Linking the Character of the Metal–Ligand Bond to the Ligand NMR Shielding in Transition-Metal Complexes: NMR Contributions from Spin–Orbit Coupling

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Supporting Information

ABSTRACT: Relativistic effects significantly affect various spectroscopic properties of compounds containing heavy elements. Particularly in Nuclear Magnetic Resonance (NMR) spectroscopy, the heavy atoms strongly influence the NMR shielding constants of neighboring light atoms. In this account we analyze paramagnetic contributions to NMR shielding constants and their modulation by relativistic spin–orbit effects in a series of transition-metal complexes of Pt(II), Au(I), Au(III), and Hg(II). We show how the paramagnetic NMR shielding and spin–orbit effects relate to the character of the metal–ligand (M–L) bond. A correlation between the (back)-donation character of the M–L bond in d10 Au(I) complexes and the propagation of the spin–orbit (SO) effects from M to L through the M–L bond influencing the ligand NMR shielding via the Fermi-contact mechanism is found and rationalized by using third-order perturbation theory. The SO effects on the ligand NMR shielding are demonstrated to be driven by both the electronic structure of M and the nature of the trans ligand, sharing the σ-bonding metal orbital with the NMR spectator atom L. The deshielding paramagnetic contribution is linked to the σ-type M–L bonding orbitals, which are notably affected by the trans ligand. The SO deshielding role of σ-type orbitals is enhanced in d10 Hg(II) complexes with the Hg 6p atomic orbital involved in the M–L bonding. In contrast, in d4 Pt(II) complexes, occupied π-type orbitals play a dominant role in the SO-altered magnetic couplings due to the accessibility of vacant antibonding σ-type MOs in formally open 5d-shell (d⁵). This results in a significant SO shielding at the light atom. The energy- and composition-modulation of σ- vs π-type orbitals by spin–orbit coupling is rationalized and supported by visualizing the SO-induced changes in the electron density around the metal and light atoms (spin–orbit electron deformation density, SO-EDD).

1. INTRODUCTION

Nuclear Magnetic Resonance (NMR) spectroscopy is an indispensable structural tool in the modern analytical arsenal of chemists and structural biologists. This spectroscopic method matured at the end of the 20th century by an expansion of multidimensional chemical-shift correlation techniques¹ and a sophisticated mapping of nuclear-spin relaxation processes.¹,² Despite very early discoveries of immense importance of nuclear magnetic shielding as a probe to internal structure of matter, its link to the chemical bond concepts is not always well established and understood. This applies particularly to the molecules of open-shell nature or systems containing heavy element(s).

The NMR shielding constant (σ) for any atom can be formally split into the diamagnetic (σd) and paramagnetic (σp) contributions. This partitioning is not unique but provides an intuitive picture of the shielding mechanism. The diamagnetic contribution reflects the total ground-state electron density around the NMR spectator atom and is relatively invariant to the change in its chemical environment. In contrast, the

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In this contribution, we provide a chemical link between the structurally altered paramagnetic contributions to the light atom NMR shielding constants and the energy characteristics of M–L bonding in a series of transition-metal complexes of Pt(II), Au(I), Au(III), and Hg(II), Figure 1. Both the relativistic spin–orbit effects on the NMR chemical shifts have been recognized and related to the mechanism of the indirect nuclear spin–spin coupling as early as in the late 1970s.19–21 During the recent three decades, several factors have been described to influence the SO effects of Heavy Atom on the Light Atom (HALA).6 s-character of the light atom in the HA–LA bond,11 energy gap involved between occupied and vacant molecular orbitals,22,23 orbital character of the heavy atom in the HA–LA bond,24 formal oxidation state of the heavy atom,23 and covalence/ionicity of the HA–LA bond.8,23,26 All these factors are related to the character of the HA–LA bond.

In the field of transition-metal (M) complexes, the spin–orbit contribution to the NMR shielding constant of the ligand spectator atom L, \( \sigma^{SO}(L) \), has recently been shown to correlate quantitatively with the \( \sigma^{SO}(L) \) whereas the symbol for MO symmetry is specified by the bond of \( \sigma^{SO}(L) \) tensors are rationalized.

2. THEORETICAL BACKGROUND

In the following text, the symbol \( \sigma \) refers to the NMR shielding constant but denotes also the symmetry of the M–L bonding MOs. The symbol for NMR shielding constant typically contains a superscript representing contribution term (e.g., \( \sigma^{SO}(L) \)), whereas the symbol for MO symmetry is specified by the bond of \( \sigma^{SO}(L) \) tensors are rationalized.

In the absence of SO coupling (nonrelativistic theory), paramagnetic contribution to the NMR shielding constant of a ligand atom L \( \sigma(L) \) is theoretically formulated by the Ramsey-type coupling formula (neglecting contribution from kernels, see the Supporting Information).4

\[ \sigma = \sigma^{d} + \sigma^{p} + \sigma^{SO} \] (1)

The \( \sigma^{SO} \) can be obtained as a perturbation to nonrelativistic or scalar-relativistic one-component (1c) calculations.16–18 Traditionally, these 1c approaches are used in chemistry to establish a link between the electronic molecular structure and the shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms. In calculations of NMR shielding constant using variational treatment of shielding mechanism for individual atoms.
PARAMAGNETIC (local) a) MO—MO*  

\[ \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \]

\[ | \psi_i \rangle \sim | \psi_i \rangle \]

\[ \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \]

SPIN-ORBIT (nonlocal) b) MO—MO—MO* (SO/FC)  

\[ \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \]

\[ | \psi_i \rangle \sim | \psi_i \rangle \]

\[ \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \]

c) MO—MO—MO* (SO/FC)  

\[ \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \]

\[ | \psi_i \rangle \sim | \psi_i \rangle \]

\[ \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \]

\[ \Delta \sigma^p(L) \approx \frac{\sum_{\text{occ}} \sum_{\text{vac}} \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle \sum_{\text{occ}} \sum_{\text{vac}} \langle \psi_i | \sum_j \epsilon_{ij} \gamma_j \psi_i \rangle | \psi_i \rangle}{e_i - e_j} \]  

(4)

Here \( \psi_i \) (\( \psi_v \)) stands for occupied (vacant) one-electron energy, and \( \mathbf{r}_i \) is the position vector relative to the coordinates of the ligand spectator atom L. The Ramsey formula describes magnetic coupling between individual occupied-vacant MO-pairs through the angular momentum operator, \( \hat{L}_M \), and the paramagnetic nuclear-spin–electron-orbit (PSO) operator (\( \hat{l}_M \)). Since PSO is of highly local nature (electron orbital motion coupled with nuclear magnetic moment of the spectator atom L) the trend-determining contributions to \( \sigma^p(L) \) arise from the magnetically coupled MO++MO* pairs that have both: a significant admixture of AOs centered on L and a small energy gap \( e_i - e_j \). In compounds 1–4, the paramagnetic shielding constant of the aromatic nitrogen/carbon is dominated by the Ramsey-type couplings between the occupied \( \sigma_{M-L} \) (\( 2p_z \) character of L) or \( \sigma_{L-C} \) (\( 2p_y \) character of L) and vacant \( \pi^* \)-type (\( 2p_z \) character of L) MOs.  

