

Supporting Information

Zn...Zn interactions at Nickel and Palladium Centers

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X-ray Crystallography: The X-ray intensity data for **1**, **2** and **4** · C₇H₈ were measured on an Oxford Diffraction Xcalibur2 diffractometer with a Sapphire2 CCD and graphite-monochromated Mo-K_α radiation. Those for **3** and **5** · 3 C₇H₈ were collected on an Agilent Technologies SuperNova diffractometer with an Atlas CCD and Cu-K_α radiation from multilayer X-ray optics. The crystals were coated with a perfluoropolyether, picked up with a glass fiber or a cryo loop and immediately mounted in the nitrogen cold gas stream of the diffractometer. The data were processed with the CrysAlisPro software [29]. Absorption corrections based on multiple-scanned reflection were carried out with ABSPACK in CrysAlisPro. The crystal structures were solved by direct methods with SHELXS-97 and refined with SHELXL-2014 [30].

The crystal of **2** was a non-merohedral twin with the twin operation corresponding to a twofold rotation about the [001] direction. The twin law is:

$$\begin{pmatrix} -1 & 0 & -0.0564 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The twinning was taken into account by using the HKLF 5 option of SHELXL. Refinement of the fractional contributions of the two twin components yielded a ratio of 0.5891(6):0.4109(6). The crystal of **4** · C₇H₈ was twinned by pseudo-merohedry. The twin operation is a twofold rotation about the [1 $\bar{1}$ 0] direction. The twin law is:

$$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The ratio of the twin components refined to 0.7792(7):0.2208(7). A Cp* ligand in **5** · 3 C₇H₈ and several toluene molecules in **4** · C₇H₈ and **5** · 3 C₇H₈ are disordered. Split models were refined with appropriate geometric restraints and rigid groups and restraints on atomic displacement parameters (ADPs). Anisotropic ADPs were introduced for all non-hydrogen atoms except for some disordered parts. Hydrogen atoms were placed at idealized positions and refined with the appropriate riding model. Crystal data and refinement details for **1–3**, **4** · C₇H₈ and **5** · 3 C₇H₈ are listed in Table S1.

CCDC 1478226 (1), 1478227 (2), 1478225 (3), 1478229 (4 · C₇H₈), 1478228 (5 · 3 C₇H₈) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

Table S1. Crystal data and refinement details for 1–3, 4 · C₇H₈ and 5 · 3 C₇H₈.

	1	2	3	4 · C ₇ H ₈	5 · 3 C ₇ H ₈
empirical formula	C ₂₀ H ₄₅ NiP ₃ Zn ₂	C ₂₈ H ₅₄ NiP ₂ Zn ₄	C ₄₂ H ₇₂ N ₄ Ni ₂ Zn ₄	C ₅₇ H ₈₆ N ₂ PdZn ₄	C ₉₇ H ₁₅₀ P ₂ Pd ₃ Zn ₆
<i>M_r</i>	567.92	772.84	1011.93	1167.15	2089.52
<i>T</i> (K)	107(2)	104(2)	102(2)	100(2)	100(2)
<i>λ</i> (Å)	0.71073	0.71073	1.54184	0.71073	1.54184
crystal size (mm ³)	0.56 × 0.36 × 0.27	0.25 × 0.19 × 0.13	0.08 × 0.05 × 0.03	0.26 × 0.24 × 0.23	0.11 × 0.09 × 0.08
crystal system, space group	triclinic, <i>P</i> -1	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	orthorhombic, <i>Pbca</i>	triclinic, <i>P</i> -1
<i>a</i> (Å)	9.2494(4)	11.8240(9)	11.9881(6)	25.6662(6)	12.2816(3)
<i>b</i> (Å)	10.0833(4)	17.8591(10)	17.8532(7)	25.5792(6)	13.0205(4)
<i>c</i> (Å)	15.9728(6)	16.3145(9)	12.4745(7)	35.0042(8)	29.8246(8)
<i>α</i> (°)	100.172(3)	90	90	90	100.247(2)
<i>β</i> (°)	92.322(3)	92.362(5)	109.769(6)	90	97.965(2)
<i>γ</i> (°)	109.339(4)	90	90	90	90.646(2)
<i>V</i> (Å ³)	1375.66(10)	3442.1(4)	2512.5(2)	22981.0(9)	4644.8(2)
<i>Z</i>	2	4	2	16	2
<i>ρ</i> _{calc} (mg m ⁻³)	1.371	1.491	1.338	1.349	1.494
<i>μ</i> (mm ⁻¹)	2.585	3.392	3.120	1.988	6.886
<i>F</i> (000)	596	1600	1056	9728	2160
<i>θ</i> range for data collection (°)	2.992 - 28.929	2.859 - 29.167	4.423 - 75.079	2.864 - 28.882	3.452 - 74.188
index ranges	-12 ≤ <i>h</i> ≤ 11 -11 ≤ <i>k</i> ≤ 12 -21 ≤ <i>l</i> ≤ 21	-15 ≤ <i>h</i> ≤ 15 -23 ≤ <i>k</i> ≤ 23 -21 ≤ <i>l</i> ≤ 20	-12 ≤ <i>h</i> ≤ 14 -15 ≤ <i>k</i> ≤ 21 -15 ≤ <i>l</i> ≤ 13	-34 ≤ <i>h</i> ≤ 33 -32 ≤ <i>k</i> ≤ 33 -43 ≤ <i>l</i> ≤ 46	-10 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 16 -35 ≤ <i>l</i> ≤ 37
reflections collected / unique	13105 / 6303	14063 / 14063	9131 / 4945	208231 / 28690	43311 / 18285
observed reflections [<i>I</i> > 2σ(<i>I</i>)]	5583	8985	3802	18902	15057
<i>R</i> _{int}	0.0290	-	0.0285	0.1063	0.0436
Parameters / restraints	250 / 0	317 / 0	247 / 0	1193 / 185	1058 / 364
goodness-of-fit on <i>F</i> ²	1.051	0.940	1.056	1.084	1.013
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0348	0.0370	0.0371	0.0585	0.0349
<i>wR</i> ₂ (all data) ^a	0.0961	0.0977	0.1054	0.1725	0.0910
Residuals (e Å ⁻³)	1.224 / -0.793	1.142 / -0.563	0.884 / -0.492	2.340 / -1.122	1.167 / -1.201

$$R_1 = \frac{\sum ||F_{obs}| - |F_{cal}||}{\sum |F_{obs}|}; wR_2 = \frac{\sum w(F_{obs}^2 - F_{cal}^2)}{\sum w(F_{obs}^2)}; GOF = \frac{\sum [w(F_{obs}^2 - F_{cal}^2)^2]}{(N_{obs} - N_{par})}^{1/2}$$

