Dynamic N.M.R. Behaviour of {6,7,8,9-η^4-*nido*-decaborato(2−)}bis(dimethylphenylphosphine)platinum(II), [Pt(η^4-$B_{10}H_{12}$)(PMe_2Ph)$_2$]; a Novel Type of Metalloborane Fluxionality

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Summary Variable temperature ^1H-{^{31}P} and ^1H-{^{11}B} n.m.r. spectroscopy show that the [η^4-$B_{10}H_{12}$]$^{2-}$ ligand in [Pt($B_{10}H_{12}$)(PMe_2Ph)$_2$] undergoes a novel type of non-dissociative rotation about an axis approximately in the Pt^{II} co-ordination plane; $\Delta G^{\ddagger}$ for the process is 79 ± 5 kJ mol^{-1} at 71 °C.

THE compound $[\mathrm{Pt}(\eta^4\text{-}\mathrm{B}_{10}\mathrm{H}_{12})(\mathrm{PMe}_2\mathrm{Ph})_2]$ (Figure 1) has been found to undergo a novel type of non-dissociative borane ligand fluxionality. In this compound the Pt–P bonds are not contained within a molecular mirror plane; the two *P*-methyl groups on each phosphine ligand are therefore inequivalent and exhibit differing proton n.m.r. resonances (Figure 2, lower traces). At higher temperatures these resonances coalesce (Figure 2, upper traces) indicating the equivalence of the *P*-methyl groups and therefore effective phosphine ligand site exchange. The limiting low-temperature line separation and temperature of coalescence[1] indicate an activation energy $\Delta G^{\ddagger}$ of 79 ± 5 kJ mol^{-1} for this process at 71 °C.

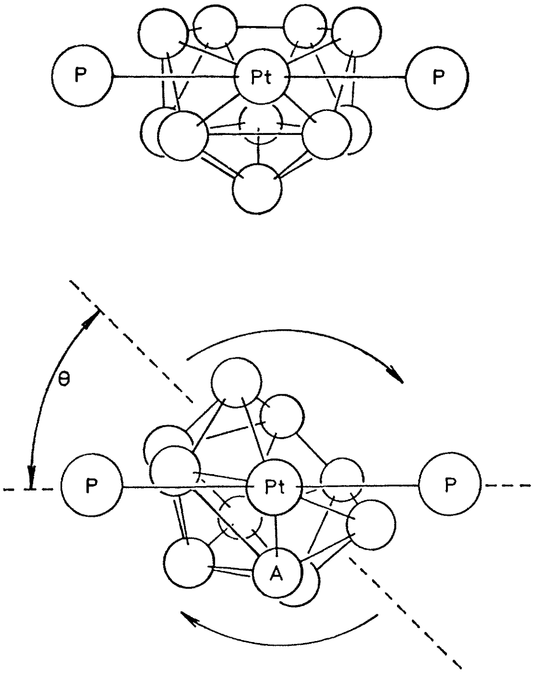

FIGURE 1. Schematic structures of $[\mathrm{Pt}(\eta^4\text{-}\mathrm{B}_{10}\mathrm{H}_{12})(\mathrm{PMe}_2\mathrm{Ph})_2]$ with carbon and hydrogen atoms omitted, showing (upper diagram) the probable minimum-energy conformation of the free molecule and (lower diagram) the nature of the rotation. The rotation is in fact associated with a differential distortion of the two Pt–P bonds and an asymmetry in the $\mathrm{B}_{10}\mathrm{H}_{12}{}^{2-}$ ligand (ref. 3).

