SYNTHESIS AND TAUTOMERISM OF PERSUBSTITUTED 1,3-DIANILS,

AND SUBSTITUENT ROTATION IN THEIR CHIRAL NICKEL COMPLEXES

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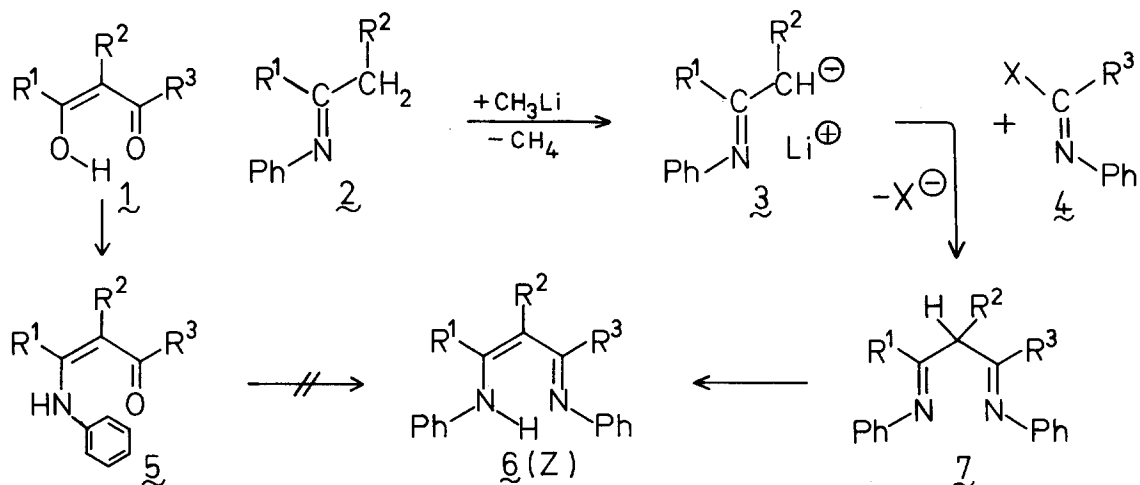Karlstr. 23, D-8000 München 2, Germany

Whereas malondianils like 6a are easily accessible from substituted malon-dialdehydes 1 ($R^1=R^3=H$), persubstituted acyclic 1,3-dianils 6 ($R^1 \neq H$) cannot be synthesized from 1,3-diketones 1. If conventional methods of C/N-condensation[1-3] are applied to "mono-anils" 5, the Beyer-Combes quinoline cyclization[4] invariably takes place. This is true even for 5g with only two bulky substituents. Therefore, we designed a different synthetic method with C/C-condensation, based on previous work by Marekov,[5] Stork,[6] and Wittig.[7]

The deprotonation of azomethines 2 is carried out in ether by addition of methyllithium. If evolution of methane does not begin instantaneously, 0.2 equivalents of N,N-diisopropyl-amine are added and the amount of methyllithium correspondingly increased. (Pinacolone-anil 2f must be refluxed with stochiometric amounts of pre-formed lithio-N,N-diisopropyl-amide for two hours.) The lithium salt 3 is then heated in ether with one equivalent of the imidic acid derivative 4 ($X = OC_2H_5$ or Cl) in an inert atmosphere for 40-80 hours. Since the primary product 7 is deprotonated by 3 with regeneration of 2, more $CH_3Li$ is added after ca. 15 and ca. 30 hours until no more methane is evolved. After hydrolysis with ice and basic work-up, the dianil is crystallized or distilled or may be purified as the perchlorate (in ethanol or 1-propanol below 70°C to avoid quinoline formation[4]). Yields (not optimized) were 26-96%.