Figure 2a)

Note that both operators in eq 4 are referenced relative to a different coordinate center (so-called gauge origin), which is either the ligand atom L or the metal center M, as indicated by the superscript. Although the exact physical theory allows an arbitrary change of the gauge origin in the angular momentum operator responsible for the interaction with external magnetic field (e.g., \( \hat{F}_M \rightarrow \hat{F}_L \)), this requires an infinite number of vacant orbitals available. In practice, however, simple and generalizing chemical concepts are useful only when a reasonably small number of the orbital excitations play a role and determine overall NMR trends. Note that the gauge origin variation will not significantly alter results of the Ramsey-type coupling for systems containing only light atoms (pyridine or benzene in compounds 1–4). Therefore, for the sake of simplicity the gauge origin is usually placed on the spectator atom L. In contrast, for systems containing a heavy atom M, the gauge origin must be placed on M, otherwise the basis-set requirements and number of significant orbital excitations will increase enormously, prohibiting to establish a simple chemical link between NMR shielding and MO bonding theory.  

In the relativistic picture, the spin–orbit (SO) coupling contribution to the paramagnetic NMR shielding of light atoms originates in our systems from the metal center M. The metal \( p \)- and \( d \)-type AOs, which contribute to the NMR-active MOs, are split by the SO coupling, and this effect can be thought of as being propagated from the central atom M to the ligand atom L via the \( M-L \) bond. There are two mechanisms — Fermi-Contact (FC) and Spin-Dipolar (SD), eq 5.  

\[ \sigma^{\text{PSO}}(L) = \sigma^{\text{SO/FC}}(L) + \sigma^{\text{SO/SD}}(L) \]  

(5)

Note that both SO/FC and SO/SD terms are represented by highly local operators related to the spectator atom L. The SO/FC term arises from the contact interaction between the nuclear and electron spins, and therefore \( \pi \) orbitals of the spectator atom L play a significant role in this mechanism.
because only those orbitals have nonvanishing density at light atoms nuclei. In contrast, the SO/SD term arises from the interaction between the nuclear and electron spin dipoles and has its origin in anisotropy of the electron spin density. For compounds investigated in this work, the SO/SD contribution to $\sigma_{SO}(L)$ comes from the 2p orbitals of the spectator atom ($^{113}\text{C}$ or $^{15}\text{N}$). It is important to emphasize that the isotropic part of $\sigma_{SO}(L)$ is typically dominated by the SO/FC mechanism (see Table S1),$^{10,17,37}$ which could be formulated in the third-order perturbation theory (PT3) formalism as (for full expressions, see the Supporting Information)

$$\sigma_{SO/FC}^{\Delta}(L) \approx -\frac{1}{c} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{s=1}^{n} \frac{(\langle \hat{\rho}_5 | \hat{\rho}_4 | \hat{M}_s \rangle ) (\langle \hat{\rho}_4 | \hat{\rho}_3 | \hat{M}_s \rangle ) (\langle \hat{\rho}_3 | \hat{\rho}_2 | \hat{M}_s \rangle )}{(\varepsilon_i - \varepsilon_s)(\varepsilon_s - \varepsilon_j)} + \text{permutations} \quad (6)$$

$$\sigma_{SO/FC}^{\sigma}(L) \approx +\frac{1}{c} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{s=1}^{n} \frac{(\langle \hat{\rho}_5 | \hat{\rho}_4 | \hat{M}_s \rangle ) (\langle \hat{\rho}_4 | \hat{\rho}_3 | \hat{M}_s \rangle ) (\langle \hat{\rho}_3 | \hat{\rho}_2 | \hat{M}_s \rangle )}{(\varepsilon_i - \varepsilon_s)(\varepsilon_s - \varepsilon_j)} + \text{permutations} \quad (7)$$

As compared to the classical nonrelativistic Ramsey-type theory (eq 4), the perturbative expressions for SO/FC$^2$ and SO/FC$^\sigma$ require a mutual interplay among three perturbative operators and involve additional occupied ($\hat{\rho}_s$) and vacant ($\hat{\rho}_s$) MOs. Because all the expressions make use of identical sets of nonrelativistic or scalar-relativistic MOs, one can establish an intuitive link between the PT3 theory and the classical Ramsey’s theory. A graphical representation of the relations is given for a specific $M$–$L$ arrangement in Figure 2.

The three perturbations involved in eqs 6 and 7 are the SO coupling, Fermi-contact, and angular-momentum operators. The role of the SO coupling term, which has in analogy to PSO a rather local character, is to provide a coupling between two metal-based p- or d-type orbitals. Note that this operator is color-coded in orange to highlight its origin to the atom M ($r_M^{-2p}$). The role of the Fermi-contact interaction term, highlighted in blue and represented by $\delta^s$ function, is associated with the electronic structure around the spectator atom L. In contrast to the PSO term, FC represents a direct interaction of the electron spin density with the spectator nucleus. The remaining MO coupling term is linked to an applied external magnetic field by means of the angular-momentum operator $I$. A mutual interplay among all three perturbations is shown schematically by a MO triangular diagram in Figure 2. As an example, we consider for a specific combination of the perturbations in Figures 2b and 2c two distinct SO/FC$^2$ (eq 6) and SO/FC$^\sigma$ (eq 7) schemes that contribute to $\sigma_{SO/FC}^{\Delta}(L)$ for systems investigated here. Note that two occupied MOs involved in SO/FC$^2$ or two vacant MOs involved in SO/FC$^\sigma$ can be identical (see Section 4.3 and the Supporting Information for more details).

