Factors controlling the relative stabilities of *cis-* and *trans*-[PtX$_2$L$_2$] isomers: Chatt and Wilkins—50 years on

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DFT computations reveal that *cis-trans* preferences in [PtX$_2$(PR$_3$)$_2$] species are due to a combination of electrostatics, π-backbonding, antisymbiosis, and solvation effects.

Werner first showed that square planar complexes of the type [PtCl$_2$L$_2$] exist as *cis* and *trans* isomers,[1] which can have profoundly different properties. For example when L = NH$_3$, the *cis* isomer is a potent anti-cancer drug whereas the *trans* isomer has essentially no therapeutic utility.[2] Coordinatively unsaturated, square-planar bis-phosphine complexes are ubiquitous in homogeneous catalysis. The key steps in many catalytic mechanisms (oxidative addition, reductive elimination, migratory insertions) require a *cis* disposition of the spectator phosphine ligands. For example, the competition between Pd-catalyzed alternating co-polymerization of CO and ethylene and alkoxycarbonylation to propanoates has been suggested to depend on the *cis* or *trans* configuration of key intermediates.[3] For chelating diphosphines, the bite angle is well known to have a large influence on the isomerization equilibrium.[4] However, the factors that control the relative stabilities of *cis* and *trans* isomers remain poorly understood, and understanding them is crucial to assessing the implication for catalysis.[5]

In 1952, Chatt and Wilkins published two seminal papers on *cis–trans* isomerism in square planar platinum(II) and related complexes,[6] and provided a lucid discussion of the possible causes of energy differences between isomers: steric effects, electrostatic interactions, differences in bond energies, and differential solvation factors. Solvation was shown to be particularly important in later studies,[7] with *cis* isomers generally strongly favoured by polar solvents.[8] In this contribution, an understanding of the origins of these effects at an atomistic level is provided using density functional theory (DFT) computations with the BP86 functional.†

Table 1 shows the relative energies of *cis* and *trans* isomers of a series of square planar species [MX$_2$L$_2$] (M = Pt, Pd). Steric effects have been suggested to account for the *cis* diiodide and dibromide being more disfavoured than the dichloride.[9] Our computations confirm the relative energy differences (see **1–3**), but the optimised structures show no sign of repulsion between the iodines. For example, the optimised XPtX, PPtX and PPtP angles are almost identical (±1°) for the *cis* isomers of **1–3**. Based on our experience,[10] steric strain of more than 1–2 kcal mol^{-1} would lead to observable geometry changes, so it seems unlikely that sterics play an important role in determining the *cis–trans* preference in these cases.

Electrostatic interactions between the partial negative charges on X and the partial positive charges on M and L are different in *cis* and *trans* isomers, with the alternating charge arrangement for the latter more favourable. Using the calculated atomic charges and gas-phase structures for *cis-* and *trans*-[PtCl$_2$(PMe$_3$)$_2$] (*e.g.* Q$_{cis}$(Cl) = −0.50 e, r_{Cl-Cl} = 3.31 Å), and assuming, as Chatt and Wilkins did, that the charges can be treated as five point charges interacting in a vacuum, gives an electrostatic energy difference (EED) of −20.2 kcal mol^{-1} (as in Table 1, the negative sign indicates a lower energy for the *trans* isomer). Although the EED computed in this way is probably somewhat too large, because the groups—especially the phosphines—are not point charges as assumed, the order of magnitude provides the main explanation for our computational observation that, in most cases, *trans* isomers are more stable in the gas phase.

The EED can be used to rationalise some of the trends in the total gas phase energy differences in Table 1. For example, the EEDs of [PtCl$_2$(PMe$_3$)$_2$] and [PdCl$_2$(PMe$_3$)$_2$] (−20.2 and −24.4 kcal mol^{-1}) differ by −4.2 kcal mol^{-1}, closely, if probably fortuitously, matching the −4.4 kcal mol^{-1} difference between the gas phase ΔH$_{isom}$ (**1** and **7**). The greater destabilisation of the *cis* isomer for the Pd compound is due to slightly more ionic bonding. However, many other trends cannot be explained using only the EED estimate of the isomerisation energy. For example, the EEDs of [PtCl$_2$(PMe$_3$)$_2$] (−20.2), [PtI$_2$(PMe$_3$)$_2$] (−15.2 kcal mol^{-1}) and [PtMe$_2$(PMe$_3$)$_2$] (−28.4 kcal mol^{-1}) (**1**, **3** and **6**) do not match the gas-phase energy differences.

