Organogallium- and Organozinc-rich Palladium and Platinum Clusters

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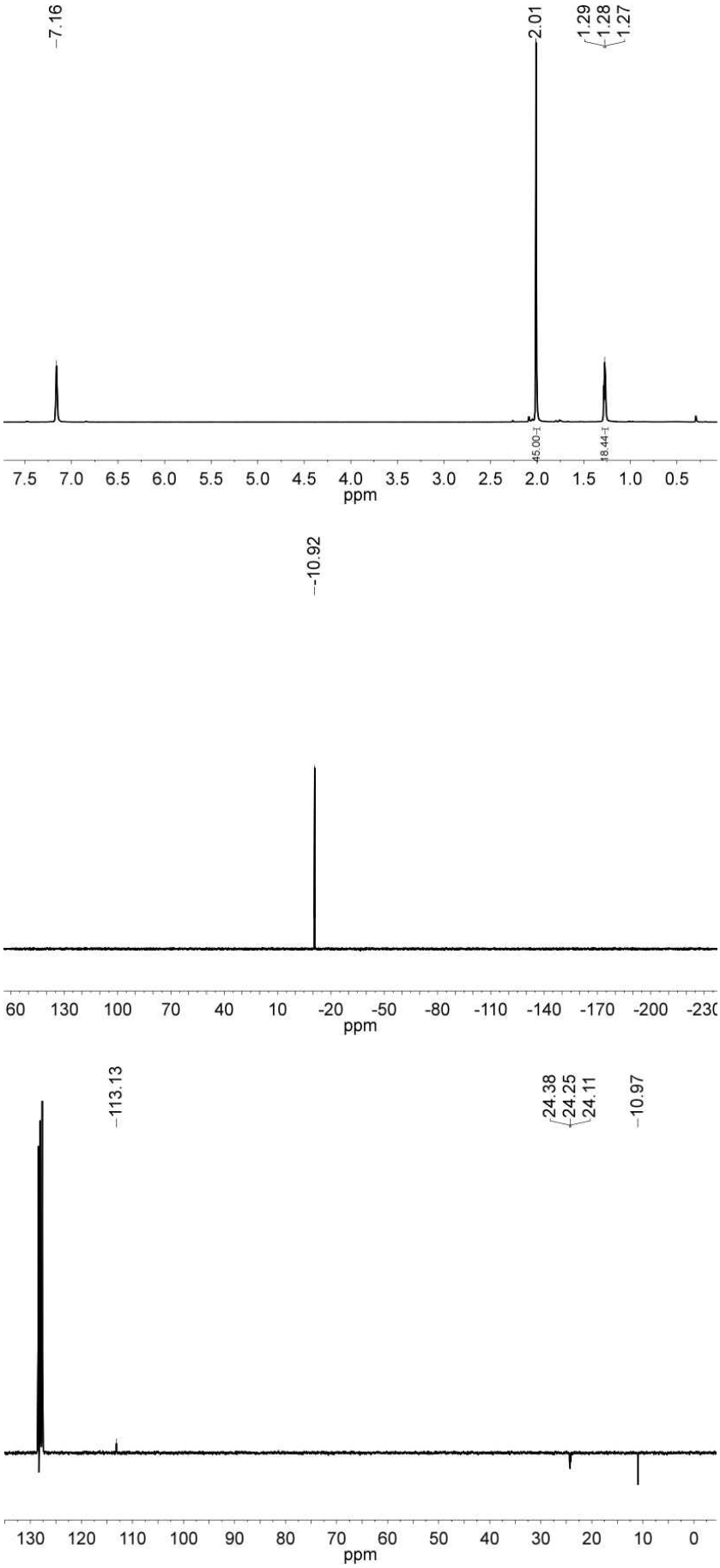
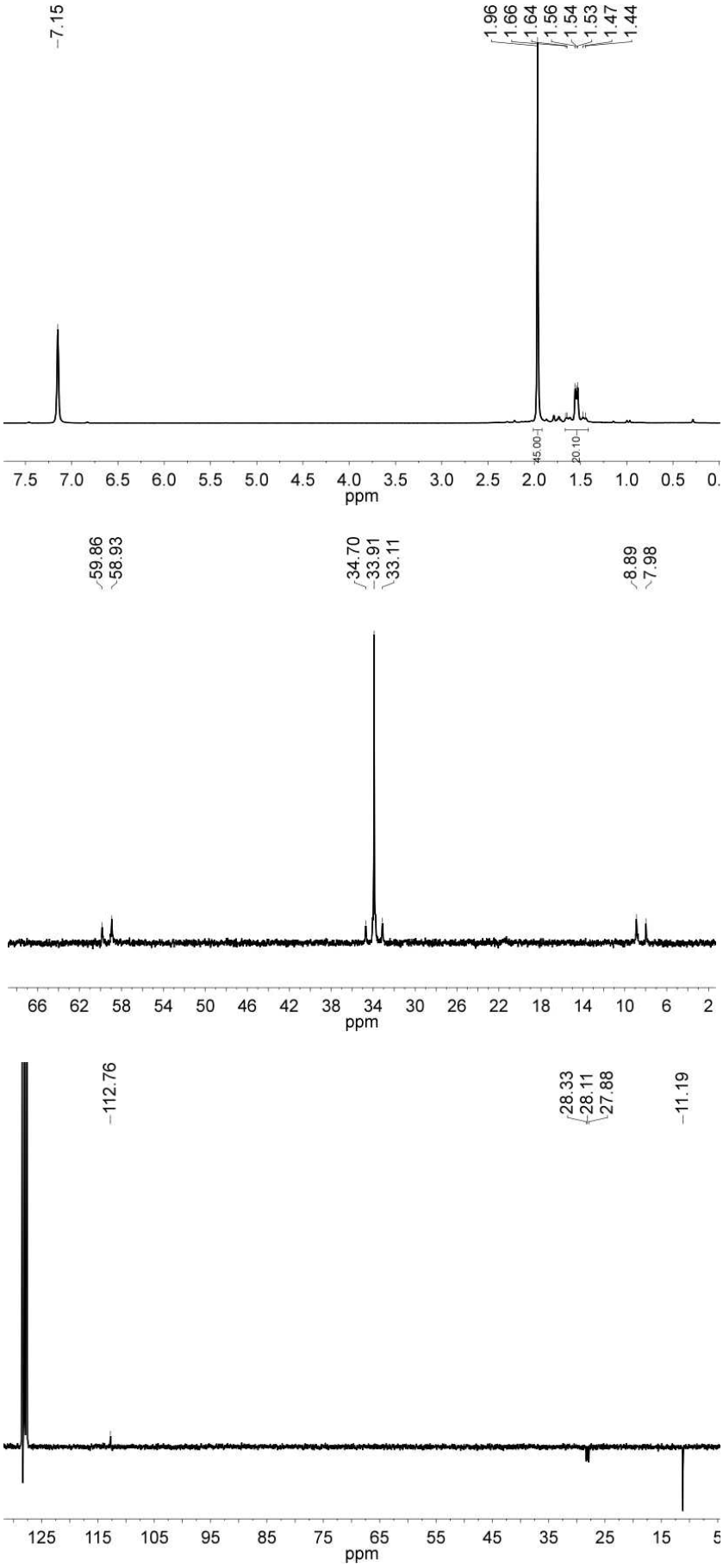
Table S1. Important crystallographic data of compounds **1a - 3b**

