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New coinage metal-coordinated intermetalloid E_{10} clusters $(R_3P)AuGe_9(Hyp)_3Pt(PPh_3)$ (R = Bu, Et)

Christian Gienger, Claudio Schrenk and Andreas Schnepf

Detailed experimental procedure:

Reactions were performed in an N_2 atmosphere using standard Schlenk technique. Solids were handled in a GS glovebox in an Ar atmosphere. Solvents were dried with sodium and benzophenone and distilled prior to use. Pentane was dried with CaH_2 and distilled prior to use. $Pt(PPh_3)_4$ was acquired from Sigma Aldrich and used as received. $R_3PAuGe_9Hyp_3$ (R = Et, Bu) were synthesized according to literature procedures.[S1]

NMR spectroscopy

NMR spectra were recorded on a Bruker AVIII-300WB spectrometer or a Bruker AVII+500 spectrometer. ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra are referenced to Me_4Si and ^{31}P-NMR spectra are referenced to 85 % H_3PO_4 as external standards. ^{1}H-NMR spectra were calibrated to the residual proton signal of the solvent (C_6D_6 7.16 ppm, toluene-d_8 2.08 ppm).[S2]

$(Bu_3P)Au(PPh_3)PtGe_9(Hyp)_3$ 1

$Pt(PPh_3)_4$ (173 mg, 139 μmol) and $Bu_3PAuGe_9Hyp_3$ (250 mg, 139 μmol) were separately weighed into a 100 ml round bottom flask and dissolved in 25 ml of THF each. The solutions were stirred and cooled to -78 °C. The bright red solution of $Bu_3PAuGe_9Hyp_3$ was then added to the yellow solution of $Pt(PPh_3)_4$ via a steel cannula. The solution becomes orange when the addition is finished and warmed to room temperature while stirring overnight. The solution

turned into a dark red and the solvent was then removed in vacuo. The remaining dark red-brown solid was extracted with pentane and stored at -30 °C for crystallization. To obtain crystals suitable for single crystal diffraction analysis, the resulting orange crystals have been recrystallized in heptane. Orange rod shaped crystals haven been received in 30 % yield. As can be seen in figure S7 the reaction is in an equilibrium state as both

+$Bu_3PAuGe_9Hyp_3$ and $Pt(PPh_3)_4$ are still present in the mixture before purification. We can estimate about 67 % of the crude product consisting of **1**, but only 30 % can be isolated in crystalline form.

^{1}H-NMR (300 MHz, C_6D_6): δ = 0.36 (s broad, 54 H, -$Si(SiMe_3)_3$), 0.73 (s, broad, -$Si(SiMe_3)_3$), 0.89 (t, 9 H, $PCH_2CH_2CH_2\mathit{CH_3}$, $^3J_{HH}$ = 6.80 Hz), 0.96-1.24 (m, broad, 18 H, $P\mathit{CH_2CH_2CH_2}CH_3$)*, 1.11-1.22 (m, 12 H, $P\mathit{CH_2CH_2}CH_2CH_3$)*, 7.10, 7.24, 7.32, 8.39 (m, broad, 15 H, PPh_3), 6.94-7.06 and 7.72-7.79 (m, $Pt(PPh_3)_4$), $^{31}P\{^1H\}$-NMR (121.5 MHz, C_6D_6), -5.35 (s, PPh_3), 24.72 (s, $Pt(PPh_3)_4$), 41.35 (d, -PPh_3, $^3J_{PP}$ = 1.16 Hz), 46.45 (d, -P^nBu_3, $^3J_{PP}$ *= 1.16 Hz*), ^{29}Si-inept-nd-NMR (99.4 MHz, toluene-d_8) -3.64 (m, decomposition product**), -8.57 (m, $Si(\mathit{Si}Me_3)_3$), -9.77 (m, $Si(\mathit{Si}Me_3)_3$), -95.98 ((m, $\mathit{Si}(SiMe_3)_3$), -104.90 ((m, $\mathit{Si}(SiMe_3)_3$) ppm.

