Supporting Information

Proximity Enforced Agostic Interactions Involving Closed-Shell Coinage Metal Ions

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**References**
Experimental Section

General. Reagents were obtained commercially (Sigma-Aldrich, Germany) and were used as received. Dry solvents were collected from a SPS800 mBraun solvent system. 5-bromo-6-diphenylphosphinoacenaphthene was prepared according to literature procedures.¹ ¹H-, ¹³C-, ²⁹Si- and ³¹P-NMR spectra were recorded at r.t. using a Bruker Avance-360 spectrometer and are referenced to tetramethylsilane (¹H, ¹³C, ²⁹Si) and phosphoric acid (85% in water) (³¹P). Chemical shifts are reported in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). Electron impact mass spectroscopy (HREIMS) was carried out using a Finnigan MAT 95. The ESI MS spectra were obtained with a Bruker Esquire-LC MS. Acetonitrile solutions (c = 1·10⁻⁶ mol l⁻¹) were injected directly into the spectrometer at a flow rate of 3 µl min⁻¹. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 5 l min⁻¹ and a pressure of 5 psi, respectively. Pressure in the mass analyzer region was usually about 1·10⁻⁵ mbar. Spectra were collected for one minute and averaged. The nozzle-skimmer voltage was adjusted individually for each measurement. Details of IR and vibrational dynamics measurements as well as X-ray and neutron diffraction experiments are given below in their respective chapters.

Synthesis of Bis(5-diphenylphosphinacenaphth-6-yl)methylsilane (1). To a suspension of 5-bromo-6-diphenylphosphinoacenaphthene (5.00 g, 12.0 mmol, 2.00 eq.) and diethyl ether (50 mL), N,N,N',N'-tetramethylethylenediamine (1.39 g, 12.0 mmol, 2.00 eq.) and n-buthyllithium (12.0 mmol, 2.5 M in n-hexane, 2.00 eq.) were added at –78°C and stirred for 1 h. The suspension was allowed to warm to r.t. and stirred for further 30 min. The suspension was cooled to –78°C and dichloromethylsilane (0.69 g, 6.00 mmol, 1.00 eq.) was added and the reaction mixture was allowed to warm to r.t. overnight. Volatile parts were removed under reduced pressure and dichloromethane (50 mL) was added to the residue. After aqueous...
workup the solvent was removed by rotary evaporation and the slightly brownish solid residue was washed with $n$-hexane and recrystallized from tetrahydrofuran affording bis(5-diphenylphosphinacenaphth-6-yl)methylsilane (1) as colorless crystals suitable for neutron diffraction measurements (2.59 g, 3.60 mmol, 60%, m.p. > 230°C).

$^1$H NMR (360.3 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 7.74 (m, 2H, H-3 or H-4), 7.35 (d, $^3$J$^\(1\)H-$^\(1\)$H) = 6.9 Hz, 1H, H-7 or H-8), 7.30 (d, $^3$J$^\(1\)$H-$^\(1\)$H = 6.7 Hz, 1H, H-7 or H-8), 7.26-7.18 (m, 8H), 7.12 – 6.95 (m, 12H), 7.06 – 7.00 (m, 1H, SiH), 6.79 (m, 2H, H-4 orH-3), 3.31 (m, 8H, H-1,2), 1.04 (dd, $^3$J$^\(1\)$H-$^\(1\)$H = 3.1 Hz, $^3$J$^\(31\)$P-$^\(1\)$H) = 1.6 Hz, 3H, CH$_3$).

$^{13}$C{$^1$H} NMR (90.6 MHz, CD$_2$Cl$_2$): $\delta$ = 150.2 (s, qC, C$_c$ or C$_d$), 148.7 (s, qC, C$_d$ or C$_e$), 141.0 (d, $^3$J$^{31}$P-$^{13}$C) = 2.0 Hz, qC, C$_a$ or C$_b$), 139.6 (d, $^5$J$^{31}$P-$^{13}$C) = 16.2 Hz, CH, C$_7$), 139.4 (s, CH, C$_4$), 133.3 (d, $^3$J$^{31}$P-$^{13}$C) = 17.7 Hz, qC, C$_5$ or C$_6$), 133.3 (d, $^3$J$^{31}$P-$^{13}$C) = 18.8 Hz, CH, C$_o$), 131.7 (d, $^3$J$^{31}$P-$^{13}$C) = 16.9 Hz, qC, C$_5$ or C$_6$), 128.6 (d, $^3$J$^{31}$P-$^{13}$C) = 5.9 Hz, CH, C$_m$), 128.1 (s, CH, C$_p$), 128.0 (d, $^1$J$^{31}$P-$^{13}$C) = 19.7 Hz, qC, C$_o$), 120.0 (s, CH, C$_3$ or C$_8$), 119.7 (s, CH, 8 or C$_3$), 30.5(s, CH$_2$, C$_1$ or C$_2$), 30.4 (s, CH$_2$, C$_2$ or C$_1$), 1.3 (t, $^3$J$^{31}$P-$^{13}$C) 13.4 Hz, CH$_3$). $^{29}$Si NMR (71.6 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = –23.3 (d, $^1$J$^{1}$H-$^{29}$Si) = 228.6 Hz).

$^{29}$Si{$^1$H} NMR (71.6 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = –23.8 (t, $^1$J$^{29}$P-$^{29}$Si) = 21.3 Hz). $^{31}$P NMR (145.9 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = –17.9 - (–18.1) (m). $^{31}$P{$^1$H} NMR (145.9 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = –18.2 (s). HREIMS: calcd for C$_{49}$H$_{39}$P$_2$Si [M-H]$^+$, 717.229632; found, 717.22785.

**Synthesis of Bis(5-diphenylphosphinacenaphth-6-yl)methylsilane-copper(I)chloride (1∙CuCl).** Copper(I) chloride (0.14 g, 1.39 mmol, 1.00 eq.) was added to a solution of 1 (1.00 g, 1.39 mmol, 1.00 eq.) in dichloromethane (10 mL) and the reaction mixture was stirred under refluxed for 4 h. The solvent was removed by rotary evaporation and the slightly brownish residue was washed with diethyl ether and $n$-hexane. The residue was recrystallized from dichloromethane/acetone yielding bis(5-diphenylphosphinacenaphth-6-yl)methylsilane-
copper(I) chloride (1·CuCl) as colourless crystals suitable for neutron diffraction measurements (0.75 g, 0.92 mmol, 66%, m.p. 180°C (dec.)).

$^1$H NMR (360.3 MHz, CDCl$_3$): $\delta$ [ppm] = 7.75 (m, 5H), 7.51 - 7.28 (m, 9H), 7.13 – 6.91 (m, 15H), 7.00 (t, $J$($^{31}$P-$^1$H) = 19.3 Hz, 1H, SiH), 3.27 (m, 8H, H-1,2), –0.25 (s, 3H, CH$_3$).

$^{13}$C($^1$H) NMR (90.6 MHz, CDCl$_3$): $\delta$ [ppm] = 150.8 (s, qC, C$_c$ or C$_d$), 149.9 (s, qC, C$_d$ or C$_c$), 140.3 (m), 140.1 - 139.8 (m), 138.8 (s), 135.1 – 134.5 (m), 132.2 (m), 132.2 (m), 129.8 (s), 129.2 - 128.3 (m), 128.1 - 126.9 (m), 125.0 - 124.0 (m), 119.5 (s, C$_3$ or C$_8$), 30.0 (s, CH$_2$, C$_1$ or C$_2$), 29.8 (s, CH$_2$, C$_2$ or C$_1$), 2.3 (s, CH$_3$). $^{29}$Si NMR (71.6 MHz, CDCl$_3$): $\delta$ [ppm] = –29.0 (d, $J$($^{1}$H-$^{29}$Si) = 161.6 Hz). $^{29}$Si($^1$H) NMR (71.6 MHz, CDCl$_3$): $\delta$ [ppm] = –29.0 (t, $J$($^{31}$P-$^{29}$Si) = 5.0 Hz).

