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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 $\sigma^{\text{iso}}(\text{SO})$ 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 $\sigma^{\text{iso}}(\text{SO})$ X *trans*-philicity descriptors and the *R*(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 $\sigma^{\text{iso}}(\text{SO})$ 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.

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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)₅L]^{−/0/+} complexes employing the calculated $\sigma^{\text{iso}}_{13}\text{C}$ 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 σ - or the σ - and π -subspaces. In this context the strength of *trans*-philicity could be explained in terms of σ -donation and π -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 $P_L = E_{1/2}[\text{Cr}(\text{CO})_6] - E_{1/2}[\text{Cr}(\text{CO})_5\text{L}]$.^{11–13}

In a following paper¹⁴ we applied the *trans*-philicity concept in the realm of square planar Pt(II) 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 -donor, σ -donor/ π -acceptor ligands). The *trans*-philicity and *trans*-influence ladders are built employing the calculated σ^{iso} X NMR shielding constants and the *R*(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: $\sigma^{\text{iso}}(\text{SO})$ 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 $\sigma^{\text{iso}}(\text{SO})$ X NMR shielding constants (X = CH₃, NH₂, Cl) and *P_L*, *R*(Pt–X), WBI(Pt–X) and *Q_{Pt}* (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.¹⁵ The geometries of the complexes were fully optimized, without symmetry constraints, employing the 1999 hybrid functional of Perdew, Burke, and Ernzerhof^{16–19} 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(PMe₃)₂(X)L]ⁿ (*n* = 0, 1, 2; X = H, CO, CH₃, NH₂, OH₂, Cl) complexes was done in solution (benzene solvent) using the all electron SARC_ZORA basis set^{20,21} 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.²² Hereafter the computational protocol used in DFT calculations is abbreviated as PBE0/SARC-ZORA(Pt) ∪ 6-31+G(d)(E)/PCM. All stationary points have been identified as minima (number of imaginary frequencies *N*_{Imag} = 0). Natural Bond Orbital (NBO) population analysis was performed using Weinhold's methodology.^{23,24} Magnetic shielding tensors have been computed with the gauge-including atomic orbitals DFT method,^{25,26} 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,^{27,28} using the ADF2019 code.²⁹ For simplicity we will denote the isotropic shielding constants as $\sigma^{\text{iso}}(\text{SO})$ 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-workers³⁰ to probe the *trans* influence on ¹H NMR hydride shifts in square-planar platinum(II) complexes predicting accurate ¹H NMR hydride shifts matching experimental data available. We also performed calculations of the ¹H NMR hydride shifts for selected complexes employing the GIAO (SO-ZORA)/PBE0/TZ2P-J/COSMO and the results are given in the ESI† (Table S1). It can be seen that both computational protocols provide ¹H NMR hydride shifts comparable to ¹H NMR hydride shifts calculated by Kaupp and co-workers³⁰ and the experiment. The deviations observed are due to the fact that in our calculations the ¹H NMR hydride shifts are calculated for the optimized geometries of the platinum(II) complexes in solution (benzene solvent), while the calculations performed by Kaupp and co-workers³⁰ referred to the gas-phase optimized geometries. Notice that the estimated *R*(Pt–H) bond lengths for the optimized geometries in solution, as it was expected, are longer by 0.053 Å relative to the *R*(Pt–H) bond lengths of the optimized geometries in gas-phase (Table S2, ESI†). Obviously the estimated *R*(Pt–H) bond lengths accounts well for the observed deviations of the ¹H NMR hydride shifts.

Results and discussion

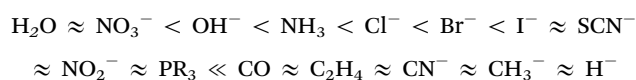
Selection of the NMR probes

trans-Philicity ladders have been built for square planar *trans*-[Pt(PMe₃)₂(X)L]ⁿ (*n* = 0, 1, 2; X = H, CO, CH₃, NH₂, OH₂, Cl) complexes for a broad series of ligands L (44 ligands) employing ¹H, ¹³C, ¹⁵N, ¹⁷O and ³⁵Cl 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 σ^{iso} *trans*-philicity descriptors. The selection of the NMR probes (X) was based on their electronic characteristics, *e.g.* employing the strong σ -donor H[−] and CH₃[−] ligands, the σ -donor/ π -acceptor CO ligand, the σ -donor/ π -donor NH₂[−] and Cl[−] ligands and the weak σ -donor/weak π -donor OH₂ ligand. Moreover the selected probes are ligands of broad relevance across platinum chemistry. The H[−] and CH₃[−] ligands are formed in catalytic processes involving activation and functionalization of C–H bonds or oxidative addition reactions.^{31–34} and dehydrocoupling reactions of compounds with element-hydrogen bonds.³⁵ The Cl[−] ligand is a good leaving group for the anticancer *cis*-Pt(NH₃)₂Cl₂ (*cis*-platin) drug, the OH₂ ligand occurs in the hydrolysis products of *cis*-platin, while the NH₂[−] ligand models the guanine base of DNA which is generally conceived to be a major bio-molecular target of the classic Pt(II) drugs.^{36–38} *trans*-Influence ladders have also been constructed employing the *R*(Pt–X) structural parameters. The relative *trans*-philicity strengths are expressed by the $\Delta\sigma^{\text{iso}}$ X NMR *trans*-philicity metrics defined as the difference between the calculated σ^{iso} X NMR shielding constants for the complete set of ligands and the σ^{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 $\Delta R(\text{Pt–X})$ metrics.

trans-Philicity ladders constructed by the strong σ -donor H[−] and CH₃[−] NMR probes

The *trans*-philicity ladders for the *trans*-Pt(PMe₃)₂(H)L and *trans*-[Pt(PMe₃)₂(CH₃)L]^{0/+} complexes involving the ¹H and ¹³C NMR probes quantified by the $\Delta\sigma^{\text{iso}}(\text{SO})$ ¹H and ¹³C NMR metrics along with the *trans*-influence ladders quantified by the $\Delta R(\text{Pt–H})$ and $\Delta R(\text{Pt–CH}_3)$ metrics are shown in Chart 1. The calculated $\sigma^{\text{iso}}(\text{SO})$ ¹H and ¹³C NMR shielding constants are given in the ESI† (Tables S3 and S4).

Perusal of Chart 1 reveals that the ¹H and ¹³C NMR *trans*-philicity ladders retrieve well the experimentally established *trans* orienting series:³⁹



Chval *et al.*³⁹ thoroughly investigated the mechanism of anation reactions in square planar *trans*-Pt[(NH₃)₂T(H₂O)]^{+/+} complexes (T = H₂O, NH₃, OH[−], F[−], Cl[−], Br[−], H₂S, CH₃S[−], SCN[−], CN[−], PH₃, CO, CH₃[−], H[−], C₂H₄) employing DFT computational methods. The authors showed that for *trans* ligands with a very strong σ -donation (*e.g.* CH₃[−] and H[−]) the substitution



