Supporting Information for

Heterometallic Ni-Pt Chini-Type Carbonyl Clusters: An Example of Molecular Random Alloy Clusters

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**Figure S2**
IR spectrum ($\nu_{\text{CO}}$ region) recorded in thf of [NBu$_4$]$_2$[Ni$_9$(CO)$_{18}$].
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IR spectrum ($\nu_{\text{CO}}$ region) recorded in thf of $[\text{NBu}_4]_2[\text{Pt}_6(\text{CO})_{12}]$.

Figure S4
IR spectrum ($\nu_{\text{CO}}$ region) recorded in thf of $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}]$. 
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**Figure S7**
IR spectrum ($\nu_{\text{CO}}$ region) recorded in CH$_3$CN after work-up of the reaction mixture of $[\text{NBu}_4]_2[\text{Pt}_6(\text{CO})_{12}]$ and $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (1:1 molar ratio).
**Figure S8**

IR spectrum ($\nu_{\text{CO}}$ region) recorded in thf of the raw reaction mixture of $[\text{NBu}_4]_2[\text{Pt}_6(\text{CO})_{12}]$ and $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (1:2 molar ratio).

**Figure S9**

IR spectrum ($\nu_{\text{CO}}$ region) recorded in CH$_3$CN after work-up of the reaction mixture of $[\text{NBu}_4]_2[\text{Pt}_6(\text{CO})_{12}]$ and $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (1:2 molar ratio).
**Figure S10**

IR spectrum ($\nu_{\text{CO}}$ region) recorded in thf of the raw reaction mixture of $[\text{NBu}_4]_2[\text{Pt}_6(\text{CO})_{12}]$ and $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (2:1 molar ratio).

**Figure S11**

IR spectrum ($\nu_{\text{CO}}$ region) recorded in CH$_3$CN after work-up of the reaction mixture of $[\text{NBu}_4]_2[\text{Pt}_6(\text{CO})_{12}]$ and $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (2:1 molar ratio).
**Figure S12**
IR spectrum ($\nu_{\text{CO}}$ region) recorded in THF of the raw reaction mixture of [NBu$_4$]$_2$[Pt$_9$(CO)$_{18}$] and [NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] (1:1 molar ratio).

**Figure S13**
IR spectrum ($\nu_{\text{CO}}$ region) recorded in CH$_3$CN after work-up of the reaction mixture of [NBu$_4$]$_2$[Pt$_9$(CO)$_{18}$] and [NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] (1:1 molar ratio).
Figure S14

ESI-MS spectrum in CH₃CN (ES–) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 1.25).
Table S1
Peak assignment of the ESI-MS spectrum (ES−) of \([\text{NBu}_4]_2[\text{Pt}_6-x\text{Ni}_x(\text{CO})_{12}]\) (\(x = 1.25\)).

