Activation Parameters for Rotation about an $M–C_{carb}$ Bond from Temperature Dependent ^1H N.m.r. Spectra of Rh^I Carbene Complexes

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Summary Restricted rotation on the n.m.r. time scale about the $Rh–C_{carb}$ bond in complexes $[RhL^{Et}(Y)Y'(Z)]$ $[L^{Et} = \overline{CN(Et)CH_2CH_2N}(Et)]$ is demonstrated; for *trans*-$[Rh(L^{Et})_2(CO)Cl]$, variable temperature observations provide rotational activation parameters including a relatively low activation energy ($\leqslant 10$ kcal mol^{-1}) and a negative activation entropy.

X-RAY structural results for various transition-metal carbene complexes[1] show that the view of the $M–C_{carb}$ bond as having substantial double bond character is incompatible with the reasonably long $M–C_{carb}$ bond length: *e.g.*, for Pt^{II}, 2·020(16) Å in *trans*-$[PtCl_2(PEt_3)\{C(NPhCH_2)_2\}]$[2] compared with 2·079(14) Å in *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$.[3] We now describe variable temperature ^1H n.m.r. experiments, from which activation parameters for $Rh–C_{carb}$ rotation are derived, and which provide an alternative probe into the nature of the $M–C_{carb}$ bond. This is the first time that such data have become available for a monohapto *C*-ligating donor, except for high symmetry small molecules such as $MeBF_2$ (E_a, 13·8 cal mol^{-1} from microwave spectra[4]).

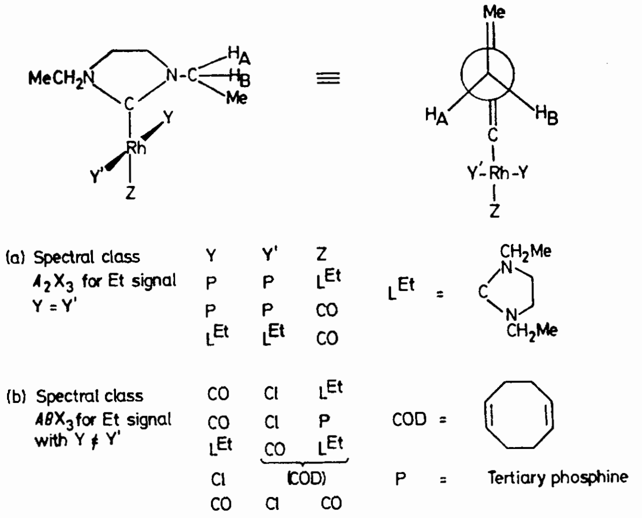

FIGURE 1. Newman projection along the N–Et bond of Rh^I carbene complexes $[RhL^{Et}(Y)Y'(Z)]$ (with the L^{Et} and $Rh(Y)Y'(Z)$ planes orthogonal) and ^1H n.m.r. spectral classifications of ethyl signal: A_2X_3 ($Y = Y'$) or ABX_3 ($Y \neq Y'$).

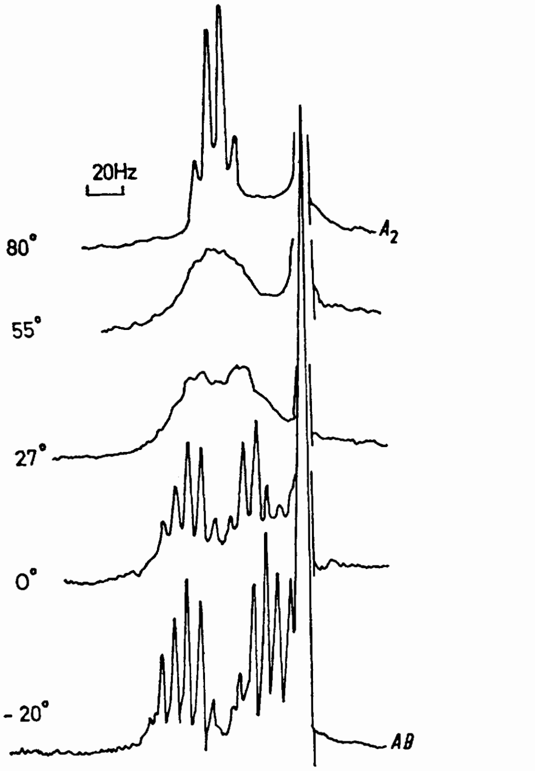

FIGURE 2. Variable temperature ^1H n.m.r. spectrum in $CDCl_3$ at 100 MHz of ethyl signal for trans-$[Rh(L^{Et})_2(CO)Cl]$, showing *AB* and A_2 parts of ABX_3 and A_2X_3 spin systems, respectively.