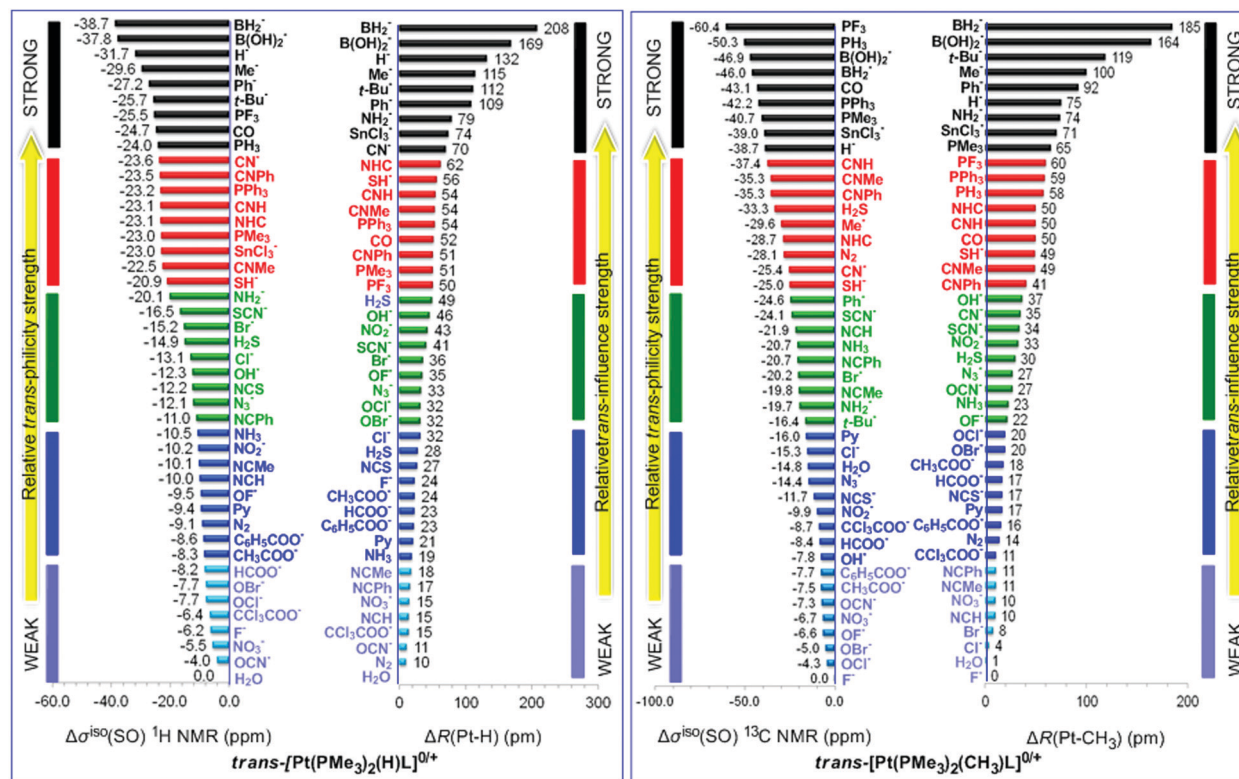
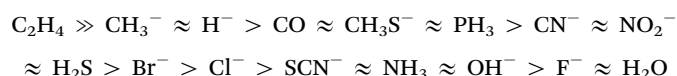


Chart 1 *trans*-Philicity ladders for the *trans*-[Pt(PMe₃)₂(H)L]^{0/+} and *trans*-[Pt(PMe₃)₂(CH₃)L]^{0/+} complexes quantified by the $\sigma^{\text{iso}}(\text{SO})$ ¹H and $\sigma^{\text{iso}}(\text{SO})$ ¹³C NMR shielding constants referenced to the $\sigma^{\text{iso}}(\text{SO})$ ¹H and $\sigma^{\text{iso}}(\text{SO})$ ¹³C shielding constants of *trans*-[Pt(PMe₃)₂(H)(OH₂)]⁺ ($\sigma^{\text{iso}}(\text{SO})$ ¹H = 67.0 ppm) and *trans*-[Pt(PMe₃)₂(CH₃)(F)] ($\sigma^{\text{iso}}(\text{SO})$ ¹³C = 239.8 ppm) reference compounds respectively along with the *trans*-influence ladders quantified by the $\Delta R(\text{Pt}-\text{H})$ and $\Delta R(\text{Pt}-\text{CH}_3)$ structural parameters referenced to $\Delta R(\text{Pt}-\text{H})$ and $\Delta R(\text{Pt}-\text{CH}_3)$ parameters of *trans*-[Pt(PMe₃)₂(H)(OH₂)]⁺ ($R(\text{Pt}-\text{H})$ = 1584 pm) and *trans*-[Pt(PMe₃)₂(CH₃)(F)] ($R(\text{Pt}-\text{CH}_3)$ = 2092 pm) reference compounds respectively.

proceeds by a dissociative interchange (*I_d*) mechanism, for *trans* ligands with strong π -back donation (e.g. C₂H₄) the substitution proceeds by a two step associative mechanism and for *trans* ligands with weak σ -donation and π -back-donation the substitution reactions proceed by an associative interchange (*I_a*) mechanism. According to the computed activation energies the T ligands follow the *trans* effect sequence:



The calculated $\sigma^{\text{iso}}(\text{SO})$ shielding constants for selected *trans*-Pt(PMe₃)₂(H)L for which experimental data are available^{40–44} (cf. Table S1, ESI†) demonstrate that the calculated $\sigma^{\text{iso}}(\text{SO})$ shielding constants are accurate metrics to deploy the ligands L in reliable *trans*-philicity ladders (*trans*-philicity sequences).

Comparison of the ¹H and ¹³C NMR *trans*-philicity ladders reveals that the two ladders are almost identical. In both ladders the strong σ -donors (H[−], Me[−], BH₂[−], B(OH)₂[−] and SnCl₃[−]) occupy the rungs with very strong *trans*-philicity (black rungs), the C-donor ligands the rungs with strong *trans*-philicity (red rungs) while the N- and O-donor ligands occupy the rungs with moderate to weak *trans*-philicity (green and blue rungs). However in many cases the ligands L follow different orders along the *trans*

orienting series. In particular the strong σ -donors *t*-Bu[−] and Ph[−] ligands occupy remarkably different rungs in the ¹H and ¹³C NMR *trans*-philicity ladders. The *t*-Bu[−] and Ph[−] ligands are found in the black rungs of the ¹H NMR *trans*-philicity ladder and the green rungs of the ¹³C NMR *trans*-philicity. However this is not the case in the respective *trans*-influence sequences (ladders). It is important to be noticed that Kaupp and co-workers³⁰ applying quantitative relativistic DFT methodology in a series of square planar Pt(*n*) complexes and exploring correlations between the calculated ¹H shifts and the *trans* ligand influence series established the *trans*-influence sequence: NO₃[−] < ONO[−] < NO₂[−] < Cl[−] < Br[−] < SCN[−] ≈ I[−] < CN[−] < Ph[−] < Me[−] < SiR₃[−] ≈ BR₂[−], which is exactly the same with the *trans*-philicity series shown in the $\sigma^{\text{iso}}(\text{SO})$ ¹H NMR *trans*-philicity ladder (Chart 1). In a following publication Kaupp and co-workers⁴⁵ 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 5d⁸ and 5d¹⁰ electron configurations, with related effects even for 5d⁶ complexes using relativistic quantum-chemical analyses. The authors showed that the *trans* ligand effects on the shieldings are exclusively dominated by two mixed σ/π -type spinors.

Generally with only minor deviations related with the position of a few ligands in the *trans*-influence and ¹H NMR *trans*-philicity ladders the two ladders go parallel to each other.



