NMR probe effects on trans-pHilicity and trans-influence ladders in square planar Pt(II) complexes†

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Quantitative trans-pHilicity ladders for a broad series of ligands in square planar trans-[Pt(PMe3)2(X)L]n+ (n = 0, 1, 2; X = H, CO, CH3, NH2, OH2, Cl) complexes are built employing the isotropic $\delta^{iso}(SO)$ X NMR shielding constants, calculated by DFT computational protocols at the SO-ZORA level of theory, as the trans-pHilicity descriptors. Linear relationships between the $\delta^{iso}(SO)$ X trans-pHilicity descriptors and the RI(Pt-X) descriptors of trans-influence demonstrate the relation of trans-pHilicity with trans-influence. The electronic features of the probes are crucial factors that manipulate trans-pHilicity. The isotropic $\delta^{iso}(SO)$ X NMR descriptors of trans-pHilicity linearly correlated with the ligand electronic $P_L$ constants and other popular electronic/structural descriptors related with the L–Pt–X bonding, revealed the origin of trans philicity. The trans-pHilicity ladders constructed by the six different probes go roughly parallel with only minor deviations related with the position of L in the rungs of the ladders.

Introduction

There have been numerous studies concerning the effect of a ligand on the lability of other ligands in transition metal complexes. The great majority of these investigations have been concerned with the trans-effect in square planar metal complexes and has been shown to be more important than the cis-effect which is thought to be very small and difficult to predict.1–8 In parallel with the trans-effect term Pidcock et al.9 introduced the trans-influence term. Across the periodic table the trans-influence operates, whereby tightly bonded ligands selectively lengthen mutually trans metal–ligand bonds. The trans-influence is fundamentally important and underpins the trans-effect, a kinetic rate effect where the order of substitution of ligands at a metal centre can be controlled.

Recently we aimed to gain a comprehensive understanding of the trans-effect/trans-influence phenomena for a broad series of octahedral [Cr(CO)6L] complexes employing the calculated $\delta^{iso}$ 13C NMR shielding constants as the trans-effect/trans-influence metrics introducing the concept of trans-pHilicity to cover both kinetic and equilibrium phenomena.10 trans-PHilicity combines two discriminate electronic effects responsible for the electron density transfer either through the $\sigma$- or the $\pi$-subspaces. In this context the strength of trans-pHilicity could be explained in terms of $\sigma$-donation and $\pi$-back-donation, both being electronic effects. These electronic effects have previously been quantified by well-established ligand electronic parameters, such as the $P_L$ constants defined as $P_L = E_{1/2}[Cr(CO)6] - E_{1/2}[Cr(CO)5L]^{11–13}$

In a following paper14 we applied the trans-pHilicity concept in the realm of square planar Pt(n) complexes where both trans-influence and trans-effects have frequently been epitomized and probe whether and to what extent the cis ligands affect trans philicity. Having in mind that trans-effect/trans-influence phenomena operate mutually along a linear L–M–X framework we report herein on the effect of the leaving group X (used as a NMR probe) on the trans-pHilicity and trans-influence ladders for a broad series of square planar trans-[Pt(PMe3)2(X)L]n+ (n = 0, 1, 2; X = H, CO, CH3, NH2, OH2, Cl) complexes involving a wide variety of L (44 ligands) with diverse electronic features (σ-donor, σ-donor/π-acceptor ligands). The trans-pHilicity and trans-influence ladders are built employing the calculated $\delta^{iso}$ X NMR shielding constants and the RI(Pt-X) bond lengths respectively. Linear correlations between NMR parameters and the well established ligand electronic parameter $P_L$ and other popular electronic/structural descriptors related with the L–Pt–X bonding threw light on the underlying principles and the origin of trans philicity and validates the broad relevance across inorganic and organometallic chemistry.

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† Electronic supplementary information (ESI) available: $\delta^{iso}(SO)$ X NMR shielding constants [X = H, CH3, CO, NH2, OH2, Cl] calculated at the SO-ZORA level of theory [Tables S1–S8]; linear plots of the correlations between the $\delta^{iso}(SO)$ X NMR shielding constants [X = CH3, NH2, Cl] and $P_L$, RI(Pt-X), WBI(Pt-X) and Qn (Fig. S1–S4). See DOI: 10.1039/d0nj01336f
and catalysis, disposing a powerful tool in the arsenal of modelling and designing techniques.