| m/z | Relative intensity | Ion | Code | Sum of the peaks intensities |
|-----|-------------------|-----|------|-----------------------------|
| 1749 | 10 | \([\text{Pt}_6(\text{CO})_{12}][\text{NBu}_4]\)^− | Pt$_6$+NBu$_4$ | 10 |
| 1612 | 4 | \([\text{Pt}_5\text{Ni}(\text{CO})_{12}][\text{NBu}_4]\)^− | Pt$_5$Ni+NBu$_4$ | |
| 725 | 10 | [Pt$_5$Ni(\text{CO})$_{15}$]$^{2−}$ | Pt$_5$Ni+3CO | 199 |
| 711 | 10 | [Pt$_5$Ni(\text{CO})$_{14}$]$^{2−}$ | Pt$_5$Ni+2CO | |
| 697 | 100 | [Pt$_5$Ni(\text{CO})$_{13}$]$^{3−}$ | Pt$_5$Ni+1CO | |
| 683 | 45 | [Pt$_5$Ni(\text{CO})$_{12}$]$^{3−}$ | Pt$_5$Ni | |
| 669 | 30 | [Pt$_5$Ni(\text{CO})$_{11}$]$^{3−}$ | Pt$_5$Ni−1CO | |
| 629 | 25 | [Pt$_4$Ni$_2$(\text{CO})$_{13}$]$^{2−}$ | Pt$_4$Ni$_2$+1CO | 65 |
| 614 | 35 | [Pt$_4$Ni$_2$(\text{CO})$_{12}$]$^{2−}$ | Pt$_4$Ni$_2$ | |
| 601 | 5 | [Pt$_4$Ni$_2$(\text{CO})$_{11}$]$^{2−}$ | Pt$_4$Ni$_2$−1CO | |
| 561 | 8 | [Pt$_3$Ni$_3$(\text{CO})$_{13}$]$^{2−}$ | Pt$_3$Ni$_3$+1CO | 28 |
| 547 | 20 | [Pt$_3$Ni$_3$(\text{CO})$_{12}$]$^{2−}$ | Pt$_3$Ni$_3$ | |
| 492 | 20 | [Pt$_2$Ni$_4$(\text{CO})$_{13}$]$^{2−}$ | Pt$_2$Ni$_4$+1CO | 35 |
| 478 | 15 | [Pt$_3$Ni$_3$(\text{CO})$_{12}$]$^{2−}$ | Pt$_2$Ni$_4$ | |
| 424 | 15 | [PtNi$_5$(\text{CO})$_{13}$]$^{−}$ | PtNi$_5$+1CO | 15 |
Isotopic pattern of the peak at m/z 424 of the ESI-MS spectrum in CH₃CN (ES−) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 1.25). Upper traces: calculated isotopic pattern for [PtNi₅(CO)₁₃]²⁻. Lower trace: experimental isotopic pattern.
Figure S16

Isotopic pattern of the peak at m/z 492 of the ESI-MS spectrum in CH$_3$CN (ES-) of [NBu$_4$]$_2$[Pt$_{6-x}$Ni$_x$(CO)$_{12}$] ($x = 1.25$). Upper traces: calculated isotopic pattern for [Pt$_2$Ni$_4$(CO)$_{13}$]$^{2-}$. Lower trace: experimental isotopic pattern.
Figure S17
Isotopic pattern of the peak at m/z 547 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_{6-\ x}$Ni$_{x}$(CO)$_{12}$] (x = 1.25). Upper traces: calculated isotopic pattern for [Pt$_3$Ni$_3$(CO)$_{12}$]$^{2-}$. Lower trace: experimental isotopic pattern.
Figure S18
Isotopic pattern of the peak at m/z 614 of the ESI-MS spectrum in CH₃CN (ES–) of [NBu₄]₂[Pt₆–
ᵸNiᵸ(CO)₁₂] (x = 1.25). Upper traces: calculated isotopic pattern for [Pt₄Ni₂(CO)₁₂]²⁻. Lower trace:
experimental isotopic pattern.
Figure S19

Isotopic pattern of the peak at m/z 683 of the ESI-MS spectrum in CH₃CN (ES–) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 1.25). Upper traces: calculated isotopic pattern for [Pt₅Ni(CO)₁₂]²⁻. Lower trace: experimental isotopic pattern.
Figure S20

Isotopic pattern of the peak at m/z 697 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$-xNi$_x$(CO)$_{12}$] (x = 1.25). Upper traces: calculated isotopic pattern for [Pt$_5$Ni(CO)$_{13}$]$_2^-$. Lower trace: experimental isotopic pattern.
Figure S21
Isotopic pattern of the peak at m/z 1749 of the ESI-MS spectrum in CH₃CN (ES–) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 1.25). Upper traces: calculated isotopic pattern for {[Pt₆(CO)₁₂][NBu₄]}⁻. Lower trace: experimental isotopic pattern.
Figure S22

ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_{9}$(CO)$_{18}$] + 1.2[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up.
Table S2
Peak assignment of the ESI-MS spectrum (ES–) of [NBu4]2[Pt9(CO)18] + 1.2[NBu4]2[Ni6(CO)12] after work-up.