	1a	**1b**	**2**	**3a**	**3b**
empirical formula	$C_{36}H_{63}Ga_3P_2Pd_2$	$C_{36}H_{63}Ga_3P_2Pt_2$	$C_{39}H_{72}Ga_3P_3Pd_3$	$C_{28}H_{69}P_5Pd_2Zn_4$	$C_{28}H_{54}P_2PtZn_4$
molecular weight	979.76	1156.39	1162.24	1034.96	909.22
temperature (K)	105(2)	105(2)	105(2)	105(2)	105(2)
wavelength Mo-K_α (Å)	0.71073	0.71073	0.71073	0.71073	1.54184
crystal size (mm)	0.39 x 0.28 x 0.08	0.22 x 0.11 x 0.05	0.25 x 0.22 x 0.16	0.27 x 0.14 x 0.11	0.11 x 0.10 x 0.05
crystal system, space group	monoclinic, *P2(1)/m*	monoclinic, *P2(1)/m*	monoclinic, *P2(1)/c*	tetragonal, *P4(3)*	Monoclinic, *P2(1)/n*
a (Å)	18.0920(5)	17.9964(6)	23.3586(3)	12.44770(10)	11.7556(4)
b (Å)	15.1214(4)	15.2155(4)	17.7180(2)	12.44770(10)	18.4752(7)
c (Å)	18.3971(4)	18.3239(4)	23.6868(3)	27.5483(6)	16.4826(6)
α (Å)	90.00	90.00	90.00	90.00	90.00
β (Å)	103.738(2)	103.664(3)	101.709(2)	90.00	91.654(3)
γ (Å)	90.00	90.00	90.00	90.00	90.00
cell volume ($Å^{-3}$)	4889.0(2)	4875.5(2)	9599.2(2)	4268.48(10)	3578.3(2)
Z	4	4	8	4	4
density $\rho_{calc.}$ (mg m^{-3})	1.331	1.575	1.608	1.611	1.688
absorption coefficient μ(mm^{-1})	2.438	7.439	2.884	3.240	11.052
F (000)	1976	2229	4656	2096	1800
2θ range for data collection (°)	2.93 - 25.00	3.03 - 25.00	2.85 - 25.00	2.96 - 25.00	3.59 - 70.00
index ranges	-21<=h<=21	-21<=h<=21	-27<=h<=27	-14<=h<=14	-12<=h<=14
	-17<=k<=17	-17<=h<=18	-21<=k<=21	-14<=k<=14	-22<=k<=22
	-21<=l<=21	-21<=l<=21	-28<=l<=28	-32<=l<=32	-20<=l<=20
reflexions collected	44900	36232	135402	47546	12040
unique reflexions	8937	8910	16877	7495	12040
R_{int}	0.0532	0.0883	0.0308	0.0363	0.0204
data/restraints/parameters	8937/48/438	8910/60/433	16877/0/907	7495/1/375	1204070/336
absorption correction	empirical (abspack)	empirical (abspack)	empirical (abspack)	empirical (abspack)	empirical (abspack)
goodness-of-fit on F^2 (GOF)	1.052	0.957	1.239	1.021	1.045
final R indices [I > 2σ(I)]	R_1 = 0.0466	R_1 = 0.0492	R_1 = 0.0454	R_1 = 0.0440	R_1 = 0.0502
	wR_2 = 0.1154	wR_2 = 0.0990	wR_2 = 0.0964	wR_2 = 0.1072	wR_2 = 0.1317
R indices (all data)[a]	R_1 = 0.0716	R_1 = 0.0862	R_1 = 0.0632	R_1 = 0.0500	R_1 = 0.0578
	wR_2 = 0.1254	wR_2 = 0.1114	wR_2 = 0.1033	wR_2 = 0.1109	wR_2 = 0.1398
largest difference peak and hole (e $Å^{-3}$)	1.304 and -1.474	1.812 and -2.718	1.246 and -0.718	0.453 and -0.363	3.138 and -1.800

