rh-N21 2.117(5), Rh-N1 2.068(5), Rh-C32 2.122(6), Rh-C33 2.136(5), Rh-C35 2.110(6), Rh-C36 2.121(6); N1-Mo-C2 36.6(3), Mo-C2-N1 70.9(3), Mo-N1-C2 72.5(3), C10-Mo-C20 77.7(4), Mo-C10-O10 166.9(6), Mo-C20-O20 174.4(7), N1-Rh-N21 80.2(2), C22-C2-N1 118.1(5), Rh-N1-C2 109.8(4), Rh-N21-C22 112.3(4), N21-C22-C2 116.4(5).

The ^{1}H-NMR spectra show that **4** forms two diastereomers **a** and **b**, which rapidly interconvert in solution at room temperature. The high-temperature limiting spectrum for **4a/4b** is observed at 100°C, while the low-temperature limiting spectrum, with separate signals for **4a** and **4b** in the intensity ratio 98:2, is observed at −70°C.[10] It is not possible, as yet, to make any statements about the structure of **4b**.

The finding that the reactions of **3a/3b** and **3c/3d** with $[Rh(nbd)Cl]_2$ lead to the same product **4a/4b** can only be explained in terms of an intermediate **2a**. The intermediate **2a** is formed from both **3a/3b** as well as from **3c/3d**; the asymmetry of all former three-membered ring atoms is removed, leading under the strongly alkaline conditions used in the synthesis,[9] to establishment of the equilibrium **3a/3b**$\rightleftarrows$**3c/3d**, even in the absence of $[Rh(nbd)Cl]_2$. It therefore follows that epimerization of the intermediates **2b** and **2c** (with π-coordinated imine ligand) via **2a** (with σ-coordinated imine ligand) is more rapid than the reaction with $[Rh(nbd)Cl]_2$: Otherwise, if the complex **4a** ($R_{Mo}R_NS_C$) is formed from **3a/3b**, then **3c/3d** would have to yield a Rh-complex **4c** with $S_{Mo}S_NR_C$ configuration, which is not observed.

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[1] J. D. Morrison (Ed.): *Asymmetric Syntheses, Vol. 5*, Academic Press, London 1985.

[2] H. Brunner, H. Schwägerl, J. Wachter, G. M. Reisner, I. Bernal, *Angew. Chem. 90* (1978) 478; *Angew. Chem. Int. Ed. Engl. 17* (1978) 453.

[3] H. Brunner, H. Schwägerl, J. Wachter, *Chem. Ber. 112* (1979) 2079.

[4] Type B (310/25 mm) LiChroprep Si60 (40–63 µm), toluene/ether 50:1.

[5] **3a/3b**: IR (cyclohexane): $\tilde{\nu}$(CO) = 1940, 1850 cm^{-1}; ^{1}H-NMR (250 MHz, [D$_8$]toluene), 100°C: δ = 1.59 (d, 3 H, J = 6.8 Hz, CHCH_3), 3.11 (m, 1 H, CH$_3$CH), 3.72 (d, 1 H, J = 6.9 Hz, MoCH), 5.29 (m, 1 H, NH), 4.89 (s, 5 H, Cp), 6.26–7.96 (m, 9 H, phenyl and pyridyl).—**3a**, −70°C: δ = 1.51 (d, 3 H), 3.04 (m, 1 H), 3.67 (d, 1 H), 5.38 (m, 1 H), 4.70 (s, 5 H), 6.18–7.86 (m, 9 H).—**3b**, −70°C: δ = 4.91 (s, Cp).—**3c/3d**: IR (cyclohexane): $\tilde{\nu}$(CO) = 1940, 1850 cm^{-1}; ^{1}H-NMR (250 MHz, [D$_8$]toluene), 100°C: δ = 1.21 (d, 3 H, J = 6.7 Hz, CHCH_3), 3.06 (m, 1 H, CH$_3$CH), 3.76 (d, 1 H, J = 7.2 Hz, MoCH), 5.37 (m, 1 H, NH), 4.75 (s, 5 H, Cp), 6.38–8.02 (m, 9 H, phenyl and pyridyl).—**3c**, −70°C: δ = 1.05 (d, 3 H), 2.51 (m, 1 H), 3.61 (d, 1 H), 5.30 (m, 1 H), 4.59 (s, 5 H), 6.27–7.93 (m, 9 H).—**3d**, −70°C: δ = 4.67 (s, Cp).

[6] **3a**: Space group $P2_12_12_1$, a = 10.084(2), b = 13.516(2), c = 29.203(5) Å, Z = 8 (two independent molecules), 7237 reflections (Mo$_{K\alpha}$ radiation, $2\theta_{max}$ = 60°C), η = 1.06(7), R_w = 0.036.—**3c**: space group $P2_12_12_1$, a = 6.795(1), b = 11.744(2), c = 24.110(3) Å, Z = 4, 4422 reflections ($2\theta_{max}$ = 63°), η = −1.19(9) for the opposite configuration, R_w = 0.029.—**4a**: space group $P2_12_12_1$, a = 8.948(2), b = 14.048(3), c = 20.007(4) Å, Z = 4, 4479 reflections ($2\theta_{max}$ = 55°), η = 1.05(9), R_w = 0.034. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-51778, the names of the authors, and the full citation of the journal.

[7] D. Rogers, *Acta Crystallogr. A 37* (1981) 734.