A Newman projection along the N–Et bond of L^{Et} in carbene complexes $[RhL^{Et}(Y)Y'(Z)]$ is shown in Figure 1. The conformation about the $Rh–C_{carb}$ bond is selected so that the L^{Et} and $Rh(Y)Y'(Z)$ planes are perpendicular, as has been demonstrated in the crystalline state (*X*-ray) for numerous carbene-d^8-metal complexes (including Rh^I [5]).[1,3,5]

In solution, restricted rotation about the Rh–C_{carb} bond, on the n.m.r. time scale, is expected to show a ^1H n.m.r. signal for the methylene protons of the N–CH_2–Me group which is first order (A_2X_3) for Y = Y′ or second order (ABX_3) for Y $\neq$ Y′. Complexes of each type have been prepared and show these spectral features (Figure 1).

^1H n.m.r. experiments in $CDCl_3$ at 100 MHz for two of the less symmetrical complexes, $[RhL^{Et}(CO)Cl(PPh_3)]$ and *trans*-$[Rh(L^{Et})_2(CO)Cl]$, show that the ABX_3 pattern observed at ambient temperature coalesces at <90° into A_2X_3. Figure 2 shows the 100 MHz variable temperature ^1H n.m.r. features for the latter complex from −20—+80°.

With *trans*-$[Rh(L^{Et})_2(CO)Cl]$, the coalescence temperature has been measured for (i) the N–CH_2–Me ^1H signal both at 60 and 100 MHz, and (ii) the ring methylene protons for $\overline{\mathrm{CN(Et)CH_2CH_2N}}\mathrm{(Et)}$ at 220 MHz (splitting was too small to be observed at the lower frequencies). These observations permit only an approximate analysis of activation parameters to be made at present (since $\Delta\nu_{AB}$ is not temperature-invariant): $E_a \leqslant 10$ kcal mol^{-1}, $\Delta G^{\ddagger}$ *ca.* 16 kcal mol^{-1}, $\Delta H^{\ddagger} < 9$ kcal mol^{-1}, and $\Delta S^{\ddagger}$ *ca.* −20 e.u. (The errors inherent in $\Delta S^{\ddagger}$ calculations make the last figure inexact,[6] but certainly $\Delta S^{\ddagger}$ is significantly negative.) Molecular models demonstrate the possibility of substantial steric interaction between the N–CH_2–Me group and the ligands Y′ and Y. Accordingly, a highly ordered transition state for Rh–C_{carb} rotation is expected and supported by the negative $\Delta S^{\ddagger}$. The activation energy is relatively low and comparable to that found for rotation about a C–C single bond in sterically-hindered *o,o*′-disubstituted biphenylenes, *e.g.*, *ca.* 13 kcal mol^{-1} in *dl*-2,2′-bis(acetoxymethyl)biphenyl.[7]

Single-temperature or temperature-independent ^1H n.m.r. observations on some Pt^{II} carbene complexes, using non-chelating carbene ligands, have been interpreted in terms of Pt–C_{carb} restricted rotation.[8] The use of a chelating carbene ligand such as L^{Et} has the advantage of eliminating ambiguities or complications arising from rotation about $\mathrm{C\overset{\cdots}{-}N}$ or $\mathrm{C\overset{\cdots}{-}O}$.[1]

Evaluation of more accurate activation parameters from detailed line shape analysis and the influence of solvent are now in progress, in collaboration with E. O. Bishop and M. D. Lambert. Of particular interest will be the use of this procedure as a probe for determining the *trans*-influence of a group Z (*trans*- to L^{Et}) to M–C_{carb} rotation in $[ML^{Et}Z(Y)Y']$ (Y and Y′ constant, M a d^8 metal ion).

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