$^{31}$P NMR (145.9 MHz, CDCl$_3$): $\delta$ [ppm] = –7.1 - (–11.9) (m).

$^{31}$P($^1$H) NMR (145.9 MHz, CDCl$_3$): $\delta$ [ppm] = -10.1 (s). ESI MS (CH$_2$Cl$_2$/MeCN 1:10, positive mode): m/z 781.4 (C$_{49}$H$_{40}$P$_2$SiCu) for [M-Cl]$^+$. 

Synthesis of Bis(5-diphenylphosphinacenaphth-6-yl)methylsilane-silver(I) chloride (1·AgCl). Silver(I) chloride (0.20 g, 1.39 mmol, 1.00 eq.) was added to a solution of 1 (1.00 g, 1.39 mmol, 1.00 eq.) in dichloromethane (10 mL), and the reaction mixture was stirred under reflux with the exclusion of light for 4 h. The solvent was removed by rotary evaporation and the slightly grayish solid was washed with diethyl ether and n-hexane. The residue was recrystallized from dichloromethane/n-hexane, affording bis(5-diphenylphosphinoacenaphth-6-yl)methylsilane-silver(I) chloride (1·AgCl) as colorless crystals suitable for neutron diffraction measurements (1.08 g, 1.25 mmol, 90%, m.p. 175°C (dec.)).

$^1$H NMR (360.3 MHz, CDCl$_3$): $\delta$ [ppm] = 7.86 (tdq, $J$($^{31}$P-$^1$H) = 14.9 Hz, $J$($^{109/107}$Ag-$^1$H) = 6.8 Hz, $J$($^1$H-$^1$H) = 2.7 Hz, 1H, SiH), 7.57 (m, 4H), 7.47 (d, $^3$J($^1$H-$^1$H) = 6.9 Hz, 2H, H-7 or H-8), 7.26 (m, 6H), 7.21 – 7.12 (m, 6H), 7.07 – 6.97 (m, 10H), 3.28 (m, 8H, H-1,2), -0.42 (d,
$^3J(1^H-1^H) = 1.9$ Hz, $3H, CH_3$). $^{13}C(1^H)\text{NMR (90.6 MHz, CDCl}_3\text{): } \delta [\text{ppm}] = 151.2$ (s, qC, Cc or Cd), 150.1 (s, qC, Cc or Cd), 140.3 (m), 140.0 (s), 139.6 (s), 138.2 (m), 135.6 (m), 134.8 (m), 133.4 (m), 132.2 (m), 130.0 (m), 129.0 (m), 128.6 (m), 128.1 (m), 125.3 (m), 119.7 (s, CH, C3 or C8), 119.5 (s, CH, C3 or C8), 29.9 (s, CH2, C1 or C2), 29.7 (s, CH2, C1 or C2), 2.5 (s, CH3). $^{29}Si\text{NMR (71.6 MHz, CDCl}_3\text{): } \delta [\text{ppm}] = -20.6$ (d, $^1J(1^H-^{29}Si) = 185.8$ Hz). $^{29}Si(1^H)\text{NMR (71.6 MHz, CDCl}_3\text{): } \delta [\text{ppm}] = -20.4$ (m). $^{31}P\text{NMR (145.9 MHz, CDCl}_3\text{): } \delta [\text{ppm}] = -0.8$ (d, $J(^{109/107}Ag-^{31}P) = 387.0$ Hz). $^{31}P(1^H)\text{NMR (145.9 MHz, CDCl}_3\text{): } \delta [\text{ppm}] = -0.8$ (d, $J(^{109/107}Ag-^{31}P) = 411.1/356.3$ Hz). ESI MS (CH$_2$Cl$_2$/MeCN 1:10, positive mode): m/z 827.4 ($C_{49}H_{46}P_2SiAg$) for [M-Cl]$^+$. 
NMR Spectra of Bis(5-diphenylphosphinacenaphth-6-yl)methylsilane (1):

Figure S1. $^1$H-NMR-Spectrum of 1 (CD$_2$Cl$_2$, 360.3 MHz)

Figure S2. $^{13}$C($^1$H)-NMR-Spectrum of 1 (CD$_2$Cl$_2$, 71.6 MHz)
Figure S3. $^{29}$Si-NMR-Spectrum of 1 (CD$_2$Cl$_2$, 71.6 MHz)

Figure S4. $^{29}$Si$\{^1$H$\}$-NMR-Spectrum of 1 (CD$_2$Cl$_2$, 71.6 MHz)
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NMR Spectra of Bis(5-diphenylphosphinacenaphth-6-yl)methylsilane-copper(I)chloride (1·CuCl):

**Figure S8.** $^1$H-NMR-Spectrum of 1·CuCl (CDCl$_3$, 360.3 MHz)

**Figure S9.** $^{13}$C{$^1$H}-NMR-Spectrum of 1·CuCl (CDCl$_3$, 90.6 MHz)
Figure S10. $^{29}\text{Si}$-NMR-Spectrum of 1-CuCl (CDCl$_3$, 71.6 MHz)

Figure S11. $^{29}\text{Si}^{[1]}\text{H}$-NMR-Spectrum of 1-CuCl (DCCl$_3$, 71.6 MHz)
Figure S12. $^{31}$P-NMR-Spectrum of 1·CuCl (CDCl$_3$, 145.9 MHz)

Figure S13. $^{31}$P{$^{1}$H}$\cdot$NMR-Spectrum of 1·CuCl (CDCl$_3$, 145.9 MHz)
Figure S14. $^1$H-$^{29}$Si-HSQC NMR-Spectrum of 1-CuCl (CDCl$_3$).
NMR Spectra of Bis(5-diphenylphosphinacenaphth-6-yl)methylsilane-silver(I)chloride (1∙AgCl):

Figure S15. $^1$H-NMR-Spectrum of 1∙AgCl (CDCl$_3$, 360.3 MHz)

Figure S16. $^{13}$C{${^1}$H}-NMR-Spectrum of 1∙AgCl (CDCl$_3$, 90.6 MHz)
Figure S17. $^{29}$Si-NMR-Spectrum of 1$\cdot$AgCl (CDCl$_3$, 71.6 MHz)

Figure S18. $^{29}$Si-$^1$H-NMR-Spectrum of 1$\cdot$AgCl (CDCl$_3$, 71.6 MHz)
Figure S19. $^{31}$P-NMR-Spectrum of 1∙AgCl (CDCl$_3$, 145.9 MHz)

Figure S20. $^{31}$P{$^{1}$H}-NMR-Spectrum of 1∙AgCl (CDCl$_3$, 145.9 MHz)
Figure S21. $^1$H-$^{29}$Si-HSQC NMR-Spectrum of 1·AgCl (CDCl$_3$).
IR and vibrational dynamics. Steady-state IR measurements were performed with an Equinox 55 (Bruker). We investigated 1, 1·AgCl, and 1·CuCl with femtosecond time-resolved pump-probe spectroscopy. The samples were dissolved in chloroform in a 200 µm solution, placed between two CaF2 windows. The pump-probe technique was used to measure the vibrational population relaxation time after direct excitation of the investigated Si-H stretching bands. For this purpose, we used two optical parametric amplifiers (OPA), generating 300 fs pulses tuned in the range of 1200-3000 cm⁻¹ at a repetition rate of 2 kHz. The OPAs are pumped by the commercial Yb:KGW 200 fs laser Pharos. The experimental set-up was reported elsewhere. In brief, two IR OPAs were used to generate IR pump and probe pulses at a repetition rate of 2 kHz. The energy of the pump pulses was about 1.5 µJ at frequencies of 1960 cm⁻¹, 2120 cm⁻¹, and 2170 cm⁻¹ and a spectral width of about 50 cm⁻¹ (FWHM). The system response was about 500 fs. The probe beam was spectrally dispersed after the sample in a spectrograph and detected by a double-array of 2×10 MCT detectors. The detector allows for detection of 10 frequencies at the same time. We selected a grating of 150 l/mm and achieved a spectral resolution of about 6 cm⁻¹ in the spectral range of 2000 cm⁻¹. The transient signals were recorded for different delay times between pump and probe pulses to collect the vibrational dynamics before and after IR excitation on a time scale of about 30 ps.