Phosphanes, nitriles, CO, NO₂[−], OH[−], and N₂ exert strong *trans*-influence ($R(\text{Pt-H}) = 1625\text{--}1638\text{ pm}$), while the O-donor ligands along with halides, isocyanides, SH₂, N₃[−], NCS[−], Py, NH₃, N₂ and OH₂ ligands exert moderate to weak *trans*-influence ($R(\text{Pt-H}) = 1584\text{--}1620\text{ pm}$). Noteworthy in both ¹H and ¹³C NMR *trans*-philicity ladders the *trans*-philicity of phosphane ligands follows the order: PF₃ > PH₃ > PPh₃ > PMe₃. According to the σ-donor/π-acceptor ratio, PF₃, PH₃ and PMe₃ follow the trend⁴⁶ PF₃ < PH₃ < PMe₃, while according to the ν(C≡O) stretching vibrational frequencies for Ni(CO)₃L complexes follow the order⁴⁷ PF₃ > PPh₃ > PMe₃ in line with the *trans*-philicity sequence for the phosphane ligands. Similarly the ¹H and ¹³C NMR *trans*-philicity ladders reproduce the experimentally established *trans*-influence sequences, Br[−] > Cl[−] > F[−] and NH₃ > Py.

In the *trans*-[Pt(PMe₃)₂(CH₃)L]^{0/+} complexes the *trans*-influence ladder match better to the ¹³C NMR *trans*-philicity 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 σ-donor (H[−], Me[−] and *t*-Bu[−], SnCl₃[−]), the C-donor (CO and isocyanides) along with the BH₂[−], B(OH)₂[−] and phosphane ligands occupy the rungs with strong to very strong *trans*-influence and *trans*-philicity. Similarly the N- and O-donor ligands occupy the rungs with moderate to weak *trans*-influence and *trans*-philicity, but in many cases follow different orders along the *trans* orienting series.

trans-Philicity ladder constructed by the σ-donor/π-acceptor CO probe

The *trans*-philicity ladder for the *trans*-[Pt(PMe₃)₂(CO)L]⁺²⁺ complexes quantified by the Δσ^{iso} ¹³C NMR metrics along with the *trans*-influence ladder quantified by the Δ*R*(Pt-CO) structural parameters are shown in Chart 2. The calculated σ^{iso}(SO) ¹³C NMR shielding constants are given in the ESI† (Table S5).

The ¹³CO NMR *trans*-philicity ladder matches better to the ¹H NMR than the ¹³CH₃ NMR ladders (Chart 1). Comparison of the aforementioned *trans*-philicity ladders illustrates clearly that the electronic features of the probes are crucial factors that tune deploy of ligands L in the *trans*-philicity ladders. In particular nitriles NCR (R = H, Me, Ph) occupy the pale blue rungs with weak *trans*-philicity in the ¹³CO NMR *trans*-philicity ladder and the blue rungs with moderate *trans*-philicity in the ¹³CH₃ and ¹H NMR *trans*-philicity ladders. It can also be seen that various classes of ligands in the three ladders follow the trends:

Strong σ-donor ligands:

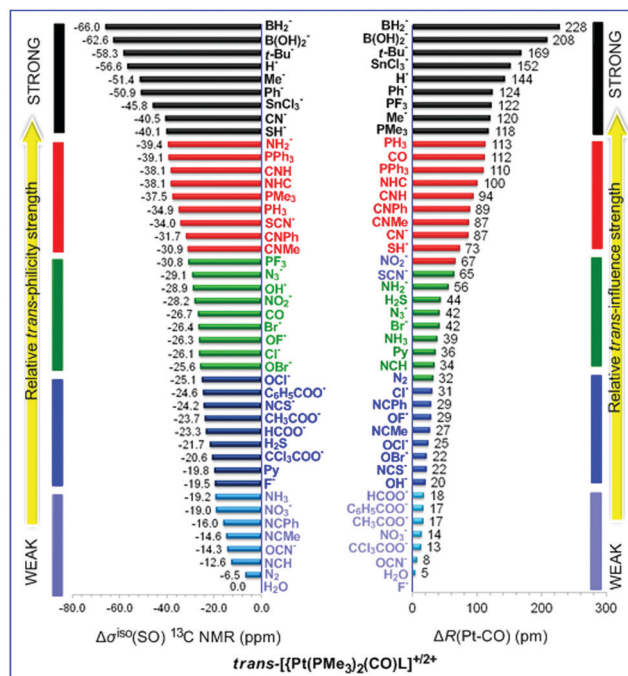
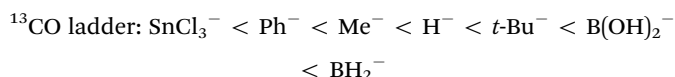
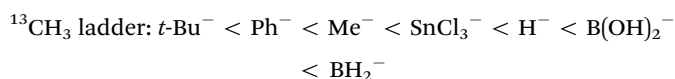
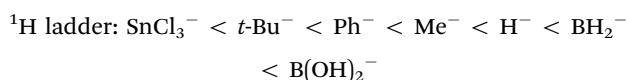
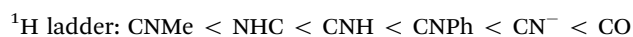
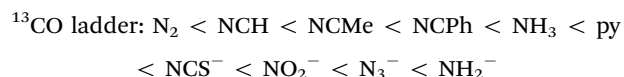
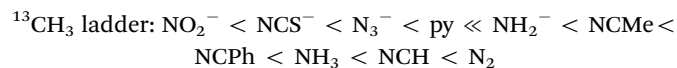
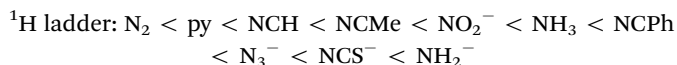


Chart 2 *trans*-Philicity ladder for the *trans*-[Pt(PMe₃)₂(CO)L]⁺²⁺ complexes quantified by the σ^{iso}(SO) ¹³C NMR shielding constants referenced to the σ^{iso}(SO) ¹³C shielding constants of *trans*-[Pt(PMe₃)₂(CO)(OH)₂]⁺²⁺ (σ^{iso}(SO) ¹³C = 48.8 ppm) reference compound along with the *trans*-influence ladder quantified by the Δ*R*(Pt-CO) structural parameters referenced to Δ*R*(Pt-CO) parameters of *trans*-[Pt(PMe₃)₂(CO)(F)]⁺ (*R*(Pt-CO) = 1936 pm) reference compound.

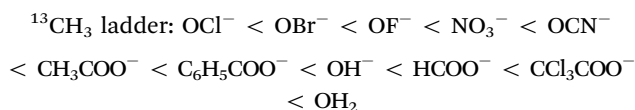
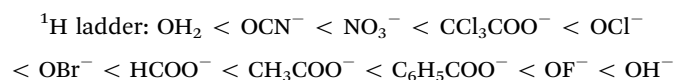
C-Donor ligands:

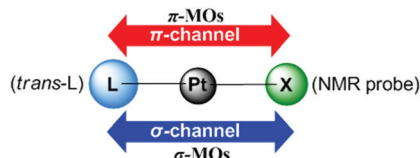


N-Donor ligands:



O-Donor ligands:





Scheme 1 Electron density transfer pathways (σ - and π -channels) between the *trans* L ligands and the X NMR probes supported by σ - and π -MOs.