* Co-crystallized heptane and pentane lead to an impossible to determine fine structure in the alkyl signal region.

** ^{29}Si-NMR spectrum was recorded after the VT measurement, so the signal at -3.64 ppm is attributed to the small amount of a decomposition product realized at higher temperatures.

$(Et_3P)Au(PPh_3)PtGe_9(Hyp)_3$ 2

$Pt(PPh_3)_4$ (105 mg, 87 µmol) and $Et_3PAuGe_9Hyp_3$ (150 mg, 87 µmol) were separately weighed into a 100 ml round bottom flask and dissolved in 25 ml of THF each. The solutions were stirred and cooled to -78 °C. The bright red solution of $Et_3PAuGe_9Hyp_3$ was then added to the yellow solution of $Pt(PPh_3)_4$ via a steel cannula. The solution becomes orange when the addition is finished and warmed to room temperature while stirring overnight. The solution turned into a dark red and the solvent was then removed in vacuo. The remaining dark red-brown solid was extracted with pentane and stored at -30 °C for crystallization. $(Et_3P)Au(PPh_3)PtGe_9(Hyp)_3$ was obtained in the form of red blocks, suitable for single crystal x-ray diffraction with 27 % yield.

NMR-spectra

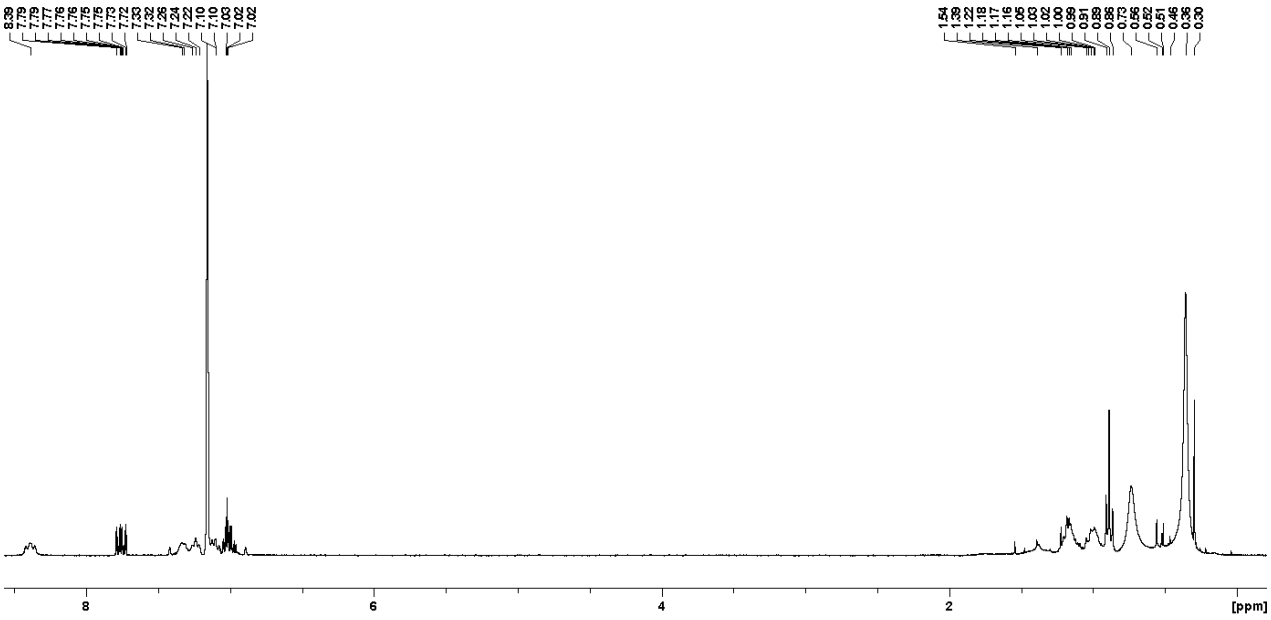

Figure S1: ^{1}H-NMR-spectrum of **1** in C_6D_6 at room temperature.