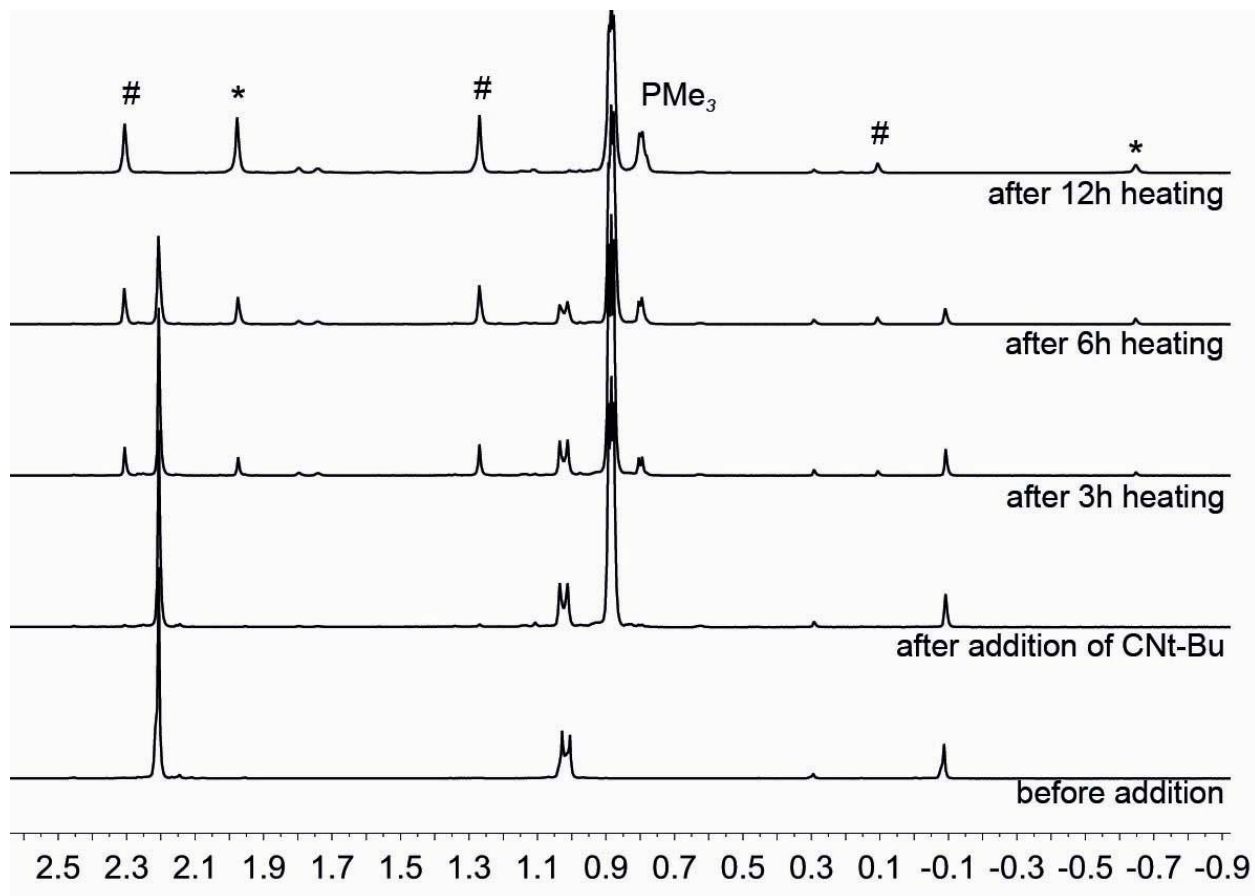


Figure S1: ^1H NMR reaction of **2** with an excess of NC^tBu : resonances marked with an # represent signals from **3**, whereas resonances marked with an * represent signals from the side product Cp^*ZnMe .