The decrease of the wave number of the stretching vibration of the Si-H bond from $\nu_{\text{SiH}} = 2173$ cm⁻¹ in 1 to $\nu_{\text{SiH}} = 2118$ cm⁻¹ (1·AgCl) and $\nu_{\text{SiH}} = 1932$ cm⁻¹ (1·CuCl) is depicted in Figure S19,left. The frequency position of the Si-H stretching vibration in 1·AgCl, and 1·CuCl is reduced by 2.6%, and 12.5%, respectively. Furthermore, the bandwidth (FWHM) of the Si-H stretching is (56±3) cm⁻¹, (60±3) cm⁻¹, and (110±20) cm⁻¹ for 1 (red line in Figure S22,left), 1·AgCl (green line in Figure S22,left), and 1·CuCl (gray line in Figure S22,left), respectively.
Figure S22. **Left:** Infrared absorption spectra of 1 (red line), 1·AgCl (green line), 1·CuCl (blue line), and background corrected 1·CuCl (gray line) dissolved in chloroform. Sharp negative absorption spikes are due to water vapour absorption. Center of absorption is indicated (dotted lines).

**Right:** Transient dynamics of the Si-H stretching vibration: (a) excited state decay averaged from 2079 cm$^{-1}$ to 2092 cm$^{-1}$ (red dots), and bleaching recovery averaged from 2153 cm$^{-1}$ to 2174 cm$^{-1}$ (black squares) of 1, fits with the time constant of 7(1) ps for both dynamics, system response (gray line); (b) excited state decay of 1·AgCl at 2053 cm$^{-1}$ (wine dots) and fit with a time constant of 0.56(9) ps (wine line); bleaching recovery of 1·AgCl at 2123 cm$^{-1}$ (green squares), fit with time constant of 0.77(9) ps (green line), system response (gray line); (c) excited state signal at 1895 cm$^{-1}$ of 1·CuCl (orange dots), bleaching recovery at 1930 cm$^{-1}$ of 1·CuCl (blue squares) and fit (blue line) with time constant of 1.6(5) ps; system response (gray line).
The transient signals at different frequencies are displayed in Figure S22,right. The dynamics shown in Figure S22,right reveal distinct vibrational excited state and bleaching recovery times upon excitation of the Si-H vibration: Excitation of the Si-H stretching vibration of 1 at 2170 cm\(^{-1}\) shows an instantaneous bleaching signal in the spectral range above 2120 cm\(^{-1}\), and an excited state absorption signal below 2120 cm\(^{-1}\). The anharmonicity between the ground and excited vibrational state is 88(5) cm\(^{-1}\). Both signals decay with the same time constant of 7(1) ps, indicating a weak coupling of the Si-H stretching vibration to other vibrational modes. Excitation of the Si-H stretching vibration of 1-AgCl at 2120 cm\(^{-1}\) shows an instantaneous bleaching signal in the spectral range above 2080 cm\(^{-1}\), and an excited state absorption signal below 2080 cm\(^{-1}\) (see Figure S23). The anharmonicity is 80(10) cm\(^{-1}\), similar to 1. Nevertheless, the bleaching signal at 2123 cm\(^{-1}\) decays with 0.77(9) ps, and the excited state at 2053 cm\(^{-1}\) decays with 0.56(9) ps, much faster than the dynamics in 1. The faster decay of the excited state in 1-AgCl compared with the bleaching signal shows energy relaxation to other vibrations prior to back relaxation to the Si-H stretching ground state. This means that the coupling of the Si-H stretching vibration to other vibrational modes is stronger than for 1. Excitation of 1-CuCl at 1960 cm\(^{-1}\) leads to an instantaneous bleaching of the Si-H stretching vibration above 1900 cm\(^{-1}\), decaying at 1930 cm\(^{-1}\) with a time constant of 1.6(5) ps. The excited state absorption is expected to be red-shifted and should appear below 1900 cm\(^{-1}\). The dynamics of the positive signal at 1895 cm\(^{-1}\) presented in Figure S22,right are comparable to our system response. Thus, it is not possible to decide whether the measured dynamics are due to nonlinear artefacts or due to a very fast decay of the excited state. If the presented dynamics represent a nonlinear artefact, the excited state decay should absorb at more red-shifted frequencies outside of our frequency window. In both cases, the excited state dynamics of the Si-H stretching vibration of 1-CuCl is altered due to stronger covalent coupling to other vibrational modes either accepting efficiently the energy from the excited
state or shifting the excited state absorption to lower frequencies via anharmonic coupling.\textsuperscript{4} Comparison of the absorption frequencies with bond lengths show a linear decrease of the frequencies with increasing Si-H bond lengths (see Figure S24), similar to the behaviour of the hydrogen bonded O-H stretching vibration.\textsuperscript{5}

\textbf{Figure S23}. Absorbance difference spectra of 1 (black dots), and 1\cdot AgCl (blue squares) for delay times of about 1 ps. Positive signals show absorption in the vibrational excited state; negative signals show bleaching signals of the vibrational ground state.
Figure S24. Frequency dependence of the Si-H stretching vibration as a function of the measured Si-H distance in Å (black dots). The error bars for frequency and distance uncertainties are given. The fit indicates a linear dependence (red line) with a slope of -9900 cm\(^{-1}\) per Ångstrom.
**X-Ray Diffraction Measurements.** Intensity data of 1, 1·CuCl and 1·AgCl were collected at 150 K on a Bruker Venture D8 diffractometer with a Photon 100 detector in shutterless mode using a microfocus source (0.7107 Å). All structures were solved using the dual-space algorithm in ShelXT and refined against F^2 with the use of SHELXL within the WinGX program package. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were located from the Fourier difference map and refined freely (except those for the THF solvent molecule which were included in geometrically calculated positions using a riding model).

For 1·CuCl, a transparent colorless plate-like crystal with dimensions 0.09 mm × 0.16 mm × 0.30 mm was used for the X-ray crystallographic analysis. The total exposure time was 23.36 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 94197 reflections to a maximum θ angle of 28.28° (0.75 Å resolution).

For 1·AgCl, a transparent grey block-like crystal with approximate dimensions 0.17 mm × 0.31 mm × 0.43 mm, was used for the X-ray crystallographic analysis. The total exposure time was 23.82 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 172655 reflections to a maximum θ angle of 40.567° (0.55 Å resolution). Data were corrected for absorption effects using numerical absorption correction (SADABS). The ratio of minimum to maximum apparent transmission was 0.849.

For ligand 1, a brown block-like crystal with approximate dimensions 0.20 mm x 0.22 mm x 0.24 mm, was used for the X-ray crystallographic analysis. The total exposure time was 144.08 hours. The frames were integrated with the Bruker SAINT software package using a
narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 284871 reflections to a maximum θ angle of 45.474° (0.50 Å resolution).