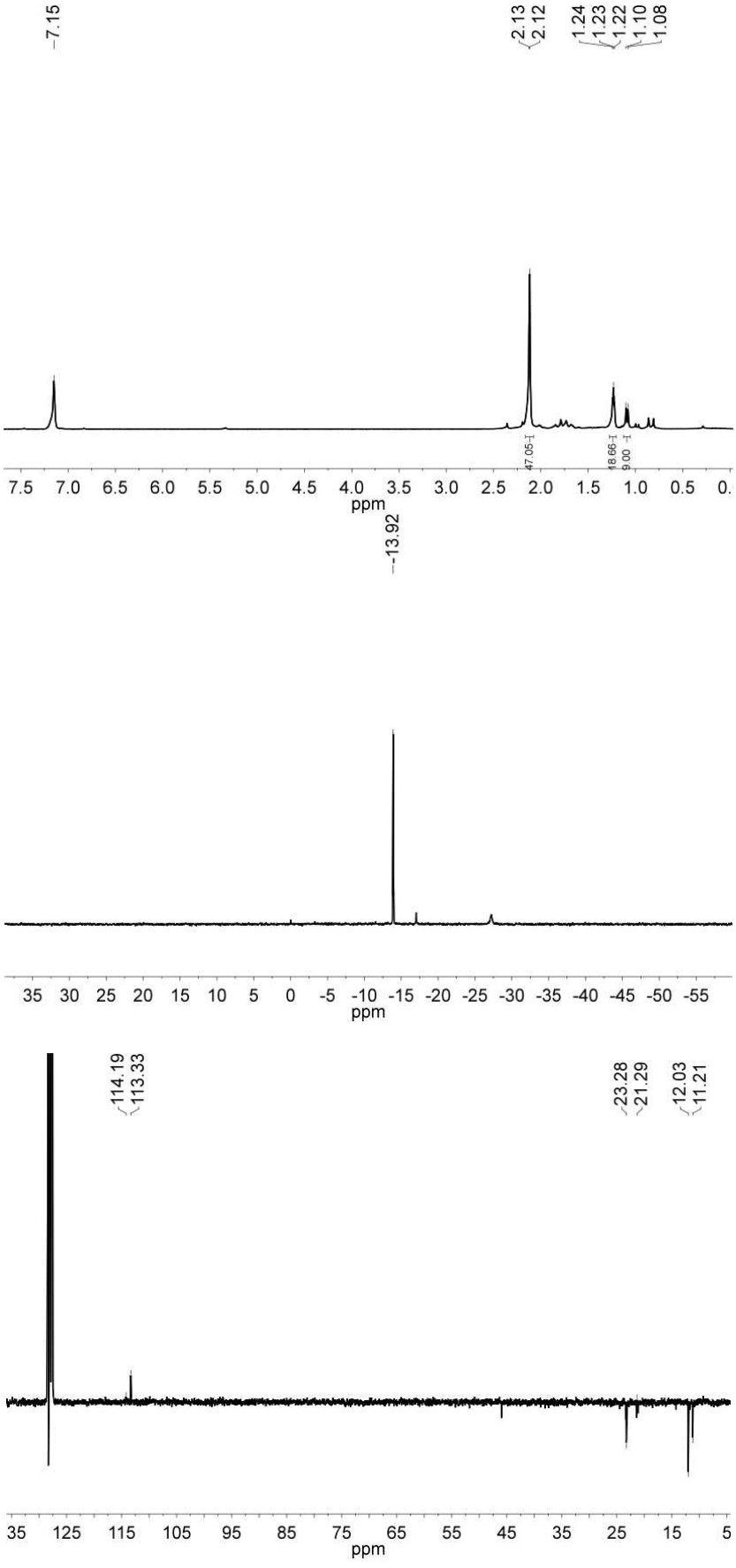
$$R_1 = \sum \left| |F_{obs}| - |F_{cal}| \right| / \sum |F_{obs}|^{1/2}; wR_2 = \left[\sum w\left(F_{obs}^2 - F_{cal}^2\right) / \sum w\left(F_{obs}^2\right)^2 \right]^{1/2}; GOF = \left\{ \sum \left[w\left(F_{obs}^2 - F_{cal}^2\right)^2 \right] / \left(N_{obs} - N_{par}\right) \right\}^{1/2}$$