In contrast to classical Ramsey-type coupling (Figure 2a), the SO/FC contribution is governed by electronic structure around both the metal atom M (SO coupling term in orange) and the ligand atom L (FC interaction term in blue). Therefore, SO-active MOs must be of a reasonable energy gap (see eqs 6 and 7) and of a particular symmetry and character of L and M.$^{71}$ This implies the central role of the M–L bond in propagating the SO effects.$^{9,25,27}$

3. METHODS

3.1. Molecular Structures. The structures of Au(I), Au(III), Hg(II), and Pt(II) complexes 1–4 were minimized in vacuo using the PBE0$^{38}$ functional and the def2-TZVPP basis sets for light atoms$^{39}$ as implemented in Turbomole 6.3.1 code. The relativistic effective-core potentials (ECPs)$^{51}$ substituting 60 core electrons (MDF-60) were used for the heavy Pt, Au, and Hg atoms together with corresponding basis sets of def2-TZVPP quality.$^{38,51}$ This computational level is referred to as PBE0/def2-TZVPP in this work and has been justified as the preferred choice in previous methodological studies of various transition-metal complexes.$^{9,27,42,45}$

3.2. Electronic Structure Calculations. The Molecular Orbital (MO) Analysis was performed using the ADF software package.$^{46,47}$ The PBE0 functional with the QZ4P basis set for the metal atom and TZ2P basis sets for light atoms$^{48,49}$ was used. Scalar-relativistic effects were treated using zero-th-order regular approximation (ZORA) and spin–orbit effects using spin–orbit ZORA (SO-ZORA) as implemented in the ADF program.$^{50–52}$

EDA-NOCV Analysis$^{53}$ was performed at the ZORA level (see previous paragraph) involving the Energy Decomposition Analysis (EDA)$^{54,55}$ of Ziegler and Rauk.$^{56–58}$ as implemented by Bickelhaupt and Baerends in ADF.$^{55}$ According to EDA, the interaction energy $E_{\text{int}}$ can be described as

$$E_{\text{int}} = E_{\text{el}} + E_{\text{Pauli}} + E_{\text{Orb}} \quad (8)$$

where $E_{\text{el}}$ is quasi-classical electrostatic component, $E_{\text{Pauli}}$ is Pauli repulsion term, and $E_{\text{Orb}}$ is orbital component representing charge-transfer between interacting fragments as well as polarization of individual fragments. The contribution from the orbital term obtained by standard EDA decomposition was linked to Natural Orbitals for Chemical Valence (NOCV) analysis$^{53,59}$ to decompose the electron deformation energy (EDD)$^{60,61}$ associated with bond formation into the individual components of the bond. We used this approach to quantify the energy stabilization ($E_{\text{NOCV}}$) brought about by individual pairings of occupied and vacant orbitals (NOCV channels).

QTAIM Analysis (Quantum Theory of Atoms in Molecules) was performed using the PBE functional, the def2-SVP basis set for light atoms$^{39}$ and MWB-60 ECP with def2-TZVPP for gold and mercury.$^{51}$ Auxiliary s-type core electron functions were added manually to the molecular wave functions to model the ECP core electrons of Au and Hg atoms.$^{62}$ The wave function was analyzed, and the delocalization index between all pairs of atoms was computed by the AIMAll suite of programs.$^{63}$ The delocalization index, DI(M+L), quantifies the magnitude of electron sharing between two atomic basins and is a direct measure of covalence.$^{64}$

3.3. NMR Shielding Constants. Two-Component Nuclear Magnetic Shielding was calculated by using the ADF2014 and ADF2016 codes at the scalar-relativistic ZORA and two-component SO-ZORA levels$^{55,66}$ including GIAO (gauge including atomic orbitals)$^{67}$ The comparison between direct $\sigma_{SO}$ ADF output and $\sigma_{SO} - \sigma_{AI}$ values is given in Table S2. The hybrid functional PBE0 (for comparison of PBE and PBE0 data, see Figure S1) with the QZ4P basis set for metal atoms and the TZ2P basis set for light atoms was used in these calculations (referred to as 2c)$^{8,27,45,69}$ The spin–orbit contribution to the paramagnetic NMR shielding, $\sigma_{SO}^{\sigma}$, was calculated as the difference between 2c and 1c paramagnetic.
Table 1. Correlation among Calculated Au–N Bond Lengths ($r_{\text{Au–N}}$), $\sigma^{SO}(^{15}\text{N})$-Tensors, Interaction Energies ($E_{\text{Int}}^{\text{Au–N}}$), Orbital Contributions to the Interaction Energies ($E_{\text{Int}}^{\text{orb}}$), the Four Most Important EDA-NOCV Channels for Au–N Bonds, and the QTAIM Delocalization Indices DI(Au–N) for PyAuX Complexes 1a–1k

<table>
<thead>
<tr>
<th>compd - trans X</th>
<th>$r_{\text{Au–N}}$</th>
<th>$\sigma^{SO}(^{15}\text{N})$</th>
<th>$\Delta E_{\text{Int}}$</th>
<th>DI(Au–N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a - F</td>
<td>2.002</td>
<td>$+13.3$</td>
<td>-30.8</td>
<td>0.90</td>
</tr>
<tr>
<td>1b - OH</td>
<td>2.024</td>
<td>$+13.8$</td>
<td>-30.4</td>
<td>0.86</td>
</tr>
<tr>
<td>1c - Cl</td>
<td>2.045</td>
<td>$+4.5$</td>
<td>-28.2</td>
<td>0.82</td>
</tr>
<tr>
<td>1d - Br</td>
<td>2.059</td>
<td>$-9.4$</td>
<td>-22.8</td>
<td>0.80</td>
</tr>
<tr>
<td>1e - CN</td>
<td>2.075</td>
<td>$-8.9$</td>
<td>-22.7</td>
<td>0.75</td>
</tr>
<tr>
<td>1f - SH</td>
<td>2.084</td>
<td>$-15.4$</td>
<td>-20.3</td>
<td>0.67</td>
</tr>
<tr>
<td>1g - SeH</td>
<td>2.092</td>
<td>$-18.1$</td>
<td>-19.2</td>
<td>0.69</td>
</tr>
<tr>
<td>1h - H</td>
<td>2.141</td>
<td>$-19.2$</td>
<td>-19.4</td>
<td>0.64</td>
</tr>
<tr>
<td>1i - CH$_3$</td>
<td>2.128</td>
<td>$-19.6$</td>
<td>-19.4</td>
<td>0.62</td>
</tr>
<tr>
<td>1j - GeH$_3$</td>
<td>2.179</td>
<td>$-20.8$</td>
<td>-19.4</td>
<td></td>
</tr>
<tr>
<td>1k - SiH$_3$</td>
<td>2.201</td>
<td>$-30.0$</td>
<td>-19.4</td>
<td></td>
</tr>
</tbody>
</table>

For the orientation of principal components of the $^{15}\text{N}$ NMR shielding tensor wrt the coordination system, see Figure 3. Note that the differences in $\sigma^{SO}$ originate mainly from the tangential ($\sigma^{SO}_{\text{t}}$) and perpendicular ($\sigma^{SO}_{\text{p}}$) components of the $^{15}\text{N}$ NMR shielding tensor. $^b$For the definition of $E_{\text{Int}}$, $E_{\text{orb}}$, and EDA-NOCV channels, see Methods: Section 3.2. $^c$Bond lengths are given in Å, $\sigma^{SO}(^{15}\text{N})$ are given in ppm, DI are given in au, and $E_{\text{NOCV}}$ are given in kcal-mol$^{-1}$.