| m/z | Relative intensity | Ion Code | Code | Sum of the peaks intensities |
|-----|--------------------|----------|------|-------------------------------|
| 1749 | 5 | \{[Pt_6(CO)_{12}][NBu_4]\}^- | Pt_6+NBu_4 | 5 |
| 698  | 100 | [Pt_5Ni(CO)_{13}]^{2-} | Pt_5Ni+1CO | |
| 683  | 50 | [Pt_5Ni(CO)_{12}]^{2-} | Pt_5Ni | 185 |
| 669  | 35 | [Pt_5Ni(CO)_{11}]^{2-} | Pt_5Ni–1CO | |
| 629  | 25 | [Pt_4Ni_2(CO)_{13}]^{2-} | Pt_4Ni_2+1CO | |
| 615  | 50 | [Pt_4Ni_2(CO)_{12}]^{2-} | Pt_4Ni_2 | 85 |
| 601  | 10 | [Pt_4Ni_2(CO)_{11}]^{2-} | Pt_4Ni_2–1CO | |
| 561  | 15 | [Pt_3Ni_3(CO)_{13}]^{2-} | Pt_3Ni_3+1CO | 45 |
| 546  | 30 | [Pt_3Ni_3(CO)_{12}]^{2-} | Pt_3Ni_3 | |
| 492  | 20 | [Pt_2Ni_4(CO)_{13}]^{2-} | Pt_2Ni_4+1CO | 35 |
| 478  | 15 | [Pt_2Ni_4(CO)_{12}]^{2-} | Pt_2Ni_4 | |
| 424  | 18 | [PtNi_5(CO)_{13}]^{2-} | PtNi_5+1CO | 18 |
Figure S23

Isotopic pattern of the peak at m/z 546 of the ESI-MS spectrum in CH₃CN (ES−) of 
[NBu₄]₂[Pt₉(CO)₁₈] + 1.2[NBu₄]₂[Ni₆(CO)₁₂] after work-up. Upper traces: calculated isotopic pattern 
for [Pt₃Ni₃(CO)₁₂]²⁻. Lower trace: experimental isotopic pattern.
Figure S24

Isotopic pattern of the peak at m/z 615 of the ESI-MS spectrum in CH₃CN (ES–) of [NBu₄]₂[Pt₉(CO)₁₈] + 1.2[NBu₄]₂[Ni₆(CO)₁₂] after work-up. Upper traces: calculated isotopic pattern for [Pt₄Ni₂(CO)₁₂]²⁻. Lower trace: experimental isotopic pattern.
Figure S25
Isotopic pattern of the peak at m/z 683 of the ESI-MS spectrum in CH$_3$CN (ES$^–$) of
[NBu$_4$]$_2$[Pt$_9$(CO)$_{18}$] + 1.2[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [Pt$_3$Ni(CO)$_{12}$]$^{2–}$. Lower trace: experimental isotopic pattern.
Figure S26
Isotopic pattern of the peak at m/z 698 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{18}$] + 1.2[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [Pt$_3$Ni(CO)$_{13}$]$^2$–. Lower trace: experimental isotopic pattern.
Figure S27

Isotopic pattern of the peak at m/z 1749 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{12}$] + 1.2[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for {[Pt$_6$(CO)$_{12}$][NBu$_4$]}–. Lower trace: experimental isotopic pattern.
Figure S28

ESI-MS spectrum in CH₃CN (ES−) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (mixture of x = 3.24, 4.15, 4.16).
Table S3
Peak assignment of the ESI-MS spectrum (ES−) of ([NBu4]2[Pt6−xNi_x(CO)12]) (mixture of x = 3.24, 4.15, 4.16).