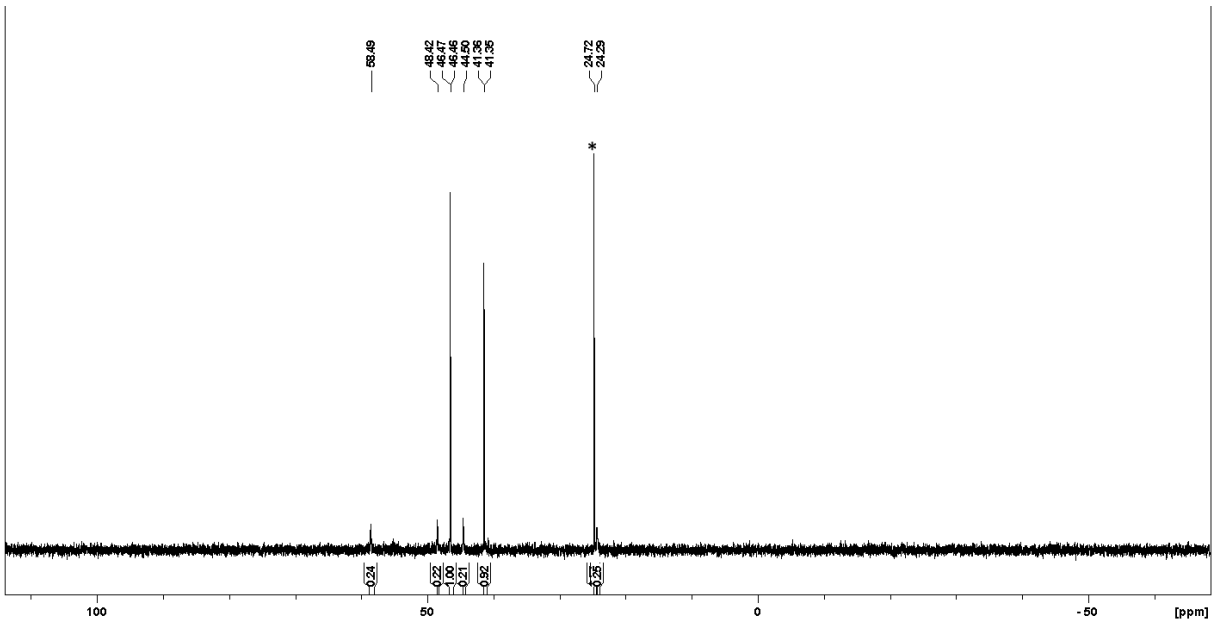

Figure S2: ^{31}P-NMR-spectrum of **1** in C_6D_6 at room temperature. * denotes cocrystallized $Pt(PPh_3)_4$