For Ph₃SiH, a translucent colorless block-like crystal with approximate dimensions 0.198 mm × 0.260 mm × 0.289 mm was used for the X-ray crystallographic analysis. The total exposure time was 97.03 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 181987 reflections to a maximum θ angle of 40.248° (0.54 Å resolution). It should be noted that the crystal structure of Ph₃SiH has already been reported⁹, albeit at a different temperature. In order to derive the molecular structure from Laue-type neutron diffraction measurements at 150 K, the single-crystal X-ray diffraction measurements had to be repeated at 150 K to establish the cell constants and starting geometry. As this structure was derived at a different temperature in comparison to the known structure, a new CIF was deposited at the CCDC.

The PLATON/SQUEEZE tool¹⁰ was applied to calculate the void space and extract its contribution from the reflection list for the structures of 1·CuCl and 1·AgCl. This treatment was necessary because the heavily disordered solvent molecule(s) could neither be identified nor refined in any meaningful way. The final models cited are given without disordered solvent contributions.

Pertinent crystal and refinement data are collected in Table S1. Figures were created using DIAMOND¹¹ and Mercury.¹² Crystallographic data including structure factors for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1875891-1875893, 1875895. They can be downloaded free of charge from https://www.ccdc.cam.ac.uk/structures/.
Table S1. Crystallographic, measurement and refinement details of the X-ray structure determinations of Ph₃SiH, 1 and 1MCl

<table>
<thead>
<tr>
<th></th>
<th>1·AgCl</th>
<th>1·CuCl</th>
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<tr>
<td>Chemical formula</td>
<td>C₄₀H₄₀AgCl₂Si</td>
<td>C₄₀H₄₀ClCu₂Si</td>
<td>C₄₀H₄₀P₂Si·C₄H₈O</td>
<td>C₁₈H₁₆Si</td>
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<tr>
<td>Mr (g/mol)</td>
<td>862.16</td>
<td>817.83</td>
<td>790.94</td>
<td>260.40</td>
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<td>triclinic, P bar</td>
<td>triclinic, P bar</td>
<td>monoclinic, P2₁/c</td>
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<td>α, β, γ (°)</td>
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<td>90, 110.362(1), 90</td>
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<tr>
<td>V (Å³)</td>
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<td>2134.64(10)</td>
<td>2047.60(7)</td>
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<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
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<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
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<tr>
<td>μ (mm⁻¹)</td>
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<td>0.71</td>
<td>0.18</td>
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**Data collection**

<table>
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<tr>
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<td>284871, 34336, 26753</td>
<td>181987, 9136, 8087</td>
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<td>0.064</td>
<td>0.034</td>
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<td>1.003</td>
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<td>(Å⁻¹)</td>
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<td>---------</td>
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<tr>
<td></td>
<td>Refinement</td>
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<tr>
<td></td>
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<td>0.028, 0.083, 1.10</td>
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<td>10593</td>
<td>34336</td>
<td>9136</td>
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<tr>
<td>No. of parameters</td>
<td>647</td>
<td>647</td>
<td>674</td>
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<td>H-atom treatment</td>
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<td>All H-atom parameters refined</td>
<td>H atoms treated by a mixture of independent and constrained refinement</td>
<td>All H-atom parameters refined</td>
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<td>$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å⁻³)</td>
<td>1.05, −0.75</td>
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<td>1875893</td>
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**Neutron Diffraction Measurements.**

The neutron diffraction experiments were carried out at the Australian Centre for Nuclear Scattering (ACNS, formerly Bragg Institute) of ANSTO (formerly the Australian Nuclear Science and Technology Organization) using the Laue technique in the KOALA instrument. The polychromatic wavelength beam (ranging from 0.50 to 4.00 Å) is produced in the OPAL research reactor and most fast neutrons are eliminated through the TG3 thermal guide before arriving at the instrument. The low and high wavelength cutoff varies as a function of crystal quality for the different compounds analyzed here (see Table S2). The Laue patterns were recorded from the stationary crystal with a large cylindrical image plate at a temperature of 150K using the open flow nitrogen cryostat COBRA. Two different crystal orientations that differ to each other by an angle of about 90 degrees were measured to obtain an optimum completeness. The total exposure times for each orientation vary between 2.78 to 5.56 hours (10,000 and 20,000 seconds, respectively). Indexing, integration and wavelength
normalization were performed using the LaueG software.\textsuperscript{14} All pertinent details regarding the measurements are given in Table S2.

For the indexing of the Laue diffraction patterns, the unit cell parameters obtained from the X-ray experiments (at the same temperature) were employed. This step is necessary for the Laue method due to the polychromatic wavelength distribution.

The CRYSTALS software\textsuperscript{15} was used to perform structure refinement of the neutron data commenced from non-hydrogen atom positions of the final structure model from the X-ray diffraction experiments. A scale-factor refinement was followed by refinement of the positional and anisotropic displacement parameters (ADPs). Hydrogen atoms were located from the difference Fourier map. Final cycles of refinement used ADPs and free position refinement for all atoms, including hydrogens.

Both $\mathrm{I\cdot AgCl}$ and $\mathrm{I\cdot CuCl}$ contain highly disordered solvent molecules which could not be modeled for the X-ray data nor the neutron data. Therefore, the PLATON/SQUEEZE\textsuperscript{6} tool was applied to calculate the void space and extract its contribution from the reflection list. The final models cited are given without disordered solvent contributions. The refinement of these structures was performed with the SHELXL program.

Some of the structures also include refinement of an extinction parameter that led to a convergent geometry of high precision and quality. For details about the refinements see Table S2, and the CIFs (CCDC-1875890,1875894,1875896,1875897) deposited with the Cambridge Structural Database. They can be downloaded free of charge from https://www.ccdc.cam.ac.uk/structures/.
Table S2. Measurement and refinement details of the neutron structure determinations of Ph₃SiH, 1 and 1MCl. Crystallographic details are identical to those in Table S1.