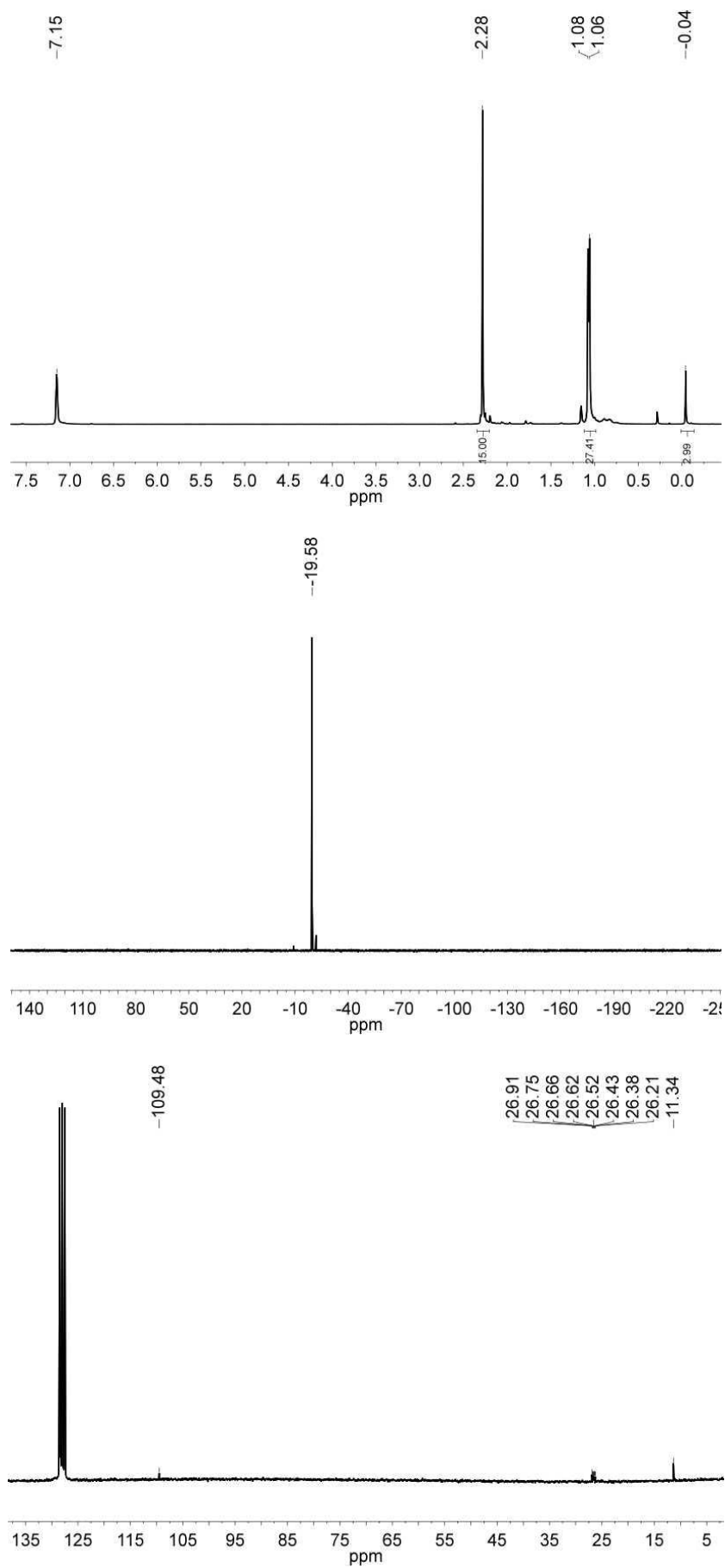


Figure S2. ^1H , ^{31}P and ^{13}C NMR spectra of **1**

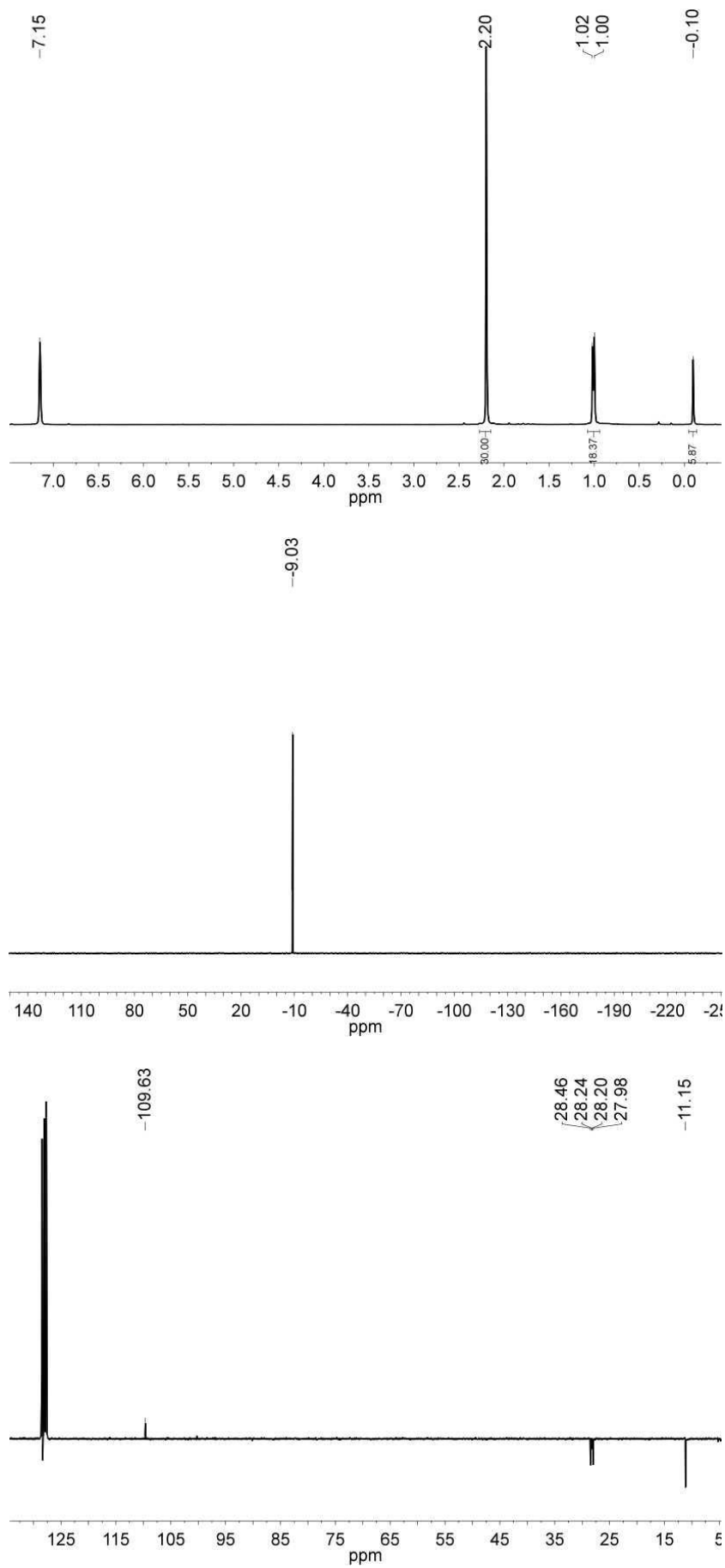


Figure S3. ^1H , ^{31}P and ^{13}C NMR spectra of **2**

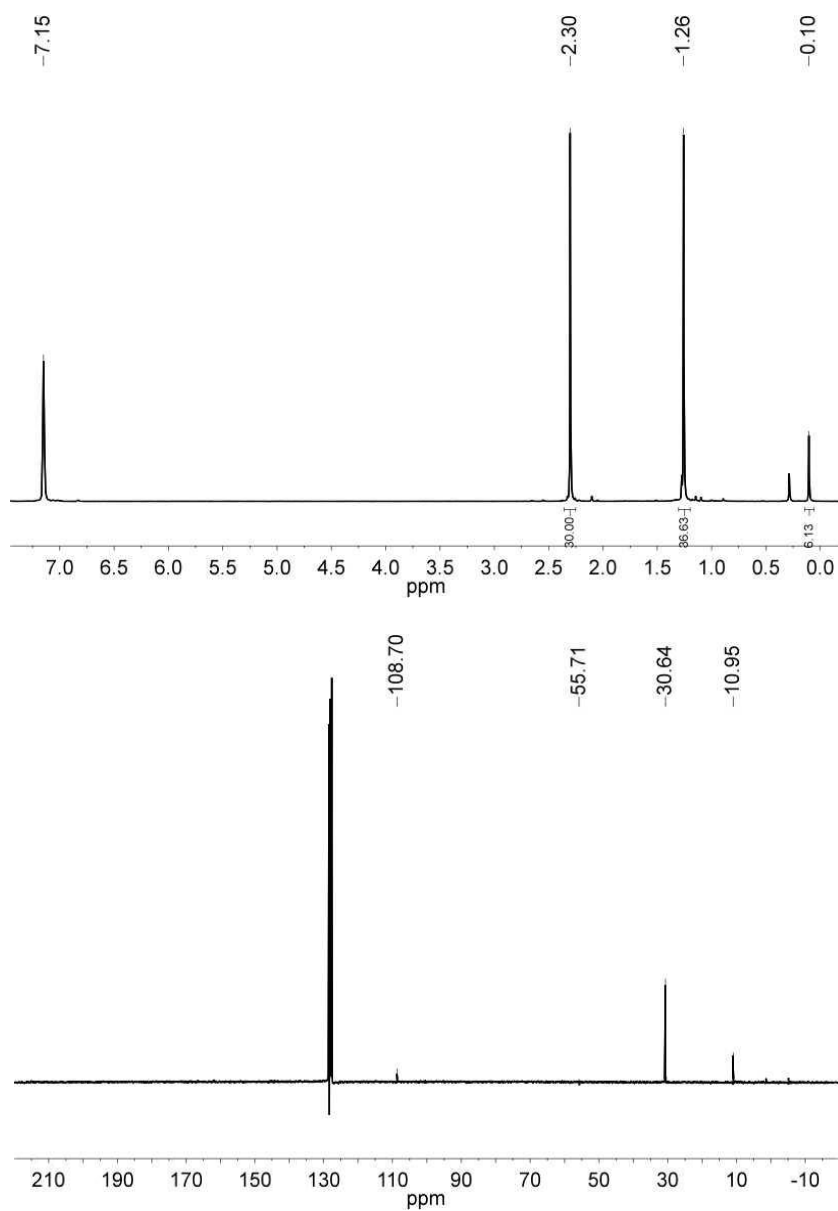