**Computational methods**

All calculations were performed using the Gaussian 09, version D.01 program suite. The geometries of the complexes were fully optimized, without symmetry constraints, employing the 1999 hybrid functional of Perdew, Burke, and Ernzerhof as implemented in the Gaussian09, version D.01 program suite. The PBE0 functional mixes the Perdew–Burke–Ernzerhof (PBE) exchange energy and Hartree–Fock exchange energy in a set 3 to 1 ratio, along with the full PBE correlation energy. Geometry optimization of the square planar $trans$-$[Pt(PMe_3)_2(X)H]$ ($n = 0, 1, 2; X = H, CO, CH_3, NH_2, OH_2, Cl$) complexes was done in solution (benzene solvent) using the all electron SARC_ZORA basis set for Pt central atom and the 6-31+G(d) basis set for all main group elements (E). Solvent effects were accounted for by means of the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEF-PCM) being the default self-consistent reaction field (SCRF) method. Hereafter the computational protocol used in DFT calculations is abbreviated as PBE0/SARC-ZORA(Pt) $\cup$ 6-31+G(d)[E]/PCM. All stationary points have been identified as minima (number of imaginary frequencies $N_{\text{imag}} = 0$). Natural Bond Orbital (NBO) population analysis was performed using Weinhold’s methodology. Magnetic shielding tensors have been computed with the gauge-including atomic orbitals DFT method, as implemented in the Gaussian09 series of programs. The NMR shielding constants were calculated by inclusion of spin-orbit (SO) effects at the 2-component-spin–orbit-ZORA (SO-ZORA) level of theory, using the ADF2019 code. For simplicity we will denote the isotropic shielding constants as $\sigma^\text{iso}(SO)$ calculated at the GIAO (SO-ZORA)/PBE0/TZ2P/COSMO level of theory. The GIAO (SO-ZORA)/PBE0/TZ2P/COSMO computational protocol was chosen for it was successfully used by Kaupp and co-workers to probe the trans influence on $^1$H NMR hydride shifts in square-planar platinum(n) complexes predicting accurate $^1$H NMR hydride shifts matching experimental data. We also performed calculations of the $^1$H NMR hydride shifts for selected complexes employing the GIAO (SO-ZORA)/PBE0/TZ2P/COSMO and the results are given in the ESI† (Table S1). It can be seen that both computational protocols provide $^1$H NMR hydride shifts comparable to $^1$H NMR hydride shifts calculated by Kaupp and co-workers and the experiment. The deviations observed are due to the fact that in our calculations the $^1$H NMR hydride shifts are calculated for the optimized geometries of the platinum(n) complexes in solution (benzene solvent), while the calculations performed by Kaupp and co-workers referred to the gas-phase optimized geometries.

Notice that the estimated $\delta$(Pt–H) bond lengths for the optimized geometries in solution, as it was expected, are longer by 0.053 Å relative to the $\delta$(Pt–H) bond lengths of the optimized geometries in gas-phase (Table S2, ESI†). Obviously the estimated $\delta$(Pt–H) bond lengths accounts well for the observed deviations of the $^1$H NMR hydride shifts.

**Results and discussion**

**Selection of the NMR probes**

$trans$-Philicity ladders have been built for square planar $trans$-$[Pt(PMe_3)_2(X)H]$ ($n = 0, 1, 2; X = H, CO, CH_3, NH_2, OH_2, Cl$) complexes for a broad series of ligands $L$ (44 ligands) employing $^1$H, $^{13}$C, $^{15}$N, $^{17}$O and $^{35}$Cl NMR probes. We selected six different common NMR probes in order to answer the question whether the nature of the NMR probe affects the $trans$-philicity sequences (ladders) and the $\sigma^\text{iso}$ $trans$-philicity descriptors. The selection of the NMR probes (X) was based on their electronic characteristics, e.g. employing the strong $\sigma$-donor $^+$ and $CH_3$ ligands, the $\sigma$-donor/$\pi$-acceptor CO ligand, the $\sigma$-donor/$\pi$-donor NH$_2$ and Cl$^-$ ligands and the weak $\sigma$-donor/weak $\pi$-donor OH$_2$ ligand. Moreover the selected probes are ligands of broad relevance across platinum chemistry. The $^+$ and CH$_3$ ligands are formed in catalytic processes involving activation and functionalization of C–H bonds or oxidative addition reactions, and dehydrocoupling reactions of compounds with element-hydrogen bonds. The Cl$^-$ ligand is a good leaving group for the anticancer cis-Pt(NH$_3$)$_2$Cl$_2$ (cis-platin) drug, the OH$_2$ ligand occurs in the hydrolysis products of cis-platin, while the NH$_2$ ligand models the guanine base of DNA which is generally conceived to be a major bio-molecular target of the classic Pt(n) drugs. $trans$-Influence ladders have also been constructed employing the $\delta$(Pt–X) structural parameters. The relative $trans$-philicity strengths are expressed by the $\delta^\text{iso}$ $X$ NMR $trans$-philicity metrics defined as the difference between the calculated $\sigma^\text{iso}$ $X$ NMR shielding constants for the complete set of ligands and the $\sigma^\text{iso}$ $X$ NMR shielding constant of the complex containing the ligand exhibiting the weakest $trans$-philicity. Similarly the relative $trans$-influence strengths are expressed by the $\Delta\delta$(Pt–X) metrics.

**$trans$-Philicity ladders constructed by the strong $\sigma$-donor $^+$ and CH$_3$ $^-$ NMR probes**

The $trans$-philicity ladders for the $trans$-Pt(PMe$_3$)$_2$(H)L and $trans$-$[Pt(PMe_3)_2(CH_3)H]$ ladders involving the $^1$H and $^{13}$C NMR probes quantified by the $\delta^\text{iso}(SO)$ $^1$H and $^{13}$C NMR metrics along with the $trans$-influence ladders quantified by the $\Delta\delta$(Pt–H) and $\Delta\delta$(Pt–CH$_3$) metrics are shown in Chart 1. The calculated $\sigma^\text{iso}(SO)$ $^1$H and $^{13}$C NMR shielding constants are given in the ESI† (Tables S3 and S4).