| m/z  | Relative intensity | Ion Code                                                          | Sum of the peaks intensities |
|------|--------------------|------------------------------------------------------------------|-----------------------------|
| 1338 | 2                  | ${[\text{Pt}_3\text{Ni}_3(\text{CO})_{12}][\text{NBu}_4]}^-$       | -                           |
| 1202 | 5                  | ${[\text{Pt}_2\text{Ni}_4(\text{CO})_{12}][\text{NBu}_4]}^-$       | -                           |
| 1068 | 8                  | ${[\text{PtNi}_5(\text{CO})_{12}][\text{NBu}_4]}^-$               | -                           |
| 930  | 10                 | ${[\text{Ni}_6(\text{CO})_{12}][\text{NBu}_4]}^-$                | -                           |
| 753  | 5                  | $[\text{Pt}_6(\text{CO})_{12}]^-$                                 | 5                           |
| 657  | 8                  | $[\text{Pt}_5\text{Ni}(\text{CO})_{10}]^-$                      | $\text{Pt}_5\text{Ni}–2\text{CO}$ |
| 589  | 14                 | $[\text{Pt}_4\text{Ni}_2(\text{CO})_{10}]^-$                    | $\text{Pt}_4\text{Ni}_2–2\text{CO}$ |
| 548  | 10                 | $[\text{Pt}_3\text{Ni}_3(\text{CO})_{12}]^-$                    | $\text{Pt}_3\text{Ni}_3$ |
| 535  | 5                  | $[\text{Pt}_3\text{Ni}_3(\text{CO})_{11}]^-$                    | $\text{Pt}_3\text{Ni}_3–1\text{CO}$ |
| 521  | 60                 | $[\text{Pt}_3\text{Ni}_3(\text{CO})_{10}]^-$                    | $\text{Pt}_3\text{Ni}_3–2\text{CO}$ |
| 506  | 20                 | $[\text{Pt}_3\text{Ni}_3(\text{CO})_{9}]^-$                     | $\text{Pt}_3\text{Ni}_3–3\text{CO}$ |
| 480  | 55                 | $[\text{Pt}_2\text{Ni}_4(\text{CO})_{12}]^-$                    | $\text{Pt}_2\text{Ni}_4$ |
| 466  | 10                 | $[\text{Pt}_2\text{Ni}_4(\text{CO})_{11}]^-$                    | $\text{Pt}_2\text{Ni}_4–1\text{CO}$ |
| 452  | 60                 | $[\text{Pt}_2\text{Ni}_4(\text{CO})_{10}]^-$                    | $\text{Pt}_2\text{Ni}_4–1\text{CO}$ |
| 412  | 30                 | $[\text{PtNi}_5(\text{CO})_{12}]^-$                             | $\text{PtNi}_5$ |
| 398  | 50                 | $[\text{PtNi}_5(\text{CO})_{11}]^-$                             | $\text{PtNi}_5–1\text{CO}$ |
| 384  | 70                 | $[\text{PtNi}_5(\text{CO})_{10}]^-$                             | $\text{PtNi}_5–2\text{CO}$ |
| 344  | 100                | $[\text{Ni}_6(\text{CO})_{12}]^-$                               | $\text{Ni}_6$ |
| 330  | 95                 | $[\text{Ni}_6(\text{CO})_{11}]^-$                               | $\text{Ni}_6–1\text{CO}$ |
| 316  | 30                 | $[\text{Ni}_6(\text{CO})_{10}]^-$                               | $\text{Ni}_6–1\text{CO}$ |
Figure S29
Isotopic pattern of the peak at m/z 344 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$-$x$Ni$_x$(CO)$_{12}$] (mixture of $x = 3.24, 4.15, 4.16$). Upper traces: calculated isotopic pattern for [Ni$_6$(CO)$_{12}$]$^{2-}$. Lower trace: experimental isotopic pattern.
Figure S30
Isotopic pattern of the peak at m/z 412 of the ESI-MS spectrum in CH$_3$CN (ES−) of [NBu$_4$]$_2$[Pt$_6$-$x$Ni$_x$(CO)$_{12}$] (mixture of $x$ = 3.24, 4.15, 4.16). Upper traces: calculated isotopic pattern for [PtNi$_5$(CO)$_{12}$]$^{2−}$. Lower trace: experimental isotopic pattern.
Figure S31