The horseshoe-shaped (Z)-structures for 6a-e follow from the symmetry of the $^1$H nmr spectrum and/or the NH absorption at about $\delta = 14$ ppm[8] in $CCl_4$. Because of its bulky $R^1$ substituent, 8f assumes the (E)-configuration characterized by its _trans_ coupling constant $J(R^2,R^3) = 12$ Hz[9] and NH resonance at $\delta = 7.70$ ppm. The liquid, analytically pure[10] mixture 7/8g consists of 25% 7g (NH 3.72 ppm) and 75% 8g (CH$_2$ 3.35 ppm), whereas 6/7h[10] contains 60% 7h (CH 3.57 ppm, t with J = 7 Hz) as well as the horseshoe 6h (NH 12.5 ppm). Crystallization from ligroin was employed to separate 8i (NH 5.40 ppm, equilibrium concentration 85% in $CCl_4$) from 7i (CH 5.03 ppm, 15%).

We performed a structural proof of C/C-condensation for 7/8g by acid hydrolysis; 71% of dipivaloyl-methane 1g were isolated as the copper complex and identified with authentic specimens. The alternate possibility of N-iminoalkylation was normally not observed.

| 1-9 | R$^1$ | R$^2$ | R$^3$ | m.p. °C of dianil [b.p./Torr] | |
|------|-------|-------|-------|------|------|
| a | H | (naphthyl) | H | 126–128 | (6a) |
| b | CH$_3$ | (cyclohexenyl, H) | CH$_3$ | 112–113 | (6b) |
| c | CH$_3$ | (naphthyl) | CH$_3$ | 154.5–155.5 | (6c) |
| d | CH$_3$ | SC$_6$H$_5$ | CH$_3$ | 103–105 | (6d) |
| e | (CH$_2$)$_6$ | | CH$_3$ | – | (6e) |
| f | tC$_4$H$_9$ | H | H | 98–99.5 | (8f) |
| g | tC$_4$H$_9$ | H | tC$_4$H$_9$ | – | (7,8g) |
| h | nC$_3$H$_7$ | C$_2$H$_5$ | nC$_3$H$_7$ | [140/10$^{-3}$] | (6,7h) |
| i | CH$_3$ | C$_6$H$_5$ | tC$_4$H$_9$ | 102–103.5 | (8i) |
| i | CH$_3$ | C$_6$H$_5$ | tC$_4$H$_9$ | 93–95 | (7i) |
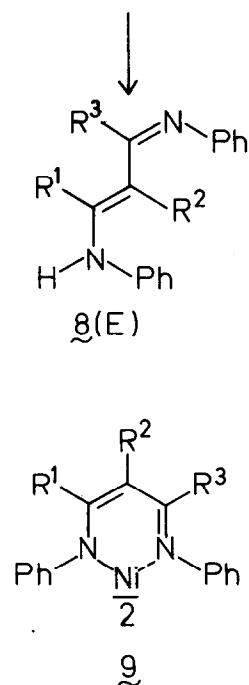
Tetrahedral, fully paramagnetic[11] nickel complexes[10] 9 were prepared in 0 – 86% yields from the 1,3-dianils by treatment with methyllithium and heating with [(C$_2$H$_5$)$_4$N]$_2$NiBr$_4$ in THF for 12–86 hours under N$_2$.[12] After evaporation and extraction with hexane or benzene, 9 crystallizes from dry ethyl acetate (precipitation with ethanol if necessary). We select here cases 9a, b, and d with symmetrical ligands (axial chirality[13,14]) for a study of substituent rotation.