Figure S4. ^1H and ^{13}C NMR spectra of **3**

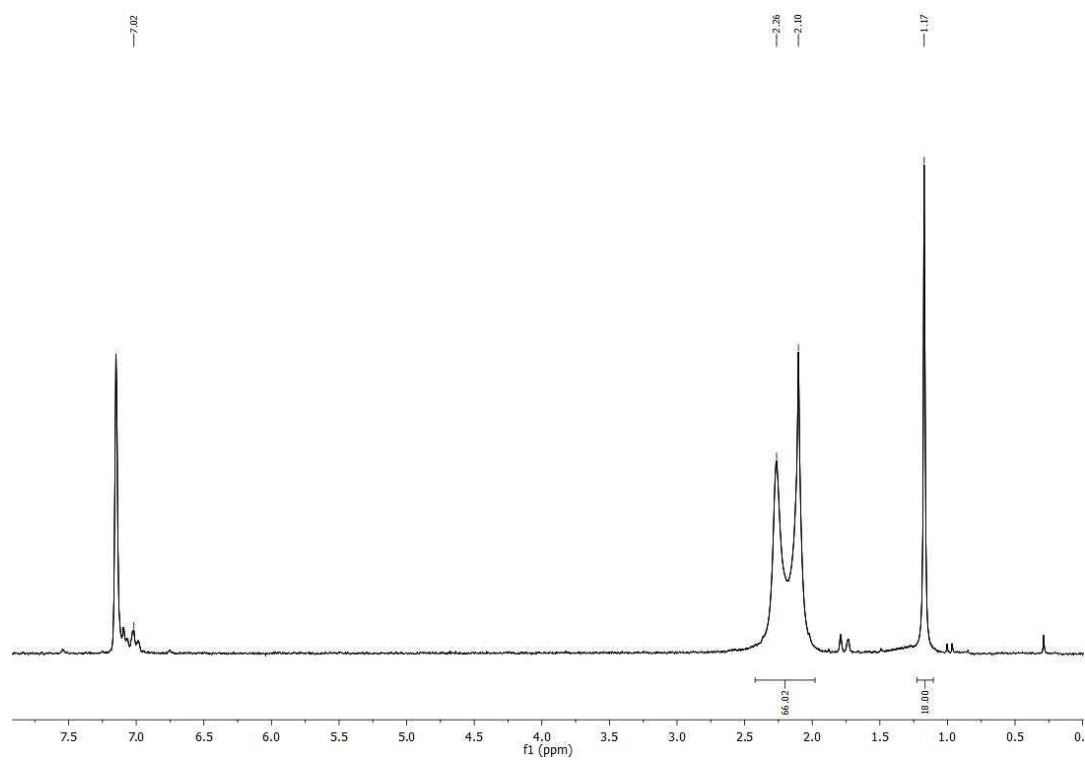


Figure S5. ^1H NMR spectra of **4**. Besides the product signals, signals for two toluene molecules, which co-crystallize, can be observed