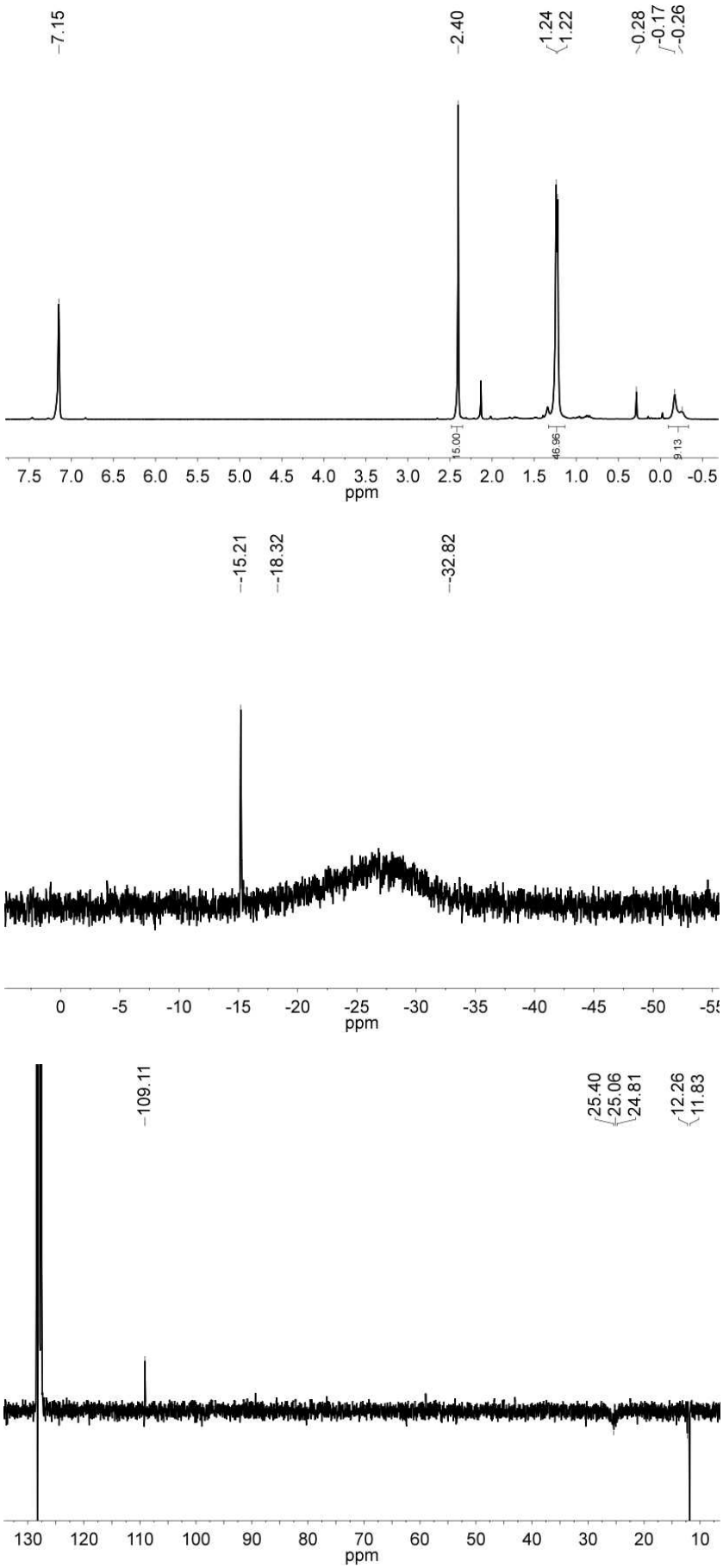
^{1}H, ^{31}P and ^{13}C NMR spectra of **1a**



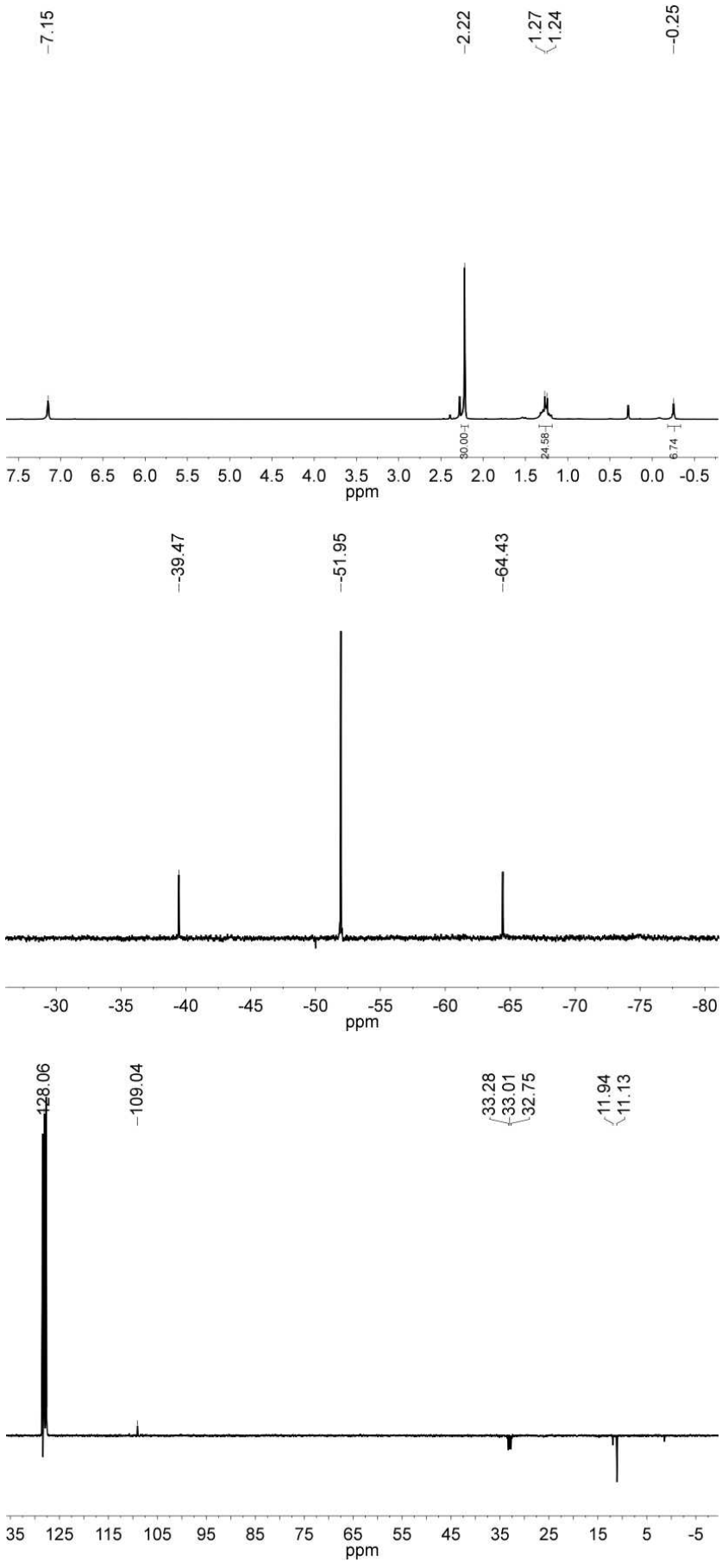
^{1}H, ^{31}P and ^{13}C NMR spectra of **1b**