Perusal of Chart 1 reveals that the $^1$H and $^{13}$C NMR $trans$-philicity ladders retrieve well the experimentally established trans orienting series:

$H_2O \approx NO_3^- < OH^- < NH_2^- < Cl^- < Br^- < I^- \approx SCN^-$
$\approx NO_3^- \approx PR_3 < CO \approx C_2H_4 \approx CN^- \approx CH_3^- \approx H^+$

Chval et al. thoroughly investigated the mechanism of anation reactions in square planar $trans$-Pt([NH$_3$]$_2$T[H$_2$O])]$^{2+}$ complexes ($T = H_2O, NH_3, OH^-, F^-, Cl^-, Br^-, H_2S, CH_3S^-, SCN^-, CN^-, PH_3, CO, CH_3^+, H^+, C_2H_4$) employing DFT computational methods. The authors showed that for $trans$ ligands with a very strong $\sigma$-donation (e.g. CH$_3^+$ and H$^+$) the substitution
proceeds by a dissociative interchange \((\lambda_1)\) mechanism, for \textit{trans}\ ligands with strong \(\pi\)-back donation (e.g. \(\text{C}_2\text{H}_4\)) the substitution proceeds by a two step associative mechanism and for \textit{trans}\ ligands with weak \(\sigma\)-donation and \(\pi\)-back-donation the substitution reactions proceed by an associative interchange \((\lambda_2)\) mechanism. According to the computed activation energies the \(\text{T}\) ligands follow the \textit{trans} effect sequence:

\[
\text{C}_2\text{H}_4 \gg \text{CH}_3^- \simeq \text{H}^+ > \text{CO} \simeq \text{CH}_3\text{S}^- \simeq \text{PH}_3 > \text{CN}^- \simeq \text{NO}_2^- \simeq \text{H}_2\text{S} > \text{Br}^- > \text{Cl}^- > \text{SCN}^- \simeq \text{NH}_3 \simeq \text{OH}^- > \text{F}^- \simeq \text{H}_2\text{O}
\]

The calculated \(\sigma^{\text{iso}}(\text{SO})\) shielding constants for selected \textit{trans}-\(\text{Pt}((\text{PEr})_2)(\text{H})\) systems for which experimental data are available\(^{40-44}\) (\(\text{cf. Table S1, ESI}\)) demonstrate that the calculated \(\sigma^{\text{iso}}(\text{SO})\) shielding constants are accurate metrics to describe the ligands \(\text{L}\) in reliable \textit{trans}-philicity ladders (\textit{trans}-philicity sequences).

Comparison of the \(\text{H}^1\) and \(\text{C}^{\text{13}}\) NMR \textit{trans}-philicity ladders reveals that the two ladders are almost identical. In both ladders the strong \(\sigma\)-donors (\(\text{H}^+, \text{Me}^-, \text{BH}_2^-, \text{B}(\text{OH})_2^-\) and \(\text{SnCl}_3^-\)) occupy the rungs with very strong \textit{trans}-philicity (black rungs), the \(\text{C}\)-donor ligands the rungs with strong \textit{trans}-philicity (red rungs) while the \(\text{N}\)- and \(\text{O}\)-donor ligands occupy the rungs with moderate to weak \textit{trans}-philicity (green and blue rungs). However in many cases the ligands \(\text{L}\) follow different orders along the \textit{trans}\-orienting series. In particular the strong \(\sigma\)-donors \(\text{tBu}^-\) and \(\text{Ph}^-\) ligands occupy remarkably different rungs in the \(\text{H}^1\) and \(\text{C}^{\text{13}}\) NMR \textit{trans}-philicity ladders. The \(\text{tBu}^-\) and \(\text{Ph}^-\) ligands are found in the black rungs of the \(\text{H}^1\) NMR \textit{trans}-philicity ladder and the green rungs of the \(\text{C}^{\text{13}}\) NMR \textit{trans}-philicity. However this is not the case in the respective \textit{trans}-influence sequences (ladders). It is important to be noticed that Kaupp and co-workers\(^{45}\) applying quantitative relativistic DFT methodology in a series of square planar \(\text{Pt}(\text{I})\) complexes and exploring correlations between the calculated \(\text{H}^1\) shifts and the \textit{trans} ligand influence series established the \textit{trans}-influence sequence: \(\text{NO}_3^- < \text{ONO}^- < \text{NO}_2^- < \text{Cl}^- < \text{Br}^- < \text{SCN}^- \simeq \text{I}^- < \text{CN}^- < \text{Ph}^- < \text{Me}^- < \text{SiR}_3^- \simeq \text{BR}_3^-\), which is exactly the same with the \textit{trans}-philicity series shown in the \(\sigma^{\text{iso}}(\text{SO})\) \(\text{H}^1\) NMR \textit{trans}-philicity ladder (Chart 1). In a following publication Kaupp and co-workers\(^{45}\) presented the results of a extensive investigation of the ligand effects on the NMR shifts of metal-bound nuclei in 5d transition-metal complexes, encompassing both 5d\(^4\) and 5d\(^{10}\) electron configurations, with related effects even for 5d\(^4\) complexes using relativistic quantum-chemical analyses. The authors showed that the \textit{trans} ligand effects on the shieldings are exclusively dominated by two mixed \(\sigma/\pi\)-type spinors.

Generally with only minor deviations related with the position of a few ligands in the \textit{trans}-influence and \(\text{H}^1\) NMR \textit{trans}-philicity ladders the two ladders go parallel to each other.
Phosphines, nitriles, CO, NO$_2^-$, OH$^-$, and N$_2$ exert strong trans-influence ($\delta$(Pt-H) = 1625–1638 pm), while the O-donor ligands along with halides, isocyanides, SH$_2$, N$_3^-$, NCS$^-$, Py, NH$_3$, N$_2$ and OH$_2^-$ ligands exert moderate to weak trans-influence ($\delta$(Pt-H) = 1584–1620 pm). Noteworthy in both $^1$H and $^{13}$C NMR trans-pillicity ladders the trans-pillicity of phosphine ligands follows the order: PF$_3$ > PH$_3$ > PPh$_3$ > PMe$_3$. According to the \( \sigma \)-donor/\( \pi \)-acceptor ratio, PF$_3$, PH$_3$ and PMe$_3$ follow the trend $^{46}$ PF$_3$ < PH$_3$ < PMe$_3$, while according to the $\nu$(C=O) stretching vibrational frequencies for Ni(CO)$_3$L complexes follow the order $^{47}$ PF$_3$ > PPh$_3$ > PMe$_3$ in line with the trans-pillicity sequence for the phosphane ligands. Similarly the $^1$H and $^{13}$C NMR trans-pillicity ladders reproduce the experimentally established trans-influence sequences, Br$^-$ > Cl$^-$ > F$^-$ and NH$_3$ > Py.