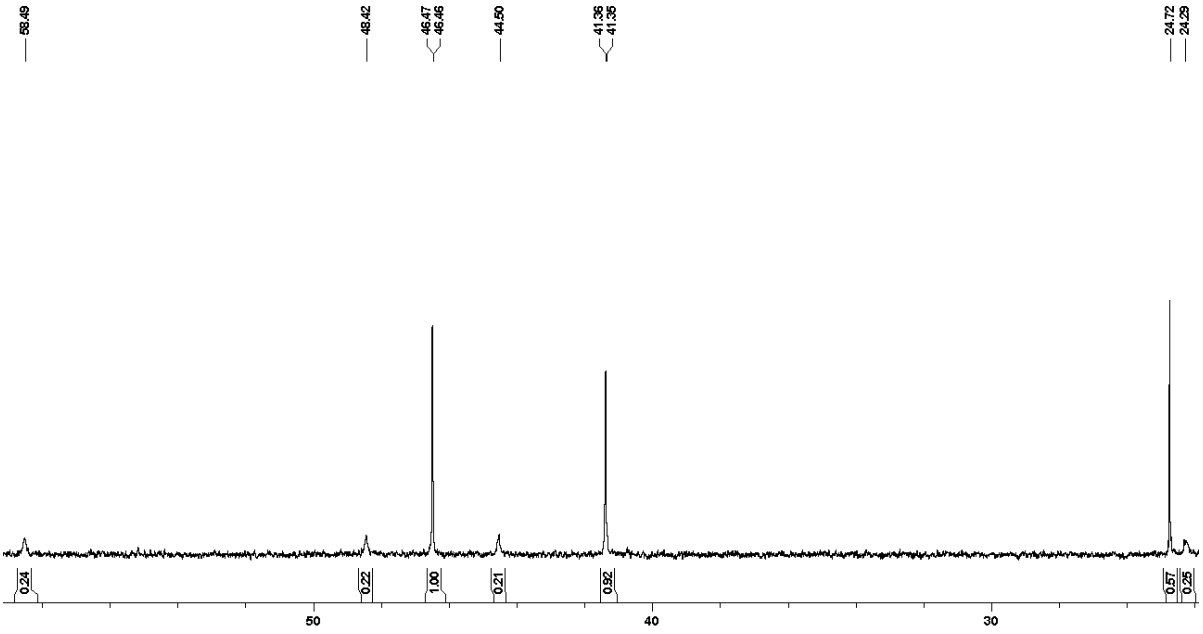

Figure S3: ^{31}P-NMR-spectrum of **1** in C_6D_6 at room temperature, to show the platinum satellites with coupling constants of $^{1}J_{P\text{-}Pt}$ = 2077.65 Hz and $^{3}J_{P\text{-}Pt}$ = 241.18 Hz.