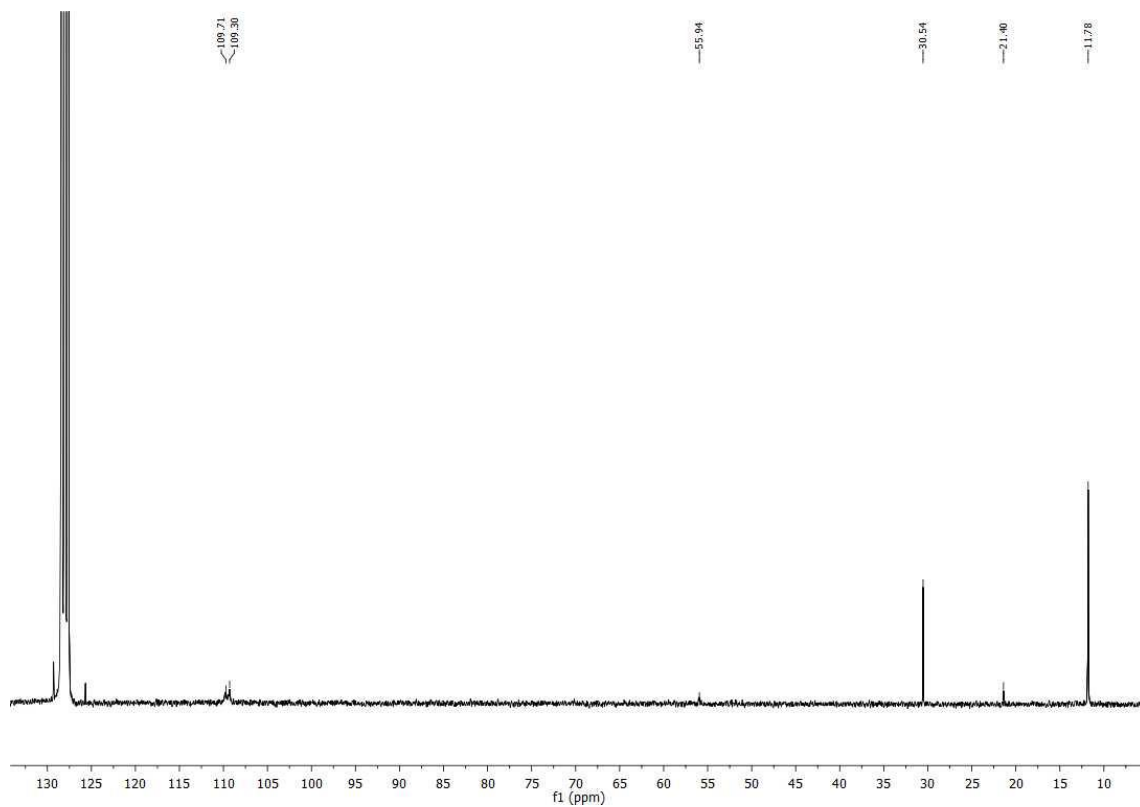


Figure S6. ^{13}C NMR spectra of **4**

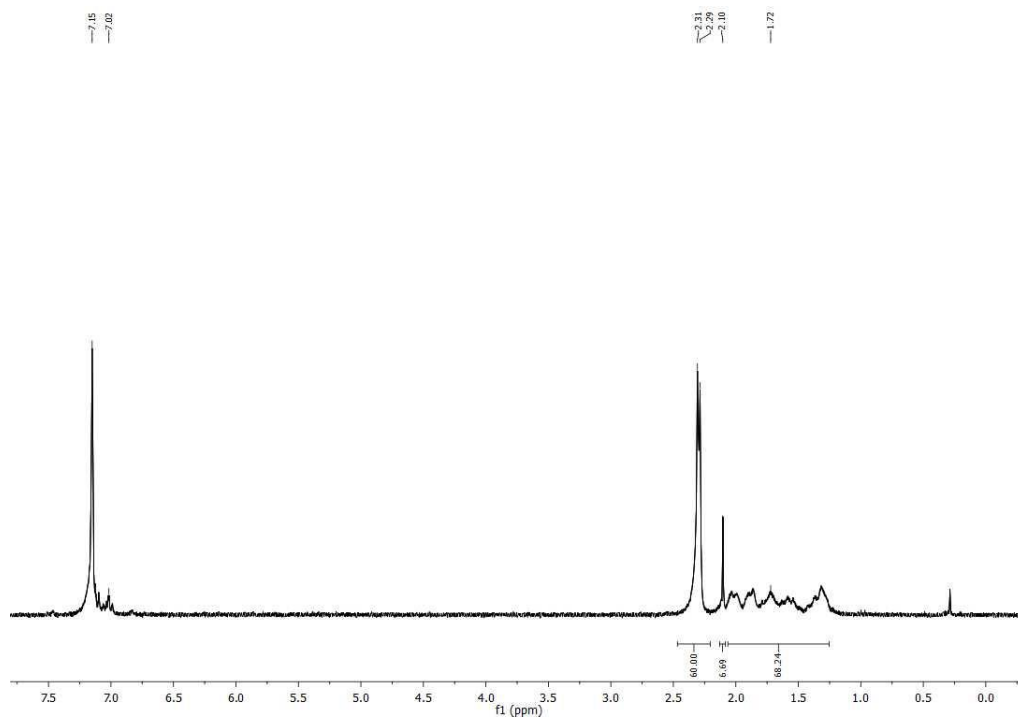


Figure S6. ^1H NMR spectra of **5**. Besides the product signals, signals for toluene which co-crystallize can be observed