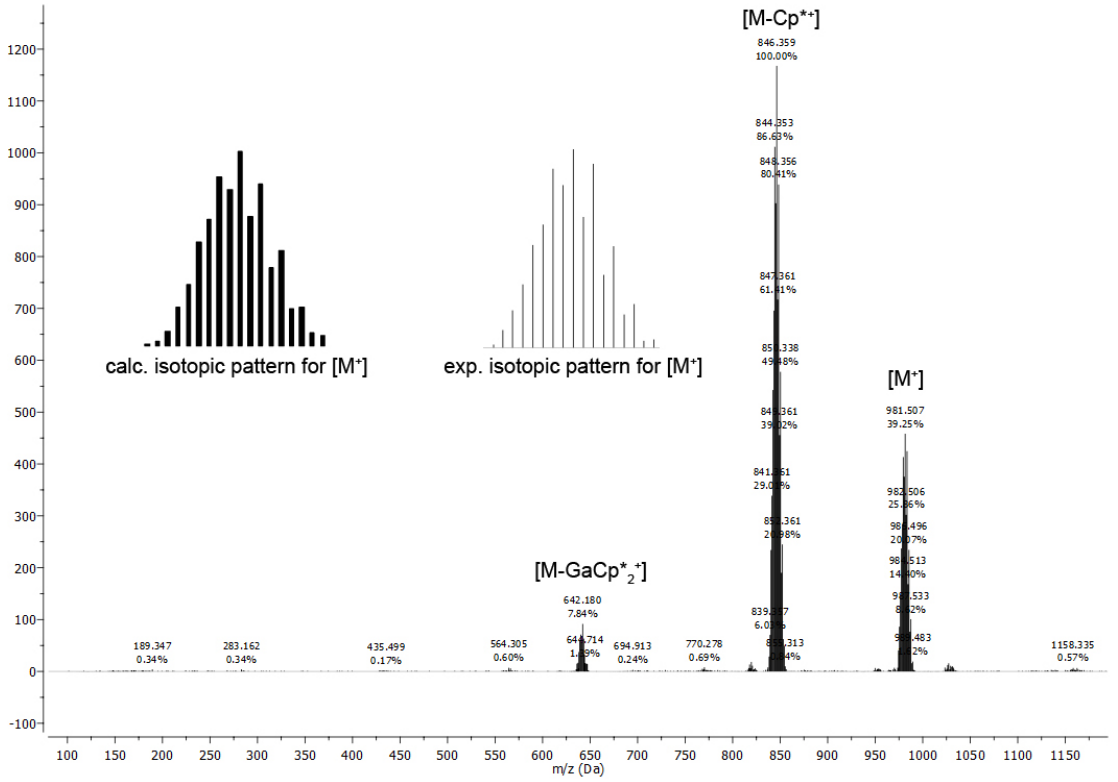
^{1}H, ^{31}P and ^{13}C NMR spectra of **2**



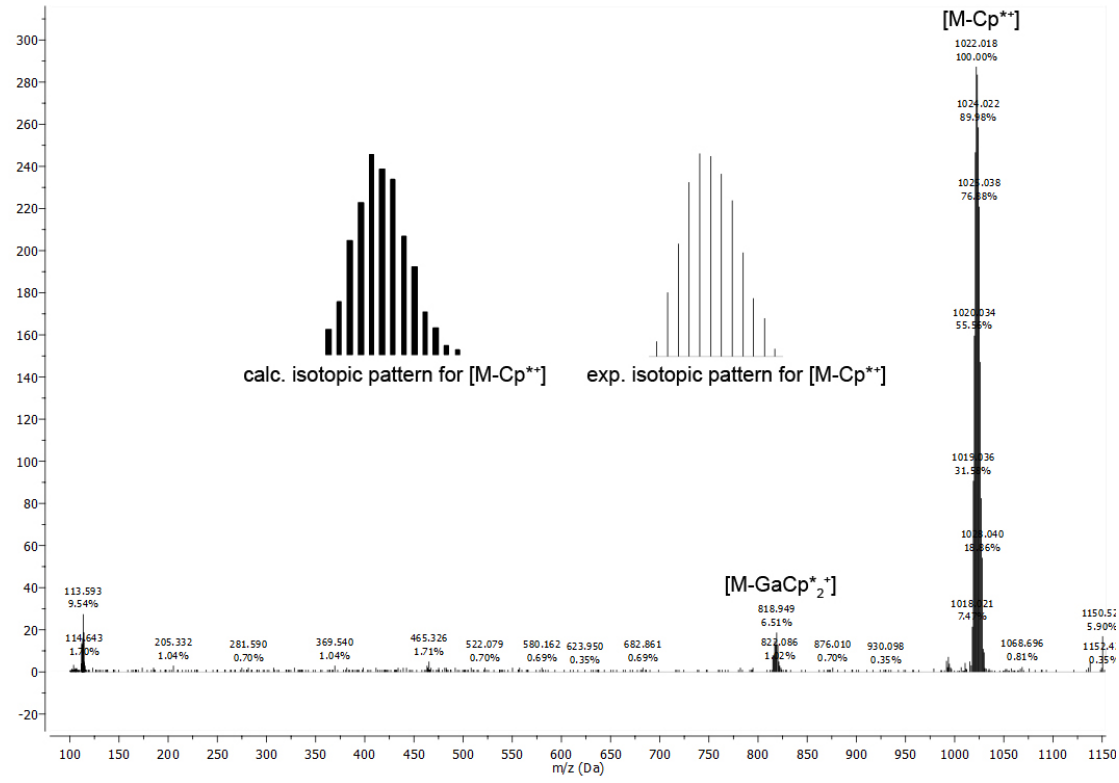
^{1}H, ^{31}P and ^{13}C NMR spectra of **3a**



