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Inequivalence in the ^{1}H-NMR Spectra of Alkene-(amine)platinum(II) Complexes

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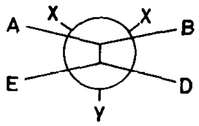
Inequivalence is very well-known to occur between atoms such as hydrogen in systems such as CH_2Q-CHRS where free rotation occurs in the C–C bond and where, in particular in this context, the inter-bond angles involving hydrogen are approximately 120°. We report here an example where the inter-bond geometry is more subtle.

When viewed along an axis containing the centre of the C=C bond, the platinum and the nitrogen atoms, a *trans*-alkene-amine platinum complex,



(I)

such as *trans*-[$Pt^{II}Cl_2(\eta^2$-CAB=CDE)(NXXY)], can be depicted as in (I). Then even if there is free rotation in the alkene–Pt–N axis, the X are inequivalent if A ≠ B ≠ E ≠ D, if A=D ≠ B=E and if A=B=E=D.

During work on alkene-amine-platinum(II) complexes [1], we observed that *trans*-[$PtCl_2(\eta^2$-*trans*-MeCH=CHMe)$NHMe_2$] provided an illustration of the second case. In contrast, in the analogous *cis*-butene complex, where A=E ≠ B=D no such inequivalence would be expected, nor is it indeed observed. A curious feature of the *trans*-butene system is that the inequivalence is observed on only one side of the molecule.

In solution in $CDCl_3$ between –40 and 25 °C, the $NHCH_3$ peak in the ^{1}H-NMR spectrum of *trans*-[$PtCl_2$(*trans*-MeCH=CHMe)$NHMe_2$] appears as a quartet with platinum satellites. (Throughout platinum satellites are observed as expected, with the same fine structures as their parent peak except where stated otherwise). Either treatment with D_2O or irradiation of the NH proton reduces the quartet to a doublet illustrating that the $N(CH_3)_2$ are inequivalent. (The former reduces the satellites to doublets. However, use of the latter technique only simplifies the main peak; irradiation at the guessed position of an NH satellite reduces one of the CH_3 satellites to a doublet, coupling being negative.) Full data are given in Table I.

The CCH_3 and $CHCH_3$ peaks are complex (as in the parent *trans*-2-butene ligand), the former being somewhat like the central quartet of the proton resonance of CH_2=CF_2 [2]. However on irradiation at CH and at CH_3 frequencies, the CH_3 and CH resonances respectively are reduced to singlets. Similarly irradiation of a CH or a CH_3 satellite simplifies one of the CH_3 or CH satellites respectively (coupling again being negative). No doublet structure could be detected.

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TABLE I. ^{1}H-NMR Spectra of *trans*-[$Pt(Cl)_2(\eta^2$-alkene)($NHMe_2$)].[a]

alkene	π-CH_2=	π-CH=	CH_3CH=	$NHCH_3$
propene	4.4(c), 4.56(c) J(Pt–H) *ca.* 63 Hz	5.5(c) J(Pt–H) 65 Hz	1.85(d) J(Pt–H) 34.5 Hz J(H–H) 7 Hz	2.75(d) J(Pt–H) 33 Hz J(NH–CH_3) 6 Hz
1-butene	4.45(c), 4.52(c) J(Pt–H) *ca.* 60 Hz	5.4(c) J(Pt–H) 61 Hz		2.75(d) J(Pt–H) 34 Hz J(NH–CH_3) 6 Hz
cis-2-butene		5.5(q) J(Pt–H) 68 Hz	1.75(d) J(Pt–H) 33 Hz J(H–H) 5 Hz	2.75(d) J(Pt–H) 33 Hz J(NH–CH_3) 6 Hz
trans-2-butene		5.34(c) J(Pt–H) 62 Hz	1.79(d), 1.82(d) J(Pt–H) 38 Hz J(H–H) 4.5 Hz	2.83(d), 2.90(d) J(Pt–H) 34 Hz
3-methyl-1-butene	4.2(d), 4.4(d) J(Pt–H) 60 Hz	5.25(c) J(Pt–H) 62 Hz		2.74(c), 2.82(d) J(Pt–H) 34 Hz J(H–H) 7.5 Hz

[a] In $CDCl_3$ at 25 °C. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, c = complex.