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

Phosphanes:

^1H ladder: $\text{PMe}_3 < \text{PPh}_3 < \text{PH}_3 < \text{PF}_3$

^{13}CO ladder: $\text{PMe}_3 < \text{PPh}_3 < \text{PH}_3 < \text{PF}_3$

$^{13}\text{CH}_3$ ladder: $\text{PF}_3 < \text{PH}_3 < \text{PMe}_3 < \text{PPh}_3$

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 $\text{L} \rightarrow \text{Pt} \rightarrow \text{CO}$ 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 NH_2^- ligands in rungs of higher *trans*-philicity relative to their positions in the ^1H and $^{13}\text{CH}_3$ NMR ladders. Coordination of the σ -donor/ π -donor ligands to $[\text{Pt}(\text{PMe}_3)_2(\text{CO})]^{2+}$ 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 ^{13}CO 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 phosphanes occupy the rungs of very strong *trans*-influence, the C-donors the rungs of strong *trans*-influence, the N-donors, hypohalites, SH_2 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 NH_2 probe

The *trans*-philicity ladder for the *trans*- $[\text{Pt}(\text{PMe}_3)_2(\text{NH}_2)\text{L}]^{0/+}$ complexes quantified by the $\Delta\sigma^{\text{iso}}(^{15}\text{N})$ NMR metrics along with the *trans*-influence ladder quantified by the $\Delta R(\text{Pt}-\text{NH}_2)$ parameters are shown in Chart 3. The calculated $\sigma^{\text{iso}}(^{15}\text{N})$ NMR shielding constants are given in the ESI† (Table S6).

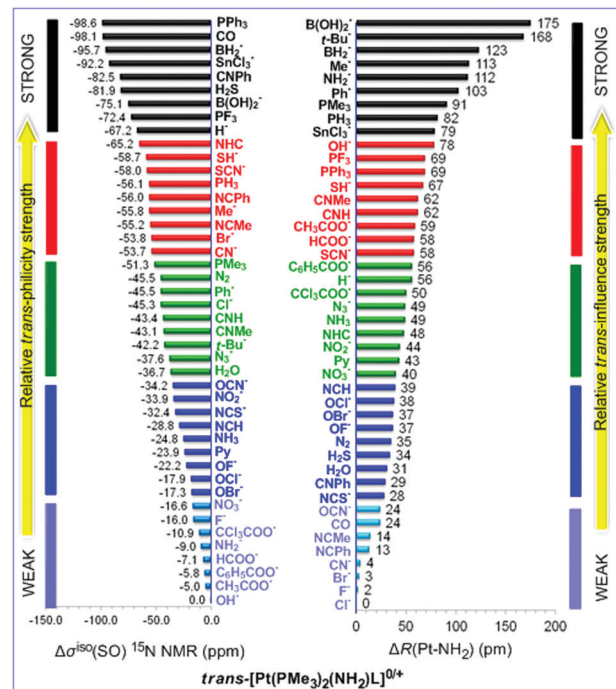


Chart 3 *trans*-Philicity ladder for the *trans*- $[\text{Pt}(\text{PMe}_3)_2(\text{NH}_2)\text{L}]^{0/+}$ complexes quantified by the $\Delta\sigma^{\text{iso}}(^{15}\text{N})$ NMR shielding constants referenced to the $\sigma^{\text{iso}}(^{15}\text{N})$ NMR shielding constants of *trans*- $[\text{Pt}(\text{PMe}_3)_2(\text{NH}_2)(\text{OH})]$ ($\sigma^{\text{iso}}(^{15}\text{N}) = 322.5$ ppm) reference compound along with the *trans*-influence ladder quantified by the $\Delta R(\text{Pt}-\text{NH}_2)$ structural parameters referenced to $\Delta R(\text{Pt}-\text{NH}_2)$ parameters of *trans*- $[\text{Pt}(\text{PMe}_3)_2(\text{NH}_2)(\text{Cl})]$ ($R(\text{Pt}-\text{NH}_2) = 2042$ pm) reference compound.

In the ^{15}N NMR *trans*-philicity ladder the O-donor ligands occupy the rungs with weak *trans*-philicity, the strong σ -donor and phosphane 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 ^{15}N NMR *trans*-philicity ladder matches better to the $^{13}\text{CH}_3$ ladder, with only minor deviations related with the position of L in the rungs of the two ladders, rather than to the ^{13}CO and ^1H NMR *trans*-philicity ladders. However in the *trans*-influence ladder remarkable changes in the *trans*-influence sequences relative to the ^{15}N 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, NH_3 and nitriles) deviating from the experimentally established *trans* orienting series.

trans-Philicity ladder constructed by the weak σ -donor/weak π -donor OH_2 probe

The *trans*-philicity ladder for the *trans*- $[\text{Pt}(\text{PMe}_3)_2(\text{OH}_2)\text{L}]^{+/2+}$ complexes quantified by the $\Delta\sigma^{\text{iso}}(^{17}\text{O})$ NMR descriptors along with the *trans*-influence ladder quantified by the $\Delta R(\text{Pt}-\text{OH}_2)$ structural parameters are shown in Chart 4. The calculated



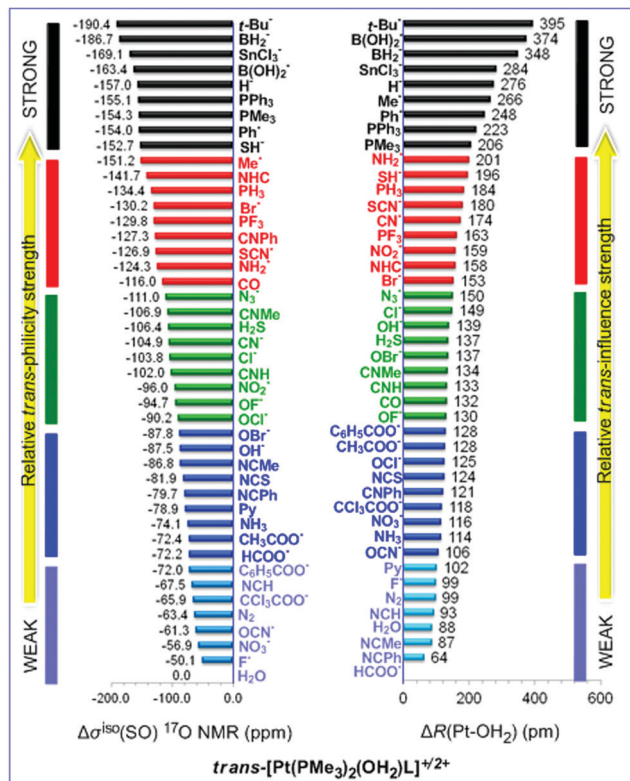


Chart 4 *trans*-Philicity ladder for the *trans*-[Pt(PMe₃)₂(OH₂)L]⁺²⁺ complexes quantified by the $\sigma^{\text{iso}}(\text{SO})$ ¹⁷O NMR shielding constants referenced to the $\sigma^{\text{iso}}(\text{SO})$ ¹⁷O = 513.8 ppm reference compound along with the *trans*-influence ladder quantified by the $\Delta R(\text{Pt}-\text{OH}_2)$ structural parameters referenced to $\Delta R(\text{Pt}-\text{OH}_2)$ parameters of [trans-Pt(PMe₃)₂(OH₂)(OOCH)]⁺ ($R(\text{Pt}-\text{OH}_2)$ = 2100 pm) reference compound.