In the trans-[Pt(PMe$_3$)$_2$(CH$_3$)$_2$] complexes the trans-influence ladder match better to the $^{13}$C NMR trans-pillicity ladder. The two ladders are almost similar showing only minor local order inversions of a few ligands along the trans orienting series. In both ladders the strong trans-$\sigma$-donor (H', Me$^-$ and t-Bu$^-$, SnCl$_3$), the C-donor (CO and isocyanides) along with the BH$_2^-$, B(OH)$_2^-$ and phosphane ligands occupy the rungs with strong to very strong trans-influence and trans-pillicity. Similarly the N- and O-donor ligands occupy the rungs with moderate to weak trans-influence and trans-pillicity, but in many cases follow different orders along the trans orienting series.

**trans-pillicity ladder constructed by the $\sigma$-donor/$\pi$-acceptor CO probe**

The trans-pillicity ladder for the trans-[Pt(PMe$_3$)$_2$(CO)$_2$] complexes quantified by the $\Delta\delta^{13}$C NMR metrics along with the trans-pillicity ladder quantified by the $\Delta\delta$(Pt-CO) metrics are shown in Chart 2. The calculated $\delta^{13}$C NMR shielding constants are given in the ESI† (Table S5).

The $^{13}$C NMR trans-pillicity ladder matches better to the $^1$H NMR than the $^{13}$CH$_3$ NMR ladders (Chart 1). Comparison of the aforementioned trans-pillicity ladders illustrates clearly that the electronic features of the probes are crucial factors that tune deploy of ligands L in the trans-pillicity ladders. In particular nitriles NCR (R = H, Me, Ph) occupy the pale blue rungs with weak trans-pillicity in the $^{13}$CO NMR trans-pillicity ladder and the blue rungs with moderate trans-pillicity in the $^{13}$CH$_3$ and $^1$H NMR trans-pillicity ladders. It can also be seen that various classes of ligands in the three ladders follow the trends:

**Strong $\sigma$-donor ligands:**

$^1$H ladder: SnCl$_3^-$ < t-Bu$^-$ < Ph$^-$ < Me$^-$ < H$^-$ < BH$_2^-$

$^{13}$CH$_3$ ladder: t-Bu$^-$ < Ph$^-$ < Me$^-$ < SnCl$_3^-$ < H$^-$ < B(OH)$_2^-$

$^{13}$CO ladder: SnCl$_3^-$ < Ph$^-$ < Me$^-$ < H$^-$ < t-Bu$^-$ < B(OH)$_2^-$

**C-Donor ligands:**

$^1$H ladder: CNMe < NHCl < CNH < CNPh < CN$^-$ < CO

$^{13}$CH$_3$ ladder: CN$^-$ < NHCl < CNPh < CNMe < CNH < CO

$^{13}$CO ladder: CO < CNMe < CNPh < NHC < CNH < CN$^-$

**N-Donor ligands:**

$^1$H ladder: N$_2$ < py < NCH < NCMe < NO$_2^-$ < NH$_3$ < NCPH < N$_3^-$ < NCS$^-$ < NH$_2^-$

$^{13}$CH$_3$ ladder: NO$_2^-$ < NCS$^-$ < N$_3^-$ < py < NH$_3^-$ < NCMe < NCPH < NH$_3^-$ < NHC < N$_2^-$

$^{13}$CO ladder: N$_2$ < NCH < NCMe < NCPH < NH$_3$ < py < NCS$^-$ < NO$_2^-$ < N$_3^-$ < NH$_2^-$

**O-Donor ligands:**

$^1$H ladder: OH$_2^-$ < OCN$^-$ < NO$_3^-$ < CCl$_3$COO$^-$ < OCl$^-$

$^{13}$CH$_3$ ladder: OCl$^-$ < OBr$^-$ < OF$^-$ < NO$_3^-$ < OCN$^-$

$^{13}$CO ladder: OCl$^-$ < OBr$^-$ < OF$^-$ < NO$_3^-$ < OCN$^-$ < CH$_3$COO$^-$ < C$_6$H$_5$COO$^-$ < OH$^-$ < HOOC$^-$ < CCl$_3$COO$^-$ < OH$_2^-$

**Chart 2** trans-Pillicity ladder for the trans-[Pt(PMe$_3$)$_2$(CO)L]$^{2+/3+}$ complexes quantified by the $\delta^{13}$C NMR shielding constants referenced to the $\delta^{13}$C NMR shielding constants of trans-[Pt(PMe$_3$)$_2$(CO)(OH)$_2$]$^{2+}$ ($\delta^{13}$C = 48.8 ppm) reference compound along with the trans-influence ladder quantified by the $\Delta\delta$(Pt–CO) structural parameters referenced to $\Delta\delta$(Pt–CO) parameters of trans-[Pt(PMe$_3$)$_2$(CO)(F)]$^{+}$ ($\Delta\delta$(Pt–CO) = 1936 pm) reference compound.
The deviations observed might be due to the synergic contribution of the σ-donor and π-acceptor capacity of the probes to the mutual electron density transfer L→Pt→CO pathways (channels) taken place through the σ- and/or the σ- and π-subspaces (Scheme 1).

