Unlocking Structural Diversity in Gold(III) Hydrides: Unexpected Interplay of cis / trans-Influence on Stability, Insertion Chemistry and NMR Chemical Shifts

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1. Relevant $^1$H and $^{13}$C NMR spectra

Figure S1. $^1$H NMR spectrum of 4 (THF–$d_8$, 253K); * denote residual protonated THF–$d_8$.

Figure S2. $^{13}$C{$^1$H} NMR spectrum of 4 (THF–$d_8$, 253K); * denote THF–$d_8$. 

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Figure S3. Two sections of the $^1$H NOESY NMR spectrum of 4 (THF–$d_8$, 253K); red arrows in the scheme denote dipolar contacts.

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Figure S6. $^1$H NMR of 5 obtained by procedure b (THF–d$_8$, 263K); * denote residual protonated THF–d$_8$, o denotes silicone grease.
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Figure S10. $^{13}$C({$^1$H}) NMR of 6 (THF–$d_8$, 223K); * denote THF–$d_8$, +: py–BEt$_3$. 

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Figure S12. $^{13}$C($^1$H) NMR of 7 (THF–$d_8$, 253K); * = THF–$d_8$, +: DMAP–BEt$_3$, x: pyridine, o: free DMAP.

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Figure S18. $^{13}$C($^1$H) NMR of 11 obtained by procedure a (THF–$d_8$, 297 K); * denote residual protonated THF–$d_8$, + = py–BEt$_3$. 
Figure S19. $^1$H NMR of 12 generated in situ (THF–d$_8$, 297 K); * denote residual protonated THF–d$_8$, + = py–BET$_3$.

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**Figure S28.** A section of the $^1$H NMR spectrum of 17 (THF–$d_8$, 297K); * denote residual protonated solvent.
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Figure S30. $^{13}$C($^1$H) NMR of 18 (THF–d$_8$, 297K); x is assigned to Li[MeO–BEt$_3$] formed after the reduction. * denote THF–d$_8$. 

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Figure S34. $^1$H COSY NMR spectrum of complex 20 (CD$_2$Cl$_2$, 213K); * denotes side product.
Figure S35. $^1$H NMR spectrum of complex 21 (213K, CD$_2$Cl$_2$); * denotes residual protonated CD$_2$Cl$_2$, o denotes silicone grease, += unreacted 3a.

Figure S36. $^1$H NMR spectrum of complex 22a (253K, CD$_2$Cl$_2$); * denotes residual protonated CD$_2$Cl$_2$, o denotes silicone grease.
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Figure S41. Overlay of the hydride regions of the $^1$H NMR spectra of (a) (C=N^C)AuH, (b) 20, (c) 21, and (d) 22a (in CD$_2$Cl$_2$, 213 K).

2. Photoisomerization Experiments

Figure S42. Evolution of the aromatic region of the $^1$H NMR spectrum of 17 upon irradiation with UV light for 2 hours (room temperature, THF–d$_8$).
**Figure S43.** Evolution of the aromatic region of the $^1$H NMR spectrum of 12 upon irradiation with UV light for 2 hours (room temperature, THF–$d_8$).

**Figure S44.** A section of the $^1$H NOESY NMR spectrum of 17 after photoisomerization (297K, CD$_2$Cl$_2$).
3. X-Ray Crystallography

Complex 9: colorless crystal grown by slow evaporation under N\textsubscript{2} of a solution of the crude in diethyl ether. The crystal was mounted on a MiTeGen MicroMesh and fixed in a cold nitrogen stream at 100 K. Diffraction intensities were recorded at 100 K on a Rigaku 007HF equipped with Varimax confocal mirrors and an AFC11 goniometer and Rigaku, HyPix 6000 detector with Enhance (Cu) X-ray Source. Data collection, refinement and reduction was performed using the CrysAlisPro 1.171.39.9g (Rigaku OD, 2015) suite of programs and the absorption correction performed at this stage.\textsuperscript{[S1]} The structure was solved in P2\textsubscript{1}/n symmetry using SHELXT\textsuperscript{[S2]} and refined by full-matrix least-squares methods on F\textsuperscript{2} with SHELXL.\textsuperscript{[S3]} The asymmetric unit is formed by four gold molecules and one molecule of diethyl ether, what arises to the stoichiometry 9·1/4 Et\textsubscript{2}O.