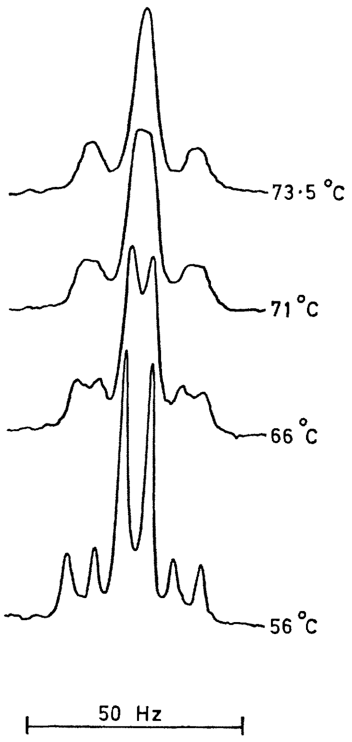

FIGURE 2. 100 MHz ^{1}H spectra of the *P*-methyl protons in $[\mathrm{Pt}(\eta^4\text{-}\mathrm{B}_{10}\mathrm{H}_{12})(\mathrm{PMe}_2\mathrm{Ph})_2]$ in $\mathrm{C}_6\mathrm{D}_6$ solution at various temperatures. Non-selective (broad-band noise) $\{^{31}\mathrm{P}\}$ decoupling has been used to simplify the spectra which are otherwise complicated by couplings $^2J(^{31}\mathrm{P}\text{–}^{31}\mathrm{P})$, $^2J(^{31}\mathrm{P}\text{–}^{1}\mathrm{H})$ and $^4J(^{31}\mathrm{P}\text{–}^{1}\mathrm{H})$; the 'satellite' lines arising from couplings $^3J(^{195}\mathrm{Pt}\text{–}^{1}\mathrm{H})$ remain.

We attribute the effective site exchange to mutual ligand rotation as in Figure 1 (lower diagram). Retention of the *P*-methyl coupling $^3J(^{195}\mathrm{Pt}\text{–}^{1}\mathrm{H})$ shows that this does not occur *via* phosphine ligand dissociation, and retention of the various[2] specific couplings $^2J(^{195}\mathrm{Pt}\text{–}^{1}\mathrm{H})$ and $^3J(^{195}\mathrm{Pt}\text{–}^{1}\mathrm{H})$ within the metalloborane cluster similarly precludes borane ligand dissociation and shows that the platinum atom remains associated with the same 4 boron atoms throughout. In addition, single-crystal *X*-ray diffraction analyses[3] of $[\mathrm{Pt}(\eta^4\text{-}\mathrm{B}_{10}\mathrm{H}_{12})(\mathrm{PMe}_2\mathrm{Ph})_2]$ and its 2-(2′-*nido*-decaboranyl) derivative $[\mathrm{Pt}(\eta^4\text{-}\mathrm{B}_{20}\mathrm{H}_{24})(\mathrm{PMe}_2\mathrm{Ph})_2]$ (which also exhibits the same dynamic n.m.r. effect) show that significant rotations θ (Figure 2) of *ca.* 21 and 8°, respectively, are readily produced by crystal packing forces; in addition, rotation in the sense represented in Figure 2 is accompanied by some displacement of the platinum atom towards the boron atom A.

Intramolecular dynamic behaviour is well-known in boron hydride and metalloborane derivatives but definitive examples so far reported have been confined to hydrogen shifts or to boron hydride bridge-terminal pseudorotation. The phenomenon reported here is therefore without precedent and may require both an η^4 ligand and a Pt$^{\mathrm{II}}$-type metal electronic configuration for sufficient stabilization of the transition-state. We have so far found no evidence for similar dynamic behaviour with η^3 ligands such as $\mathrm{B}_3\mathrm{H}_7{}^{2-}$, $\mathrm{B}_8\mathrm{H}_{12}{}^{2-}$, or $[\mathrm{Pt}(\mathrm{B}_8\mathrm{H}_{10})(\mathrm{PMe}_2\mathrm{Ph})_2]^{2-}$.

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[1] R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1977, 528, D. Kost, E. H. Carlson, and M. Raban, *J. Chem. Soc., Chem. Commun.*, 1971, 656.

[2] Observable in $^1\mathrm{H}\text{–}\{^{11}\mathrm{B}\}$ experiments; J. D. Kennedy and B. Wrackmeyer, *J. Magn. Reson.*, 1980, **38**, in the press.

[3] Unpublished work in collaboration with Dr. W. S. McDonald and (in part) J. Staves; to be submitted to *J. Chem. Soc., Dalton Trans.*