Projecting 10 (9b) along the axis C$^3$NiC$^{3'}$ from the right, one obtains 11 with R configuration.[14] The cyclohexenyl double bonds are symbolized by two
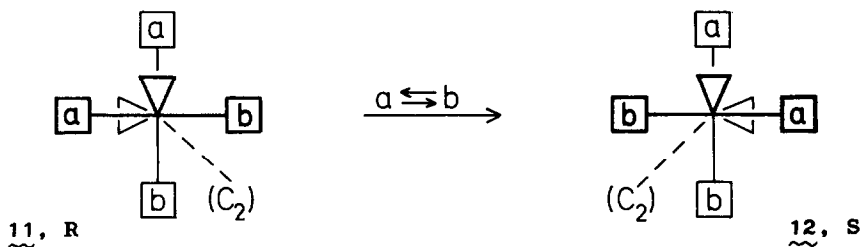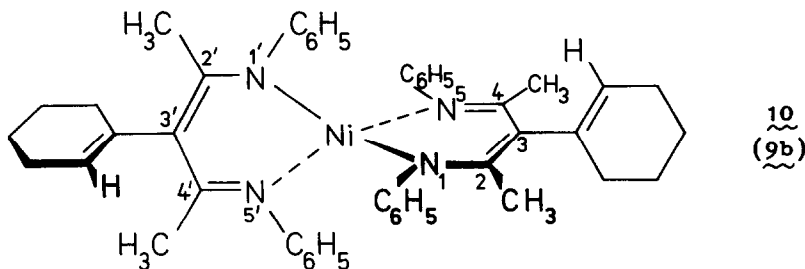
wedges ◁, one above the horizontal and one to the left of the vertical
(rear) chelate ring. For chemically equivalent groups ☐ (CH$_3$ or aromatic p-
hydrogen) we expect two $^1$H nmr absorptions (a,b) of equal intensity, but only
one for ◁ due to the symmetry axis (C$_2$). Rotations by 180° of the rear cyc-
lohexenyl substituent or of the rear ligand as a whole (i.e., nickel inver-
sion) will produce enantiomer 12 with interchanged chemical shifts a and b.
Since nickel inversion needs more than 23 kcal/mol,[13] the smaller barrier of
cyclohexenyl rotation may be obtained from the a/b coalescence of the p-hydro-
gen signals of the anilino moieties in 10. We find $\Delta G^{\neq}$ = 16 kcal/mol (320 K)
in (Cl$_2$CD)$_2$, in reasonable agreement with barriers for 2,2'-dimethyl-biphenyl
derivatives[15] having similar methyl/hydrogen repulsions in a planar transition
state. Due to weaker repulsions, nmr non-equivalences in 13 disappear at 240 K
with $\Delta G^{\neq}$ = 9.8 kcal/mol in (Cl$_2$CD)$_2$; the relevant $\delta$ values[11] (ppm) are shown
in 13 for ☐ = 2-H and 4-H.

14 (9a) is a model for the non-planar[16] 1-phenyl-naphthalene whose rotatio-
nal barrier is unknown.[17] Enantiomerization requires $\Delta G^{\neq}$ = 15.2 kcal/mol at
351 K in (Cl$_2$CD)$_2$. Hindered rotation of the phenyl groups about their bonds
to nitrogen is not observed for 9a (14) but detectable for 9b (10; $\Delta G^{\neq}$ =
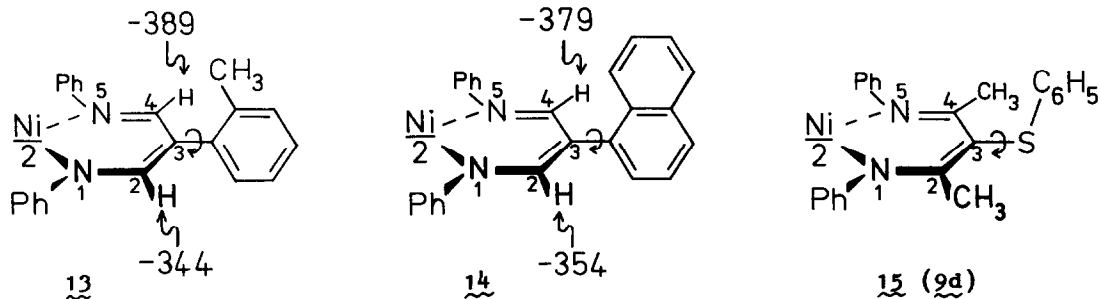
12.1 kcal/mol at 238 K), $\underset{\sim}{9c}$ (17.7 kcal/mol at 330 K), and $\underset{\sim}{9d}$ ($\underset{\sim}{15}$; 12.8 kcal/mol at 253 K).

The highest barrier $\Delta G^{\ddagger} = 17.4$ kcal/mol (340 K) found for $\underset{\sim}{15}$ ($\underset{\sim}{9d}$) in $(Cl_2CD)_2$ deserves special attention. It could be due to rotation of the $SC_6H_5$ group about the bond to $C^3$ or to inversion of divalent sulfur via a linear transition state and therefore constitutes another[18] lower energy limit for the latter process.

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