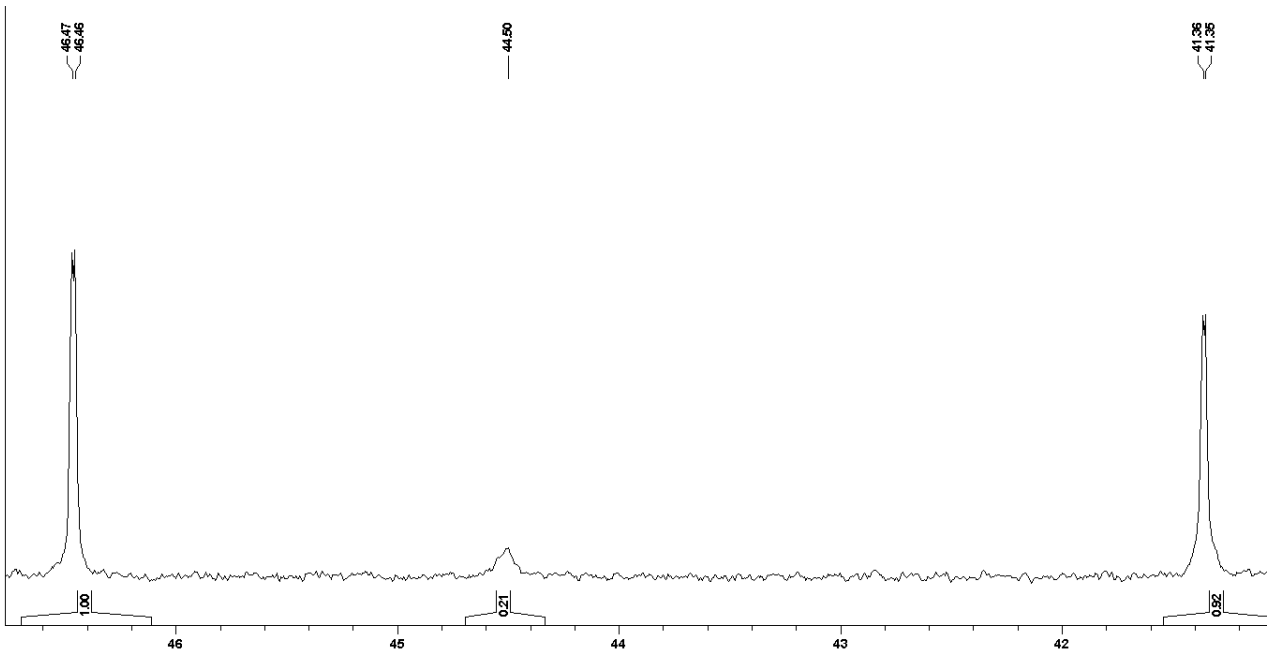

Figure S4: : ^{31}P-NMR-spectrum of **1** in C_6D_6 at room temperature, to show the $^3J_{P\text{-}P}$ coupling in the cluster.

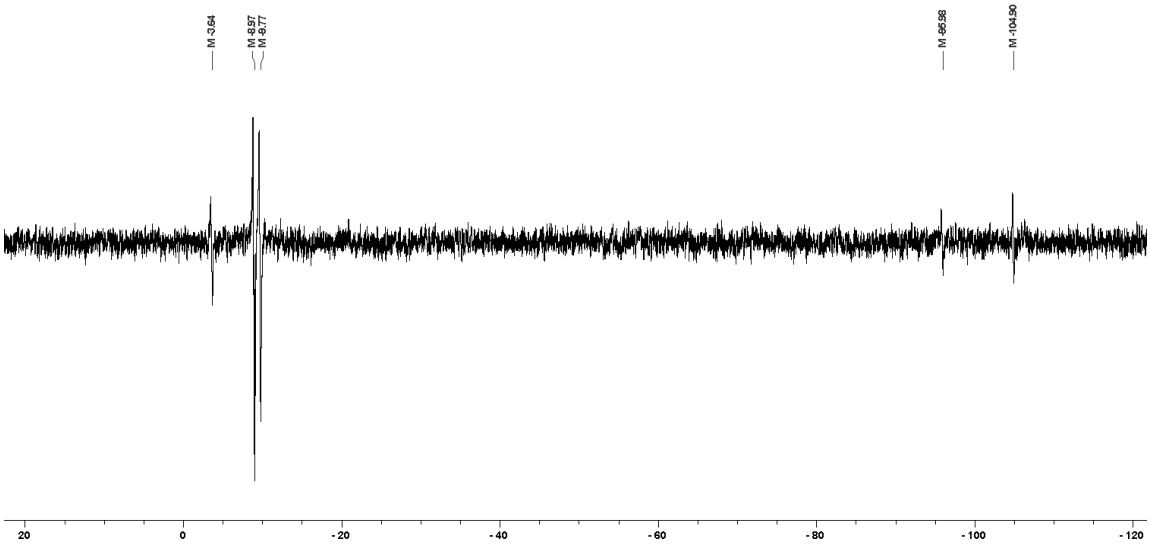

Figure S5: ^{29}Si-ineptd-nd-NMR-spectrum of **1** in toluene-d_8 at room temperature.