TABLE II. ^{13}C-NMR Spectra of *trans*-[$PtCl_2(\eta^2$-alkene)$NHMe_2$].^{a}

alkene	π-CH_2=	CH=	CH_3CH=	$NHCH_3$
ethene	74.8, 156 Hz			41.8, 13 Hz
Propene	71.1, 153 Hz	98.2, 144 Hz	20.9, 27 Hz	41.7, 15 Hz
1-butene	69.2, 154 Hz	104.6, 151 Hz		41.5, 13 Hz
cis-2-butene		89.8, 145 Hz	15.3, 22 Hz	41.7, 14 Hz
trans-2-butene		92.1, 148 Hz	20.3, 33 Hz	41.7, 13 Hz

^{a}In $CDCl_3$ at 25 °C. First figure: δ values in p.p.m.; second figure: J(Pt–C).

The inequivalence is thus noteworthy in two ways. It is curious, though not impossible in principle, that the interactions between the alkene and amine are not sufficiently close in size for the effect to appear mutual. Secondly, the distance over which the effect is felt suggests that orbitals on the platinum must be involved.

In contrast the spectrum of *trans*-[$PtCl_2(\eta^2$-cis-MeCH=CHMe)$NHMe_2$] is much more straightforward. The CCH_3 and $CHCH_3$ peaks are much simpler than in the complex of the *trans* alkene (just as they are in the parent ligands) being a doublet and quartet respectively, suggesting that J(CH=CH) is negligible. The $NHCH_3$ resonance is a simple doublet collapsing to a singlet on treatment with D_2O; there is no detectable inequivalence.

In principle *trans*-[$PtCl_2(\eta^2$-MeCH=CH_2)$NHMe_2$] should also exhibit inequivalence since it corresponds to $A \neq B=E=D$ in (I) above. In fact the $CHCH_3$ peak is a simple doublet (although that in free propene is more complex) while the $NHCH_3$ resonance is a doublet which collapses to a singlet with D_2O. Inequivalence is not detectable. Nor is it in *trans*-[$PtCl_2(\eta^2$-EtCH=CH_2)$NHMe_2$]. However the $NHCH_3$ spectrum of *trans*-[$PtCl_2(\eta^2$-^{i}PrCH=CH_2)$NHMe_2$] like that of the *trans*-2-butene complex, is a quartet which collapses to a doublet in D_2O.

The absence of inequivalence in the propene and 1-butene complexes may arise because the RC=C plane is not perpendicular to that containing the $PtCl_2N$ atom (where R is the Me or Et group). Such twisting away from the perpendicular has been proposed many times [3–6]. {It is, of course known that optically active forms of *trans*-[$PtCl_2$(ol)-$NHMeCH_2Ph$] (ol = propane, *trans*-2-butene, phenylethene) do not isomerize readily [7], so that it seems fair to assume that full rotation around the C=C axis does not occur in our compounds.} Hence the alkyl group, R, in the RCH=CH_2 ligands may be twisted too far away from the platinum for its effect to be significant. Only when R is large as in ^{i}PrCH=CH_2 is its effect sufficiently great to be transmitted by the platinum to the $NHMe_2$ group.

There is no significant difference in spectra between –40 °C and 25 °C, which suggests free rotation of the alkene-platinum bond. This occurs at room temperature in platinum-alkene complexes containing *cis* groups more bulky than chloride, but is quenched on cooling [3, 8].

No inequivalences are observed in the ^{13}C resonances of the propene, 1-butene and the *trans*-2-butene complexes, where they might be seen in principle. However both δ and J values of the coordinated alkenes vary considerably from complex to complex, *cf.* CH= and CH_3CH between the *cis*- and *trans*-2-butene compounds (Table II). This is compatible with the supposition that the angle between the RC=C and $PtCl_2N$ plane varies considerably between complexes.

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