According to Scheme 1 the electronic features of the trans L ligands and X NMR probes are the crucial determinants of the net charge transfer from the trans L ligands to X NMR probes that manipulates trans-philicity. In this context trans-philicity (trans effect/trans-influence) originates from electronic effects. The electronic nature of trans-philicity accounts well for the positions of the σ-donor/π-donor SH+, SCN− and NH2− ligands in rungs of higher trans-philicity relative to their positions in the 1H and 13CH3 NMR ladders. Coordination of the σ-donor/π-donor ligands to [Pt(PMe3)2(CO)]2+ reference standard adds more electron density on the CO probe by electron density transfer through the π-channel that increases the downfield shifts, hence increasing trans-philicity and moving the positions of σ-donor/π-donor ligands in rungs of higher trans-philicity in the 13CO NMR trans-philicity ladder.

Generally in the trans-influence ladder the majority of the ligands occupy the proper rungs of the ladder, e.g. the strong σ-donors and phosphines occupy higher trans-influence, the C-donors the rungs of strong trans-influence, the N-donors, hypohalites, SH3 and Cl− the rungs of moderate trans-influence and the O-donors along with F− the rungs of weak trans-influence.

trans-Philicity ladder constructed by the strong σ-donor/π-donor NH2 probe

The trans-philicity ladder for the trans-[Pt(PMe3)2(NH2)L]0/+ complexes quantified by the Δσiso15N NMR metrics along with the trans-influence ladder quantified by the ΔR(Pt–NH2) parameters are shown in Chart 3. The calculated σiso(SO)15N NMR shielding constants of the trans-[Pt(PMe3)2(NH2)L]0/+ complexes along with the trans-influence ladder quantified by the ΔR(Pt–NH2) structural parameters referenced to ΔR(Pt–NH2) parameters of trans-[Pt(PMe3)2(NH2)Cl]0/+ (R(Pt–NH2) = 2042 pm) reference compound.

In the 15N NMR trans-philicity ladder the O-donor ligands occupy the rungs with weak trans-philicity, the strong σ-donor and phosphe ligands the rungs with strong trans-philicity, while the N- and C-donor ligands occupy rungs with strong, moderate and weak trans-philicity. Noteworthy the 15N NMR trans-philicity ladder matches better to the 13CH3 ladder, with only minor deviations related with the position of L in the rungs of the two ladders, rather than to the 13CO and 1H NMR trans-philicity ladders. However in the trans-influence ladder remarkable changes in the trans-influence sequences relative to the 15N NMR trans-philicity sequences are observed. Specifically in the trans-influence ladder the O-donor ligands are placed in the rungs of moderate to strong trans-influence. In the trans-influence sequences phosphanes are placed in the rungs with weak to very weak trans-influence. The same holds true for some of the C-donor ligands (CO, CN− and isocyanides) and N-donor ligands (NHC, Py, NH3 and nitriles) deviating from the experimentally established trans orienting series.

trans-Philicity ladder constructed by the weak σ-donor/weak π-donor OH2 probe

The trans-philicity ladder for the trans-[Pt(PMe3)2(OH2)L]0/+ complexes quantified by the Δσiso17O NMR descriptors along with the trans-influence ladder quantified by the ΔR(Pt–OH2) structural parameters shown in Chart 4. The calculated...
$\sigma^{iso}(SO)$ $^{17}O$ NMR shielding constants are given in the ESI† (Table S7).

Interestingly the $^{17}O$ NMR trans-philicity ladder is almost identical with the $^1H$ NMR (Chart 1) and $^{13}CO$ NMR (Chart 2) trans-philicity ladders with only marginal deviations related with local inversion of the trans-philicity order of some ligands. On the other hand the trans-influence ladder quantified by the $R$(Pt–OH$_2$) parameters deploy trans-influence sequences, which do not match the experimentally established trans orienting series. In effect the strong $\sigma$ donor BH$_2^-$, B(OH)$_2^-$, H, SnCl$_3^-$, Me$^-$, $t$-Bu$^-$ and Ph$^-$ anionic ligands along with phosphanes, CN$^-$, NH$_2^-$, SH$^-$, SCN$^-$ and NO$_3^-$ ligands occupy the rungs with very strong trans-influence in the trans-influence ladder in line with the experimentally established trans orienting series. However the O-donor (RCOO$^-$, OX$^-$, OCN$^-$ and OH$^-$) ligands along with NH$_3$, N$_3^-$, Br$^-$, Cl$^-$, NCS$^-$ and PH$_3^-$ occupy the rungs with strong to moderate trans-influence deviating from the experimentally established trans orienting series. Similarly the C-donor (isocyanides and CO) ligands along with the N-donor (nitriles, NH$_3$, Py and N$_2$) and PF$_3$ ligands are placed in the rungs of weak trans-influence also deviating from the experimentally established trans orienting series.

**Chart 4** trans-Philicity ladder for the trans-[Pt(PMe$_3$)$_2$(OH$_2$)L]$^{1/+}$ complexes quantified by the $\sigma^{iso}(SO)$ $^{17}O$ NMR shielding constants referenced to the $\sigma^{iso}(SO)$ $^{17}O$ shielding constants of trans-[Pt(PMe$_3$)$_2$(OH$_2$)H]$^{1/+}$ ($\sigma^{iso}(SO)$ $^{17}O = 513.8$ ppm) reference compound along with the trans-influence ladder quantified by the $\Delta R$(Pt–OH$_2$) structural parameters referenced to $\Delta R$(Pt–OH$_2$) parameters of [trans-Pt(PMe$_3$)$_2$(OH$_2$)(OOCH)]$^+$ ($\Delta R$(Pt–OH$_2$) = 2100 ppm) reference compound.