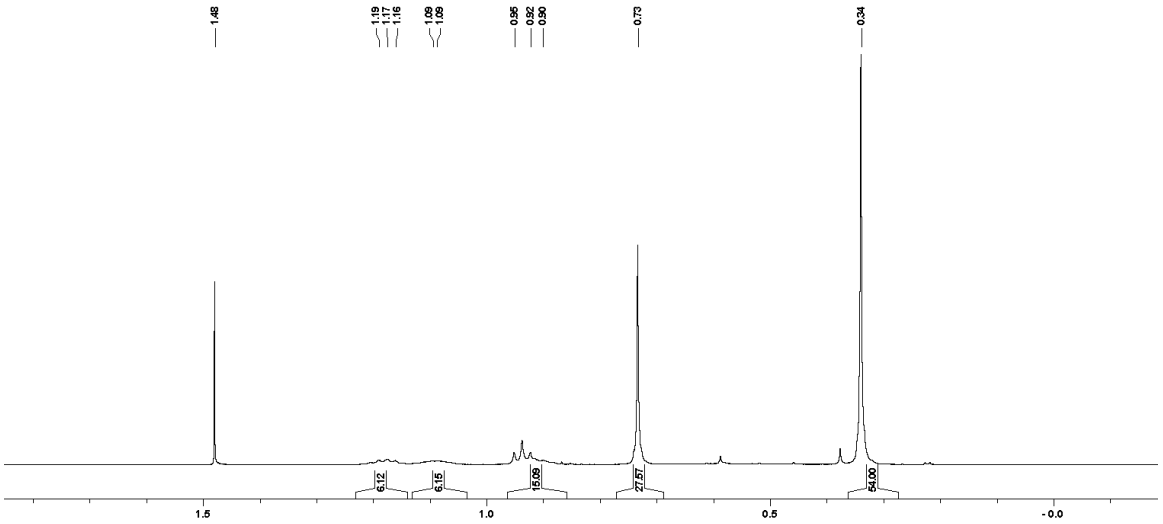

Figure S6: Part of the ^{1}H-NMR-spectrum of **1** in toluene-d_8 at -40 °C.

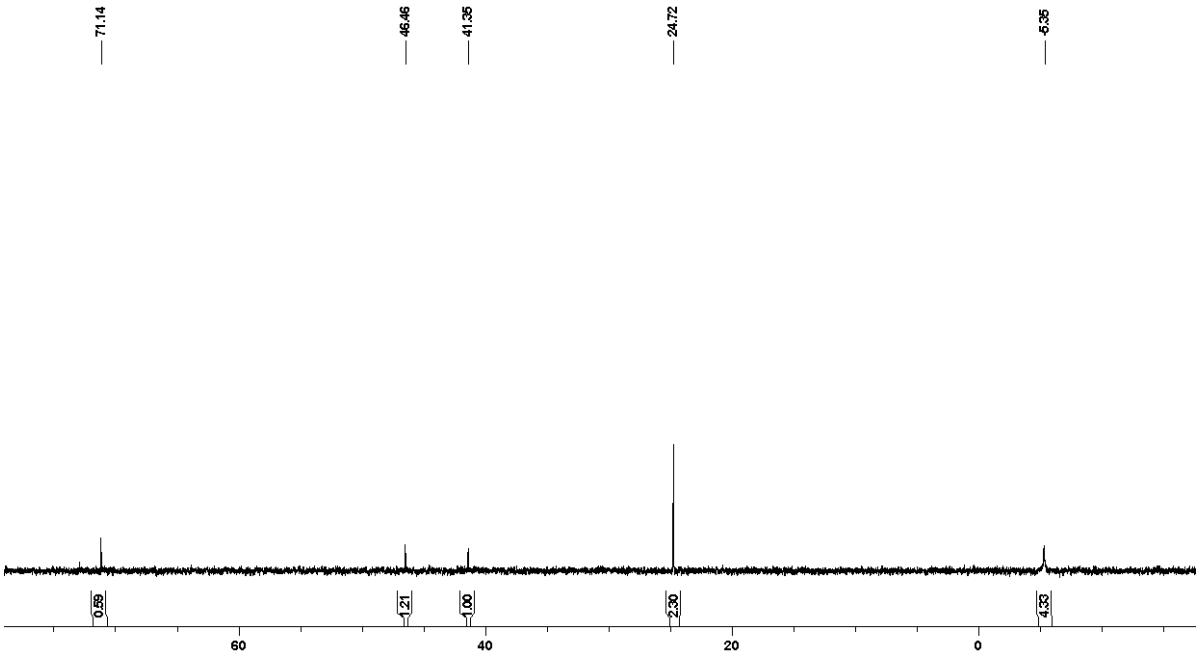

Figure S7: ^{31}P-NMR spectrum of the crude reaction mixture before purification. Besides the product peaks, all reactands and free PPh_3 can be identified. The integrals hint that there are about 67 % of **1** compared to $Pt(PPh_3)_4$.