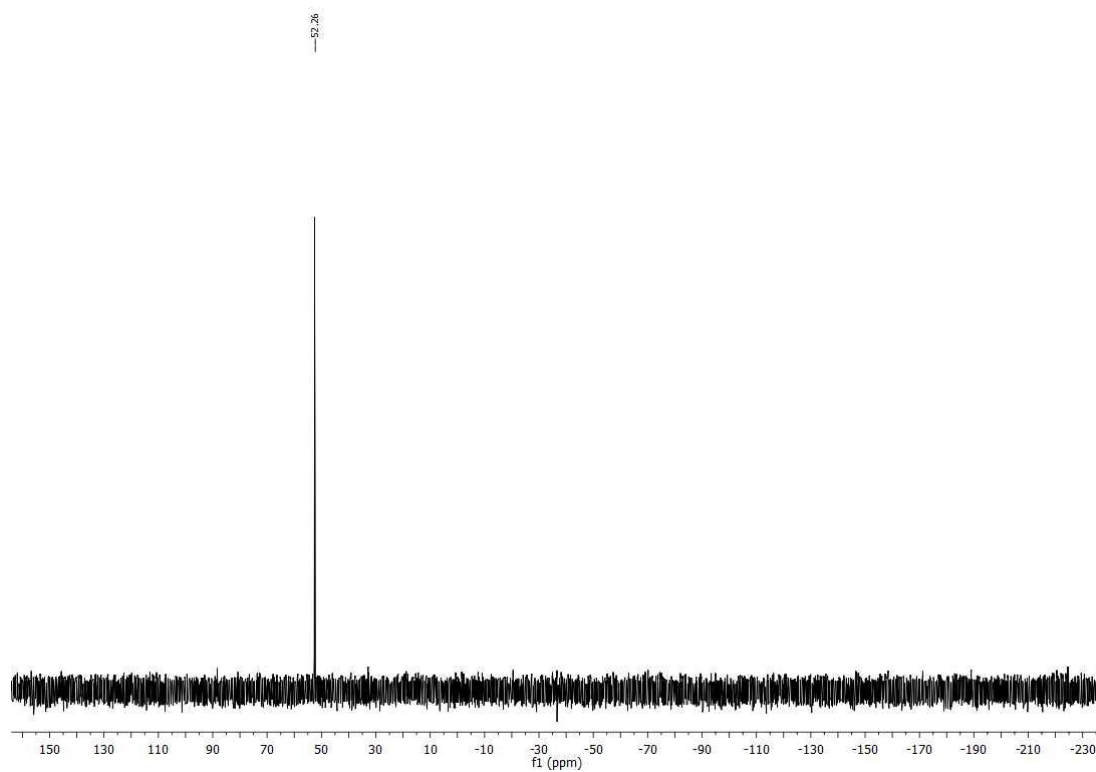


Figure S7. ^{31}P NMR of **5**

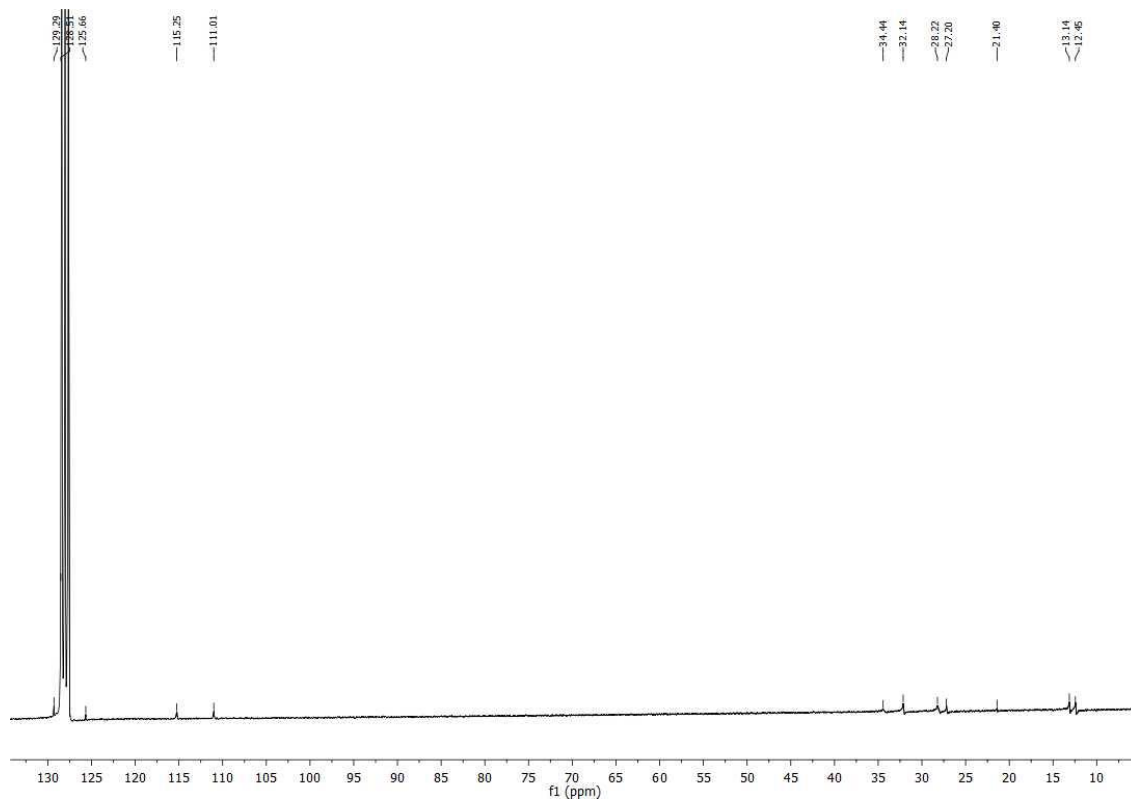


Figure S8. ^{13}C NMR spectra of **5**. Besides the product signals, signals for toluene which co-crystallize can be observed

Further Information on Continuous Shape Measure (CShM)

Continuous shape measure (CShM) is a mathematical method for the comparison of two different polyhedra. In this method, N vertices of a polyhedron are given by their position vectors Q_i ($i = 1, 2, 3 \dots, N$), as well as N vertices of an second polyhedron with the position vectors P_i ($i = 1, 2, 3 \dots, N$). The smallest distance $S_Q(P)$ of the position vectors between both polyhedrons is expressed with the following equation

$$S_Q(P) = \frac{1}{N} \min \sum_{i=1}^N |Q_i - P_i|^2 \cdot 100$$

The polyhedrons tested were centered in the origin and standardized ($|V_i| = |V_j|/\overline{|V_j|}$) first. Final values of $0 \leq S_Q(P) \leq 100$ can be obtained, which serve as a quantitative measure for the analogousness of both polyhedra. With $S_Q(P) = 0$ the polyhedron represents exact overlap of both polyhedrons, while increasing values denote increasing distortions. In our approach, we have chosen a computer-aided method for finding the minimum distance, i.e. for identifying the best superimposition of both polyhedra: The two polyhedra with the transition metal centre in the origin were superimposed. One of the two polyhedra is then rotated around three independent axes by 360° in steps of $360/n$ degrees resulting in n^3 different superimpositions. For each step a “minimum distance” of the polyhedral vertices is calculated by permutation of all plausible vertex combinations. This procedure results in n^3 distance values, the smallest one representing the most ideal superimposition of the two polyhedra. For this superimposition, the shape measure $S_Q(P)$ is calculated as described above. Figure S9a to S9c show the most ideal superimposition for the corresponding ideal polyhedrons and those extracted from molecular structures of **1** and **2**.

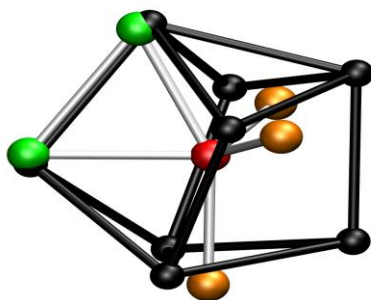


Figure S9a: Superimposition of a dodecahedron (black) and the fragment $[\text{NiZn}_2\text{P}_3]$ extracted from the molecular structure of **1** (coloured), concerning Zn atoms

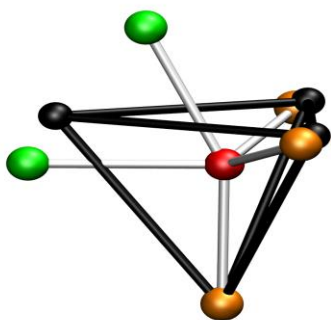


Figure S9b: Superimposition of a tetrahedron (black) and the fragment $[\text{NiZn}_2\text{P}_3]$ extracted from the molecular structure of **1** (coloured), concerning P atoms

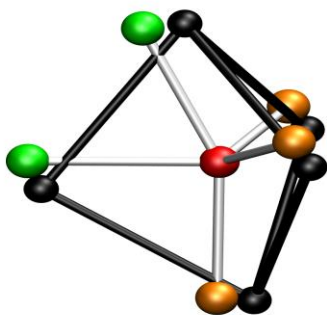


Figure S9c: Superimposition of a trigonalbipyramid (black) and the fragment $[\text{NiZn}_2\text{P}_3]$ extracted from the molecular structure of **1** (coloured), concerning Zn and P atoms

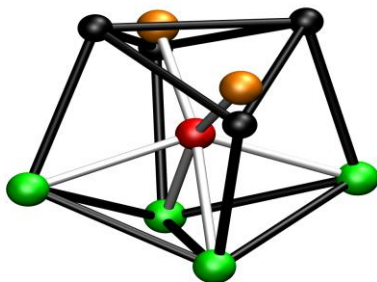


Figure S10a: Superimposition of a dodecahedron (black) and the fragment $[\text{NiZn}_4\text{P}_2]$ extracted from the molecular structure of **2** (coloured), concerning Zn atoms