$\sigma^{\text{iso}}(\text{SO})$ ¹⁷O NMR shielding constants are given in the ESI† (Table S7).

Interestingly the ¹⁷O NMR *trans*-philicity ladder is almost identical with the ¹H NMR (Chart 1) and ¹³CO 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 $R(\text{Pt}-\text{OH}_2)$ parameters deploy *trans*-influence sequences, which do not match the experimentally established *trans* orienting series. In effect the strong σ donor BH₂[−], B(OH)₂[−], H[−], SnCl₃[−], Me[−], *t*-Bu[−] and Ph[−] anionic ligands along with phosphanes, CN[−], NH₂[−], SH[−], SCN[−] and NO₂[−] 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 NHC, N₃[−], Br[−], Cl[−], NCS[−] and PH₃ 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, NH₃, Py and N₂) and PF₃ ligands are placed in the rungs of weak *trans*-influence also deviating from the experimentally established *trans* orienting series.

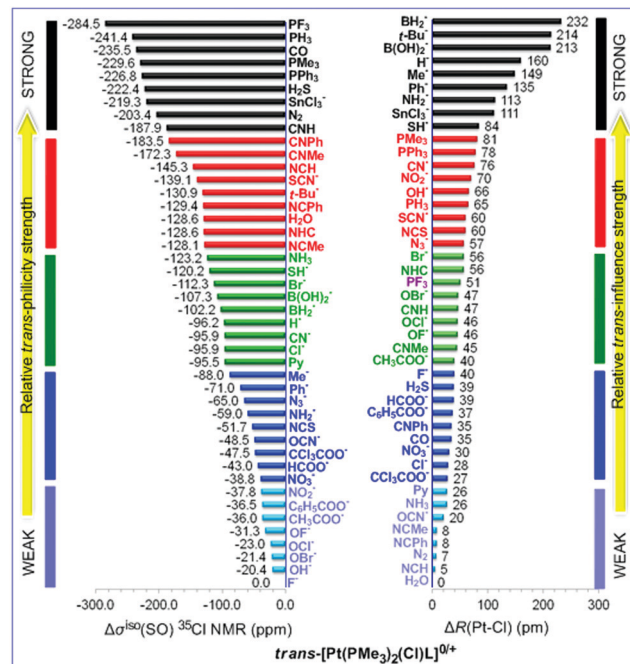


Chart 5 *trans*-Philicity ladder for the *trans*-[Pt(PMe₃)₂(Cl)L]^{0/+} complexes quantified by the $\sigma^{\text{iso}}(\text{SO})$ ³⁵Cl NMR shielding constants referenced to the $\sigma^{\text{iso}}(\text{SO})$ ³⁵Cl shielding constants of *trans*-[Pt(PMe₃)₂(Cl)(F)] ($\sigma^{\text{iso}}(\text{SO})$ ³⁵Cl = 1225.2 ppm) reference compound along with the *trans*-influence ladder quantified by the $\Delta R(\text{Pt}-\text{Cl})$ structural parameters referenced to $\Delta R(\text{Pt}-\text{Cl})$ parameters of *trans*-[Pt(PMe₃)₂(Cl)(OH₂)]⁺ ($R(\text{Pt}-\text{Cl})$ = 2355 pm) reference compound.

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

Chart 5 shows the *trans*-philicity ladder for the *trans*-[Pt(PMe₃)₂(Cl)L]^{0/+} complexes quantified by the $\Delta\sigma^{\text{iso}}(\text{SO})$ ³⁵Cl NMR descriptors along with the *trans*-influence ladder quantified by the $\Delta R(\text{Pt}-\text{Cl})$ structural descriptors. The calculated $\sigma^{\text{iso}}(\text{SO})$ ³⁵Cl NMR shielding constants are given in the ESI† (Table S8).

The ³⁵Cl NMR *trans*-philicity ladder has an analogous structure to the corresponding ¹H, ¹³CO and ¹⁷O 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 σ -donor, phosphane and SH₂ ligands. The strong σ -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, NH₃, NH₂[−], N₃[−] and NO₂[−]) along with the SH[−], SCN[−], CN[−], Br[−], Cl[−] and OH₂ 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 σ donor BH₂[−], B(OH)₂[−], H[−], SnCl₃[−], Me[−], *t*-Bu[−] and Ph[−] anionic ligands along with NH₂[−], OH[−], SH[−], CN[−], Br[−], N₃[−] 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_2^- , 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 $\sigma^{\text{iso}}(\text{SO})$ 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 threw some light on the still intriguing physics of the *trans*-influence phenomena we investigated relationships between the isotropic $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CH}_3$, ${}^{13}\text{CO}$, ${}^{15}\text{N}$, ${}^{17}\text{O}$ and ${}^{35}\text{Cl}$) shielding constants and the well established ligand electronic parameters P_L (a measure of the overall electron attracting or releasing quality of L).¹⁴ Representative linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$, ${}^{17}\text{OH}_2$) vs. P_L are shown in Fig. 1. Linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^{13}\text{CH}_3$, ${}^{15}\text{NH}_2$, ${}^{35}\text{Cl}$) 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 $\sigma^{\text{iso}}(\text{SO})$ ${}^1\text{H}$ vs. P_L , $\sigma^{\text{iso}}(\text{SO})$ ${}^{17}\text{O}$ vs. P_L (Fig. 1) and $\sigma^{\text{iso}}(\text{SO})$ ${}^{15}\text{NH}_2$ vs. P_L (Fig. S1, ESI†) the ligands are grouped into four families, in the $\sigma^{\text{iso}}(\text{SO})$ ${}^{13}\text{CO}$ vs. P_L , and $\sigma^{\text{iso}}(\text{SO})$ ${}^{35}\text{Cl}$ vs. P_L

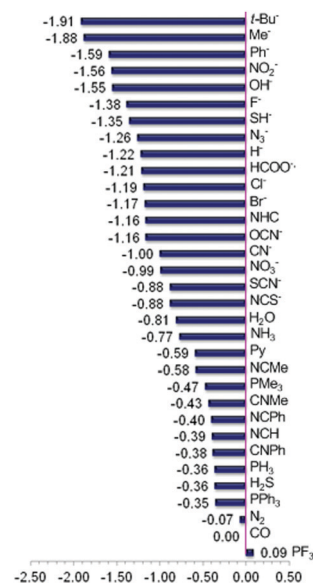


Chart 6 P_L constants ladder (values taken from ref. 14).

correlations (Fig. S1, ESI†) into two ligand families, while in the $\sigma^{\text{iso}}(\text{SO})$ ${}^{13}\text{CH}_3$ vs. P_L , correlations into three ligand families.

Generally the O-, N-, C- and σ -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 $\sigma^{\text{iso}}(\text{SO})$ ${}^1\text{H}$ vs. P_L correlations (Fig. 1) and the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^{13}\text{CH}_3$, ${}^{15}\text{NH}_2$ and ${}^{35}\text{Cl}$) 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 $\sigma^{\text{iso}}(\text{SO})$ X NMR shielding constants. Conversely in the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^{13}\text{CO}$ and ${}^{17}\text{OH}_2$) vs. P_L correlations (Fig. 1) increase of the negative value of P_L constant increases the upfield shifts of the $\sigma^{\text{iso}}(\text{SO})$ 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 $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^{13}\text{CO}$ and ${}^{17}\text{OH}_2$) and $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CH}_3$, ${}^{15}\text{NH}_2$ and ${}^{35}\text{Cl}$) could be explained by the synergism of the *trans* L and X ligands to balance the electron density transfer along the L–Pt–X framework through the σ - and π -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 H^- and CH_3^- NMR probes are strong σ -donors ligands. The same holds true for the NH_2^- and Cl^- NMR probes with their σ -donor capacity enhanced by the weak π -donor capacity of these probes (these ligands are found at the top of the P_L ladder). On the other hand H_2O and CO NMR probes are weak σ -donors with the σ -donor capacity of the latter further diminished by its strong π -acceptor capacity (H_2O and CO ligands are found at the low part of the P_L ladder).