Non-hydrogen atoms were refined with anisotropic thermal parameters. The thermal parameters of some carbon atoms were modeled using EADP and ISOR restrictions to avoid alerts related with too large U\textsubscript{eq} parameters compared with neighboring atoms. Hydrogen atoms, with the exception of the hydride atoms, were included in idealized positions. Several peaks of residual density were found in the final model but with no chemical meanings. No missed symmetry was reported by PLATON.\textsuperscript{[S4]} Computer programs used in this analysis were run through WinGX.\textsuperscript{[S5]} Scattering factors for neutral atoms were taken from reference.\textsuperscript{[S6]}

Complex 12: Colorless plates grown by slow evaporation at room temperature of a saturated solution of the pure crude material in a mixture ca. 50:50 CH\textsubscript{2}Cl\textsubscript{2}:toluene. The crystal was mounted on a MiTeGen MicroMesh and fixed in a cold nitrogen stream at 100 K. Diffraction intensities were recorded at 100 K on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector with Mo K\textalpha X-ray Source. Data collection, refinement and reduction was performed using the CrysAlisPro 1.171.39.9g (Rigaku OD, 2015) suite of programs and the absorption correction performed at this stage.\textsuperscript{[S1]} The structure was solved using SHELXT\textsuperscript{[S2]} and refined by full-matrix least-squares methods on F\textsuperscript{2} with SHELXL.\textsuperscript{[S3]} The crystal showed orthorhombic P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} symmetry with a Flack parameter of 0.421(3) indicative of a racemic crystal.\textsuperscript{[S7]}

Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions. No missed symmetry was reported by PLATON.\textsuperscript{[S4]} Computer programs used in this analysis were run through WinGX.\textsuperscript{[S5]} Scattering factors for neutral atoms were taken from reference.\textsuperscript{[S6]}

Complex 17: Colorless crystals grown by slow diffusion of petrol into a saturated solution of the complex in CH\textsubscript{2}Cl\textsubscript{2}. The crystal was mounted on a MiTeGen MicroMesh and fixed in a cold
nitrogen stream at 100 K. Diffraction intensities were recorded at 100 K on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector with Mo Kα X-ray Source. Data collection, refinement and reduction was performed using the CrysAlisPro 1.171.39.9g (Rigaku OD, 2015) suite of programs and the absorption correction performed at this stage.\textsuperscript{[S1]} The structure was solved in orthorhombic Pbca symmetry using SHELXT\textsuperscript{[S2]} and refined by full-matrix least-squares methods on F\textsuperscript{2} with SHELXL.\textsuperscript{[S3]} No missed symmetry was reported by PLATON.\textsuperscript{[S4]}

Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions. The thermal parameters of some carbon atoms and O2 were modelled using EADP and ISOR restrictions to avoid alerts related with too large U\textsubscript{eq} parameters compared with neighboring atoms. Several peaks of residual density were found in the final model but with no chemical meaning. The check-cif reveals two A alerts; the first one is generated by the residual electron density most likely due to a low quality of the crystal; the second A alert is generated by the presence of a short intermolecular H-H distance. However, this distance involves the NBu\textsubscript{4} groups and we observed positional disorder in the butyl groups that are most likely responsible of the problem. Our attempts to model this disorder gave poor convergence in the refinement. Computer programs used in this analysis were run through WinGX.\textsuperscript{[S5]} Scattering factors for neutral atoms were taken from reference \textsuperscript{[S6]}.

[(C^C)(AuPMe\textsubscript{3})\textsubscript{2}]\textsubscript{x}, Orange crystals identified as [(C^C)(AuPMe\textsubscript{3})\textsubscript{2}]\textsubscript{x} were found during the crystallization process of (C^C)AuH(PMe\textsubscript{3}). One crystal was mounted on a MiTeGen MicroMesh and fixed in a cold nitrogen stream at 100 K. Diffraction intensities were recorded at 100 K on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector with Rigaku (Cu) X-ray Source. Data collection, refinement and reduction was performed using the CrysAlisPro 1.171.39.9g (Rigaku OD, 2015) suite of programs and the absorption correction performed at this stage.\textsuperscript{[S1]} The structure was solved in monoclinic P2\textsubscript{1}/c symmetry using SHELXT\textsuperscript{[S2]} and refined by full-matrix least-squares methods on F\textsuperscript{2} with SHELXL.\textsuperscript{[S3]} No missed symmetry was reported by PLATON.\textsuperscript{[S4]} Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions. The check-cif reveals the presence of one A alert related with a low fraction of measured theta but the model is unambiguous. Several peaks of residual density were found in the final model but with no chemical meaning. Computer programs used in this analysis were run through WinGX.\textsuperscript{[S5]} Scattering factors for neutral atoms were taken from reference \textsuperscript{[S6]}.

[(C^C)Au(\mu-OH)]\textsubscript{2}: Yellow crystals of [(C^C)Au(\mu-OH)]\textsubscript{2} were grown by slow evaporation in air of a diethyl ether solution of (C^C)AuH(Ptol\textsubscript{3}). The crystal was mounted on a MiTeGen
MicroMesh and fixed in a cold nitrogen stream at 100 K. Diffraction intensities were recorded at 100 K on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector with Mo Kα X-ray Source. Data collection, refinement and reduction was performed using the CrysAlisPro 1.171.39.9g (Rigaku OD, 2015) suite of programs and the absorption correction performed at this stage. The structure was solved in monoclinic P2₁/c symmetry using SHELXT and refined by full-matrix least-squares methods on F² with SHELXL. No missed symmetry was reported by PLATON. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions. Computer programs used in this analysis were run through WinGX. Scattering factors for neutral atoms were taken from reference.