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<th>1·CuCl</th>
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<td>Radiation type</td>
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<td>neutron, (\lambda_{\text{min}} = 0.90 \text{ Å})</td>
<td>neutron, (\lambda_{\text{min}} = 0.85 \text{ Å})</td>
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<td>Maximum resolution (Å)</td>
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<td>0.85</td>
<td>0.70</td>
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<td>Crystal size (mm)</td>
<td>1.2 × 0.9 × 0.8</td>
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<td>No. of measured, independent and observed ([I &gt; 2\sigma(I)]) reflect.</td>
<td>32643, 5986, 3953</td>
<td>54576, 9308, 6172</td>
<td>25892, 5425, 3618</td>
<td>27048, 3817, 2333</td>
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<tr>
<td>(R_{\text{int}}(\text{all}), R_{\text{int}}(I &gt; 4\sigma(I)))</td>
<td>0.134, 0.066</td>
<td>0.107, 0.056</td>
<td>0.106, 0.050</td>
<td>0.150, 0.063</td>
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<td><strong>Refinement</strong></td>
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<tr>
<td>(R(F), wR(F^2), S)</td>
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<td>No. of param.</td>
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<td>847</td>
<td>946</td>
<td>316</td>
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<td>(w = 1/[\sigma^2(F_o^2) + (0.0188P)^2 + 56.0799P]) &amp; (w = 1/[\sigma^2(F_o^2) + 40.9811P]) &amp; (w = 1/[\sigma^2(F_o^2) + 2F_c^2]/3) &amp; (w = 1/[\sigma^2(F_o^2) + 2F_c^2]/3)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>where (P = (F_o^2 + 2F_c^2)/3) &amp; where (P = (F_o^2 + 2F_c^2)/3) &amp; Chebychev polynomial with coefficients (A_i = 7.02, -4.64, 2.32, 1.65^S) &amp; Chebychev polynomial with coefficients (A_i = 1.04, -0.60, 0.51^S)</td>
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<td></td>
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<tr>
<td>(\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (\text{fm}^{-3}))</td>
<td>0.90, −2.21</td>
<td>0.89, −0.97</td>
<td>0.55, −0.81</td>
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<td>not refined</td>
<td>not refined</td>
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* This is the number of reflections in the refinement, either in SHELX all unique after squeeze (for 1·AgCl and 1·CuCl) or \(F > 3\sigma(F)\) in Crystals (for 1 and Ph₃SiH).  
$ w = 1.0/[A_0*T_0(x) + A_1*T_1(x) + \cdots + A_{n-1}]\cdot T_{n-1}(x) ]$
The final geometries of 1 and 1-MCl derived from the single-crystal neutron diffraction experiments are shown in Figure 1 in the main text, and geometrical parameters are summarized in Table S3. The crystal structure of 1 contains one molecule of THF in its asymmetric unit. For both 1-MCl compounds the crystal structures contain disordered solvent molecules that could not be modelled, see discussion above. The silicon hydride bond length of 1.484(7) Å in 1 is elongated to 1.509(7) Å in 1-CuCl and 1.492(10) Å in 1-AgCl. For those three crystal structures there are no intermolecular interactions involving the silane hydrogen atom. In addition to 1 and 1-MCl, we also determined the structure of triphenylsilane Ph₃SiH by neutron diffraction, where the Si-H distance is 1.494(6) Å. The Si-H bonds of Ph₃SiH and 1 are similar, but for Ph₃SiH one intermolecular interaction (distance smaller than the sum of van-der-Waals radii) involving the hydridic H atom is present that explains the slight elongation. In all four cases, the silicon atom has a distorted tetrahedral arrangement. The geometrical goodness is 9.9(15)° for Ph₃SiH, 4.9(19)° for 1 as well as 1-CuCl, and 4.1(30)° for 1-AgCl. In both metal complexes, the metal atoms also exhibit a tetrahedral ligand arrangement with a P1-M-P2-angle of 126.26(16)° for M = Cu (1-CuCl) and 122.3(2)° for M = Ag (1-AgCl). The Si1-H1-M-angles are 117.6(4)° for M = Cu (1-CuCl) and 122.7(6)° for M = Ag (1-AgCl), indicating the presence of an interaction of the metal atoms with the Si-H bond.

The Si-Me bond distance elongates slightly from 1 to 1-MCl (1.866(5), 1.870(5), 1.881(8) Å for 1, 1-CuCl and 1-AgCl, respectively). The Si-P distances are asymmetric for 1 (3.227(6) and 3.328(5) Å) indicating interactions of different strengths within the molecule, but these distances become longer and more symmetric for 1-MCl (3.442(5) and 3.455(5) Å for 1-CuCl; 3.558(9) and 3.549(9) for 1-AgCl). The angles for P1-Si-Me are 173.3(2), 170.0(3) and 174.2(4) ° or 1, 1-CuCl and 1-AgCl, respectively. However, the angles for Si-P2-Ph are considerably more distorted from the linear arrangement in 1, (154.2(2) degrees) than in
1-MCl (171.9(2) and 173.3(3)° for 1-CuCl and 1-AgCl). A superposition of the geometries can be found in Figure 1(d) of the main document.

Table S3. Experimental interatomic distances [Å] and angles [°] of 1, 1-CuCl and 1-AgCl derived from neutron diffraction measurements.

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<th>1-MCl (M = Cu)</th>
<th>1-AgCl (M = Ag)</th>
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<td><strong>Peri-region Distances</strong></td>
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<tr>
<td>P(1)--Si(1)</td>
<td>3.227(6)</td>
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<td>0.257(5)</td>
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<td><strong>Central Acenaphthyl Ring Torsion Angles</strong></td>
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<td>C::(13)-(14)-(19)-(18)</td>
<td>-176.9(2)</td>
<td>-177.7(3)</td>
</tr>
<tr>
<td>C::(43)-(44)-(49)-(48)</td>
<td>175.1(2)</td>
<td>-178.8(2)</td>
</tr>
<tr>
<td>Bond</td>
<td>Angle (°) 1</td>
<td>Angle (°) 2</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>C(15)-(14)-(19)-(10)</td>
<td>-177.9(2)</td>
<td>-174.1(3)</td>
</tr>
<tr>
<td>C(45)-(44)-(49)-(40)</td>
<td>173.2(2)</td>
<td>-177.4(2)</td>
</tr>
</tbody>
</table>

* Splay angle: Σ of the three bay region angles – 360°.

*C*omponents 1, 1·CuCl and 1·AgCl show an out-of-plane displacement of the peri-substituents. The out of plane angle was calculated as the distance from the atom to the plane defined by 5 atoms out of the 6 membered ring adjacent to that atom.

### Leaving group angle

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°) 1</th>
<th>Angle (°) 2</th>
<th>Angle (°) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1)-P(2)-C(50)</td>
<td>154.2(2)</td>
<td>171.9(2)</td>
<td>173.3(3)</td>
</tr>
<tr>
<td>P(1)-Si(1)-C(5)</td>
<td>173.3(2)</td>
<td>170.0(3)</td>
<td>174.2(4)</td>
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</tbody>
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### Angles involving H(1)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°) 1</th>
<th>Angle (°) 2</th>
<th>Angle (°) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1)-H(1)-P(1)</td>
<td>86.5(3)</td>
<td>85.4(3)</td>
<td>84.1(5)</td>
</tr>
<tr>
<td>Si(1)-H(1)-P(2)</td>
<td>95.6(3)</td>
<td>100.6(4)</td>
<td>103.6(5)</td>
</tr>
<tr>
<td>P(1)-H(1)-P(2)</td>
<td>107.2(3)</td>
<td>83.2(2)</td>
<td>86.0(3)</td>
</tr>
</tbody>
</table>

### Angles between planes

<table>
<thead>
<tr>
<th>Plane</th>
<th>Angle (°) 1</th>
<th>Angle (°) 2</th>
<th>Angle (°) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1)-C(10)-C(19)</td>
<td>P(1)-C(18)-C(19)</td>
<td>4.8</td>
<td>12.12</td>
</tr>
<tr>
<td>Si(1)-C(40)-C(49)</td>
<td>P(2)-C(48)-C(49)</td>
<td>20.86</td>
<td>15.27</td>
</tr>
</tbody>
</table>

#### Plane containing C:40-41-42-43-44-45-46-48-49-3-4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle (°) 1</th>
<th>Angle (°) 2</th>
<th>Angle (°) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>18.93</td>
<td>18.50</td>
</tr>
<tr>
<td>1·CuCl</td>
<td>18.93</td>
<td>-</td>
<td>5.06</td>
</tr>
<tr>
<td>1·AgCl</td>
<td>18.50</td>
<td>5.06</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Plane containing P(1)-Si(1)-P(2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle (°) 1</th>
<th>Angle (°) 2</th>
<th>Angle (°) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>4.80</td>
<td>6.69</td>
</tr>
<tr>
<td>1·CuCl</td>
<td>4.8</td>
<td>-</td>
<td>1.89</td>
</tr>
<tr>
<td>1·AgCl</td>
<td>6.69</td>
<td>1.89</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Torsion angles with phenyl rings