Details for Quantum chemical calculations:

Quantum-chemical calculations were carried out with the RI-DFT[S5] version of the Turbomole[S3] program package by employing the BP86-functional.[S4] The basis sets were of SVP[S6] quality. The TmoleX client[S7] was used as graphical user interface and for illustrating the molecular orbitals.

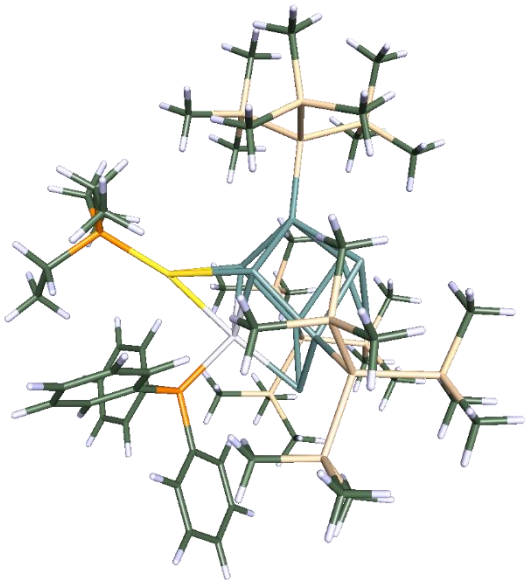

Figure S8: Geometry optimized structure of **2**

Point group: C_1

Energy: -25113.90050436305 Hartree

Lowest vibrational eigenvalue: 5.30 cm^{-1}

HOMO-LUMO-gap: 1.816 eV

Atomic coordinates:

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Au -1.968202 0.212830 -2.024790
Pt 0.181018 -0.723608 -0.574254
Ge 0.175649 1.842114 -0.963739
Ge -1.846827 0.240354 0.801914
P -3.795581 0.570773 -3.503041
Ge -0.028643 -0.936869 2.305776
Ge 2.330544 0.918334 0.272583
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Orbital Pictures of 2