Figure S45. Electron density maps for each of the Au coordination planes of the 4 different molecules found in the asymmetric unit of complex 9 revealing the presence of negative regions indicative of the Au-H(hydride) bond.
Figure S46. (left) Molecular view of [(C^C)(AuPMe$_3$)$_2$]. Non-hydrogen atoms represented as ellipsoids with 50% probability level and hydrogens omitted for clarity. Selected bond distances (Å) and angles (°): Au1-C1 2.084(5), Au2-C8 2.076(4), Au1-P1 2.290(1), Au2-P2 2.293(1), Au1-Au2 2.9635(3), C1-Au1-P1 179.4(1), C8-Au2-P2 176.9(1), C1-Au1-Au2 76.3(1), C8-Au2-Au1 79.7(1), P1-Au1-Au2 103.22(3), P2-Au2-Au1 98.08(3), torsion C1-Au1-Au2-C8 71.1(2), P1-Au1-Au2-P2 73.00(5). (right) Part of the polymer chain of [(C^C)(AuPMe$_3$)$_2$], showing aurophilic interactions.

Figure S47. Molecular view of [(C^C)Au(μ-OH)$_2$]. Non-hydrogen atoms represented as ellipsoids with 50% probability level. Selected bond distances (Å) and angles (°): Au1-C1 2.002(3), Au1-C12 1.998(3), Au1-O1 2.113(2), Au1-O1’ 2.118(2), C1-Au1-C12 81.1(1), C1-Au1-O1 99.5(1), O1-Au1-O1’ 80.35(9), O1’-Au1-C12 99.1(1), C1-Au1-O1 178.4(1), C12-Au1-O1 178.8(1).
4. Computational Details

All structures were fully optimized at the PBE0 level of theory, including an atom-pairwise correction for dispersion forces via Grimme’s D3 model with Becke–Johnson (BJ) damping in the Turbomole program package. A quasirelativistic energy-consistent small-core pseudopotential (effective-core potential, ECP) in conjunction with Gaussian-type orbital valence sets of quality (8s7p6d1f)/[6s4p3d1f] and (11s10p8d2f)/[6s5p3d2f] was used for gold and iodine, respectively, whereas all other atoms have been treated with an all-electron def2-TZVP basis set. Frequency calculations at the same level of theory (PBE0-D3(BJ)/ECP/def2-TZVP) were performed to verify that all stationary points are minima with no imaginary frequency.

The two-component relativistic all-electron DFT calculations of the NMR nuclear shieldings and nuclear spin-spin J-couplings were performed using the Amsterdam Density Functional (ADF) program suite, employing the PBE0 exchange-correlation functional in conjunction with Slater-type orbital basis sets of triple-ζ doubly polarized (TZ2P) quality and an integration accuracy of 5.0. The ZORA calculations of NMR shieldings were done by using gauge-including atomic orbitals (GIAOs) and including the previously neglected terms from the exchange–correlation (XC) response kernel. The latter were shown to be particularly important for systems with large spin-orbit (SO) shielding contributions. For comparative purposes, the nuclear shieldings were also evaluated using four-component, fully relativistic DFT calculations within the matrix Dirac-Kohn-Sham (mDKS) framework employing the PBE0 hybrid functional as implemented in the ReSpect program package. The 4c-mDKS method combines GIAOs with restricted magnetically balanced (RMB) orbitals for the small component. For heavy atoms (Z > 18), the Dyall VDZ basis set was used, along with fully uncontracted IGLO-II basis sets for light ligand atoms. An integration grid of “Adaptive” size for the Lebedev angular points was applied and the following numbers of radial grid points were used for the indicated atoms: H, B, C, N, O, F: 60; P, S, Cl: 72; I: 80; Au: 96. All 4c-mDKS calculations were performed without fitting the electron and spin densities. In the case of complexes with pendant alkyl chains, the bulky tert-butyl groups were replaced by hydrogen atoms in NMR shielding calculations (these were, however, kept in structure optimizations).

The computed ¹H nuclear shieldings were converted to chemical shifts (δ, in ppm) relative to the shielding of tetramethylsilane (TMS), considering (C^N^C)AuH (complex A in Chart 1) as a secondary standard, with a hydride shift value of –6.51 ppm (measured in CD₂Cl₂).

Molecular orbital (MO) analyses of the NMR shifts and natural localized molecular orbital (NLMO) analyses were carried out using the NBO 5.0 module in the ADF code. The (two identical) shielding contributions of degenerate MOs or spinors were summed and are reported as...
contributions of one parental MO or spinor. When discussing the effect of a given occupied MO, the sum of the so-called U1 (first-order changes in MO coefficients) and S1 (first-order changes in overlap matrix) contributions reported by ADF are given, together with gauge contributions for the $\sigma^p$ and $\sigma^p+SO$ contributions.