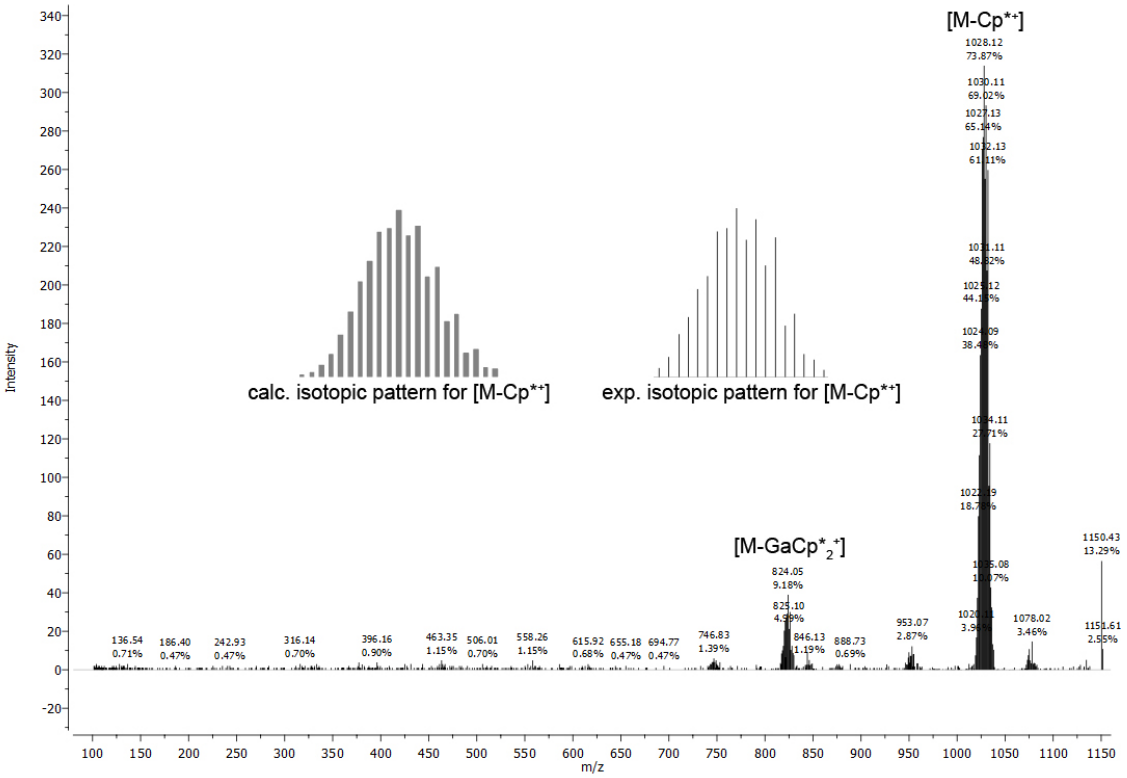
^{1}H, ^{31}P and ^{13}C NMR spectra of **3b**



