Geometric Isomerism in Dinuclear Cycloplatinated Tri-tert-butylphosphine and Trimesitylphosphine Complexes

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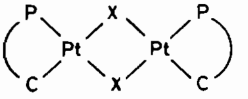
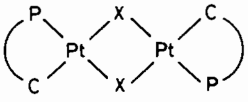
On further pursuing our initial investigation of the cyclometallation of trimesitylphosphine ($Pmes_3$) [1], we found [2] that the resulting product with Pt(II) is really a mixture of two products. This mixture is very stable as a solid and analyzes as one compound having the formula, $[Pt(P\frown C)X]_2$ ($P\frown C = Pmes_2C_6H_2(CH_3)_2CH_2$; X = Cl, Br, I) [2]. If redissolved, the two product species always appear in the same time-independent major:minor product ratio, as confirmed by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy.

We have assigned the two products as geometric isomers: *cis* (syn) and *trans* (anti) for the minor and major products respectively. The *trans*-configuration should be the more thermodynamically stable isomer for steric reasons. Also, because the two phosphorus centres in this arrangement are each *trans* to a more covalent Pt–X bond, weaker coupling to ^{195}Pt should be expected relative to the *cis*-arrangement. Our reasoning and subsequent assignments [2] are corroborated by the very recent characterization of *cis*/*trans*-$[Pt_2X_4(PR_3)_2]$ [3].



cis



trans

Thus we found it very disconcerting that Goel *et al.* [4] made no mention of the *cis*-isomer in their crystal structure report for *trans*-$[Pt(P^tBu_2C(CH_3)_2CH_2)(Cl)]_2$, despite their earlier claim [5] that based on ^1H and ^{31}P NMR spectral data and some literature precedence [6], both *cis*- and *trans*-isomers occur in solution. Rather, these authors attempted to reassign the ^1H NMR spectra for $[Pt(P^tBu_2C(CH_3)_2CH_2)(X)]_2$ (X = Cl, Pz) [4, 7] on the basis of a *trans*-isomer only. Although it is true that for the pyrazolato complex only one set of ^{31}P NMR signals was observed, two sets were observed for the chloro complex [5] and these conflicting data were not addressed [4]. We had earlier also observed only one set of ^{31}P NMR signals for $[Pt(P\frown C)(Pz)]_2$ whereas the ^1H NMR spectrum clearly indicated the presence of two isomers [8].

In a paper predating Goel *et al.* [7], Shaw and co-workers [9] reported that the cycloplatination of $P(^tBu_2{}^iBu)_3$ also gives rise to a mixture of *cis*- and *trans*-isomers. These authors have pointed out that the multiplicity of signals observed in the ^{31}P NMR spectrum cannot be due to *meso* and *dl* isomers since the corresponding complex $[Pt(P^tBu_2CH_2C(CH_3)_2CH_2)(X)]_2$ [10], for which there are no asymmetric centres, gives rise to one central resonance with two sets of ^{195}Pt satellites.

The low temperature (193 K) ^{31}P spectra for either $[Pt(P\frown C)Cl]_2$ or $[Pt(P'\frown C)Cl]_2$ ($P'\frown C = P^tBu_2C(CH_3)_2CH_2$) as well as for the analogous Pd(II) species are very similar to corresponding ambient temperature spectra. Slight changes occur for actual chemical shift and coupling constant values but the resonances are not significantly broadened relative to the ambient temperature spectra. These observations allow us to rule out the possibility that restricted rotation within the chelate moieties is responsible for the multiplicity of signals observed in the Pt(II) case.

Interconversion between *cis*- and *trans*-isomers of square planar Pt(II) complexes should be highly solvent dependent [6, 11]. The *trans*-isomer by virtue of its almost negligible dipole moment should be favoured by less polar media. Thus, comparative ^{31}P NMR solvent studies were carried out for $[Pt(P\frown C)Cl]_2$ and $[Pt(P'\frown C)Cl]_2$. The results appear in Table I. The changes in major:minor isomer ratio with increasing solvent dielectric constant [12] are plotted in Fig. 1.

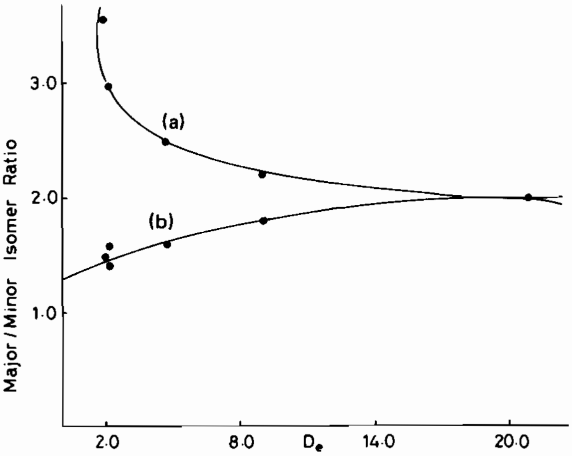


Fig. 1. The solvent dependence of *cis–trans* isomer interconversion. Changes in major/minor isomer ratio with dielectric constant (D_e) for (a) $[Pt(P\frown C)Cl]_2$ and (b) $[Pt(P'\frown C)Cl]_2$.