[8] C. W. Fong, G. Wilkinson, *J. Chem. Soc. Dalton Trans. 1975*, 1100; E. K. Barefield, D. J. Sepelak, *J. Am. Chem. Soc. 101* (1979) 6542.

[9] **4**: 0.2 mmol **3a/3b**, 0.1 mmol $[Rh(nbd)Cl]_2$, 100 mg KOH, catalytic amounts of [18]crown-6 (toluene, 2 h, 20°C). Chromatography on Al_2O_3, neutral without added water with toluene/ether 6:1.

[10] **4a/4b**: IR (cyclohexane): $\tilde{\nu}$(CO) = 1915 s, 1835 m, 1815 w sh cm^{-1}; ^{1}H-NMR (250 MHz, [D$_8$]toluene), 100°C: δ = 1.19 (s, 2 H, nbd), 1.20 (d, 3 H, J = 6.9 Hz, CHCH_3), 3.21 (q, 1 H, CH$_3$CH), 3.48 (m, 2 H, nbd), 3.57 (m, 3 H, MoCH + nbd), 3.72 (m, 2 H, nbd), 4.97 (s, 5 H, Cp), 6.03–7.76 (m, 9 H, phenyl and pyridyl).—**4a**, −70°C: δ = 0.9 (d, 3 H), 1.17 (s, 2 H), 2.87 (m, 1 H), 3.29 (s, 1 H), 3.40, 3.57, 3.83 (m, 6 H), 4.82 (s, 5 H), 5.83–7.94 (m, 9 H).—**4b**, −70°C: δ = 5.30 (s, Cp).

[11] Priority sequence used for the specification of the Mo configuration: Cp > N(MoNC ring) > C(MoNC ring), looking at the molecule from the side opposite to the two carbonyl groups. Cf. H. Brunner, *Adv. Organomet. Chem. 18* (1980) 195.

[(α-Cyanobenzyllithium · Tetramethylethylenediamine)$_2$ · Benzene]: X-ray Structure Analysis of an α-Nitrile "Carbanion"**

By *Gernot Boche*,* *Michael Marsch*, and *Klaus Harms*

The synthetic importance of α-nitrile-"carbanions" extends from dinitrile cyclization[1] to the umpolung of aldehydes with trimethylsilyl cyanide.[2] However, although numerous mechanistic investigations have been carried out,[3] and both mono- as well as di-alkali-metal compounds of acetonitriles and phenylacetylnitriles have been prepared and investigated IR spectroscopically,[4,5] an X-ray structure analysis has so far never been carried out.[6] In the following, we report on such an analysis of [(α-cyanobenzyllithium · tetramethylethylenediamine (TMEDA))$_2$ · benzene] **1** · C_6H_6[7] (Fig. 1).

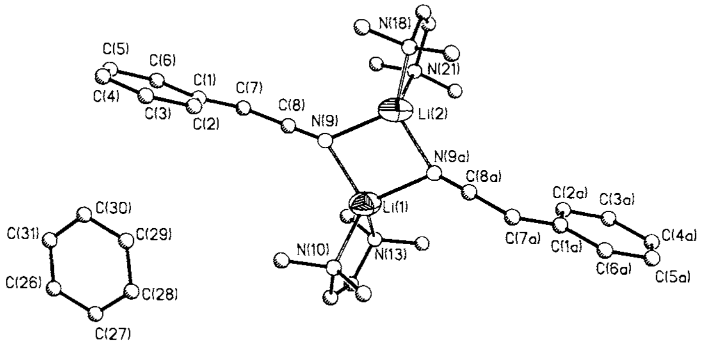
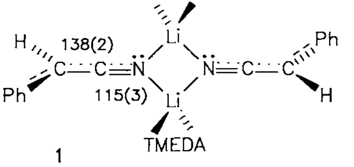


Fig. 1. Asymmetric unit of the crystal structure of **1** · C_6H_6. Space group $P2_1/n$, a=968.0(2), b=1583.4(4), c=2402.9(6) pm, β=99.46(2)°, Z=4, R=0.115 for 2292 reflections with $F > 3\sigma(F)$. The high R value is due to decomposition of the crystal in the X-ray beam. The H atoms on C-7 and C-7a were given a fixed C-H distance (96 pm) and a common isotropic temperature factor. All other H atoms were refined according to a riding model with C-H=96 pm. All calculations were carried out with the SHELXTL (Rev. 5.1) program system (*G. M. Sheldrick*, Göttingen 1985). Selected bond lengths [pm] and angles [°] (mean values: Li-N(TMEDA) 205(4), Li-N(anion) 204(3), C1-C7 143(2), C7-C8 138(2), C8-N9 115(3), Li1-Li2 264(5); C1-C7-C8 124.5 (1.0), C7-C8-N9 178.4(1.0), N9-Li1-N9a 98.2(0.5), Li1-N9-Li2 80.9 (0.5), dihedral angle C6-C1-C7-C8 179.2 (0.7). Because of the small anisotropic vibration of the nitrogen atom, an analysis of the C8-C9 bond length according to a riding model [8] gave only a slight lengthening to 117(2) pm. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-51841, the names of the authors, and the full citation of the journal.

1 · C_6H_6 crystallizes as a dimer, in which Li atoms are bonded to the N atoms of the nitrile groups and the TMEDA molecules. This solid state structure may corre-



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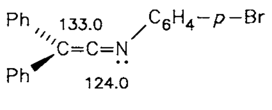

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