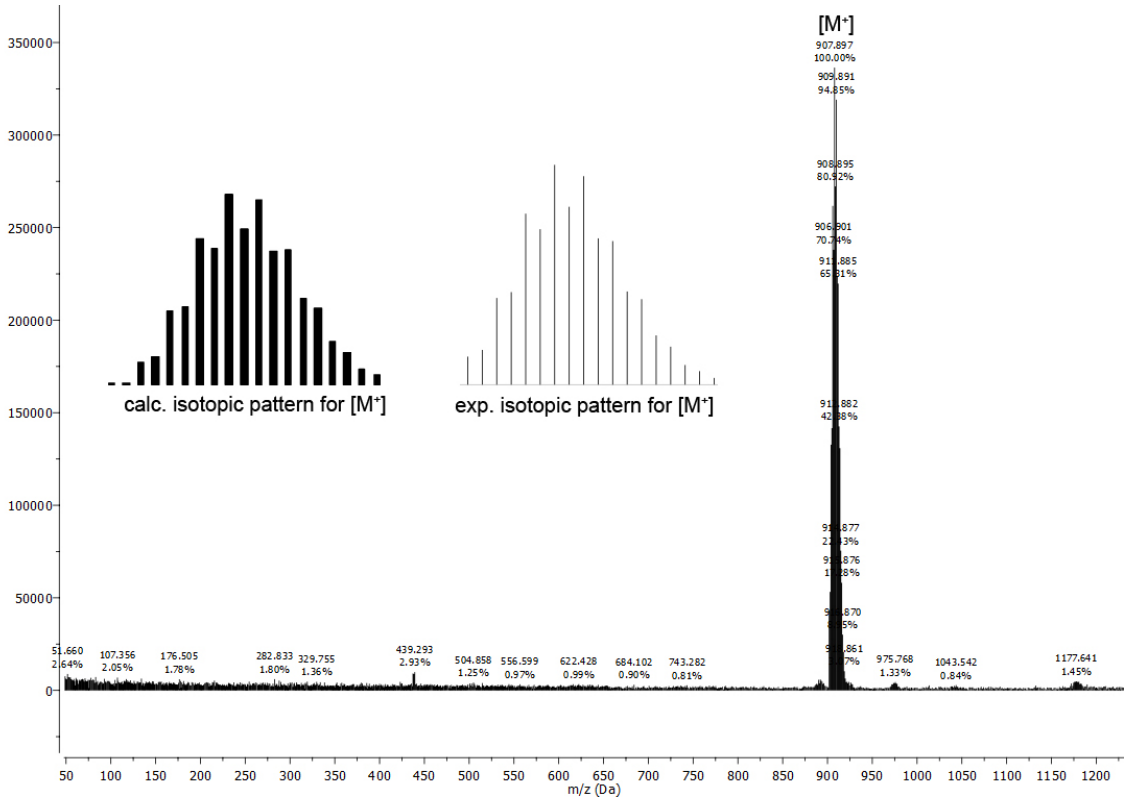
LIFDI MS (toluene) spectra of **1a**



LIFDI MS (toluene) spectra of **1b**



LIFDI MS (toluene) spectra of **2**



LIFDI MS (toluene) spectra of **3b**

Further Information on continuous shape measure

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 ..., N), as well as N vertices of an second polyhedron with the position vectors P_i (i = 1, 2, 3 ..., N). The smallest distance $S_Q(P)$ of the position vectors between both polyhedrons is expressed with the following equation

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

The polyhedrons tested were centered in the origin and standardized ($|\vec{V_i}| = |\vec{V_j}|/|\vec{V_j}|$) 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 S1a to S3c show the superimpositions of ideal polyhedra and the metal core structures extracted from the molecular structures of **3a** and **3b**.

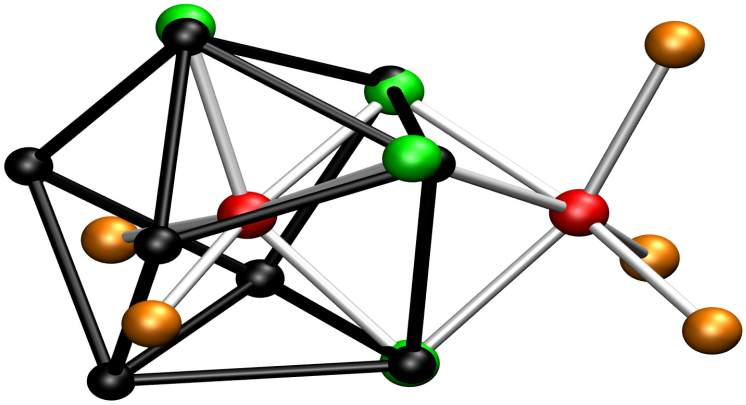


Figure S1a: Superimposition of a dodecahedron (black) and the metal fragment $[Pd_2Zn_4P_5]$ with Pd1 atom in the center extracted from the molecular structure of **3a** (coloured), concerning Zn atoms at Pd1

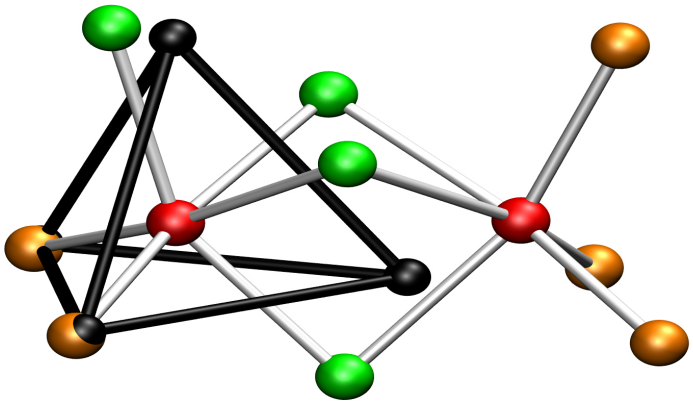


Figure S1b: Superimposition of a tetrahedron (black) and the metal fragment $[Pd_2Zn_4P_5]$ with Pd1 atom in the center extracted from the molecular structure of **3a** (coloured), concerning P atoms at Pd1

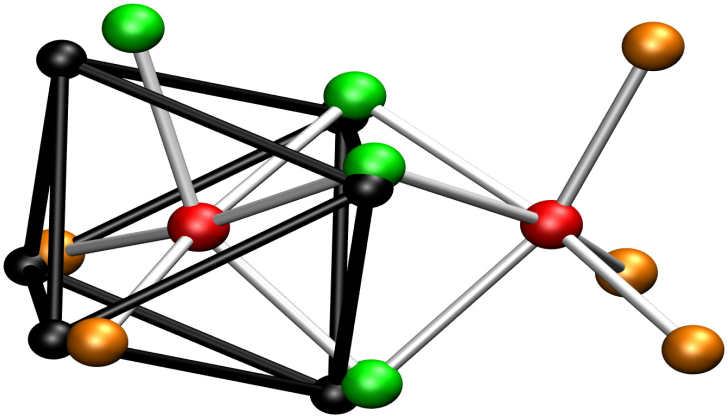


Figure S1c: Superimposition of a octahedron (black) and the metal fragment $[Pd_2Zn_4P_5]$ with Pd1 atom in the center extracted from the molecular structure of **3a** (coloured), concerning Zn and P atoms at Pd1

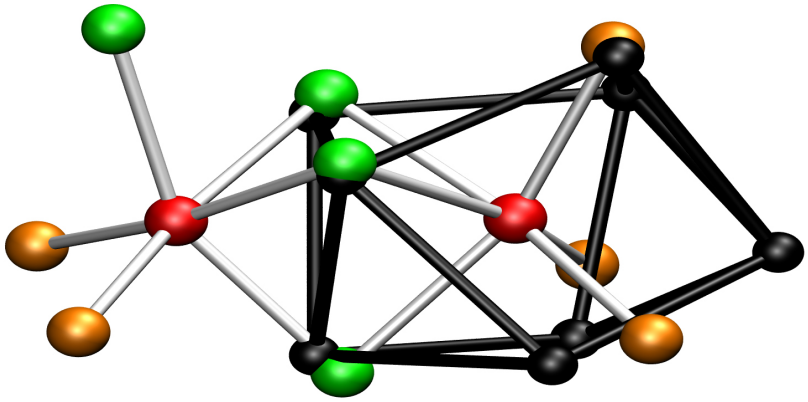


Figure S2a: Superimposition of a dodecahedron (black) and the metal fragment $[Pd_2Zn_4P_5]$ with Pd2 atom in the center extracted from the molecular structure of **3a** (coloured), concerning Zn atoms at Pd2