Quantum theory of atoms-in-molecules (QTAIM)\cite{QTAIM} analyses were performed at the PBE0/def2-TZVP/ECP level, using the Multifwn\cite{Multifwn} program interfaced with Gaussian 09.\cite{Gaussian09} In particular, we focused on QTAIM delocalization indices (DI), as a measure of the Au–H bond covalency. The DI integrates the electron density in the bonding region between two atoms in question and is closely related to the covalent bond order, reduced by bond polarity (i.e., DI = 1.0 for a “pure” covalent single bond, but DI = 0.0 for a “pure” ionic bond).
5. Results of Quantum-Chemical Calculations

![Figure S4](image)

**Figure S48.** Comparison of selected Au–L bond distances (in Ångstroms) for X-ray (data in red) and DFT (PBE0-D3(BJ)/ECP/def2-TZVP) optimized (data in blue) structures of hitherto characterized gold hydride complexes. X-ray structural data for (NHC-IPr)AuH, (C^N^C)AuH (complex A) and (C^C^N)AuH (complex B) were taken from refs. [S33], [S28] and [S34], respectively. Complex 9 was characterized in this work.

![Figure S49](image)

**Figure S49.** Computed and experimental $^{13}$C NMR shifts (in ppm vs. TMS) for Au-bound carbon atoms in selected gold(III) hydride complexes. $^{2c}$-ZORA-SO/PBE0-XC/TZ2P results (cf. Computational details).
Figure S50. Comparison of experimental and calculated $^1$H NMR hydride shifts (in ppm vs. TMS) for gold hydride complexes.

$$\delta (^1\text{H, expt.}) = 0.971 \, \delta (^1\text{H, calcd.}) + 0.337$$

RMSD = 0.39 ppm; $R^2 = 0.992$
Table S1. DFT optimized Au–H bond-lengths (in Ångstroms), NPA atomic charges, NLMO composition of Au-H bonds and computed \(^1\)H NMR hydride shieldings (in ppm) decomposed into diamagnetic ($\sigma^d$), paramagnetic ($\sigma^p$) and spin-orbit ($\sigma^{SO}$) contributions for a series of linear HAuL\(^q\) complexes.

| L    | d(Au-H) [Å] | NPA charges | NLMO analysis of Au-H bonding | \(^1\)H NMR hydride shieldings (σ) and shifts (δ) (in ppm) |
|------|-------------|-------------|-------------------------------|-----------------------------------------------------------|
|      | q(Au)       | q(H)        | %Au in Au-H                  | %Au(5d) %Au.%Au(5d) | $\sigma^d$ | $\sigma^p$ | $\sigma^{SO}$ | $\sigma^{total}$ | $\delta(^1\text{H})$ |
| OH\(_2\) | 1.546       | 0.110       | -0.184                        | 42.7 19.3 8.2 | 31.2 | 3.2 | 10.2 | 44.6 | -14.2 |
| F\(^-\) | 1.569       | 0.206       | -0.374                        | 34.5 21.2 7.3 | 33.0 | 3.5 | 7.6 | 44.1 | -13.7 |
| ONO\(_2\)^- | 1.566   | 0.197       | -0.330                        | 39.4 19.4 7.6 | 32.4 | 2.4 | 6.6 | 41.4 | -11.0 |
| py | 1.568       | 0.165       | -0.258                        | 39.9 19.1 7.6 | 31.8 | 1.6 | 5.1 | 38.5 | -8.1 |