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°) 1</th>
<th>Angle (°) 2</th>
<th>Angle (°) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(20)-P(1)-C(18)-C(19)</td>
<td>127.0(2)</td>
<td>142.9(3)</td>
<td>140.7(4)</td>
</tr>
<tr>
<td>C(30)-P(1)-C(18)-C(19)</td>
<td>-126.3(2)</td>
<td>-110.7(3)</td>
<td>-111.8(5)</td>
</tr>
<tr>
<td>C(50)-P(2)-C(48)-C(49)</td>
<td>-137.3(2)</td>
<td>163.8(2)</td>
<td>162.5(4)</td>
</tr>
<tr>
<td>C(60)-P(2)-C(48)-C(49)</td>
<td>117.0(2)</td>
<td>-88.1(3)</td>
<td>88.4(5)</td>
</tr>
</tbody>
</table>

### Distances

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å) 1</th>
<th>Distance (Å) 2</th>
<th>Distance (Å) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)-P(2)</td>
<td>4.666(4)</td>
<td>4.035(5)</td>
<td>4.295(8)</td>
</tr>
</tbody>
</table>
**Computational Methodology.** Starting from the XRD models 1, 1-CuCl, and 1-AgCl, structural optimizations in the isolated states were conducted with density functional theory (DFT) calculations at the B3PW91/6-311+G(2df,p)\textsuperscript{19} level applying Gaussian09\textsuperscript{20}. For the Cu and Ag atoms effective core potentials (ECP10/28MDF)\textsuperscript{21} and corresponding cc-pVTZ basis sets\textsuperscript{22} were utilized. Dispersion effects were modeled using Grimme’s GD3BJ parameters.\textsuperscript{23} Subsequent normal mode analysis proved all structures to be local minima on the potential energy hypersurface. The resulting IR frequencies were scaled with a basis-set dependent factor of 0.9679 as obtained from ref. \textsuperscript{24}. NMR coupling constants as well as natural atomic populations were calculated with all-electron DGDZVP basis sets at the optimized geometries using the same DFT functional. Natural populations were taken from a natural population analysis according to the natural bond orbital (NBO) procedure,\textsuperscript{25} calculated with the program NBO6.0.\textsuperscript{26} Topological analysis of the electron density according to the Atoms-In-Molecules (AIM) space-partitioning scheme was performed using AIM2000,\textsuperscript{27} whereas Electron-Localizability-Indicator (ELI-D) related real-space bonding descriptors were generated and analyzed with DGRID\textsuperscript{28} (grid step size of 0.05 au for integration and of 0.15 au for visualization). For the fine grids of ELI-D and Laplacian of electron density shown in Figure 2, the self-written unpublished software cuQCT was used that calculates grid files in a highly parallelized manner on GPUs. NCI grids were computed with NCIplot (grid step size of 0.10 au).\textsuperscript{29} Bond paths are displayed with AIM2000, ELI-D and NCI figures are displayed with MolIso\textsuperscript{30} and VMD\textsuperscript{31}. The determination of the compliance constants and compliance coupling constants were carried out with the COMPLIANCE software (version 3.0.2)\textsuperscript{32} using the respective Gaussian *.log file containing the frequency analysis.

AIM provides a bond paths motif resembling the molecular structure, which also includes weak secondary contacts (e.g. hydrogen bonds, dihydrogen bonds, agostic interactions). Atomic and fragmental charges are obtained by integration of AIM atomic basins. By forming basins of electron pairs, ELI-D gives access to electron populations within

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1.  
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26.  
27.  
28.  
29.  
30.  
31.  
32.  

---
chemical bonds and lone-pairs, which makes this method especially suitable to characterize (polar-)covalent and dative bonds. Highly polar or ionic contacts, however, do not form ELI-D basins between the interacting atoms. Fortunately, this gap is perfectly filled by the NCI, which is derived from the reduced electron density (ED) gradient \( s = [1/2(3\pi^2)^{1/3}||\nabla p/p^{4/3}) \), typically forming localized interatomic basins for highly polar atom-atom contacts as well as flat and extended plane-like basins between molecules or molecular fragments in regions where weak van-der-Waals like contacts occur. Accordingly, ELI-D and NCI exhibit complementary spatial distribution, suggesting at least partial spatial separation of covalent and non-covalent bonding aspects.\(^{33}\) Further discrimination of non-covalent bonding into steric/repulsive, non-bonding, and attractive is enabled by mapping the sign of the second eigenvalue of the Hessian times the ED (\( \text{sign}(\lambda_2)p \)) on the NCI basin surface (\( \lambda_2 > 0 \), red colored: steric; \( \lambda_2 \approx 0 \), green colored: non-bonding; \( \lambda_2 < 0 \), blue colored: attractive). NCI is known to be more sensitive against very weak interactions than AIM topology, or in other words not all weak interactions which are visible in NCI result in the formation of an AIM bond path.\(^{34}\) Combining AIM and ELI-D affords quantification of bond polarities with the Raub-Jansen-Index (RJI),\(^{35}\) which is the electron population distribution of an ELI-D basins intersecting two or more adjacent AIM atomic basins. Consequently, homo-polar bonds are characterized by RJI values between 50 and 60%, whereas highly polar or dative bonds show RJI values above 90%. The majority of bonds – polar covalent interactions – lie in between. In conjunction with geometric and energetic considerations, the applied set of RSBI and orbital representations provides a holistic scheme of the Si-H…M contacts. The concept of generalized compliance constants\(^{36}\) greatly augments the set of real-space bonding descriptors described above. By generating a compliance matrix (the inverse of the Hessian matrix), weak interactions between atoms are unraveled and due to them being independent of the coordinate system they can be directly compared for similar chemical environments. A compliance constant (the inverse of the relaxed force constant) determines the force necessary
to displace a given coordinate, e.g. the Si-H bond, while all other atoms of the molecules are allowed to be relaxed (leading to the name *relaxed* force constant) with higher values of the compliance constant representing weaker bonds. This leads to a more accurate analysis of the local environment, especially when compared to an analysis of fixed force constants.32

**Table S4**  AIM and ELI-D derived bonding indicators. Values derived from the inclusion of empirical dispersion are given in italics.