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TABLE I. Solvent Dependence for Isomerism in $[\mathrm{Pt}(\overset{\frown}{\mathrm{PC}})\mathrm{Cl}]_2$ and $[\mathrm{Pt}(\overset{\frown}{\mathrm{P'C}})\mathrm{Cl}]_2$[a, b]

Solvent	Chelate[a]	Major isomer δ (ppm) ($^1J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ (Hz))	Minor isomer δ (ppm) ($^1J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ (Hz))	Major/ Minor
CCl_4	$\overset{\frown}{\mathrm{PC}}$	9.15 (5075)	9.78 (5175)	3.5
C_6D_6	$\overset{\frown}{\mathrm{PC}}$	9.17 (5068)	9.48 (5154)	3.0
$CDCl_3$	$\overset{\frown}{\mathrm{PC}}$	8.35 (5118)	9.20 (5191)	2.7
CD_2Cl_2	$\overset{\frown}{\mathrm{PC}}$	8.66 (5090)	9.37 (5159)	2.2
$(CH_3)_2CO$	$\overset{\frown}{\mathrm{PC}}$	8.42 (5088)	9.75 (5144)	2.0
C_6H_{12}	$\overset{\frown}{\mathrm{P'C}}$	−14.75 (3765)	−15.28 (3773)	1.5
CCl_4	$\overset{\frown}{\mathrm{P'C}}$	−15.15[c]	−15.48[c]	1.4
C_6D_6	$\overset{\frown}{\mathrm{P'C}}$	−15.75 (3738)	−16.22 (3763)	1.6
$CDCl_3$	$\overset{\frown}{\mathrm{P'C}}$	−15.28[c]	−15.66[c]	1.6
CD_2Cl_2	$\overset{\frown}{\mathrm{P'C}}$	−14.75 (3747)	−15.13 (3772)	1.8
$(CH_3)_2CO$	$\overset{\frown}{\mathrm{P'C}}$	−13.84 (3745)	−14.30 (3757)	2.0

[a] $\overset{\frown}{\mathrm{PC}} = \mathrm{Pmes_2C_6H_2(CH_3)_2CH_2}$; $\overset{\frown}{\mathrm{P'C}} = \mathrm{P^tBu_2C(CH_3)_2CH_2}$. [b] Free ligand positions for $CDCl_3$ are −35.77 ppm for $\mathrm{Pmes_3}$ and +60.90 ppm for $\mathrm{P^tBu_3}$. [c] Not assignable.

The changes observed, although not dramatic, do show definite but opposite trends for the two systems studied. Our earlier assignments for *cis*/*trans*-$[\mathrm{Pt}(\overset{\frown}{\mathrm{PC}})\mathrm{Cl}]_2$ are corroborated since the major isomer is indeed less favoured by more polar solvents. Perhaps surprisingly the major isomer for $[\mathrm{Pt}(\overset{\frown}{\mathrm{P'C}})\mathrm{Cl}]_2$ appears to have the *cis*-geometry. This 'reversal' must mean that the *cis–trans* interconversion rate for $[\mathrm{Pt}(\overset{\frown}{\mathrm{P'C}})\mathrm{Cl}]_2$ is much slower than that for $[\mathrm{Pt}(\overset{\frown}{\mathrm{PC}})\mathrm{Cl}]_2$ which is in line with the less dramatic curvature in the plot observed for the former complex. It should be pointed out that there is a much higher degree of similarity between the two isomers in $[\mathrm{Pt}(\overset{\frown}{\mathrm{P'C}})\mathrm{Cl}]_2$ compared with $[\mathrm{Pt}(\overset{\frown}{\mathrm{PC}})\mathrm{Cl}]_2$. This in turn might be related to the differences between 5- and 4-membered chelates and/or aromatic and aliphatic tertiary phosphine ligands.

The geometry assignments made for either complex are reasonable and show internal consistency. In each case, coupling to $^{195}\mathrm{Pt}$ is higher for the *cis*-isomer and the *cis*-isomer is further shifted than the *trans*-isomer from free ligand positions.

The above solvent study indicates that *cis–trans* isomeric interconversion is a real and perhaps controllable process for either $[\mathrm{Pt}(\overset{\frown}{\mathrm{PC}})\mathrm{Cl}]_2$ or $[\mathrm{Pt}(\overset{\frown}{\mathrm{P'C}})\mathrm{Cl}]_2$. Although the corresponding Pd(II) analogues are more kinetically labile, formation of *cis*-$[\mathrm{Pd}(\overset{\frown}{\mathrm{PC}})\mathrm{Cl}]_2$ should be feasible [9, 13] and we are pursuing the possibility further.

Acknowledgements

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