Isotopic pattern of the peak at m/z 480 of the ESI-MS spectrum in CH$_3$CN (ES−) of [NBu$_4$]$_2$[Pt$_6$-$x$Ni$_x$(CO)$_{12}$] (mixture of $x = 3.24, 4.15, 4.16$). Upper traces: calculated isotopic pattern for [Pt$_2$Ni$_4$(CO)$_{12}$]$^{2−}$. Lower trace: experimental isotopic pattern.
Figure S32

Isotopic pattern of the peak at m/z 521 of the ESI-MS spectrum in CH$_3$CN (ES$^-$) of [NBu$_4$]$_2$[Pt$_6$-$_{x}$Ni$_x$(CO)$_{12}$] (mixture of x = 3.24, 4.15, 4.16). Upper traces: calculated isotopic pattern for [Pt$_3$Ni$_3$(CO)$_{10}$]$_2^-$, Lower trace: experimental isotopic pattern.
Figure S33
Isotopic pattern of the peak at m/z 930 of the ESI-MS spectrum in CH$_3$CN (ES$^-$) of [NBu$_4$]$_2$[Pt$_6$. $\chi$Ni$_{12}$]$_2$(CO)$_{12}$ (mixture of $\chi$ = 3.24, 4.15, 4.16). Upper traces: calculated isotopic pattern for $\{[Ni_6(CO)_{12}][NBu_4]\}^-$. Lower trace: experimental isotopic pattern.
Figure S34
Isotopic pattern of the peak at m/z 1068 of the ESI-MS spectrum in CH₃CN (ES–) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (mixture of x = 3.24, 4.15, 4.16). Upper traces: calculated isotopic pattern for {[PtNi₅(CO)₁₂][NBu₄]}⁻. Lower trace: experimental isotopic pattern.
Figure S35

Isotopic pattern of the peak at m/z 1202 of the ESI-MS spectrum in CH$_3$CN (ES$^-$) of [NBu$_4$]$_2$[Pt$_6$xNi$_{6-x}$(CO)$_{12}$] (mixture of $x = 3.24, 4.15, 4.16$). Upper traces: calculated isotopic pattern for $\{[Pt_2Ni_4(CO)_{12}][NBu_4]\}^-$. Lower trace: experimental isotopic pattern.
Figure S36

Isotopic pattern of the peak at m/z 1338 of the ESI-MS spectrum in CH₃CN (ES−) of [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (mixture of x = 3.24, 4.15, 4.16). Upper traces: calculated isotopic pattern for {[Pt₃Ni₃(CO)₁₂][NBu₄]}⁻. Lower trace: experimental isotopic pattern.
Figure S37

ESI-MS spectrum in CH$_3$CN (ES$^-$) of [NBu$_4$]$_2$[Pt$_{6}$(CO)$_{11}$] + 1.0[NBu$_4$]$_2$[Ni$_{6}$(CO)$_{12}$] after work-up.
Table S4
Peak assignment of the ESI-MS spectrum (ES-) of [NBu₄]₂[Pt₆(CO)₁₁] + 1.0[NBu₄]₂[Ni₆(CO)₁₂] after work-up.