<table>
<thead>
<tr>
<th>model</th>
<th>bond</th>
<th>d [Å]</th>
<th>ρ(r) [eÅ⁻³]</th>
<th>V²ρ(r) [eÅ⁻⁵]</th>
<th>G/ρ(r) [a.u.]</th>
<th>H/ρ(r) [a.u.]</th>
<th>N_{ELI}</th>
<th>V_{ELI} [Å³]</th>
<th>Y</th>
<th>RJI [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si–H</td>
<td>1.479</td>
<td>0.84</td>
<td>2.6</td>
<td>0.93</td>
<td>-0.71</td>
<td>2.00</td>
<td>13.7</td>
<td>10.01</td>
<td>82.9</td>
</tr>
<tr>
<td>1·AgCl</td>
<td>Si–H</td>
<td>1.490</td>
<td>0.82</td>
<td>2.4</td>
<td>0.91</td>
<td>-0.71</td>
<td>2.01</td>
<td>12.0</td>
<td>7.57</td>
<td>81.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.487</td>
<td>0.82</td>
<td>2.6</td>
<td>0.92</td>
<td>-0.70</td>
<td>2.02</td>
<td>11.2</td>
<td>7.25</td>
<td></td>
</tr>
<tr>
<td>1·CuCl</td>
<td>Si–H</td>
<td>1.512</td>
<td>0.77</td>
<td>2.2</td>
<td>0.88</td>
<td>-0.69</td>
<td>2.11</td>
<td>11.6</td>
<td>6.34</td>
<td>77.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.539</td>
<td>0.74</td>
<td>2.0</td>
<td>0.86</td>
<td>-0.67</td>
<td>2.26</td>
<td>12.0</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>1·AgCl</td>
<td>(Si–)H–Ag</td>
<td>2.141</td>
<td>0.26</td>
<td>2.6</td>
<td>0.81</td>
<td>-0.09</td>
<td></td>
<td></td>
<td></td>
<td>97.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.093</td>
<td>0.29</td>
<td>3.0</td>
<td>0.84</td>
<td>-0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1·CuCl</td>
<td>(Si–)H–Cu</td>
<td>1.757</td>
<td>0.43</td>
<td>4.4</td>
<td>0.97</td>
<td>-0.26</td>
<td></td>
<td></td>
<td></td>
<td>92.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.677</td>
<td>0.54</td>
<td>5.3</td>
<td>1.03</td>
<td>-0.34</td>
<td></td>
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<td></td>
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<tr>
<td>1·AgCl</td>
<td>Ag–P1</td>
<td>2.436</td>
<td>0.51</td>
<td>3.4</td>
<td>0.77</td>
<td>-0.31</td>
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<td>10.8</td>
<td>1.77</td>
<td>84.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.401</td>
<td>0.54</td>
<td>3.5</td>
<td>0.77</td>
<td>-0.32</td>
<td>2.15</td>
<td>10.1</td>
<td>1.76</td>
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<tr>
<td>1·AgCl</td>
<td>Ag–P2</td>
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<td>0.75</td>
<td>-0.29</td>
<td>2.11</td>
<td>10.5</td>
<td>1.78</td>
<td>85.0</td>
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<tr>
<td></td>
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<td>2.420</td>
<td>0.53</td>
<td>3.5</td>
<td>0.77</td>
<td>-0.31</td>
<td>2.13</td>
<td>10.0</td>
<td>1.72</td>
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<tr>
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<td>Cu–P1</td>
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<td>13.9</td>
<td>1.75</td>
<td>73.2</td>
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<tr>
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<td>2.211</td>
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<td>3.9</td>
<td>0.83</td>
<td>-0.38</td>
<td>2.52</td>
<td>12.9</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>1·CuCl</td>
<td>Cu–P2</td>
<td>2.266</td>
<td>0.55</td>
<td>3.7</td>
<td>0.82</td>
<td>-0.35</td>
<td>2.36</td>
<td>11.3</td>
<td>1.76</td>
<td>77.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.231</td>
<td>0.59</td>
<td>3.9</td>
<td>0.83</td>
<td>-0.37</td>
<td>2.33</td>
<td>9.8</td>
<td>1.73</td>
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</tr>
<tr>
<td>1·AgCl</td>
<td>Ag–Cl</td>
<td>2.452</td>
<td>0.44</td>
<td>4.5</td>
<td>0.94</td>
<td>-0.22</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>2.401</td>
<td>0.49</td>
<td>5.0</td>
<td>0.96</td>
<td>-0.24</td>
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<td></td>
<td></td>
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<tr>
<td>1·CuCl</td>
<td>Cu–Cl</td>
<td>2.254</td>
<td>0.50</td>
<td>5.4</td>
<td>1.03</td>
<td>-0.27</td>
<td>0.37</td>
<td>0.5</td>
<td>1.48</td>
<td>88.6</td>
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<tr>
<td></td>
<td></td>
<td>2.231</td>
<td>0.52</td>
<td>5.7</td>
<td>1.04</td>
<td>-0.29</td>
<td>0.42</td>
<td>0.5</td>
<td>1.48</td>
<td></td>
</tr>
</tbody>
</table>

For all bonds, ρ(r)_{hcp} is the electron density at the bond critical point, V²ρ(r)_{hcp} is the corresponding Laplacian, G/ρ(r)_{hcp} and H/ρ(r)_{hcp} are the kinetic and total energy density over ρ(r)_{hcp} ratios, N_{ELI} and V_{ELI} are the electron populations and volumes of the ELI-D basins, Y is the ELI-D value at the attractor position, RJI is the Raub-Jansen Index.
Table S5  AIM atomic and fragment charges (in e) with charges derived from the inclusion of empirical dispersion given in italics.

<table>
<thead>
<tr>
<th></th>
<th>1·CuCl</th>
<th>Diff</th>
<th>1·AgCl</th>
<th>Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>0.38</td>
<td>0.28</td>
<td>0.34</td>
<td>0.27</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.72</td>
<td>-0.68</td>
<td>-0.69</td>
<td>-0.67</td>
</tr>
<tr>
<td>Si</td>
<td>2.78</td>
<td>2.74</td>
<td>-0.04</td>
<td>2.75</td>
</tr>
<tr>
<td>H</td>
<td>-0.68</td>
<td>-0.64</td>
<td>0.04</td>
<td>-0.65</td>
</tr>
<tr>
<td>Me</td>
<td>-0.70</td>
<td>-0.68</td>
<td>0.02</td>
<td>-0.68</td>
</tr>
<tr>
<td>P1</td>
<td>1.51</td>
<td>1.53</td>
<td>0.02</td>
<td>1.57</td>
</tr>
<tr>
<td>P2</td>
<td>1.47</td>
<td>1.56</td>
<td>0.09</td>
<td>1.59</td>
</tr>
<tr>
<td>ace1</td>
<td>-1.18</td>
<td>-1.15</td>
<td>0.03</td>
<td>-1.14</td>
</tr>
<tr>
<td>ace2</td>
<td>-1.18</td>
<td>-1.18</td>
<td>0.00</td>
<td>-1.17</td>
</tr>
<tr>
<td>(ace1)ph1</td>
<td>-0.50</td>
<td>-0.44</td>
<td>0.06</td>
<td>-0.47</td>
</tr>
<tr>
<td>(ace1)ph2</td>
<td>-0.51</td>
<td>-0.48</td>
<td>0.03</td>
<td>-0.44</td>
</tr>
<tr>
<td>(ace2)ph1</td>
<td>-0.51</td>
<td>-0.46</td>
<td>0.05</td>
<td>-0.46</td>
</tr>
<tr>
<td>(ace2)ph2</td>
<td>-0.50</td>
<td>-0.47</td>
<td>0.03</td>
<td>-0.46</td>
</tr>
<tr>
<td>sum</td>
<td>0.00</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table S6. 4s and 3d atomic orbital populations of Cu in 1·CuCl, 5s and 4d atomic orbital populations of Ag in 1·AgCl, from natural population analysis (NPA). NPA atomic charges are also given. All units = e.