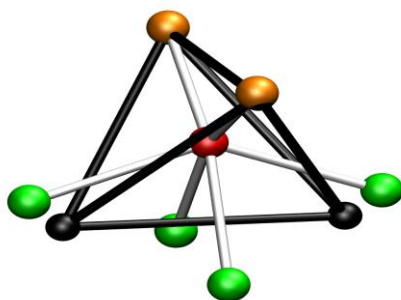


Figure S10b: Superimposition of a tetrahedron (black) and the fragment $[\text{NiZn}_4\text{P}_2]$ extracted from the molecular structure of **2** (coloured), concerning P atoms

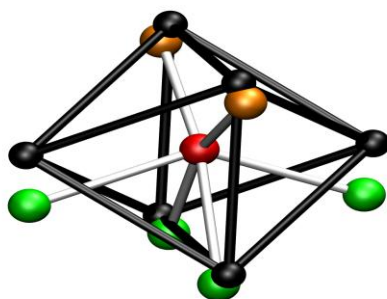


Figure S10c: Superimposition of a octahedron (black) and the fragment $[\text{NiZn}_4\text{P}_2]$ extracted from the molecular structure of **2** (coloured), concerning Zn and P atoms

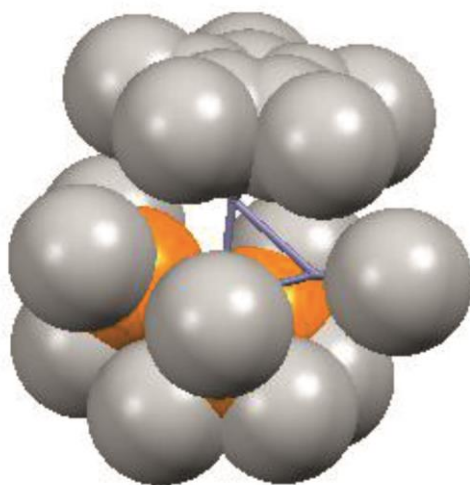


Figure S11: Space filling model for **1**.

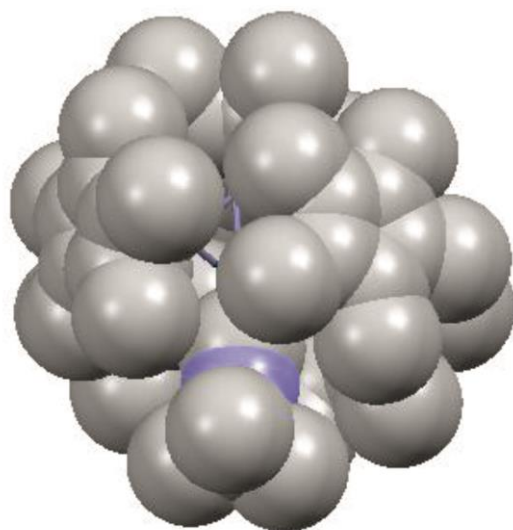


Figure S12: Space filling model for **4**.

Quantumchemical Calculations

Theoretical Methods:

The geometries of the molecules were optimized at the gradient corrected DFT level of theory using Becke's exchange functional^[1] in conjunction with Perdew's correlation functional^[2] (BP86) with the TURBOMOLE V6.3 program package.^[3] Ahlrich's def2-TZVPP basis set^[4] was used. The RI approximation^[5] was applied using auxiliary basis functions.^[6] Stationary points were characterized by the analytical calculation of the Hessian using TURBOMOLE's AOFORCE module.^[7] The level of theory is then denoted as BP86/TZVPP.

The Atom-in-Molecules (QTAIM)^[8] analyses were carried out with the program AIMAll^[9] using the BP86/TZVPP wavefunction files.

The NBO charges were obtained using the NBO 3.1 program implemented in Gaussian09.^{[10],[11]}

The EDA-NOCV calculations^[16] were carried out using the ADF(2013.01)^[12] program package at the BP86/TZ2P+ level of theory. Uncontracted Slater-type orbitals (STOs) were employed as basis functions in self-consistent field (SCF) calculations.^[13] Triple-zeta-quality basis sets were used which were augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.^[14] Scalar relativistic effects were considered using the zero-order regular approximation (ZORA).^[15]

Within the EDA, bond formation between the interacting fragments is divided into three steps: In the first step, the fragments which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation to yield the quasiclassical electrostatic attraction ΔE_{elstat} . In the second step, the product wave function becomes antisymmetrized and renormalized, which gives the repulsive term ΔE_{Pauli} , named the Pauli repulsion. The third step consists of the relaxation of the molecular orbitals to their final form to yield to stabilizing orbital interaction ΔE_{orb} . The sum of the three terms $\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$ gives the total interaction energy ΔE_{int} . For further information we refer to the literature.^[17]

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Table S2: NBO results for **1**, [(ZnCp*)(ZnMe)] and **2** (BP86/def2-TZVPP).

System	Partial Charge [<i>e</i>]	Wiberg Bond Index
1		Zn-Zn: 0.26
ZnMe	+0.31	Zn _{Me} -Ni: 0.20
ZnCp*	-0.06	ZnCp*-Ni: 0.28
Ni	-0.23	
[(ZnCp*)(ZnMe)]		Zn-Zn: 0.65
ZnMe	+0.17	-
ZnCp*	-0.17	-
2		Zn-Zn: 0.07-0.15
ZnMe	+0.32	Zn _{Me} -Ni: 0.51
ZnCp*	+0.31	ZnCp*-Ni: 0.58
Ni	-2.37	

Table S3: EDA-NOCV results in kcal/mol for **1** (BP86/TZ2P+). Occupation of the fragments: [(ZnCp*)(ZnMe)]: singlet ; [Ni(PMe₃)₃] : singlet.