Instead, one must consider the interaction between the metal and the ligands and its effect on bond energies. Bonding in Pt(II) d^8 square-planar complexes is both ionic and covalent, with the latter arising from donation from ligand σ orbitals into sd hybrids on the metal,[11] as shown in Scheme 1. This leads to a three-centre, three-orbital, four-electron bond, with one very stable bonding orbital (MOs HOMO-10 and HOMO-15 in *trans*-[PtCl$_2$(PH$_3$)$_2$]), one mostly non-bonding one (a small contribution from the metal 6p orbital gives it some bonding character), and one anti-bonding one. Where two mutually *trans* ligands are not identical, they compete to donate into the *sd* hybrid. Softer ligands, higher in the *trans* influence scale, donate electrons more effectively, and this leads to an antisymbiotic effect whereby stronger ligands prefer to bind *trans* to weaker ones.[12] Together with the order of ligand-metal bond strength Me$^-$ > PMe$_3$ > I$^-$ > Br$^-$ > Cl$^-$, this explains the gas-phase results for **1**, **2**, **3** and **6**. In *cis*-[PtCl$_2$(PMe$_3$)$_2$], PMe$_3$ is *trans* to two weaker Cl$^-$ ligands, which partially offsets the unfavourable EED effect. Although the EED is less negative for the Br$^-$ and I$^-$ species than for Cl$^-$, given the smaller partial negative charges on the heavier halides, the overall energy

Table 1 Computed BP86 gas phase and solution energies (kcal mol^{-1}) for the *cis-* to *trans*-isomerisation of [MX$_2$L$_2$] (M = Pt, Pd)

Entry	M	X	L	ΔH^a (gas-phase)	ΔG^a (CH$_2$Cl$_2$)
1	Pt	Cl	PMe$_3$	−6.0	4.5
2	Pt	Br	PMe$_3$	−7.8	2.8
3	Pt	I	PMe$_3$	−10.0	−1.5
4	Pt	Cl	PH$_3$	−1.5	6.1
5	Pt	Cl	PF$_3$	2.8	6.9
6	Pt	Me	PMe$_3$	2.9	5.9
7	Pd	Cl	PMe$_3$	−10.4	−0.6
8	Pt	Cl	PPh$_3$	−4.5	0.5
9	Pt	Cl	NH$_3$	−13.8	−4.5

^{a} The gas-phase ΔH values shown here are in fact electronic energy differences ΔE; solution ΔG values are obtained by adding the computed ΔG$_{solv}$ to the gas phase ΔE. Frequency calculations on [PtCl$_2$(PH$_3$)$_2$] show that ΔE, ΔH and ΔG are nearly identical in the gas-phase.
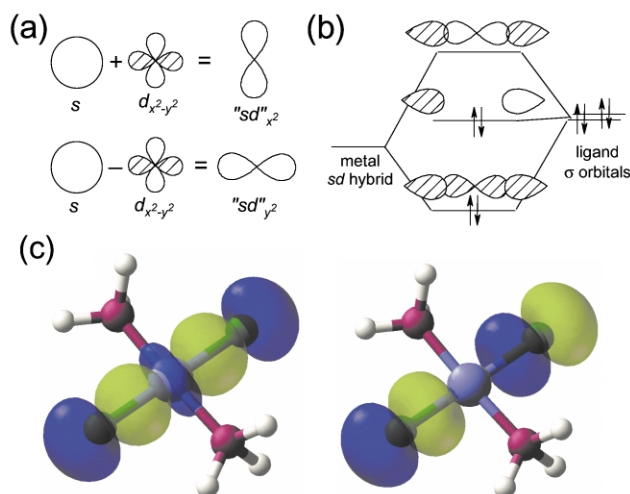
Scheme 1 (a) Formation of sd hybrid orbitals from the 6s and $5d_{x^2-y^2}$ orbitals of Pt; (b) MO diagram with generic σ orbitals on ligands; (c) Isodensity contours of the σ-sd bonding HOMO-10 and non-bonding HOMO-6 of *trans* $[PtCl_2(PH_3)_2]$.

difference is more negative, because Br^- and I^- have a stronger *trans* influence than Cl^-, so the Pt–PMe$_3$ bonds in the *cis* isomer are less strengthened by the antisymbiotic effect. For $[PtMe_2(PMe_3)_2]$, the very strongly bonding methyl group has such a great preference for binding *trans* to L that the *cis* isomer is more stable even in the gas phase, despite the unfavourable EED.