<table>
<thead>
<tr>
<th></th>
<th>1·CuCl</th>
<th>1·AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0.3513</td>
<td>0.3080</td>
</tr>
<tr>
<td>d_{xy}</td>
<td>1.9774</td>
<td>1.9847</td>
</tr>
<tr>
<td>d_{xz}</td>
<td>1.9717</td>
<td>1.9795</td>
</tr>
<tr>
<td>d_{yz}</td>
<td>1.9528</td>
<td>1.9776</td>
</tr>
<tr>
<td>d_{x^2-y^2}</td>
<td>1.9612</td>
<td>1.9681</td>
</tr>
<tr>
<td>d_{z^2}</td>
<td>1.9748</td>
<td>1.9838</td>
</tr>
<tr>
<td>sum d-orbitals</td>
<td>9.8379</td>
<td>9.8937</td>
</tr>
<tr>
<td>NPA charge</td>
<td>0.7690</td>
<td>0.7715</td>
</tr>
</tbody>
</table>
Table S7. Parts of the compliance matrix for 1, 1·CuCl and 1·AgCl. Values derived from the inclusion of dispersion are given in italics.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>Si-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–H</td>
<td>0.351</td>
<td></td>
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The values are given in units of Å mdyn⁻¹. Larger compliance constants (diagonal elements) indicate a weaker bond, whereas compliance coupling constants (off-diagonal elements) are proportional to the interaction of the coupling coordinates.
Figure S25  RSBI analysis of 1. (a) AIM bond paths motif with bond critical points (bcps, red spheres). (b) NCI iso-surface at $s(r) = 0.5$ color coded with $\text{sign}(\lambda_2)\rho$ in a.u. Blue surfaces refer to attractive forces and red to repulsive forces. Green indicates weak interactions. (c) ELI-D localization domain representation at iso-value of 1.3. (d) ELI-D distribution (unitless) color-coded onto the (Si–)H ELI-D basin.
Figure S26. RSBI analysis of 1-CuCl with the inclusion of empirical dispersion. (a) AIM bond paths motif with bond critical points (bcps, red spheres). (b) NCI iso-surface at $s(r) = 0.5$ color coded with $\text{sign}(\lambda_2)p$ in a.u. Blue surfaces refer to attractive forces and red to repulsive forces. Green indicates weak interactions. (c) ELI-D localization domain representation at iso-value of 1.3.
Figure S27. RSBI analysis of 1·AgCl with the inclusion of empirical dispersion. (a) AIM bond paths motif with bond critical points (bcps, red spheres). (b) NCI iso-surface at s(r) = 0.5 color coded with sign(λ2)ρ in a.u. Blue surfaces refer to attractive forces and red to repulsive forces. Green indicates weak interactions. (c) ELI-D localization domain representation at iso-value of 1.3.

The DFT optimized structures with and without the inclusion of empirical dispersion are virtually identical with the structures obtained by neutron diffraction. Upon inclusion of empirical dispersion effects in the optimization leads to a slight elongation of the Si-H bond in 1·CuCl from 1.5112 to 1.5357 Å (neutron: 1.509(7) Å) and a shortening of the H···Cu bond from 1.7514 to 1.6690 Å (neutron: 1.775(7) Å). For the silver analogue 1·AgCl the trend is less pronounced (Si-H 1.4901 vs. 1.4866 Å (neutron: 1.492(10) Å); H···Ag 2.1325 vs. 2.0828 Å).
Å (neutron: 2.091(11) Å). However, all general structural features are maintained proving both sets of optimized structures for their reliability for subsequent electronic analysis. AIM topologies as well as ELI-D and NCI surfaces of 1·CuCl and 1·AgCl are shown in Figures 3 and 4 as well as Figures S26 and S27 for the respective data with the inclusion of dispersion effects, the corresponding results for 1 are given in Figure S25. Quantitative results are comprised in Tables S4 and S5. Two curved (Si–H)···P bond paths are visible in the AIM topology of 1 (Fig. S25a). These weak contacts cause the formation of localized blue-colored NCI basins and increased electron localizabilities along the H-P axes, see Figures S25b and S25d. The NCI basins are fused with flat and green-colored basins representing longer and even weaker P···C and P···H contacts. In 1·MCl (M = Cu, Ag) the (Si–)H·P interactions are lost in favor of P-M and (Si-)H···M bond formation. The tetrahedral MClP2H ligand arrangement is reflected by the formation of four corresponding AIM bond paths, see Figures 3a, 4a, S26a and S27a. In that, the M–Cl and M–P bonds fall into the regime of polar-covalent interactions with ED values at the M–Cl/P bond critical points (bcp) of 0.44 to 0.57 eÅ³, a slightly positive Laplacian, considerable kinetic energy density over ED ratios (G/ρ(r) 0.75 to 1.03 a.u.), negative but less pronounced total energy density over ED ratios (H/ρ(r) −0.22 to −0.35 a.u.), and RJI values roughly between 70 and 90%. Inclusion of dispersion lead to essentially the same values with the largest differences of Δmax,p(r),bcp = +0.05 eÅ³, Δmax,G/ρ(r) = +0.02 a.u. and Δmax,H/ρ(r) = −0.03 a.u. (see Table S4). The M–Cl bonds are nevertheless significantly more ionic than the M–P bonds, which amongst other things is reflected by larger G/ρ(r) and less negative H/ρ(r) values. These seemingly small differences, however, become immediately clearer by inspection of the topological and integrated ELI-D derived properties. Whereas ELI-D basins of considerable size (10.5 to 13.9 Å³; with disp. 9.8 to 12.9 Å³), electron population (2.11 to 2.52 e; with disp. 2.13 to 2.52 e) and localizability (1.75 to 1.78; with disp. 1.70 to 1.76) are formed for the M–P bonds, only a tiny Cu–Cl basin of 0.5 Å³ carrying 0.37 e (with disp. 0.42 e) with a maximum localizability of 1.48 at the basin
attractor position is obtained. Moreover, with 89% the RJI value is highest for the Cu–Cl bond. 1 AgCl does not even exhibit such kind of Ag-Cl basin suggesting dominantly ionic Ag-Cl bonding aspects.

As shown by the experiments, the (Si–)H···Cu interaction is shorter and stronger than the corresponding (Si–)H···Ag interaction. The negligible atom-atom overlap in the (Si–)H–Ag contact causes low ED, Laplacian, and H/ρ(r) values (Table S4), whereas the high bond polarity leads to high G/ρ(r) and RJI values. In contrast, the shorter and stronger (Si–)H–Cu contact leads to higher ED, Laplacian, and G/ρ(r) values, whereas non-negligible covalent bonding aspects result in more negative H/ρ(r) and smaller RJI values. This interpretation scheme is fully supported by NCI and ELI-D surfaces, see Figures 3b/d as and 4b/d as well as Figures S26b and S27b for the NCI values including dispersion effects. In the NCI of 1 AgCl, a disc-shaped and blue-colored basin (fused with a flat and green-colored inter-ligand region) is formed along the H–Ag axis pointing towards a purely ionic (Si–)H···Ag contact, whereas a ring-shaped and mixed-colored NCI basin is formed along the H–Cu axis in 1 CuCl. Moreover, the protonated valence ELI-D basin (the H atom) is flat along the H–Ag axis and curved along the H–Cu axis.

Table S5 lists AIM atomic and fragment charges of 1, 1 CuCl and 1 AgCl. The inclusion of dispersion effects have little influence on the AIM charges as the highest deviations are found to be Δ1 CuCl = 0.04 e and Δ1 AgCl = 0.06 e, respectively. With 2.8 e and 1.5 e, the Si and P atoms show high positive atomic charges, which are typical for the AIM method. The organic ligands carry ca. –0.5 e (phenyl groups), ca –0.7 e (methyl groups), and ca. –1.2 e (acenaphthal ligands). The hydridic H atoms also carry ca. –0.7 e and show only small differences between the three compounds, which was expected since the agostic bonds are quite weak. According to AIM, the Cl atoms in 1 CuCl and 1 AgCl carry ca. –0.7 e, which is in parts compensated by the metal atom charges, being ca. 0.4 e for Cu and ca. 0.3 e for Ag. Consequently, negative net charges of –0.3 and –0.4 e are obtained for the M–Cl fragments,
which were withdrawn from the bis(5-diphenylphosphinacenaphth-6-yl)methylsilane, or in other words, the "1-fragment" of 1·MCl. Notably, the charge compensation is not accomplished by specific chemical fragments in 1·CuCl and 1·AgCl, but all chemical parts of the compound more or less equally participate in charge balancing. The highest loss of charge is 0.09 e and 0.11 e for the P2 atom in 1·CuCl and 1·AgCl.

References


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