4. RESULTS AND DISCUSSION

As described in the Introduction, the SO-induced effects on the $^{13}\text{C}$ and $^{15}\text{N}$ NMR shielding constants have recently been linked to the type of orbital magnetic couplings ($5d^* \leftrightarrow 6p^*$ vs $6p^* \leftrightarrow 6p^*$) and covalence of the HA–LA bonding. $^{23,25,26}$ Herein we perform a systematic investigation of the $\sigma^p$ and $\sigma^{SO}$ contributions for model transition-metal complexes (see Figure 1). The ultimate goal of this work is to understand how the changes in electronic structure (electron configuration of the central metal atom and character of the M–L bonding) affect the NMR shielding constants of the light atoms L. We focus on the spin–orbit-induced changes in the molecular orbitals, in particular those altering the M–L bond.

4.1. Au(I) Compounds: Effect of the Trans Substituent (X) on the Character of the M–L Bond and Ligand Spin–Orbit NMR Shielding. 4.1.1. Spin–Orbit Effects on the Ligand NMR Shielding Constants – General Trends and Structural Trans Effect along the Au(I) Series. To get a detailed understanding of the relationships between the ligand NMR chemical shifts and the nature of M–L bonding we first analyze simple linear Au(I) complexes of pyridine with various substituents (X) in the trans position to the NMR spectator atom L (Figure 1). In Table 1, compounds 1a–1k are ordered according to their structural trans effect. This arrangement nicely reflects the magnitude of $\sigma^{SO}$ and the M–L distance. $^{23}$ The strength of the trans ligand (its propensity to electron sharing) alters the character of M–L bonding which is sensitively reflected in $\sigma^p$ and $\sigma^{SO}$ of the spectator ligand...
atom L (Table S5). This enables a detailed analysis of the correlation between the $\sigma^{SO}(L)$ and the electronic structure in given complexes. As an example, the orientation of principal axes of the $^{15}$N NMR shielding tensor for compound 1a is shown in Figure 3.

As demonstrated previously, the $\sigma^{SO}(L)$ correlates exponentially with the interatomic distance and linearly with the covalence of the M–L bond, which can be characterized, for example, by the QTAIM delocalization index. Both the M–L distance and the covalence of the M–L bond are very effectively altered by the trans ligand X (see Table 1). To demonstrate this phenomenon, the relationships between the $\sigma^{SO}(^{15}$N) and the Au–N distance, $\sigma^{SO}(^{15}$N) and DI(Au$\leftrightarrow$N), $\sigma^{SO}(^{15}$N) and DI(Au$\leftrightarrow$N)/r$_{Au-N}$ separately for halogen (red, Group 17), chalcogen (green, Group 16), pnictogen (blue, Group 15), and hydrogen (black) trans substituents X, and $\sigma^{SO}(^{15}$N)$\cdot$χ$_{DM}$ for 1a–1k.

4.1.2. Structural Trans Effect on the Character of the Au–N Bond – the Localized MO Picture. To analyze the effect of the trans X substituent on the character of the Au–N bond we performed the EDA-NOCV analysis. Energy decomposition analysis provides classical electrostatic ($E_{Els}$) and orbital ($E_{Orb}$) terms which can be used for estimating the role of bond polarity and orbital interactions, respectively. The individual EDA contributions to interaction energy, $E_{Int}$ for Au–X and Au–N bonds in compounds 1a–1k are summarized in Table S6 in the Supporting Information. The important role of $E_{Orb}$ for the Au–N bond is highlighted in Table 1. To demonstrate the direct link between the character of the Au–N bond and $\sigma^{SO}$, correlations between $\sigma^{SO}(^{15}$N) and $E_{Int}(Au\leftrightarrow N)$ as well as between $\sigma^{SO}(^{15}$N) and $E_{Orb}(Au\leftrightarrow N)$ are shown in Figure 5. Similar to the DI(Au$\leftrightarrow$N) in Figure 4, $E_{Orb}$ of Au–N bond scales with the polarity of the trans X. $E_{Orb}$ can be further decomposed into energetic contributions from individual NOCV channels (occupied-vacant orbital pairs), which provide a more detailed view to the bonding situation. The contributions of the first four NOCV channels (NOCV$_1$–NOCV$_4$) to $E_{Orb}$ are summarized in Table 1 and discussed on
The first channel, NOCV₁, corresponds to the donation of the nitrogen LP (with 2pₓ AO character) to the vacant orbital at the gold atom (charge transfer from the ligand toward the Au–X fragment in the σ-space). The corresponding E₁ contributions to the M–L bond energies vary from −30.8 to −21.4 kcal mol⁻¹ for F (1a) and CH₃ (1i) trans ligands X, respectively. Considerably larger E₁ highlights a significantly stronger Au–N σ-bonding character in 1a. In parallel to the stronger σ-bonding, the π-back bonding (charge shift from metal toward pyridine moiety in the π-space) is realized by 5dₓ₃ (channel 2) and 5dₓz (channel 4) donation to nitrogen 2pₓ orbitals is also more pronounced in 1a. This is partly related to the π-space donation capacity of the trans ligand F which enables formation of the π-conjugated system; note the fluorine π-type orbitals in NOCV₂ and NOCV₄. The back-bonding is accompanied by the somewhat shorter interatomic Au–N distance in 1a, which allows for a more efficient overlap between the M (Au) and L (N) orbitals forming the π-bond. Notice also significant concentration of charge at Au for 1a in NOCV₁ (bottom left, the weak trans σ-bond). In contrast, charge-shift propagation to the trans ligand X via the strong trans σₓₓ₋ₓ bond is clearly visible from NOCV₁ for 1i (bottom right).

Thus, in the case of weak trans X, such as F, the M–X bond (here Au–F in 1a) is highly polar, which enables the formation of a more covalent Au–N bond (cf. rₓₓ₋ₓ, DI, and Eₓₓ values in Table 1). On the contrary, the more covalently bonded trans methyl ligand induces weakening of the Au–N bond in 1i. This is paralleled by the destabilization of the particular MOs, which in turn influence the ¹⁵N NMR shielding constant, see below.

**4.1.3. Electronic Structure vs Ligand NMR Shielding Constants: The MO Picture.** To understand how the ligand NMR shielding constants relate to the electronic structure, we performed Kohn–Sham molecular orbital (MO) analysis for isoelectronic systems 1a and 1i, as they have opposite spin–orbit contributions to the ¹⁵N NMR shielding constants (+13.3 ppm for 1a vs −19.6 ppm for 1i, see Table 1). The frontier MO-energy diagrams for 1a and 1i along with MO contributions to the paramagnetic NMR shielding constants (σᵣ) calculated at the 1c PBE0 level are shown in Figure 7 (for comparisons of 1c and 2c calculations at the PBE0 level, see Figure S4 and Figure S5 in the Supporting Information).