**Chart 5** trans-Philicity ladder for the trans-[Pt(PMe$_3$)$_2$(Cl)L]$_{0/+}$ complexes quantified by the $\sigma^{iso}(SO)$ $^{35}$Cl NMR shielding constants referenced to the $\sigma^{iso}(SO)$ $^{35}$Cl shielding constants of trans-[Pt(PMe$_3$)$_2$(Cl)(F)] ($\sigma^{iso}(SO)$ $^{35}$Cl = 1225.2 ppm) reference compound along with the trans-influence ladder quantified by the $\Delta R$(Pt–Cl) structural parameters referenced to $\Delta R$(Pt–Cl) parameters of trans-[Pt(PMe$_3$)$_2$(Cl)(OH)$_2$]$^{1/+}$ ($\Delta R$(Pt–Cl) = 2355 pm) reference compound.

**trans-Philicity ladder constructed by the moderate $\sigma$-donor/weak $\pi$-donor Cl probe**

Chart 5 shows the trans-philicity ladder for the trans-[Pt(PMe$_3$)$_2$(Cl)L]$_{0/+}$ complexes quantified by the $\sigma^{iso}(SO)$ $^{35}$Cl NMR descriptors along with the trans-influence ladder quantified by the $\Delta R$(Pt–Cl) structural descriptors. The calculated $\sigma^{iso}(SO)$ $^{35}$Cl NMR shielding constants are given in the ESI† (Table S8).

The $^{35}$Cl NMR trans-philicity ladder has an analogous structure to the corresponding $^1H$, $^{13}$CO and $^{17}O$ NMR trans-philicity ladders with only minor deviations related with the positions of a few ligands in the rungs of the ladders. Surprisingly the rungs with very strong trans-philicity are occupied by the C-donor (isocyanides and CO) ligands, instead of the strong $\sigma$-donor, phosphane and SH$_2$ ligands. The strong $\sigma$-donor ligands are moved to the regions of strong and moderate trans-philicity. In the regions of strong and moderate trans-philicity are also found the N-donor (nitriles, Py, NH$_3$, NH$_2^-$, N$_3^-$ and NO$_3^-$) along with the SH$^-$, SCN$^-$, CN$^-$, Br$^-$, Cl$^-$ and OH$_2$ ligands, while the O-donor (RCOO$^-$, OX$^-$, OCN$^-$ and OH$^-$) ligands and F$^-$ are correctly placed in the rungs of weak trans-philicity.

In the trans-influence ladder the strong $\sigma$ donor BH$_2^-$, B(OH)$_2^-$, H, SnCl$_3^-$, Me$^-$, $t$-Bu$^-$ and Ph$^-$ anionic ligands along with NH$_3$, OH$^-$, SH$^-$, CN$^-$, Br$^-$, N$_3^-$ and SCN$^-$ ligands are placed in the rungs of very strong and strong trans-influence, in line with the experimentally established trans orienting series. The O-donor (RCOO$^-$, OX$^-$, OCN$^-$) ligands...
along with NO$_3^-$, F$^-$, Cl$^-$ and NCS$^-$ occupy the rungs with strong to moderate trans-influence. The C-donor (isocyanides and CO) along with the N-donor (nitriles, NH$_3$, Py and N$_2$) ligands occupy the rungs of weak trans-influence deviating from the experimentally established trans orienting series.

### Correlations between the isotropic $\sigma_{iso}(SO)$ X NMR shielding constants and the ligand electronic parameter $P_L$

In order to scrutinize the underlying principles and the origin of trans philicity and throw some light on the still intriguing physics of the trans-influence phenomena we investigated relationships between the isotropic $\sigma_{iso}(SO)$ X (X = $^1$H, $^{13}$CH$_3$, $^{13}$CO, $^{15}$N, $^{17}$O and $^{35}$Cl) shielding constants and the well established ligand electronic parameters $P_L$ (a measure of the overall electron attracting or releasing quality of L). Representative linear plots of the $\sigma_{iso}(SO)$ X (X = $^1$H, $^{13}$CO, $^{17}$O) vs. $P_L$ are shown in Fig. 1. Linear plots of the $\sigma_{iso}(SO)$ X (X = $^{13}$CH$_3$, $^{15}$NH$_2$, $^{35}$Cl) vs. $P_L$ correlations are given in the ESI† (Fig. S1).

Inspection of Fig. 1 and Fig. S1 (ESI†) reveals that accurate linear relationships are obtained for similar subsets of ligands L. In the $\sigma_{iso}(SO)$ $^1$H vs. $P_L$, $\sigma_{iso}(SO)$ $^{17}$O vs. $P_L$ (Fig. 1) and $\sigma_{iso}(SO)$ $^{15}$NH$_2$ vs. $P_L$ (Fig. S1, ESI†) the ligands are grouped into four families, in the $\sigma_{iso}(SO)$ $^{13}$CO vs. $P_L$, and $\sigma_{iso}(SO)$ $^{35}$Cl vs. $P_L$ correlations (Fig. S1, ESI†) into two ligand families, while in the $\sigma_{iso}(SO)$ $^{14}$CH$_3$ vs. $P_L$, correlations into three ligand families.

Generally the O-, N-, C- and $\sigma$-donor ligands form their own families and in some cases are mixed with phosphane and S-donor ligands. Notice that the three and two ligand families result from the mixing of O- and N-donor ligands in the same family. Noteworthy in the $\sigma_{iso}(SO)$ $^1$H vs. $P_L$ correlations (Fig. 1) and the $\sigma_{iso}(SO)$ X (X = $^{13}$CH$_3$, $^{15}$NH$_2$ and $^{35}$Cl) vs. $P_L$ correlations (Fig. S1, ESI†) increase of the negative value of $P_L$ constant (increase of the electron releasing capacity of L) increases the downfield shifts of the $\sigma_{iso}(SO)$ X NMR shielding constants. Conversely in the $\sigma_{iso}(SO)$ X (X = $^{13}$CO and $^{17}$O) vs. $P_L$ correlations (Fig. 1) increase of the negative value of $P_L$ constant increases the upfield shifts of the $\sigma_{iso}(SO)$ X NMR shielding constants. It should be noticed that the values of the $P_L$ constants, taken from ref. 14 are presented herein in from of a $P_L$ constants ladder (Chart 6).