| NH\(_3\) | 1.566       | 0.120       | -0.248                        | 40.6 19.8 8.1 | 31.3 | 2.2 | 4.6 | 38.1 | -7.7 |
| NCS\(^-\) | 1.581       | 0.222       | -0.360                        | 35.3 18.7 6.6 | 32.5 | 2.6 | 2.1 | 37.3 | -6.9 |
| Cl\(^-\) | 1.587       | 0.147       | -0.380                        | 35.5 16.3 5.8 | 32.4 | 1.1 | 2.7 | 36.2 | -5.8 |
| SCN\(^-\) | 1.599       | 0.127       | -0.367                        | 36.7 15.4 5.6 | 31.8 | 0.4 | -0.4 | 31.8 | -1.4 |
| SH\(_2\) | 1.584       | 0.102       | -0.265                        | 41.1 15.6 6.4 | 31.1 | 0.1 | 0.3 | 31.5 | -1.1 |
| I\(^-\) | 1.598       | 0.098       | -0.375                        | 36.7 14.5 5.3 | 31.8 | -0.4 | -0.8 | 30.6 | -0.2 |
| L      | \(d\text{(Au-H)}\) | NPA charges | NLMO analysis of Au-H bonding | \(^1\text{H NMR hydride shieldings (σ) and shifts (δ) (in ppm)}\) |
|--------|-------------------|-------------|-----------------------------|-------------------------------------------------|
|        | \([\text{Å}]\)  | q(Au)       | q(H)                        | \%Au in Au-H | \%Au(5d) | \%Au.%Au(5d) | \(\sigma^d\) | \(\sigma^p\) | \(\sigma^{SO}\) | \(\sigma^{total}\) | \(\delta(\text{^1H})\) |
| CN\(^-\) | 1.623             | 0.164       | -0.447                      | 33.4         | 17.7      | 5.9          | 32.6         | 0.0         | -4.9            | 27.7            | 2.7       |
| C\(_6\)H\(_5\)- | 1.638             | 0.169       | -0.466                      | 32.9         | 18.0      | 5.9          | 32.0         | 0.0         | -4.2            | 27.7            | 2.7       |
| C\(_6\)F\(_5\)- | 1.621             | 0.178       | -0.422                      | 34.1         | 17.3      | 5.9          | 31.6         | 0.2         | -4.2            | 27.6            | 2.8       |
| CH\(_3\)- | 1.645             | 0.135       | -0.486                      | 32.6         | 17.6      | 5.7          | 31.8         | 0.2         | -5.2            | 26.7            | 3.7       |
| CO     | 1.607             | 0.257       | -0.329                      | 38.6         | 16.8      | 6.5          | 30.9         | 0.2         | -7.0            | 24.1            | 6.3       |
| H\(^+\) | 1.660             | 0.016       | -0.508                      | 33.0         | 15.3      | 5.0          | 31.3         | -0.6        | -7.3            | 23.4            | 7.0       |
| PH\(_3\) | 1.612             | 0.141       | -0.312                      | 40.0         | 13.6      | 5.5          | 30.7         | -1.3        | -6.6            | 22.8            | 7.6       |
| SiH\(_3\)\(^-\) | 1.667            | 0.058       | -0.487                      | 34.2         | 12.1      | 4.1          | 30.8         | -1.7        | -11.1           | 18.0             | 12.4      |