| m/z  | Relative intensity | Ion | Code        | Sum of the peaks intensities |
|------|--------------------|-----|-------------|-----------------------------|
| 753  | 18                 | [Pt₆(CO)₁₂]²⁻ | Pt₆          | 18                          |
| 684  | 10                 | [Pt₅Ni(CO)₁₂]²⁻ | Pt₅Ni       | 20                          |
| 658  | 10                 | [Pt₅Ni(CO)₁₀]²⁻ | Pt₅Ni–2CO   |                             |
| 616  | 4                  | [Pt₄Ni₂(CO)₁₂]²⁻ | Pt₄Ni₂      |                             |
| 603  | 4                  | [Pt₄Ni₂(CO)₁₁]²⁻ | Pt₄Ni₁–1CO  | 33                          |
| 588  | 25                 | [Pt₄Ni₂(CO)₁₀]²⁻ | Pt₄Ni₂–2CO  |                             |
| 548  | 30                 | [Pt₃Ni₃(CO)₁₂]²⁻ | Pt₃Ni₃      | 85                          |
| 534  | 15                 | [Pt₃Ni₃(CO)₁₁]²⁻ | Pt₃Ni₁–1CO  |                             |
| 520  | 40                 | [Pt₃Ni₃(CO)₁₀]²⁻ | Pt₃Ni₁–2CO  |                             |
| 480  | 50                 | [Pt₃Ni₄(CO)₁₂]²⁻ | Pt₃Ni₄      |                             |
| 466  | 12                 | [Pt₃Ni₄(CO)₁₁]²⁻ | Pt₃Ni₁–1CO  | 72                          |
| 453  | 10                 | [Pt₃Ni₄(CO)₁₀]²⁻ | Pt₃Ni₁–2CO  |                             |
| 412  | 50                 | [PtNi₅(CO)₁₂]²⁻ | PtNi₅       |                             |
| 398  | 15                 | [PtNi₅(CO)₁₁]²⁻ | PtNi₁–1CO   | 70                          |
| 385  | 5                  | [PtNi₅(CO)₁₀]²⁻ | PtNi₁–2CO   |                             |
| 344  | 100                | [Ni₆(CO)₁₂]²⁻  | Ni₆          | 108                         |
| 330  | 8                  | [Ni₆(CO)₁₁]²⁻  | Ni₆–1CO     |                             |
Figure S38

Isotopic pattern of the peak at m/z 344 of the ESI-MS spectrum in CH_{3}CN (ES–) of [NBu_{4}]_{2}[Pt_{6}(CO)_{11}] + 1.0[NBu_{4}]_{2}[Ni_{6}(CO)_{12}] after work-up. Upper traces: calculated isotopic pattern for [Ni_{6}(CO)_{12}]^{2–}. Lower trace: experimental isotopic pattern.
Figure S39
Isotopic pattern of the peak at m/z 412 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{11}$] + 1.0[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [PtNi$_5$(CO)$_{12}$]$^{2-}$. Lower trace: experimental isotopic pattern.
Figure S40

Isotopic pattern of the peak at m/z 480 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{11}$] + 1.0[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [Pt$_2$Ni$_4$(CO)$_{12}$]$^{2–}$. Lower trace: experimental isotopic pattern.
Figure S41

Isotopic pattern of the peak at m/z 520 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{11}$] + 1.0[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [Pt$_3$Ni$_3$(CO)$_{10}$]$^{2–}$. Lower trace: experimental isotopic pattern.
Figure S42
Isotopic pattern of the peak at m/z 588 of the ESI-MS spectrum in CH$_3$CN (ES–) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{11}$] + 1.0[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [Pt$_4$Ni$_2$(CO)$_{10}$]$^{2–}$. Lower trace: experimental isotopic pattern.
Figure S43
Isotopic pattern of the peak at m/z 754 of the ESI-MS spectrum in CH$_3$CN (ES$^-$) of [NBu$_4$]$_2$[Pt$_6$(CO)$_{11}$] + 1.0[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] after work-up. Upper traces: calculated isotopic pattern for [Pt$_6$(CO)$_{12}$]$^{2-}$. Lower trace: experimental isotopic pattern.
Figure S44

$^{195}$Pt NMR spectra of [NBu$_4$]$_2$[Pt$_6$(CO)$_{12}$] + 2[NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] in CD$_3$COCD$_3$ at 298 K recorded at different times.