Correlations between the $\sigma^{\text{iso}}(\text{SO})$ X NMR descriptors of *trans*-philicity and the $R(\text{Pt-X})$ descriptors of *trans*-influence

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

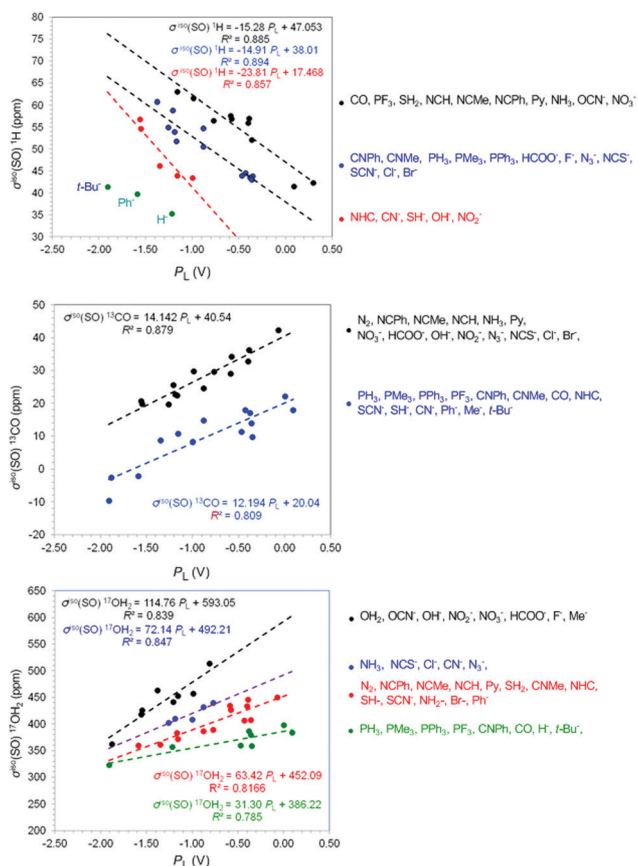


Fig. 1 Linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$ and ${}^{17}\text{OH}_2$) shieldings vs. P_L correlations for square planar *trans*-[Pt(PMe₃)₂(X)L]ⁿ ($n = 0, 1, 2$; $X = \text{H}$, CO , OH_2) complexes calculated by the GIAO(SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.



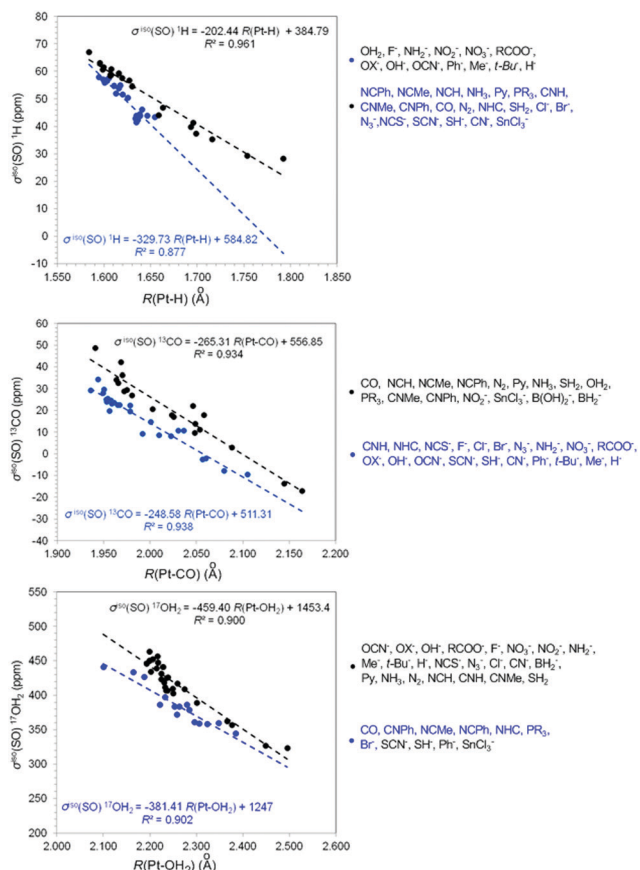


Fig. 2 Linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$ and ${}^{17}\text{OH}_2$) shieldings vs. $R(\text{Pt}-X)$ correlations for square planar $\text{trans}-[\text{Pt}(\text{PMe}_3)_2(\text{X})\text{L}]^n$ ($n = 0, 1, 2$; $X = \text{H}, \text{CO}, \text{OH}_2$)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

the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CH}_3$, ${}^{13}\text{CO}$, ${}^{15}\text{N}$, ${}^{17}\text{O}$ and ${}^{35}\text{Cl}$) *trans*-philicity descriptors and the $R(\text{Pt}-X)$ descriptors of *trans*-influence. The linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$, ${}^{17}\text{OH}_2$, ${}^{13}\text{CH}_3$, NH_2 and ${}^{35}\text{Cl}$) vs. $R(\text{Pt}-X)$. Correlations are shown in Fig. 2 and Fig. S2 (ESI†).

Accurate correlation equations can be drawn from two ligand families for the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$, ${}^{17}\text{OH}_2$) vs. $R(\text{Pt}-X)$ correlation, three ligand families for the $\sigma^{\text{iso}}(\text{SO})$ X vs. $R(\text{Pt}-X)$ $X = \text{CH}_3$ and NH_2 correlation and four ligand families for the $\sigma^{\text{iso}}(\text{SO})$ ${}^{35}\text{Cl}$ vs. $R(\text{Pt}-\text{Cl})$ correlations. The first family in the $\sigma^{\text{iso}}(\text{SO})$ X vs. $R(\text{Pt}-X)$ $X = \text{H}, \text{CO}, \text{OH}_2$ correlations involves most of the O-donor ligands mixed with some of the strong σ -donor and N-donor ligands, while the second ligand family involves all the remaining ligands.

In the $\sigma^{\text{iso}}(\text{SO})$ ${}^{13}\text{CH}_3$ vs. $R(\text{Pt}-\text{CH}_3)$ and $\sigma^{\text{iso}}(\text{SO})$ ${}^{15}\text{NH}_2$ vs. $R(\text{Pt}-\text{NH}_2)$ correlations the first family involves strong σ -donor BH_2^- , $\text{B}(\text{OH})_2^-$ and Ph^- ligands mixed with OH^- , OX^- , OCN^- , NO_2^- , NH_2^- and F^- ligands. In the second family one finds N-donor ligands along with CN^- , SCN^- , SH^- and SnCl_3^- ligands, while the third family involves the C-donor, nitriles, phosphanes, halides, H_2S and H_2O ligands.