ΔE_{int}	-49.8	
ΔE_{Pauli}	165.6	
ΔE_{elstat}	-155.3 (72.1%)	
ΔE_{orb}	-60.1 (27.9%)	
$\Delta E_{\text{orb,(1)}}$	-27.7 (46.1%)	Ni→Zn ₂
$\Delta E_{\text{orb,(2)}}$	-17.0 (28.3%)	Zn ₂ →Ni
$\Delta E_{\text{orb, rest}}$	-15.4 (25.6%)	Polarisation

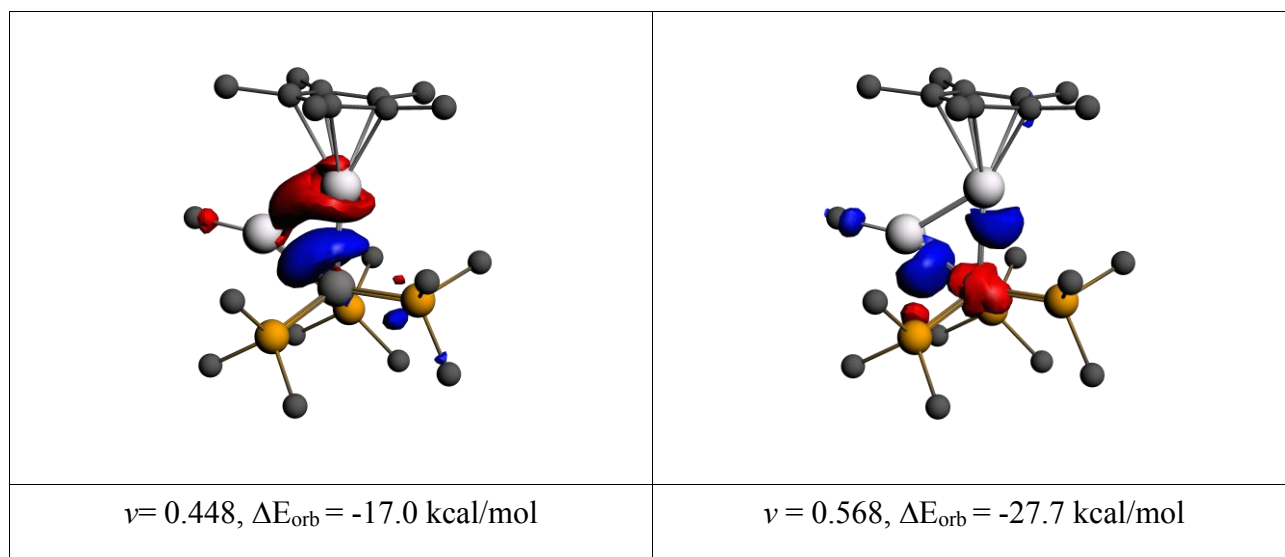


Table S4: EDA-NOCV results in kcal/mol for **2** (BP86/TZ2P+). Occupation of the fragments: ZnMe: doublet; $[\text{Ni}(\text{ZnCp}^*)_2(\text{ZnMe})(\text{PMe}_3)_2]$: doublet.

ΔE_{int}	-69.4	
ΔE_{Pauli}	209.5	
ΔE_{elstat}	-171.8 (61.6%)	
ΔE_{orb}	-107.1 (38.4%)	
$\Delta E_{\text{orb,(1)}}$	-79.2 (73.9%)	Zn→Ni
$\Delta E_{\text{orb,(2)}}$	-10.6 (9.9%)	Ni→Zn
$\Delta E_{\text{orb, rest}}$	-17.3 (16.2%)	Polarisation

Table S5: EDA-NOCV results in kcal/mol for **2** (BP86/TZ2P+). Occupation of the fragments: ZnCp: doublet; $[\text{Ni}(\text{ZnCp}^*)(\text{ZnMe})_2(\text{PMe}_3)_2]$: doublet.

ΔE_{int}	-67.0	
ΔE_{Pauli}	139.5	
ΔE_{elstat}	-137.4 (66.5%)	
ΔE_{orb}	-69.1 (33.5%)	
$\Delta E_{\text{orb,(1)}}$	-53.9 (78.0%)	Zn→Ni
$\Delta E_{\text{orb,(2)}}$	-3.8 (5.5%)	Ni→Zn
$\Delta E_{\text{orb, rest}}$	-11.4 (16.5%)	Polarisation

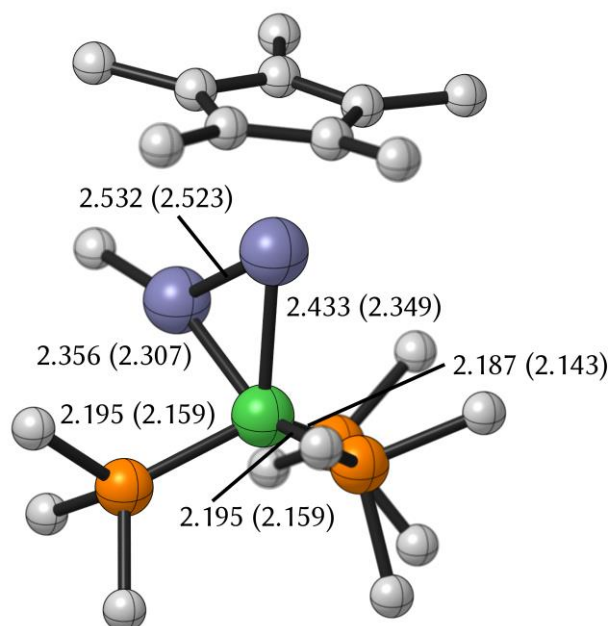


Figure S13: Calculated bond lengths [in Å] and angles [in °] of **1** (BP86/TZVPP). Experimental values are given in parentheses. Hydrogen atoms are omitted for a better view

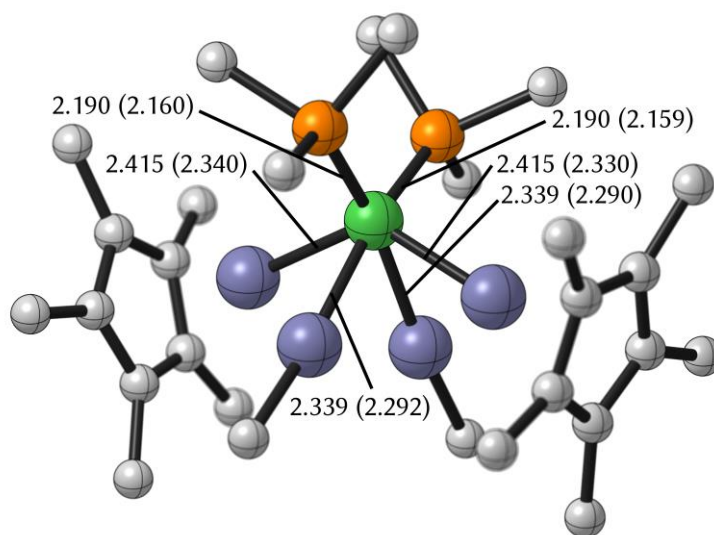


Figure S14: Calculated bond lengths [in Å] and angles [in °] of **2** (BP86/TZVPP). Experimental values are given in parentheses. Hydrogen atoms are omitted for a better view.