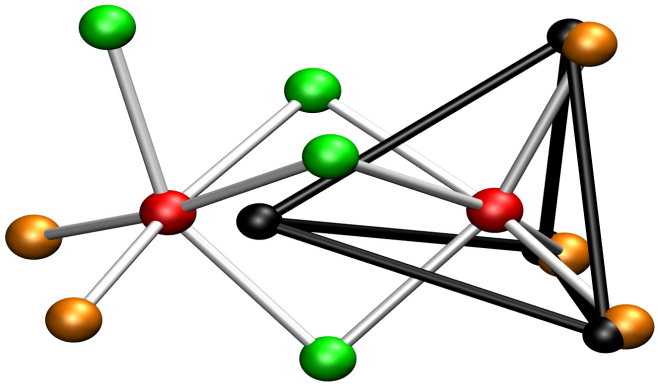


Figure S2b: Superimposition of a dodecahedron (black) and the metal fragment $[Pd_2Zn_4P_5]$ with Pd2 atom in the center extracted from the molecular structure of **3a** (coloured), concerning P atoms at Pd2

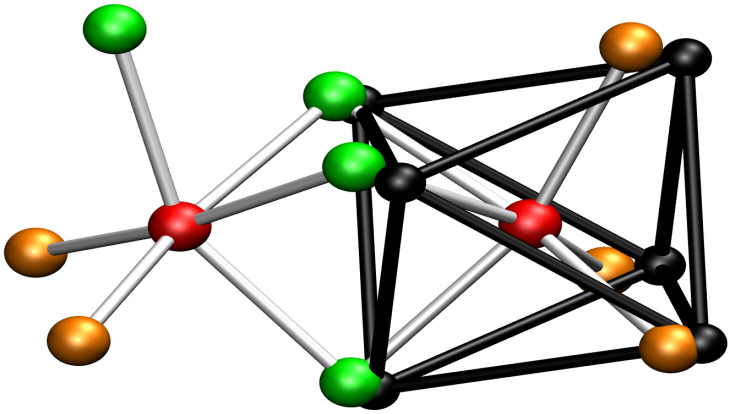


Figure S2c: Superimposition of a octahedron (black) and the metal fragment $[Pd_2Zn_4P_5]$ with Pd2 atom in the center extracted from the molecular structure of **3a** (coloured), concerning Zn and P atoms at Pd2

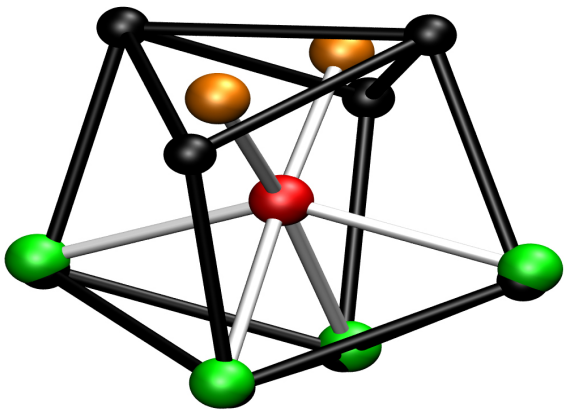


Figure S3a: Superimposition of a dodecahedron (black) and the metal fragment $[PtZn_4P_2]$ extracted from the molecular structure of **3b** (coloured), concerning Zn atoms

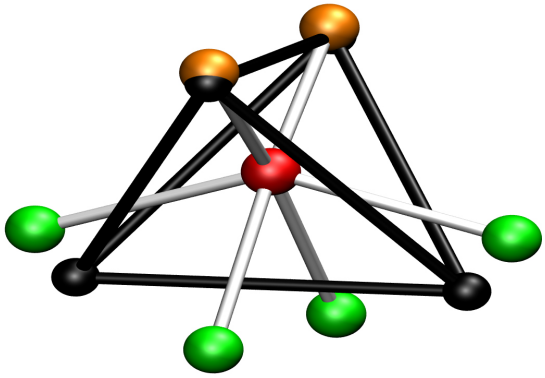


Figure S3b: Superimposition of a tetrahedron (black) and the metal fragment $[PtZn_4P_2]$ extracted from the molecular structure of **3b** (coloured), concerning Zn atoms

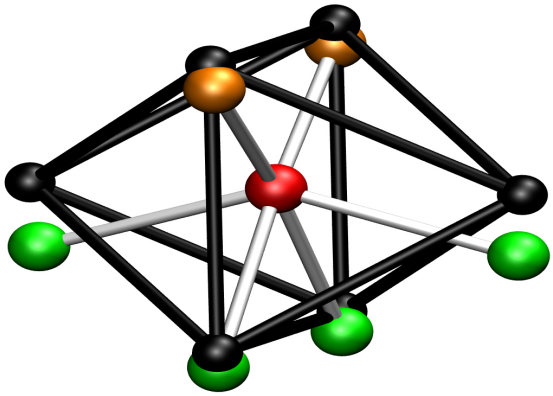


Figure S3c: Superimposition of a octahedron (black) and the metal fragment $[PtZn_4P_2]$ extracted from the molecular structure of **3b** (coloured), concerning Zn atoms