The different NMR probe effects on the $\sigma_{iso}(SO)$ X (X = $^{13}$CO and $^{17}$O) and $\sigma_{iso}(SO)$ X (X = $^1$H, $^{13}$CH$_3$, $^{15}$NH$_2$ and $^{35}$Cl) could be explained by the synergism of the $\sigma$- and $\pi$-subspaces that affects the X NMR shielding constants (compare the overall electron attracting or releasing quality of the X NMR probe given in Chart 6). The $^1$H$^-$ and CH$_3^-$ NMR probes are strong $\sigma$-donors ligands. The same holds true for the NH$_2^-$ and Cl$^-$ NMR probes with their $\sigma$-donor capacity enhanced by the weak $\pi$-donor capacity of these probes (these ligands are found at the top of the $P_L$ ladder). On the other hand H$_2$O and CO NMR probes are weak $\sigma$-donors with the $\sigma$-donor capacity of the latter further diminished by its strong $\pi$-acceptor capacity (H$_2$O and CO ligands are found at the low part of the $P_L$ ladder).

### Correlations between the $\sigma_{iso}(SO)$ X NMR descriptors of trans-philicity and the R(Pt-X) descriptors of trans-influence

To demonstrate whether trans-philicity is related with the trans-influence phenomenon we investigated relationships between

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**Fig. 1** Linear plots of the $\sigma_{iso}(SO)$ X (X = $^1$H, $^{13}$CO and $^{17}$O) shielings vs. $P_L$ correlations for square planar trans-[Pt(PMe$_3$)$_2$(X)I]$^+$ (n = 0, 1, 2; X = H, CO, OH$_2$) complexes calculated by the GIAO(SO-ZORA)/PBE0/TZ2P/ COSMO computational protocol in benzene solution.

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**Chart 6** $P_L$ constants ladder (values taken from ref. 14).
the $\sigma_{\text{iso}(SO)}$ vs. $R(\text{Pt}-\text{X})$ correlations show that accurate linear equations can be drawn from distinct ligand families. For the $\sigma_{\text{iso}(SO)}$ vs. WBI(\text{Pt}-\text{X}) (X = H, CO, OH$_2$, CH$_3$) correlations accurate linear equations are obtained for three ligand families, while for the $\sigma_{\text{iso}(SO)}$ vs. WBI(\text{Pt}-\text{X}) (X = NH$_2$, Cl) correlations from four ligand families. These ligand families are given in Fig. 3 and Fig. S3 (ESI†).

It can also be seen that in all linear relationships the increase of WBI(\text{Pt}-\text{X}) (increase of the covalency of the Pt–X bond)
increases the downfield shift of \( \sigma^{iso}(SO) X \) shielding constants. In this context the relation of the trans-philicity and trans-influence with the covalency of Pt–X bond demonstrates clearly the electronic origin of the two phenomena. Scheme 2 shows the 3D plots and composition of the natural bonding orbitals BD (Pt–X) and BD(L–Pt) for selected trans-Pt(PMe3)\( _2 \)(X)L (X = Cl, CO, CH\(_3\)) complexes.

Taking into consideration that the primary determinant of trans-philicity is likely to be covalent contributions to bonding, whether they arise from \( \sigma \) donation or \( \pi \) back-donation, in the formation of the L \( \rightarrow \) Pt dative bond electron density is transferred towards the coordination site trans to L. Interestingly, the \( \sigma^{iso}(SO) X \) X shieldings linearly correlate with the calculated WBI(Pt–X) parameters, a measure of the covalency of Pt–X bond, demonstrating that the covalent bonding contributions to the Pt–X bond and the net charge transfer from the ligand L to Pt metal center are the key factors that manipulate trans-philicity. The bonding \( \sigma \) (Pt–X) NBOs are constructed from the interaction of the sp\(^m\)d\(^n\) hybrid orbitals of the Pt(n) metal center with the s or sp\(^m\) hybrid orbitals of X and are described as \( \sigma \) (Pt–X) = \( c_1 \) (sp\(^m\)d\(^n\))\( _{Pt} \) + \( c_2 \) (sp\(^m\))\( _{X} \). The covalency of the \( \sigma \) (Pt–X) NBOs increases (higher WBI(Pt–X) values) by increasing the overlap of the (sp\(^m\)d\(^n\))\( _{Pt} \) and (sp\(^m\))\( _{X} \) hybrid orbitals. Accordingly increase of the overlap results from the overlap of more diffuse (sp\(^m\)d\(^n\))\( _{Pt} \) hybrid orbitals that exhibit higher d-orbital character illustrating the crucial role of 5d orbitals of Pt(n) in modulating the propagation of spin–orbit effects on the \( \sigma^{iso}(SO) X \) shielding constants.

The trans-philicity descriptors are linearly correlated with the natural atomic charges on the Pt central atom, \( Q_{Pt} \) (Fig. 4 and Fig. S5, ESI\(^\dagger\)). For the \( \sigma^{iso}(SO) X \) vs. \( Q_{Pt} \) correlations accurate linear equations are obtained from two, three or four ligand families, which are given in Fig. 4 and Fig. S4 (ESI\(^\dagger\)). At this point it is important to be noticed that in all correlations studied the grouping of the ligands into families is almost similar. The linear plots of the \( \sigma^{iso}(SO) X \) vs. \( Q_{Pt} \) correlations show that the increase of electron density on the Pt central atom, \( Q_{Pt} \) induces upfield shifts of \( \sigma^{iso}(SO) X \) shielding constants.