**Analysis of σ₁₋ₓ-Bonding Contributions to σᵣ(L) at the Scalar-Relativistic 1c Level.** There are two types of occupied σ-bonding MOs with significant contributions to σᵣ (N) shown in Figure 7: σ₁₋ₓ (MO55 for 1a, MO54 for 1i) and σₓₓ₋ₓ (MO54 for 1a, MO55 for 1i). They are both magnetically coupled to the vacant π-type MOs with sizable nitrogen 2pₓ, 2pᵧ AOs character. The schematic representation of the σₓₓ₋ₓ→πᵣ coupling is shown as the Ramsey-type paramagnetic contribution in Figure 2a. As the trans substituent X efficiently alters the energy of the Au–N bond, the role of the σₓₓ₋ₓ-type orbitals in σᵣ variations varies significantly in the series of compounds. The σₓₓ₋ₓ-type orbitals are notably less affected by the substituent, see Figure 7.

The weakening of the Au–N bond in 1i (the strong trans Au–CH₃ bond) relative to that in 1a can clearly be observed in the 1c Kohn–Sham MO diagram. This destabilizing effect of...
the trans methyl ligand in 1i is highlighted by the magenta lines between the corresponding $\sigma$$_{Au-N}$ orbitals, namely MO54 (1a) – MO55 (1i) and MO58 (1a) – MO60 (1i). The substituent-induced energy destabilization (manifested by decreasing the $\Delta E_{MO-MO^*}$ denominator in eq 4), accompanied by a larger N 2p character of MO55 in 1i as compared to MO54 in 1a, is responsible for a larger deshielding contribution of $\sigma$$_{Au-N}$ to $\sigma$$_{p}$ (N) ($−67.3$ ppm for 1i vs $−28.0$ ppm for 1a).

The situation is a bit more complicated for the higher-lying $\sigma$-type Au–N orbital (MO58 in 1a, MO60 in 1i). Its larger substituent-induced energy destabilization of about $+1.86$ eV ($E_{MO58(1a)} = −9.82$ eV vs $E_{MO60(1i)} = −7.96$ eV) as well as conserved nitrogen 2p character should intuitively lead to larger deshielding in 1i. The observed opposite trend ($−51.2$ ppm for 1a vs $−42.8$ ppm for 1i) can be rationalized by a notable increase in the Au 5d$^2$ character from 2% in MO58 of 1a to 28% in MO60 of 1i (for total Au d AO contributions, see Table S7). The observed large gold character in MO60 together with its energetic proximity to $\pi$-type orbitals (MO61-MO64) are the essence for a particular sensitivity of MO60 to the spin–orbit coupling and the SO-induced orbital mixing.

Analysis of $\sigma$$_{M-L}$-Bonding Contributions to $\sigma$’(L) at the Spin–Orbit Relativistic 2c Level. The MO58 in 1a has a rather small Au 5d character and is affected by SO coupling only marginally, $\sigma$$_{MO58}$ = $−3.8$ ppm (see Figure 7). In contrast, its counterpart in 1i, MO60, is split by the SO coupling into MO61 and MO62, containing admixtures from nonbonding Au 5d MOs (formally Au LPs) and $\pi$Au–X-type MOs—MO61-MO64. Note that such mixing of MOs with $\sigma$- and $\pi$-symmetry is allowed only in the presence of SO coupling. The $\sigma$/ $\pi$ mixing in 1i is the consequence of the above-mentioned destabilization of MO60 due to the strong trans effect bringing the frontier MOs of $\sigma$- and $\pi$-symmetry closer to contact. The resulting two 2c MOs in 1i with significant $\sigma$-character are coupled more efficiently with the vacant-orbital space and are responsible for the large SO-induced deshielding contribution of about $−28.3$ ppm.

Figure 7. Energy diagram and orbital contributions to $\sigma$’ from the frontier occupied Kohn–Sham MOs as obtained from 1c calculations (in blue, inner columns) for compound 1a (left) and 1i (right). The main substituent-induced changes in the $\sigma$$_{Au-N}$ space are highlighted by two magenta lines, and effects of the SO coupling on these selected orbitals are shown by arrows (2c levels in red, outer columns). The important SO-active MOs are highlighted in bold, and total $\sigma$’ values are given at the bottom.

![Figure 7](image_url)
The second $\sigma_{Au-N}$ contribution, represented by MOS4 in 1a and MOS5 in 1i, is only weakly altered by the SO coupling. These MOs are slightly energetically stabilized at the 2c level ($\Delta E_{SO}^{MO54} = -0.07 eV$, $\Delta E_{SO}^{MO55} = +0.1 eV$) and contribute less to the total paramagnetic deshielding, $\Delta \sigma_{SO} = +7.4$ ppm and $\delta \sigma_{SO} = +10.3$ ppm.

In summary, the $\sigma_{SO}$ contributions arising from the two above-mentioned $\sigma$-type MOs sum up to $\sigma_{SO} = +3.6$ ppm for 1a (3.25% of total $\sigma_{SO} = +13.3$ ppm) and $\sigma_{SO} = +18.0$ ppm for 1i (90% of total $\sigma_{SO} = -19.6$ ppm). Clearly, the sign of the $\sigma_{SO}$ values parallels the total SO-induced shielding/deshielding effect.

Contributions from $\pi$-Type M–L Bonding to $\sigma(\mathbf{L})$ in 1a. Similar to $\sigma$-bonding discussed above, the $\pi_{Au-N}$ back-bonding MOs are destabilized in 1i and play an even less important role in Au–N bonding (cf. NOCV channels in Figure 6). The lesser Au–N back-bonding efficiency in 1i (cf. $\pi$-bonding capability of trans fluorine atom in NOCV of 1a) is linked to the weak stabilization of the occupied antibonding $\pi_{Au-N}$ orbitals in 1i (upper lying Au $d_{2z}$-based and Au $d_{yz}$-based MO63 and MO64) as compared to those in 1a. Thus, small SO shielding contributions from these $\pi$-type MOs in 1a of about $\sigma_{SO} = +3.9$ ppm vanish in 1i. The $\pi$-type MOs can play a more significant or even dominant role in determining the sign of the total $\sigma_{SO}$ in other transition-metal complexes, in particular those with $\pi$-donors in the trans position such as compound 4a discussed in Section 4.3.