\(\Delta^\text{b}\) 0.121 \hspace{1cm} 0.324

\(\Delta\) \(^a\) Chemical shieldings computed at the 2c-ZORA(SO)/PBE0-XC/TZ2P level (cf. Computational details).  \(\Delta\) \(^b\) The difference between maximal and minimal value of the series.
Table S2. DFT optimized Au–H bond-lengths (in Ångstroms). NPA atomic charges. NLMO composition of Au–H bonds and computed $^1\text{H}$ NMR hydride shieldings (in ppm) decomposed into diamagnetic ($\sigma^d$), paramagnetic ($\sigma^p$) and spin-orbit ($\sigma^{SO}$) contributions for a series of trans-[HAu$^{\text{III}}$(C$_6$H$_5$)$_2$L] complexes $^a$

| L     | d(Au–H) [Å] | DI(Au–H) | q(Au) | q(H) | %Au | %Au(5d) | %Au.%Au(5d) | $^1\text{H}$ NMR shieldings/shifts [ppm] |
|-------|-------------|----------|-------|------|-----|---------|-------------|-----------------------------------------|
| OH$_2$ | 1.521       | 0.958    | 0.869 | 0.035 | 54.7 | 70.0    | 38.3        | $\sigma^d$ 1.8 $\sigma^p$ 14.6 $\sigma^{SO}$ -16.1 $\delta(1^H)$ |
| ONO$_2^-$ | 1.530     | 0.956    | 0.936 | -0.072 | 50.5 | 71.5    | 36.1        | $\sigma^d$ 1.7 $\sigma^p$ 11.6 $\sigma^{SO}$ -14.3 |
| F$^-$  | 1.534       | 0.957    | 0.975 | -0.124 | 48.7 | 72.4    | 35.3        | $\sigma^d$ 1.6 $\sigma^p$ 12.1 $\sigma^{SO}$ -14.0 |
| NCS$^-$ | 1.540      | 0.957    | 0.944 | -0.095 | 49.6 | 71.9    | 35.7        | $\sigma^d$ 1.1 $\sigma^p$ 10.1 $\sigma^{SO}$ -12.2 |
| py    | 1.539       | 0.945    | 0.890 | -0.019 | 51.2 | 71.4    | 36.5        | $\sigma^d$ 1.3 $\sigma^p$ 10.3 $\sigma^{SO}$ -11.6 |
| NH$_3$ | 1.540       | 0.949    | 0.866 | -0.024 | 53.2 | 69.8    | 37.1        | $\sigma^d$ 1.4 $\sigma^p$ 10.0 $\sigma^{SO}$ -10.8 |
| Cl$^-$ | 1.550       | 0.929    | 0.870 | -0.113 | 51.0 | 70.1    | 35.7        | $\sigma^d$ 0.1 $\sigma^p$ 8.8 $\sigma^{SO}$ -9.2 |
| SH$_2$ | 1.547       | 0.928    | 0.796 | -0.015 | 52.2 | 68.1    | 35.5        | $\sigma^d$ -0.3 $\sigma^p$ 8.7 $\sigma^{SO}$ -7.8 |
| I$^-$  | 1.563       | 0.920    | 0.808 | -0.111 | 52.7 | 68.2    | 35.9        | $\sigma^d$ -1.0 $\sigma^p$ 8.6 $\sigma^{SO}$ -7.3 |
| SCN$^-$ | 1.565    | 0.914    | 0.836 | -0.116 | 51.9 | 69.4    | 36.0        | $\sigma^d$ -0.6 $\sigma^p$ 6.6 $\sigma^{SO}$ -6.1 |
| L            | d(Au–H) [Å] | DI(Au–H) | q(Au)  | q(H)  | %Au   | %Au(5d) | %Au.%Au(5d) | \(\delta^1\)H NMR shieldings/shifts [ppm] |
|-------------|-------------|----------|--------|-------|-------|---------|-------------|------------------------------------------|
|             |             |          |        |       |       |         |             | \(\sigma^d\) | \(\sigma^o\) | \(\sigma^{SO}\) | \(\delta^1\)H |
| CN⁻         | 1.576       | 0.917    | 0.900  | -0.202| 48.0  | 70.3    | 33.7        | 32.0         | -1.4          | 4.0           | -4.1           |
| CO          | 1.559       | 0.919    | 0.853  | -0.062| 53.1  | 69.4    | 36.8        | 30.0         | -0.6          | 4.7           | -3.7           |
| C₆F₅⁻       | 1.590       | 0.917    | 0.901  | -0.195| 48.2  | 69.7    | 33.6        | 30.1         | 0.0           | 3.2           | -2.8           |
| PH₃         | 1.571       | 0.908    | 0.786  | -0.073| 53.1  | 67.2    | 35.7        | 29.5         | -1.2          | 3.5           | -1.3           |
| C₆H₅⁻       | 1.613       | 0.894    | 0.916  | -0.262| 46.2  | 69.6    | 32.2        | 30.4         | -0.4          | 1.5           | -1.0           |
| CH₃⁻        | 1.625       | 0.890    | 0.901  | -0.291| 46.0  | 68.5    | 31.5        | 29.9         | -0.4          | -0.8          | 1.7            |
| H⁻          | 1.634       | 0.876    | 0.802  | -0.343| 46.2  | 67.4    | 31.1        | 30.6         | -1.8          | -1.5          | 3.2            |
| SiH₃⁻       | 1.646       | 0.873    | 0.765  | -0.311| 46.5  | 64.9    | 30.2        | 28.8         | -1.1          | -3.6          | 6.3            |

| \(\Delta^b\) | 0.125       | 0.086    | 0.378  |       | 3.2   | 3.6     | 18.2        | 22.5         |

\(^a\) Chemical shieldings computed at the 2c-ZORA(SO)/PBE0-XC/TZ2P level (cf. Computational details). \(^b\) The difference between maximal and minimal value of the series.
Table S3. DFT optimized Au–H bond-lengths (in Ångstroms). NPA atomic charges. NLMO composition of Au–H bonds and computed $^1$H NMR hydride shieldings decomposed into diamagnetic ($\sigma^d$), paramagnetic ($\sigma^p$) and spin-orbit ($\sigma^{SO}$) contributions for a series of cis-[HAu$^{III}$(bph)L]$^q$ complexes $^a$