More direct evidence for the antisymbiotic effect and its magnitude can be obtained by computing Pt–PH$_3$ bond energies in $[PtX(PH_3)_3]^+$, shown in Table 2. In agreement with the MO diagram of Scheme 1, there is only a small *cis* influence[13] on the bond energy, but a very large variation of the *trans* Pt-PH$_3$ bond energy, in the order Cl > Br > I >> Me.

As well as changes in the σ-bonding, there will also be changes in π-donation by X lone pairs and in π-backbonding to the phosphine. In part, such effects cannot be distinguished from the σ-bonding ones: for example, Cl^- is a better π-donor than I, and this will enhance the π-backbonding to the phosphine *trans* to Cl in the same antisymbiotic way as discussed for σ-bonding. However, Table 1 clearly shows the effect of more favourable π-backbonding in the *cis* isomers due to the partipation of two different metal *d* orbitals, as already discussed by Chatt and Wilkins.[6] As the π-acceptor strength of the ligand in $[PtCl_2L_2]$ is increased for L = NH$_3$, PMe$_3$, PH$_3$, PF$_3$ (**9**, **1**, **4**, **5** in Table 1), the EED-derived preference for the *trans* isomer decreases markedly and actually disappears in the last case: *cis*-$[PtCl_2(PF_3)_2]$ is predicted to be more stable than its *trans* isomer.

The final contribution, solvation, is very important: by preferentially stabilising the *cis* form in all cases, it brings the computational results into much better agreement with experiment.[6] This effect is due to the very different polarity of the two isomers: with partial positive charges on L and negative ones on Cl, the *cis* isomer has a very large dipole moment (*e.g.* of 11.4 Debye for $[PtCl_2(PMe_3)_2]$), whereas the individual dipole moments in the *trans* isomer cancel out. The larger solvation energy for the *cis* isomer is enough, in many cases, to make it the more stable in dichloromethane solution. The exceptions are the iodo, palladium and amine compounds (**3**, **7** and **9**), where

the solvation effect, though strong, is not enough to reverse the gas-phase preference for *trans* geometry. Smaller solvation effects are obtained for $[PtCl_2(PH_3)_2]$ and especially $[PtMe_2(PMe_3)_2]$ and $[PtCl_2(PF_3)_2]$ due to lower gas-phase dipoles of the *cis* isomers (9.3, 5.4 and 5.5 Debyes, respectively). As expected, changing the polarity of the 'solvent' changes the computed energy difference. For $[PtCl_2(PMe_3)_2]$, we compute energy differences of −6.0, 0.6, 4.5, and 6.5 kcal mol^{-1} for the gas phase, benzene, dichloromethane, and acetonitrile, respectively. Whilst the quantitative results are not in perfect agreement—ΔG should be negative in benzene, as the *trans* isomer predominates experimentally[6]—the trend is well reproduced.

In conclusion, modern electronic structure methods have enabled us to revisit the classic studies by Chatt and Wilkins,[6] and to construct accurate atomistic models which assess and quantify their insights. For most compounds $[PtX_2(PR_3)_2]$, the *trans* isomer is more stable in the gas phase, mainly due to the more favourable electrostatic interactions between negative X and positive L groups. In solution, the large dipole in the *cis* isomer is better solvated, which explains why the *cis–trans* ratio is often associated with large solvent effects. For the compounds studied here, steric effects are found to be unimportant, whereas the more favourable π-backbonding in the *cis* isomers also helps to counteract the electrostatic *trans* preference. Finally, the antisymbiotic effect, which operates through ligand lone pair interactions with metal sd hybrids, is critical. It leads to stronger bonds for phosphines *trans* to chloride, and for methyl *trans* to phosphine, and plays an important role in alleviating the gas phase *trans* preference, making *cis*-$[PtMe_2(PMe_3)_2]$ more stable than its *trans* isomer, even in the gas phase.

Notes and references

We have checked that the level of theory used is adequate for these systems. Thus, using larger basis sets, different density functionals (PW91, B3LYP) or levels of theory (MP2), or adding zero-point energy, thermal and entropic contributions to the energy difference did not lead to notable deviations (>3 kcal mol^{-1}) from the results presented here. Whilst the absolute numbers presented may not be completely accurate, we are therefore confident that the trends are well reproduced.

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Table 2 BP86 gas phase bond dissociation energies (BDE) (kcal mol^{-1}) for $[PtX(PH_3)_3]^+$, for the *cis* and *trans* phosphine ligands

X	Cl	Br	I	Me
cis-BDE	50.1	50.4	47.9	46.1
trans-BDE	62.0	60.4	55.4	36.4