Configurationally Rigid Tetrahedral Nickel Complexes used for Conformational Analysis of Cycloalkene Units

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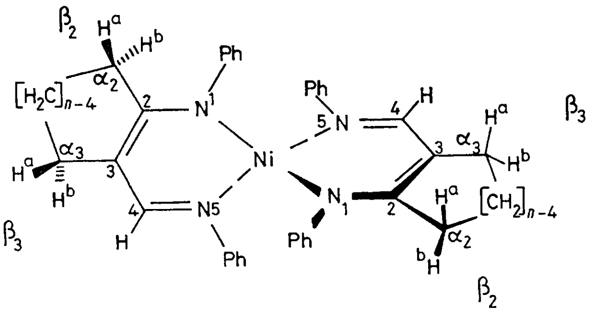
Summary Tetrahedral nickel complexes with cycloalkene substituents require more than 50 kJ mol^{-1} for configurational inversion; the conformations of these substituents may be inferred from paramagnetically induced ^1H n.m.r. shifts.

CONFORMATIONAL analysis of medium-sized cycloalkenes by n.m.r. spectroscopy has relied largely on symmetry considerations. We have exploited the angular dependence of spin transmission[1] for more direct conformational evidence. Moreover, the model compounds (**1**)—(**5**) which we have studied reveal high energy barriers preserving the hitherto unknown configurational rigidity[2] of paramagnetic, (pseudo)tetrahedral nickel complexes.

The nickel atom is a chiral centre in (**1**)—(**5**) with the (*R*) configuration.[3] Therefore, the protons H^a and H^b in any CH_2 group (β_2,β_3, *etc.*) are diastereotopic and would interchange their ^1H n.m.r. shifts (a,b) on enantiomeriza-



(1) $n = 5$
(2) $n = 6$
(3) $n = 7$
(4) $n = 8$
(5) $n = 12$

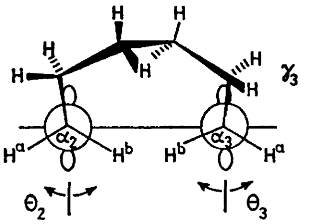
tion, *e.g.* by ligand rotation about the nickel. We find a separate signal for each pair of C_2-symmetry related protons. Since no a–b coalescences are observed on heating, we compute the following limits of barriers for configurational inversion at nickel: $\Delta G^{\ddagger} \geqslant 50{\cdot}2$ kJ mol^{-1} for (**1**) at 420 K in tetralin, $\geqslant 52{\cdot}6$ for (**2**) at 407 K in $(Cl_2CD)_2$, $\geqslant 54{\cdot}0$ for (**3**) at 465 K in tetralin, $> 49{\cdot}9$ for (**4**) at 418 K in $(Cl_2CD)_2$, and $> 44{\cdot}0$ for (**5**) at 391 K in $(Cl_2CD)_2$.

According to empirical equations (1)[1] and (2), the 'reduced' shifts[1] δ depend on the dihedral angles θ_3 (or θ_2) between the $2p_z$ axis at C^3 (or C^2) and the C(α)–H(β) bonds. One ligand of (**4**) is shown in the double Newman projection

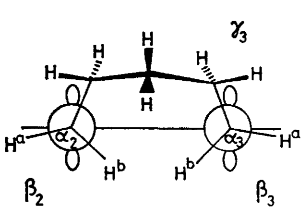
$$\delta\,(\beta_3\text{-H}) = +15 - 200\,\langle\cos^2\theta_3\rangle \text{ p.p.m.} \qquad (1)$$

$$\delta\,(\beta_2\text{-H}) = +\,3 + 96\,\langle\cos^2\theta_2\rangle \text{ p.p.m.} \qquad (2)$$

(**6**), looking along the bonds from C(α_3) and C(α_2) to the chelate ring. Apparent dihedral angles[4] $\langle\theta_{3,2}\rangle$ may be computed from the observed shifts δ *via* equations (1) and (2), yielding 55 and 64° for $\langle\theta_3\rangle$ and similar values for $\langle\theta_2\rangle$ at −50 °C. The only appropriate conformation is the 'twisted-boat-chair'[5,6] depicted in (**6**). This view is supported by the γ_3 shifts ($\delta = +\,12$ and -1 p.p.m.) since a negative shift indicates positive spin density[1] and hence an *anti* position[7] with respect to the spin-bearing $2p_z$ orbital.

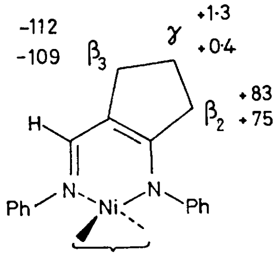


(**6**)

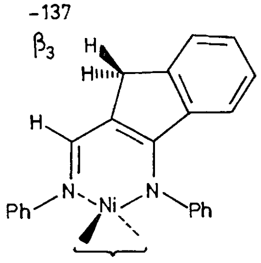


(**7**)

A local conformation like (**6**) must also prevail in the cyclododecene derivative (**5**) since very similar β_3 and β_2 shifts were found. Such 'reduced' shifts are strongly temperature dependent because of unequal invertomer populations in these chiral complexes. Values of 40 and 70° are obtained for $\langle\theta_{3,2}\rangle$ of (**3**) at −50 °C which compare well with the dihedral angles of the cycloheptene chair[8] in projection (**7**). Although these $\langle\theta\rangle$ agree with the boat conformation[6,9] as well, they rule out a twisted boat[10] for (**3**).



(**8**), δ at -40 °C



(**9**), δ at +25 °C

Dihedral angles of 20 to 40° are obtained from the δ values in (**8**). Only one β_3 signal shows up in (**9**) since $\langle\theta\rangle$ is 29° for both protons. INDO[11] calculations performed on radicals of the ligands (obviously a crude approximation) agree qualitatively with most of our shifts and with equations (1) and (2).

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