The linear relationships for the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$, ${}^{17}\text{OH}_2$, ${}^{13}\text{CH}_3$, NH_2 and ${}^{35}\text{Cl}$) vs. $R(\text{Pt}-X)$ correlations show that

the increase of the $R(\text{Pt}-X)$ descriptor of *trans*-influence increases the upfield shifts of the $\sigma^{\text{iso}}(\text{SO})$ X descriptors of *trans*-philicity.

Correlations between the $\sigma^{\text{iso}}(\text{SO})$ X NMR shielding constants and the $\text{WBI}(\text{Pt}-X)$ and Q_{Pt} electronic parameters

To probe further the electronic nature of *trans* philicity we investigated possible relationships of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CH}_3$, ${}^{13}\text{CO}$, ${}^{15}\text{NH}_2$, ${}^{17}\text{OH}_2$ and ${}^{35}\text{Cl}$) shielding constants and natural bond orbital (NBO) parameters, namely the Wiberg Bond Index of the Pt-X bond, $\text{WBI}(\text{Pt}-X)$ and the natural atomic charge on Pt metal center Q_{Pt} . Representative linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X vs. $\text{WBI}(\text{Pt}-X)$ and $\sigma^{\text{iso}}(\text{SO})$ X vs. Q_{Pt} ($X = \text{H}, \text{CO}, \text{OH}_2$) correlations are shown in Fig. 3 and 4 respectively. The linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X vs. $\text{WBI}(\text{Pt}-X)$ and $\sigma^{\text{iso}}(\text{SO})$ X vs. Q_{Pt} ($X = \text{CH}_3, \text{NH}_2, \text{Cl}$) correlations are given in the ESI† (Fig. S3 and S4).

Inspection of the linear plots given in Fig. 3 and Fig. S3 (ESI†) reveals that accurate linear equations can be drawn from distinct ligand families. For the $\sigma^{\text{iso}}(\text{SO})$ X vs. $\text{WBI}(\text{Pt}-X)$ ($X = \text{H}, \text{CO}, \text{OH}_2, \text{CH}_3$) correlations accurate linear equations are obtained for three ligand families, while for the $\sigma^{\text{iso}}(\text{SO})$ X vs. $\text{WBI}(\text{Pt}-X)$ ($X = \text{NH}_2, \text{Cl}$) correlations from four ligand families. It can also be seen that in all linear relationships the increase of $\text{WBI}(\text{Pt}-X)$ (increase of the covalency of the Pt-X bond)

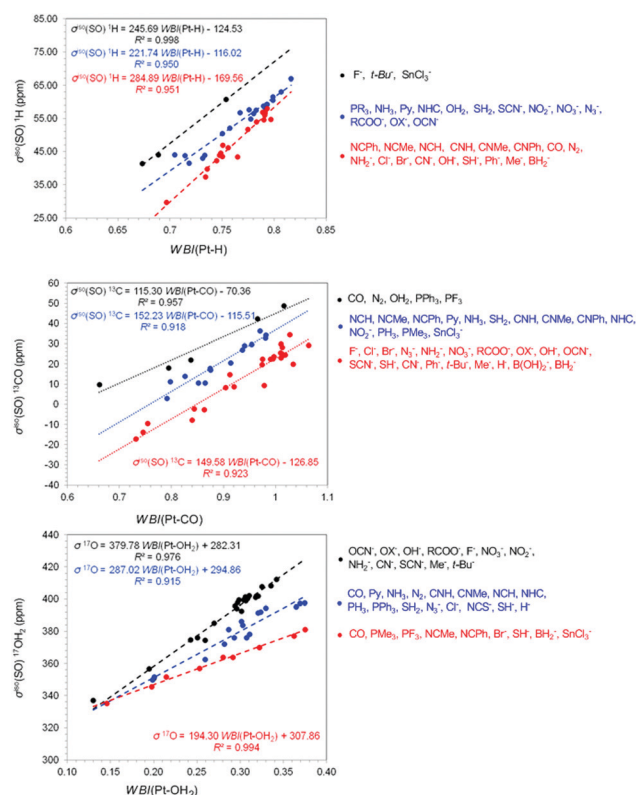


Fig. 3 Linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$ and ${}^{17}\text{OH}_2$) shieldings vs. $\text{WBI}(\text{Pt}-X)$ correlations for square planar $\text{trans}-[\text{Pt}(\text{PMe}_3)_2(\text{X})\text{L}]^n$ ($n = 0, 1, 2$; $X = \text{H}, \text{CO}, \text{OH}_2$) complexes calculated by the GIAO(SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

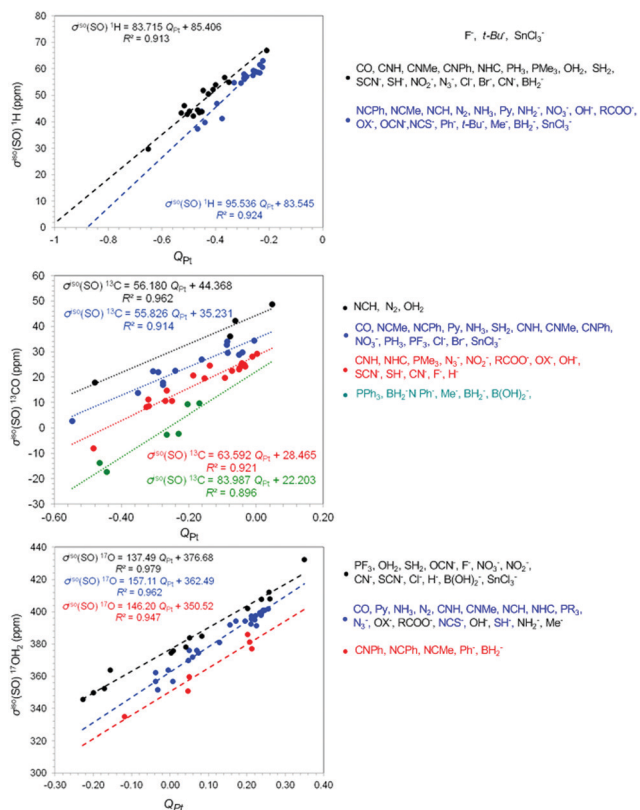
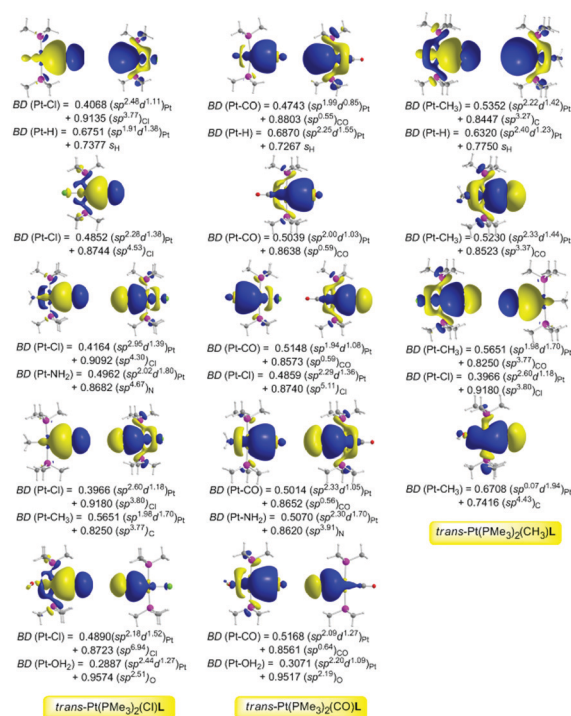