**Conclusions**

Quantitative trans-philicity ladders for a broad series of ligands (44 ligands) in square planar trans-[Pt(PMe3)\( _2 \)(X)L]\( n \) (n = 0, 1, 2; X = H, CO, CH\(_3\), NH\(_2\), OH\(_2\), Cl) complexes are built by the isotropic \( \sigma^{iso}(SO) X \) NMR trans-philicity descriptors. We also deployed the ligands under study in trans-influence sequences employing the \( R \) (Pt–X) structural descriptors. Accordingly the relation of trans-philicity with trans-influence validates the trans-philicity concept, as a unified term, avoiding confusion in the ambiguous use of the kinetic trans-effect and the structural trans-influence terms, often encountered in coordination chemistry. The relative trans-philicity strengths are expressed...
by the \( \Delta \sigma^{iso}(SO) \) X NMR trans-

philicity metrics defined as the difference between the calculated \( \sigma^{iso}(SO) \) X NMR shielding constants for the complete set of ligands and the \( \sigma^{iso}(SO) \) X NMR shielding constant of the complex containing the ligand exerting the weakest trans-

philicity phenomenon. Similarly the relative trans-

fluence strengths are expressed by the \( \Delta R(Pt-X) \) structural metrics. Important results are summarized as follows.

The NMR trans-

philicity ladders built for square planar trans-

Pt\((PMe_3)_2(X)L^n\) \((n = 0, 1, 2; X = H, CO, CH_3, NH_2, OH_2, Cl)\) complexes, involving a broad series of ligands (44 ligands) with diverse electronic features go roughly parallel to trans-

fluence ladders built by the \( \Delta R(Pt-X) \) descriptors.

The NMR trans-

philicity descriptors depend on the nature of the NMR probe. The electronic effects of the NMR probes \( (\sigma\)-donor, \( \sigma\)-donor/\( \pi\)-acceptor, \( \sigma\)-donor/\( \pi\)-donor) tune the electron density transfer \( L \rightarrow Pt \rightarrow X \) pathways, thus affecting the \( \sigma^{iso}(SO) \) trans-

philicity descriptors. For the \( \sigma\)-donor NMR probes \((^{1}H, ^{13}CO, ^{17}OH_2)\) the electron density transfer \( L \rightarrow Pt \rightarrow X \) takes place only through the \( \sigma\)-subspace (\( \sigma\)-channel), whereas for the \( \sigma\)-donor/\( \pi\)-acceptor \( ^{1}CO \) and \( \sigma\)-donor/\( \pi\)-donor \( ^{15}NH_2 \) and \( ^{35}Cl \) NMR probes the electron density transfer takes place through both the \( \sigma\)- and \( \pi\)-subspaces (\( \sigma\)- and \( \pi\)-channels). The synergic contribution of the \( \sigma\)- and \( \pi\)-electronic effects of \( L \) and \( X \) to balance the electron density transfer along the \( L \rightarrow Pt \rightarrow X \) framework are the crucial factors that manipulate trans-

philicity. Generally very strong \( \sigma\)-donor ligands and \( \sigma\)-donor/\( \pi\)-acceptor ligands exert strong trans-

philicity, \( \sigma\)-donor/\( \pi\)-donor ligands exert moderate trans-

philicity, while weak \( \sigma\)-donors exert the weakest trans-

philicity.

Excellent linear relationships between the isotropic \( \sigma^{iso}(SO) \) X shielding constants and the well established ligand electronic parameter \( P_L \) and other popular electronic/structural descriptors related with the \( L \rightarrow Pt \rightarrow X \) bonding throw light on the underlying principles and the electronic origin of trans-

philicity.

The trans-

philicity ladders constructed by the six different NMR probes go roughly parallel. Indeed all ladders are almost similar, but some minor deviations related with the position of \( L \) in the rungs of the trans-

philicity ladders are observed.

Linear relationships between the \( \sigma^{iso}(SO) \) X trans-

philicity descriptors and the \( R(Pt-X) \) descriptors of trans-

fluence demonstrate the relation of trans-

philicity with trans-

fluence phenomenon, thus validating its use as a unified concept in the realm of inorganic, organometallic, coordination chemistry and catalysis. According to the linear relationships for the \( \sigma^{iso}(SO) \) \( X = ^{1}H, ^{13}CO, ^{17}OH_2, ^{13}CH_3, NH_2 \) and \( ^{35}Cl \) vs. \( R(Pt-X) \) correlations the increase of the \( R(Pt-X) \) descriptor increases the upfield shifts of the \( \sigma^{iso}(SO) \) X shielding constants.

All linear relationships for the \( \sigma^{iso}(SO) \) \( X = ^{1}H, ^{13}CO, ^{17}OH_2, ^{13}CH_3, NH_2 \) and \( ^{35}Cl \) vs. WBI\((Pt-X) \) correlations showed that the increase of WBI\((Pt-X) \) (increase of the covalency of the Pt-X bond) increases the downfield shift of \( \sigma^{iso}(SO) \) X shielding constants. Furthermore the increase of electron density on the Pt central atom increases the upfield shifts of the \( \sigma^{iso}(SO) \) X \( X = ^{1}H, ^{13}CO, ^{17}OH_2, ^{13}CH_3, NH_2 \) and \( ^{35}Cl \) shielding constants.

Conflicts of interest

There are no conflicts to declare.

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