| L     | d(Au–H) [Å] | QTAIM | NPA charges | NLMO analysis of Au–H bonding | $^1$H NMR shieldings/shifts [ppm] |
|-------|-------------|-------|-------------|-------------------------------|-----------------------------------|
|       |             | DI(Au–H) | q(Au) | q(H) | %Au | %Au(5d) | %Au.%Au(5d) | $\sigma^d$ | $\sigma^p$ | $\sigma^{SO}$ | $\delta(^1$H) |
| H$^+$ | 1.619       | 0.916  | 0.793 | -0.314 | 44.3 | 68.4 | 30.3 | 30.3 | 0.3 | 0.5 | -0.7 |
| SCN$^-$ | 1.621     | 0.911  | 0.885 | -0.296 | 44.4 | 70.7 | 31.4 | 31.7 | -1.1 | 0.4 | -0.6 |
| CH$_3$ | 1.617       | 0.909  | 0.918 | -0.302 | 44.6 | 69.2 | 30.9 | 30.5 | -0.3 | 0.4 | -0.2 |
| SiH$_3$ | 1.618     | 0.910  | 0.760 | -0.273 | 46.6 | 73.1 | 34.0 | 30.9 | -0.5 | -0.1 | 0.1 |
| I$^-$ | 1.615       | 0.903  | 0.847 | -0.286 | 45.5 | 69.5 | 31.6 | 30.7 | -0.7 | 0.2 | 0.2 |
| C$_6$F$_5$ | 1.619  | 0.901  | 0.942 | -0.286 | 45.2 | 68.8 | 31.1 | 29.8 | 0.1 | 0.4 | 0.3 |
| CN$^-$ | 1.619       | 0.900  | 0.927 | -0.281 | 45.4 | 68.9 | 31.3 | 30.6 | -0.6 | 0.0 | 0.4 |
| NCS$^-$ | 1.622     | 0.896  | 1.016 | -0.299 | 44.8 | 68.2 | 30.5 | 29.9 | 0.1 | -0.1 | 0.6 |
| C$_6$H$_5$ | 1.618  | 0.906  | 0.934 | -0.288 | 45.0 | 68.9 | 31.0 | 30.2 | -0.5 | 0.1 | 0.7 |
| Cl$^-$ | 1.619       | 0.900  | 0.929 | -0.304 | 44.6 | 68.0 | 30.3 | 30.8 | -0.9 | -0.3 | 0.8 |
| L     | \(d(\text{Au–H})\) [Å] | QTAIM | \(q(\text{Au})\) | \(q(\text{H})\) | \(\%\text{Au}\) | \(\%\text{Au}(5\text{d})\) | \(\%\text{Au.}\%\text{Au}(5\text{d})\) | \(\delta^1\text{H}\) NMR shieldings/shifts [ppm] |
|-------|------------------|-------|----------------|-------------|----------------|----------------|----------------|----------------|
| \(\text{ONO}_2^-\) | 1.624 | 0.897 | 1.012 | -0.316 | 43.8 | 67.5 | 29.6 | 30.2 | -0.4 | -0.5 | 1.1 |
| \(\text{F}^-\) | 1.627 | 0.904 | 1.057 | -0.337 | 42.9 | 65.9 | 28.3 | 30.3 | -0.5 | -0.5 | 1.1 |
| \(\text{PH}_3\) | 1.628 | 0.882 | 0.834 | -0.285 | 45.4 | 70.0 | 31.8 | 30.2 | -0.6 | -1.2 | 2.1 |
| \(\text{SH}_2\) | 1.627 | 0.893 | 0.850 | -0.307 | 44.9 | 67.7 | 30.4 | 30.5 | -0.7 | -1.5 | 2.2 |
| \(\text{NH}_3\) | 1.628 | 0.901 | 0.933 | -0.324 | 43.8 | 66.4 | 29.1 | 29.8 | -0.1 | -2.0 | 2.7 |
| \(\text{py}\) | 1.626 | 0.896 | 0.955 | -0.310 | 44.4 | 67.3 | 29.9 | 30.2 | -1.0 | -2.3 | 3.6 |
| \(\text{CO}\) | 1.627 | 0.881 | 0.927 | -0.259 | 46.8 | 67.8 | 31.7 | 29.5 | -0.4 | -2.4 | 3.8 |
| \(\text{OH}_2\) | 1.633 | 0.874 | 0.937 | -0.347 | 42.8 | 65.0 | 27.8 | 30.0 | -0.4 | -4.2 | 5.0 |

| \(\Delta\) \(^b\) | 0.019 | 0.042 | 0.088 | | 2.2 | 1.3 | 4.7 | 5.6 |

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\(^a\) Chemical shieldings computed at the 2c-ZORA(SO)/PBE0-XC/TZ2P level (cf. Computational details). \(^b\) The difference between maximal and minimal value of the series.
Table S4. DFT optimized Au–H bond-lengths (in Ångstroms). NPA atomic charges. NLMO composition of Au–H bonds and computed $^1$H NMR hydride shieldings decomposed into diamagnetic ($\sigma^d$), paramagnetic ($\sigma^p$) and spin-orbit ($\sigma^{SO}$) contributions for a series of cis-[HAu$^m$(ppy)L]$^{n+1}$ complexes.