4.2. Au(III) Complexes: Role of Metal Oxidation State and Atomic Charge. The effects of the heavy-atom oxidation state on the $\sigma_{SO}(\mathbf{L})$ have already been reported for compounds containing p-block elements.24,76 Here we focus on the charge-neutral Au(I) and Au(III) complexes (for structures, see Figure 1). The calculated $\sigma_{SO}(15N)$ values and $E_{orb}$ for selected PyAuIIIClX complexes 2 are summarized in Table 2 (for full data sets, see Tables S8 and S9). The increasing formal positive charge on gold as going from Au(III) to Au(II) in 1 is compensated for by two additional chloride ligands, whose binding alters the energy and composition of the SO-active MOs. For compound 2a, the Au–N bonding and shielding characteristics are similar to those for 1a – a strong M–L bond with the low-lying Au $d_{2z}$-based MO and total $\sigma_{SO} = +13.3$ ppm for 1a vs $+15.3$ ppm for 2a). In contrast, compounds 1i and 2i behave somewhat differently. The destabilized MO60 in linear geometry of 1i has its counterpart in $\sigma_{Au-N}$ in 2i significantly stabilized by the different ligand field in square-planar geometry and the higher gold oxidation state (see Figure S6). This results in somewhat lower sensitivity of this $\sigma_{Au-N}$ in 2i to SO effects thus diminishing the overall SO deshielding (total $\sigma_{SO} = -19.6$ ppm for 1i vs $\sigma_{SO} = -9.4$ ppm for 2i). Note also the substituent trends in $E_{orb}$ and $E_{orb}$ in Table 2 paralleling those observed for compounds 1.

4.3. Effect of the Central Metal Atom on the $\sigma_{SO}(\mathbf{L})$ and the Character of the M–L Bonding – Comparison of Au(I) Complexes with Hg(II) and Pt(II) Compounds. As we demonstrated in previous chapters on 1a and 1i complexes, the character of Au–N bonding is reflected in $\sigma_{SO}$ of the nitrogen atom of the pyridine ligand L. The $\sigma_{SO}$ has a positive sign in 1a (shielding effect), as typically observed for the transition-metal complexes with a partially filled d-shell (e.g., platinum or iridium), whereas $\sigma_{SO}$ is negative in 1i (deshielding effect), which is common in Group 12 (e.g., mercury) and early p-block (thallium, lead) compounds.

Therefore, we analyzed a series of Hg(II) and Pt(II) compounds to investigate and reveal the origin of the SO-induced (de)shielding effects. The structure of these complexes is shown in Figure 1, and selected NMR data and bonding characteristics are summarized in Table 3 (for full data sets, see Tables S10–S13 and Figures S7 and S8 in the Supporting Information). To conserve charge neutrality of Hg(II) compounds 3a–k, the substitution of the phenyl ligand for pyridine was performed. In the following, compound 3k with strong $\sigma_{SO}$ deshielding of $-37$ ppm and compound 4a with strong $\sigma_{SO}$ shielding of $+51$ ppm are analyzed and compared in detail. Data for the remaining systems can be found in the Supporting Information.

4.3.1. Electronic Structure and Ligand NMR Shielding Constant in PhHg$^\text{III}$H$_2$ – Compound 3k. The significant role of $\sigma_{M-L}$-type MOs identified for the magnetic couplings in Au(I) compound 1i is even more pronounced in Hg(II) compound 3k, Figure 8. This is related to a larger involvement of formally vacant Hg 6p orbitals in bonding and a reduced importance of the more compact 5d-shell of Hg. In the following two subsections we discuss the role of $\sigma_{M-L}$-type MOs in $\sigma_{SO}$ and perform the analysis of the deshielding mechanism using third-order perturbation theory.

The Dominant Role of Occupied $\sigma$-Type M–L Bonding MOs for $\sigma_{SO}$. In Hg compound 3k, the highest occupied MO69 of $\sigma_{M-L}$ character, composed of 30% C 2p, 6% C 2s, and 9% Hg 6p, is effectively coupled with the vacant-orbital space resulting in $\sigma_{SO} = -57.9$ ppm. This can be seen as the Ramsey-type paramagnetic 2p$^2$ e$^2$ coupling (Figure 2a). In contrast to the scalar-relativistic $\sigma_{SO}$, the two-component contribution from MO69, $\sigma_{SO}^{RR} = -82.5$ ppm, reveals a dominant role of this orbital in total $\sigma_{SO}$ deshielding ($\sigma_{SO}^{RR} = -24.6$ ppm of total $\sigma_{SO} = -36.8$ ppm), as indicated in Figure 8. In addition to MO69, $\sigma_{SO}$ also arises from the second occupied $\sigma$-
bonding orbital MO61 (σ_{MO61} = −6.3 ppm) and from the formally closed Hg 5d shell (Σ σ_{MO53−59} = −6.4 ppm). In passing, note the significant structure-induced contraction and stabilization of the metal 5d-based orbitals in 3k compared to those in 4a—a phenomenon highlighted by the light-green background in Figure 8 (for the 2c level, see Figure S7).
This spin density is then operator \( \text{SO/FC} \) in MO69 (6% C \( 2p \)) in the presence of a magnetic field. This is in perfect agreement with the results from third-order perturbation MO analysis.

SO Contributions from Highest Occupied M–L Bonding MO69 to \( \sigma(L) \): Analysis of Deshielding Fermi-Contact Mechanism (SO/FC\(^4\)). Two types of the SO/FC mechanism \( \text{SO/FC\(^4\)} \) in eq 6 and SO/FC\(^5\) in eq 7) involving contribution to \( \sigma(L) \) from MO69 are demonstrated for couplings MO69 \( \leftrightarrow \) MO70 and MO69 \( \leftrightarrow \) MO71, as examples, in Figure S9 in the Supporting Information.

The important contribution to \( \sigma(L) \) from MO69 is represented by MO69 \( \leftrightarrow \) MO71 coupling, involving the SO/FC\(^4\) mechanism. At the 1c level, the contribution to \( \sigma(L) \) from MO69 \( \leftrightarrow \) MO71 is vanishingly small, but it gives rise to \( \sigma(L) \) of about –5 ppm at the 2c level. The third-order perturbation MO analysis provides understanding of this difference, Figure S9c. The MO69 is coupled with MO71 by the spin–orbit operator \( (\hat{r} \vec{p}) \) and the angular momentum operator \( (\hat{l}) \). The spin–orbit operator “generates” in the presence of a magnetic field an induced spin density on MO69. This spin density is then “measured” by the FC interaction operator \( (\hat{d}^\sigma) \) at the spectator nucleus L. The involvement of the FC operator implies a significant role of ligand s-character in MO69 (6% C 2s). Note that the deshielding contribution of the SO/FC\(^4\) term (eq 6) is due to the coupling between two identical occupied \( \sigma \)-bonding M–L orbitals MO69. This is in clear contrast to the shielding role of the vacant \( \sigma \)-antibonding M–L orbital in Pt compound 4a, see Section 4.3.2.