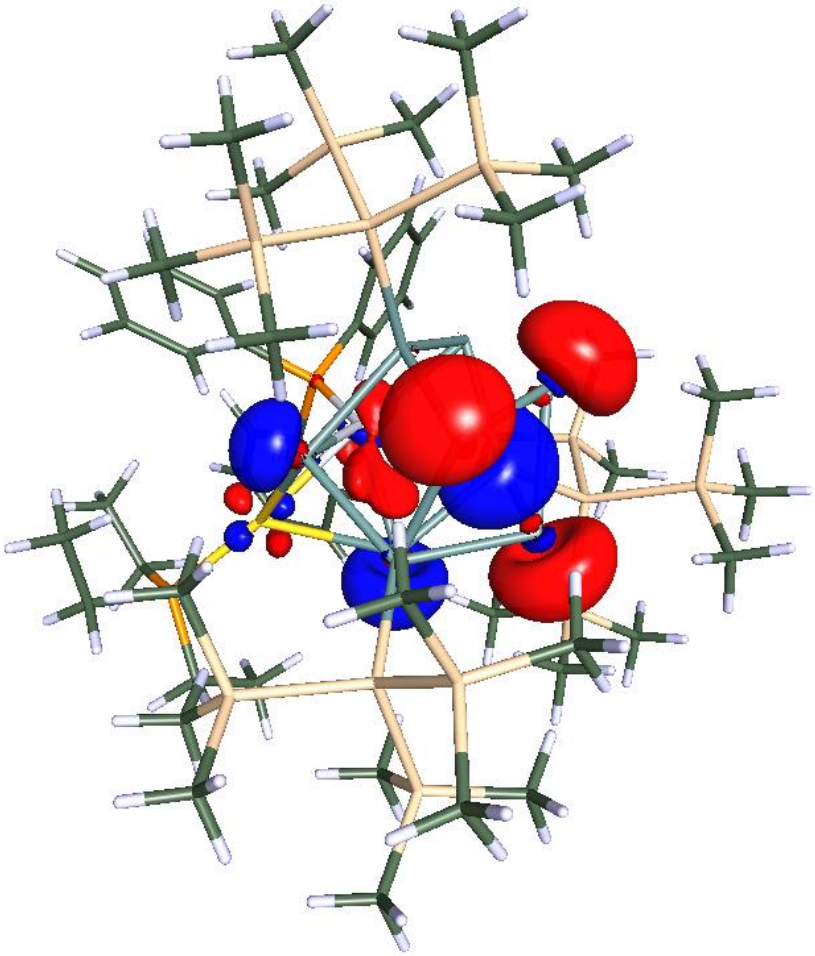

Figure S9: Orbital picture of HOMO-1 of **2**.

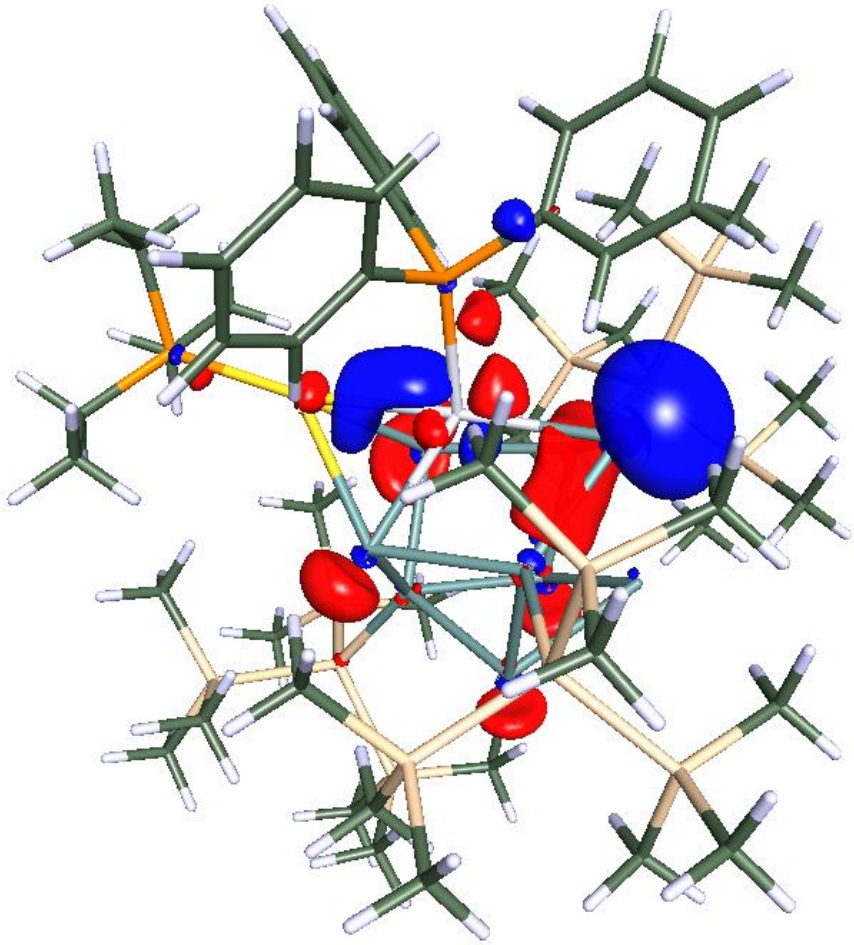

Figure S10: Orbital picture of HOMO of **2**.

Acknowledgement

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