| L     | $d$(Au–H) | QTAIM | NPA charges | NLMO analysis of Au-H bonding | $^1$H NMR shieldings/shifts [ppm] |
|-------|-----------|-------|-------------|-----------------------------|-----------------------------------|
|       | [Å]       |       | q(Au)       | q(H)                        | %Au    | %Au(5d) | %Au.%Au(5d) | $\sigma^d$ | $\sigma^p$ | $\sigma^{SO}$ | $\delta(^1$H) |
| ONO$_2^-$ | 1.547     | 0.955 | 1.013       | -0.072                      | 50.9   | 70.2    | 35.7        | 30.5      | 0.9       | 11.1            | -12.0          |
| NCS$^-$ | 1.545     | 0.952 | 1.021       | -0.049                      | 52.3   | 71.1    | 37.1        | 30.2      | 1.3       | 10.8            | -11.9          |
| F$^-$  | 1.547     | 0.957 | 1.054       | -0.085                      | 50.3   | 68.6    | 34.5        | 30.4      | 0.9       | 10.8            | -11.7          |
| SCN$^-$ | 1.543     | 0.960 | 0.863       | -0.036                      | 52.7   | 70.6    | 37.2        | 31.1      | 0.1       | 10.4            | -11.1          |
| Cl$^-$ | 1.543     | 0.942 | 0.916       | -0.054                      | 51.8   | 70.3    | 36.4        | 31.2      | 0.2       | 10.2            | -11.1          |
| I$^-$  | 1.543     | 0.941 | 0.916       | -0.054                      | 52.0   | 70.7    | 36.8        | 31.2      | 0.2       | 10.2            | -11.1          |
| H$^+$  | 1.544     | 0.953 | 0.782       | -0.069                      | 51.4   | 70.4    | 36.2        | 30.5      | 1.2       | 9.7             | -10.9          |
| CN$^-$ | 1.546     | 0.944 | 0.928       | -0.043                      | 52.1   | 70.2    | 36.6        | 30.8      | 0.5       | 9.8             | -10.6          |
| C$_6$F$_5^-$ | 1.544 | 0.958 | 0.935       | -0.047                      | 52.0   | 71.1    | 36.9        | 30.1      | 0.9       | 9.9             | -10.4          |
| CH$_3^-$ | 1.542     | 0.954 | 0.908       | -0.065                      | 51.3   | 70.4    | 36.1        | 30.6      | 0.7       | 9.0             | -9.9           |
| L        | d(Au–H) [Å] | QTAIM DI(Au–H) | NPA charges q(Au) | q(H) | %Au | %Au(5d) | %Au.%Au(5d) | $\sigma^d$ | $\sigma^p$ | $\sigma^{SO}$ | $\delta^{(1)H}$ |
|----------|-------------|----------------|-------------------|------|-----|---------|-------------|------------|------------|--------------|----------------|
| C₆H₅⁻   | 1.545       | 0.953          | 0.923             | -0.054 | 52.1 | 71.4    | 37.2         | 30.4       | 0.5        | 9.4          | -9.9          |
| SiH₃⁻    | 1.548       | 0.950          | 0.748             | -0.058 | 51.7 | 73.8    | 38.1         | 31.4       | 0.1        | 8.7          | -9.7          |
| NH₃      | 1.552       | 0.943          | 0.938             | -0.078 | 50.9 | 69.9    | 35.5         | 30.0       | 1.0        | 8.9          | -9.5          |
| py       | 1.551       | 0.942          | 0.957             | -0.062 | 51.6 | 70.3    | 36.3         | 30.2       | 0.3        | 9.3          | -9.3          |
| OH₂      | 1.556       | 0.946          | 0.936             | -0.093 | 50.4 | 69.3    | 34.9         | 30.0       | 0.9        | 8.5          | -9.0          |
| PH₃      | 1.556       | 0.927          | 0.843             | -0.062 | 51.4 | 72.1    | 37.1         | 30.6       | 0.2        | 8.1          | -8.5          |
| CO       | 1.560       | 0.918          | 0.918             | -0.048 | 51.9 | 70.7    | 36.7         | 29.5       | 0.4        | 8.1          | -7.6          |
| SH₂      | 1.556       | 0.920          | 0.841             | -0.064 | 52.2 | 69.2    | 36.1         | 30.3       | 0.5        | 6.8          | -7.1          |

$\Delta^b$ \hspace{1cm} 0.017 \hspace{1cm} 0.042 \hspace{1cm} 0.056 \hspace{1cm} 1.9 \hspace{1cm} 1.3 \hspace{1cm} 4.4 \hspace{1cm} 5.0

$^a$ Chemical shieldings computed at the 2c-ZORA(SO)/PBE0-XC/TZ2P level (cf. Computational details). $^b$ The difference between maximal and minimal value of the series.
Figure S51. Dependence of the computed $^1$H hydride shifts ($\delta_{\text{total}}$) and spin-orbit-induced shift contributions ($\delta_{\text{SO}}$) on the trans ligand L in the HAuL$_4$ series (2c-ZORA(SO)/PBE0-XC/TZ2P results; cf. Table S1 for numerical data).
**Figure S52.** Energies of the highest occupied σ(Au-H)-type MOs (indicated by blue lines) and Au(dπ) orbitals (indicated by orange lines) in trans-[HAu(C₆H₅)L₂] series (L = NH₃, PH₃, CH₃⁻, SiH₃⁻). SR-ZORA/PBE0/TZ2P results.
Figure S53. Energies of the highest occupied \( \sigma(\text{Au-H}) \)-type MOs (indicated by blue lines) and Au(\( \text{d}_\pi \)) orbitals (indicated by orange lines) in *cis*-\([\text{HAu(bph)}L]\)\(^8\) series (L = NH\(_3\), PH\(_3\), CH\(_3\), SiH\(_3\)). SR-ZORA/PBE0/TZ2P results.
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