4.3.2. Electronic Structure and Ligand NMR Shielding Constant in PyPtCl\((\text{NH}_3)\)F – Compound 4a. In contrast to mercury, platinum behaves as a “standard” 5d transition metal. Therefore, \( \sigma_{M-L} \)-type MOs (MO69, MO65) are more stabilized in 4a as compared to those in 3k (MO69, MO61), see the magenta lines in Figure 8. Simultaneously, most of the \( \pi \)-type orbitals with Pt 5d character (formal LPs and \( \pi_{M-L} \)-type MOs) are considerably higher in energy when compared to those in 3k. This is highlighted by the light-green background in Figure 8. These changes are likely caused by a lower nuclear charge of platinum and its partly unfilled \( 5d \) shell (\( d^\pi \)). It should be explicitly noted that the total \( \sigma(L) \) in 4a is dominated by the \( \sigma_{M-L} \)-type MOs at the 1c level similar to those in gold and mercury complexes. For example, MO69 (\( \sigma_{M-L} \)-type) with the nitrogen \( 2p_z \) character contributes to \( \sigma(L) \) by –56.5 ppm. This can be explained straightforwardly by the Ramsey-type (eq 4) magnetic coupling MO69 \( \leftrightarrow \) MO79 \( \ast \) (\( \sigma(L) \approx -22 \) ppm), where MO79 \( \ast \) (\( \pi_{M-L} \)-type) has a significant nitrogen \( 2p_z \) character (see Figure 10a, cf. Figure 2a). This coupling is induced by \( \vec{l} \), and hence contributes to the tangential component of the NMR shielding tensor (\( \sigma = -65 \) ppm). However, this type of low-lying \( \sigma \)-type orbital in 4a is rather SO-intact.

The Dominant Role of Occupied \( \pi \)-Type M–L Bonding MOs for \( \sigma(L) \). In general, total \( \sigma(L) \) in 4a is dominated by numerous, albeit relatively small, contributions from upper-lying \( \pi \)-type M–L orbitals (see Figure 8) resulting in a large total \( \sigma(L) \approx +50.6 \) ppm. Interestingly, many of these MOs have shielding (positive) contributions to \( \sigma(L) \) even at the 1c level, although \( \sigma(L) \) is generally associated with deshielding.\(^{55} \) For example, MO74 of N \( 2p_z \) character and \( \sigma_{M-L} \)-type is efficiently coupled at 1c by the Ramsey-type mechanism to MO82 \( \ast \) of \( N \) \( 2p_z \) character and \( \sigma_{M-L} \)-type, providing thus shielding contribution.\(^{91,47} \) See Figure 10b. The total \( \sigma(L) \) for MO74 \( \leftrightarrow \) MO82 \( \ast \) is +8 ppm at 1c but amounts to +11 ppm at the 2c level (\( \sigma(L) \approx +3 \) ppm). Other examples of SO-induced shielding contributions of \( \sigma_{M-L} \) orbitals are (i) decreased deshielding for MO67 (–17.4 ppm at 1c vs –10.4 ppm at 2c, \( \sigma(L) \approx +7.0 \) ppm) and (ii) increased shielding for upper-lying MO71–78 (\( \Sigma \sigma^\pi_{L} = +15.4 \) ppm, \( \Sigma \sigma^\pi_{L} = +37.9 \) ppm, \( \Sigma \sigma^\pi_{L} = +22.5 \) ppm), see Figure 8.

SO Contributions from Vacant M–L Antibonding MO82 \( \ast \) to \( \sigma(L) \): Analysis of Shielding Fermi-Contact Mechanism (SO/FC\(^4\)). To analyze the sign of \( \sigma(L) \) and to describe the mechanism of SO propagation, we performed the third-order
perturbation MO analysis of MO74 → MO82* σ coupling for Pt compound 4a (Figure 10c). As revealed by the analysis, the SO/FCV mechanism plays a dominant role in which the MO74 is coupled with the MO82* by the spin–orbit operator \( \langle \sigma^\delta \rangle \) and the angular momentum operator \( \hat{l} \). The spin–orbit operator “generates” in the presence of a magnetic field an induced spin density on MO82*. This spin density is then “measured” by the FC interaction operator \( \langle \delta^n \rangle \) at the spectator nucleus L. Here, for the vacant σ-type M–L antibonding orbital MO82*, the shielding contribution is dictated by the final positive sign of the SO/FCV term (eq 7). This is in contrast with the deshielding role of occupied σ-type M–L bonding orbitals in Hg compound 3k. To summarize, the sign of SO contributions to \( \sigma(L) \) is related to the character of the \( \sigma_{M\L}^{-} \) space in frontier MOs. Whereas occupied \( \sigma_{M\L}^{-} \)-bonding MOs are linked to the deshielding SO effects on the atom L (e.g., 3k), vacant \( \sigma_{M\L}^{-} \)-antibonding MOs are responsible for SO shielding (e.g., 4a). As the σ-type AOs contribute exclusively to σ-bonding, their involvement in the \( \sigma_{M\L}^{-}/\sigma_{M\L}^{\ast} \)-space is directly reflected in the sign of \( \sigma_{SO}^\ast(L) \). This is intimately related with the relative roles of σ/π bonding between M and L discussed in Section 4.3.3.

### 4.3.3. The Role of \( \sigma_{M\L}^{-} \) vs \( \sigma_{M\L}^{\ast} \) Bonds in Compounds 3k (PhHg3SiH4) and 4a (PyPtCl(NH3)F) – NOCV Analysis

The important role of σ-type M–L bonding in 4a compared to 3k is clearly identified by EDA-NOCV analysis performed for these two compounds, see Figure 11. Whereas the M–L bonding in 3k is largely of σ-character (\( \Delta_{\text{NOCV}^\ast_{\text{L}}} = 7.9 \)), governed by metal 6s AO (σ), the M–L bonding in 4a has a significant contribution from the π-space (\( \Delta_{\text{NOCV}^\ast_{\text{L}}} = 2.6 \)) with a significant contribution from metal 5d AO (σ).

### 4.4. General Considerations

The trends and findings described above can be generalized. A schematic representation of the orbital space in selected complexes together with the \( \sigma_{SO} \) values is given in Figure 12. The σ-type (red) and π-type M–L or M (blue) orbitals are highlighted in relation to the metal 5d, 6s, and 6p orbital space. Overall, the \( \sigma_{SO} \) values correlate well with the electronic structure of the complexes (relative energetic positions of σ-type vs π-type MOs and metal 5d vs 6p character) and are modulated both by the different central atom \( \delta_{SO} \) and the trans effect \( 2.7 \) of ligand X (e.g., F vs CH3, H2S, SiH3).