Fig. 4 Linear plots of the $\sigma^{\text{iso}}(\text{SO})$ X ($X = {}^1\text{H}$, ${}^{13}\text{CO}$ and ${}^{17}\text{OH}_2$) shieldings vs. Q_{Pt} correlations for square planar $\text{trans}[\text{Pt}(\text{PMe}_3)_2(\text{X})\text{L}]^n$ ($n = 0, 1, 2$; $X = \text{H}$, CO , OH_2) complexes calculated by the GIAO(SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

increases the downfield shift of $\sigma^{\text{iso}}(\text{SO})$ 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 ($X = \text{Cl}$, 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 σ donation or π back-donation, in the formation of the $\text{L} \rightarrow \text{Pt}$ dative bond electron density is transferred towards the coordination site *trans* to L. Interestingly, the $\sigma^{\text{iso}}(\text{SO})$ X shieldings linearly correlate with the calculated $\text{WBI}(\text{Pt}–\text{X})$ 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 $\sigma(\text{Pt}–\text{X})$ NBOs are constructed from the interaction of the $\text{sp}^m d^n$ hybrid orbitals of the Pt(II) metal center with the s or sp^k hybrid orbitals of X and are described as $\sigma(\text{Pt}–\text{X}) = c_1(\text{sp}^m d^n)_{\text{Pt}} + c_2(\text{sp}^k)_{\text{X}}$. The covalency of the $\sigma(\text{Pt}–\text{X})$ NBOs increases (higher $\text{WBI}(\text{Pt}–\text{X})$ values) by increasing the overlap of the $(\text{sp}^m d^n)_{\text{Pt}}$ and $(\text{sp}^k)_{\text{X}}$ hybrid orbitals. Accordingly increase of the overlap results from the overlap of more diffuse $(\text{sp}^m d^n)_{\text{Pt}}$ hybrid orbitals that exhibit



Scheme 2 3D plots and composition of the bonding natural orbitals localized on the Pt–X and L–Pt bonds for selected *trans*-[Pt(PMe₃)₂(X)L]ⁿ ($n = 0, 1, 2$; $X = \text{H}$, CO , OH_2) complexes. The X and L ligands are selected on the basis of their electronic characteristics (σ -donor, σ -donor/ π -acceptor, σ -donor/ π -donor).

higher d-orbital character illustrating the crucial role of 5d orbitals of Pt(II) in modulating the propagation of spin-orbit effects on the $\sigma^{\text{iso}}(\text{SO})$ 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[†]). For the $\sigma^{\text{iso}}(\text{SO})$ 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[†]). 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 $\sigma^{\text{iso}}(\text{SO})$ X vs. Q_{Pt} correlations show that the increase of electron density on the Pt central atom, Q_{Pt} induces upfield shifts of $\sigma^{\text{iso}}(\text{SO})$ 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 ($n = 0, 1, 2$; $X = \text{H}$, CO , CH_3 , NH_2 , OH_2 , Cl) complexes are built by the isotropic $\sigma^{\text{iso}}(\text{SO})$ X NMR *trans*-philicity descriptors. We also deployed the ligands under study in *trans*-influence sequences employing the $R(\text{Pt}–\text{X})$ 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 $\Delta\sigma^{\text{iso}}(\text{SO})$ X NMR *trans*-philicity metrics defined as the difference between the calculated $\sigma^{\text{iso}}(\text{SO})$ X NMR shielding constants for the complete set of ligands and the $\sigma^{\text{iso}}(\text{SO})$ X NMR shielding constant of the complex containing the ligand exerting the weakest *trans*-philicity phenomenon. Similarly the relative *trans*-influence strengths are expressed by the $\Delta R(\text{Pt-X})$ structural metrics. Important results are summarized as follows.

The NMR *trans*-philicity ladders built for square planar $\text{trans}[\text{Pt}(\text{PMe}_3)_2(\text{X})\text{L}]^n$ ($n = 0, 1, 2$; $\text{X} = \text{H}, \text{CO}, \text{CH}_3, \text{NH}_2, \text{OH}_2, \text{Cl}$) complexes, involving a broad series of ligands (44 ligands) with diverse electronic features go roughly parallel to *trans*-influence ladders built by the $\Delta R(\text{Pt-X})$ descriptors.

The NMR *trans* philicity descriptors depend on the nature of the NMR probe. The electronic effects of the NMR probes (σ -donor, σ -donor/ π -acceptor, σ -donor/ π -donor) tune the electron density transfer $\text{L} \rightarrow \text{Pt} \rightarrow \text{X}$ pathways, thus affecting the σ^{iso} X *trans*-philicity descriptors. For the σ -donor NMR probes (^1H , $^{13}\text{CH}_3$ and $^{17}\text{OH}_2$) the electron density transfer $\text{L} \rightarrow \text{Pt} \rightarrow \text{X}$ takes place only through the σ -subspace (σ -channel), whereas for the σ -donor/ π -acceptor ^{13}CO and σ -donor/ π -donor $^{15}\text{NH}_2$ and ^{35}Cl NMR probes the electron density transfer takes place through both the σ - and π -subspaces (σ - and π -channels). The synergic contribution of the σ - and π -electronic effects of L and X to balance the electron density transfer along the $\text{L} \rightarrow \text{Pt} \rightarrow \text{X}$ framework are the crucial factors that manipulate *trans*-philicity. Generally very strong σ -donor ligands and σ -donor/ π -acceptor ligands exert strong *trans*-philicity, σ -donor/ π -donor ligands exert moderate *trans*-philicity, while weak σ -donors exert the weakest *trans*-philicity.

Excellent linear relationships between the isotropic $\sigma^{\text{iso}}(\text{SO})$ X shielding constants 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 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 $\sigma^{\text{iso}}(\text{SO})$ X *trans*-philicity descriptors and the $R(\text{Pt-X})$ descriptors of *trans*-influence demonstrate the relation of *trans*-philicity with *trans*-influence 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 $\sigma^{\text{iso}}(\text{SO})$ X ($\text{X} = ^1\text{H}, ^{13}\text{CO}, ^{17}\text{OH}_2, ^{13}\text{CH}_3, \text{NH}_2$ and ^{35}Cl) vs. $R(\text{Pt-X})$ correlations the increase of the $R(\text{Pt-X})$ descriptor increases the upfield shifts of the $\sigma^{\text{iso}}(\text{SO})$ X shielding constants.

All linear relationships for the $\sigma^{\text{iso}}(\text{SO})$ X ($\text{X} = ^1\text{H}, ^{13}\text{CO}, ^{17}\text{OH}_2, ^{13}\text{CH}_3, \text{NH}_2$ and ^{35}Cl) vs. $\text{WBI}(\text{Pt-X})$ correlations showed that the increase of $\text{WBI}(\text{Pt-X})$ (increase of the covalency of the Pt-X bond) increases the downfield shift of $\sigma^{\text{iso}}(\text{SO})$ X shielding constants. Furthermore the increase of electron density on the Pt central atom increases the upfield shifts of the $\sigma^{\text{iso}}(\text{SO})$ X ($\text{X} = ^1\text{H}, ^{13}\text{CO}, ^{17}\text{OH}_2, ^{13}\text{CH}_3, \text{NH}_2$ and ^{35}Cl) shielding constants.

Conflicts of interest

There are no conflicts to declare.

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