Let us generalize our findings for the complexes in a series \( \Delta_{\text{q}_{L}} \) (e.g., Pt 5d-shell in 4a, the highly positive \( \sigma_{SO} \) is dominated by the SO effects on the couplings among the occupied \( \pi_{\text{L}} \) orbitals and vacant \( \pi_{\text{L}}^{\ast} \) orbitals. Spin–orbit coupling modulates the energy and Pt 5d character of both occupied and vacant orbitals, thus increasing the shielding and decreasing the deshielding MO ↔ MO* contributions (total \( \sigma_{SO} > 0 \) in Figure 12). In 1a with a formally closed Au 5d10 shell, the role of frontier \( \pi_{\text{L}} \) and \( \pi_{\text{L}}^{\ast}(\text{Au}) \) MOs in the SO shielding is significantly reduced. If the Au–L bonding is additionally destabilized by a strong trans effect, like in the Au compound 1i, the deshielding role of the occupied \( \sigma_{\text{AuL}} \)-bonding orbitals starts to dominate the \( \sigma_{SO} \). Further, the paramagnetic SO deshielding is enhanced by admixing the metal 6p orbitals into the frontier bonding \( \sigma_{\text{HgL}} \) MOs in Hg compound 3k. These frontier orbitals (HOMO in 3k) are efficiently coupled with the vacant π*-type orbital space. The closed and significantly contracted Hg 5d shell limits the contributions from \( \sigma_{\text{HgL}} \leadsto \sigma_{\text{HgL}}^{\ast} \) shielding couplings. In total, the SO effects induce increased deshielding in 3k (\( \sigma_{SO} < 0 \), see Figure 12).

Interestingly, the above-mentioned SO-induced changes in MOs are nicely reflected in a rearrangement of the ground-state electron density upon the spin–orbit coupling. To make a link between these MO changes and \( \sigma_{SO} \), the SO-induced electron deformation density (SO-EDD), calculated as a difference between the electron density at 2c and 1c levels is visualized for compounds 4a and 3k in Figure 13. SO-alteration of the metal σ-type orbitals (mainly 5d-based) in 4a shifts the electron density from the metal π-space toward the connected ligand atoms (e.g., as shown in Figure 12). In contrast, SO-alteration of the metal σ-type orbitals (mainly 6s- and 6p-based) in 3k induces accumulation of the electron density at the metal atom and its depletion at the neighboring ligand atoms (deshielding in Figure 12).
In the present work, a detailed analysis of the paramagnetic NMR shielding constants ($\sigma^p$) of the light atoms neighboring the heavy transition-metal centers in gold, mercury, and platinum complexes was performed, and intuitive chemical interpretations are provided. Particularly, we focused on the correlation between the metal–ligand (M–L) bonding characteristics and the sign of spin–orbit contributions to the ligand NMR shielding constants ($\sigma^{SO}$). A thorough Kohn–Sham molecular orbital (MO) analysis was performed, and the type and characteristics of MOs are correlated with $\sigma^p$ and $\sigma^{SO}$. The structural $trans$ effect on the ligand NMR shielding constants in Au(I) compounds can be understood by changes in the relative roles of $\sigma$-type (bonding) and $\pi$-type (back-bonding) M–L orbitals. Furthermore, the shielding or deshielding nature of the spin–orbit contribution to $\sigma^p$ is naturally linked to the type of metal atom and its electronic structure. The dominating $\sigma$-type 6$p$-based M–L bonding in Hg(II) complexes is reflected in SO-induced deshielding, whereas the enhanced $\pi$-type M–L bonding in Pt(II) complexes leads to SO-induced shielding. The details of metal–ligand bonding have been observed consistently in the energy and composition of MOs as well as characteristics obtained from the energy decomposition analysis linked with natural orbitals for chemical valence (EDA-NOCV). In addition, we analyzed the Fermi-contact mechanism of propagation of the SO effect from the metal center to the ligand atom modulating individual components of the paramagnetic NMR shielding tensor of the ligand atom. Finally, we demonstrate an intuitive chemical link between the SO-induced changes in NMR shielding constants and the SO-induced changes in electron density (SO-EDD, spin–orbit-induced electron deformation density) around the metal and ligand atom. Investigations of how general these trends are along the Periodic Table are underway with our team.

### 5. CONCLUDING REMARKS

In the present work, a detailed analysis of the paramagnetic NMR shielding constants ($\sigma^p$) of the light atoms neighboring the heavy transition-metal centers in gold, mercury, and platinum complexes was performed, and intuitive chemical interpretations are provided. Particularly, we focused on the correlation between the metal–ligand (M–L) bonding characteristics and the sign of spin–orbit contributions to the ligand NMR shielding constants ($\sigma^{SO}$). A thorough Kohn–Sham molecular orbital (MO) analysis was performed, and the type and characteristics of MOs are correlated with $\sigma^p$ and $\sigma^{SO}$. The structural $trans$ effect on the ligand NMR shielding constants in Au(I) compounds can be understood by changes in the relative roles of $\sigma$-type (bonding) and $\pi$-type (back-bonding) M–L orbitals. Furthermore, the shielding or deshielding nature of the spin–orbit contribution to $\sigma^p$ is naturally linked to the type of metal atom and its electronic structure. The dominating $\sigma$-type 6$p$-based M–L bonding in Hg(II) complexes is reflected in SO-induced deshielding, whereas the enhanced $\pi$-type M–L bonding in Pt(II) complexes leads to SO-induced shielding. The details of metal–ligand bonding have been observed consistently in the energy and composition of MOs as well as characteristics obtained from the energy decomposition analysis linked with natural orbitals for chemical valence (EDA-NOCV). In addition, we analyzed the Fermi-contact mechanism of propagation of the SO effect from the metal center to the ligand atom modulating individual components of the paramagnetic NMR shielding tensor of the ligand atom. Finally, we demonstrate an intuitive chemical link between the SO-induced changes in NMR shielding constants and the SO-induced changes in electron density (SO-EDD, spin–orbit-induced electron deformation density) around the metal and ligand atom. Investigations of how general these trends are along the Periodic Table are underway with our team.

### ASSOCIATED CONTENT

#### Supporting Information

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Tables S1—S13: SO/FC and SO/SD contributions, $\sigma^{SO}(L)$ values, MO contributions, EDA-NOCV analysis, and DI values for complexes 1−4 with orientations of the principal components of the NMR shielding tensors; Figures S1—S8: energy diagrams and orbital contributions to $\sigma^p$ from the frontier occupied Kohn–Sham MOs for 1a, 1i, 3k, and 4a at 1c, 2c, and 4c levels; Figure S9: schematic representations of SO-induced MO magnetic couplings (the SO/FC mechanism); Cartesian coordinates for 1a, 1i, 3k, and 4a (PDF)

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**Notes**

The authors declare no competing financial interest.

A related work on $^1$H NMR shielding constants in some transition-metal complexes, highlighting the role of $\sigma$- and $\pi$-type MOs, appeared during the finalization of this manuscript.92

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