- $t = 0$ h
- $t = 5$ h
- $t = 26$ h
- $t = 96$ h
Figure S45

$^{195}$Pt NMR spectra in CD$_3$COCD$_3$ at 298 K of (a) [NBu$_4$]$_2$[Pt$_6$(CO)$_{12}$], (b) [NBu$_4$]$_2$[Pt$_{6-x}$Ni$_x$(CO)$_{12}$] 
(x = 1.25), (c) [NBu$_4$]$_4$[Pt$_{6-x}$Ni$_x$(CO)$_{12}$][Cl$_{1.77}$Br$_{0.23}$] (x = 2.53), (d) [NMe$_4$]$_2$[Pt$_6$(CO)$_{12}$] + [NMe$_4$]$_2$[Ni$_6$(CO)$_{12}$] (1:1), (e) [NBu$_4$]$_2$[Pt$_{6-x}$Ni$_x$(CO)$_{12}$] (mixture of x = 3.24, 4.15, 4.16), (f) [NBu$_4$]$_2$[Pt$_6$(CO)$_{12}$] + [NBu$_4$]$_2$[Ni$_6$(CO)$_{12}$] (1:5).
Figure S46
Comparison of (top) the simulated $^{195}$Pt NMR spectrum of $[\text{Pt}_5\text{Ni(CO)}_{12}]^{2-}$ ($\delta_{\text{Pt}} -4497$ (3Pt) and -4613 (2Pt), $^1J_{\text{Pt-Pt}} = 218$ Hz) and (bottom) the experimental $^{195}$Pt NMR spectrum of $[\text{NBu}_4]_2[\text{Pt}_6\text{Ni}_3(\text{CO})_{12}]$ ($x = 1.25$) in CD$_3$COCD$_3$ at 298 K. The singlets at $\delta_{\text{Pt}}$ -4510 and -4613 ppm are due to $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ and $[\text{Pt}_3\text{Ni}_3(\text{CO})_{12}]^{2-}$, respectively.
Figure S47

VT $^{195}$Pt NMR spectra of $[\text{NBu}_4]_2[\text{Pt}_{3.7}\text{Ni}_{0.3}(\text{CO})_{12}]$ in CD$_3$COCD$_3$. 
Figure S48

VT $^{13}$C NMR spectra of [NBu$_4$]$_2$[Pt$_{5}$Ni$_{1-1}$(CO)$_{12}$] in CD$_3$COCD$_3$.
Figure S49

VT $^{195}\text{Pt}$ NMR spectra of [NBu$_4$]$_2$[Pt$_2$Ni$_4$(CO)$_{12}$] in CD$_2$COCD$_3$. 

203 K

298 K
Figure S50
VT $^{13}$C NMR spectra of [NBu$_4$]$_2$[Pt$_2$Ni$_4$(CO)$_{12}$] in CD$_3$COCD$_3$. 

203 K

298 K
Figure S51
Possible isomers of $[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]^{2-}$ ($x = 0 – 6$). Isomers $1-10$ are inter-converted by a combination of inter-molecular triangle exchange reactions and intra-molecular CO exchange. Isomers $4/4'$, $5/5'$ and $6/6'$ are inter-converted by intra-molecular triangle rotation.
Figure S52

Triangle exchange reactions between $[\text{Pt}_{6-x}\text{Ni}_x\text{(CO)}_{12}]^{2-}$ ($x = 0 – 6$) clusters.
Triangle exchange

1-(Ni3)(Ni3) + 8-(Ni3)(Pt2Ni) ↔ 1-(Ni3)(Ni3) + 8-(Ni3)(Pt2Ni)

1-(Ni3)(Ni3) + 9-(Pt3)(Pt2Ni) ↔ 3-(Pt3)(Ni3) + 8-(Ni3)(Pt2Ni)

1-(Ni3)(Ni3) + 10-(Ni3)(PtNi2) ↔ 1-(Ni3)(Ni3) + 10-(Ni3)(PtNi2)

2-(Pt3)(Pt3) + 3-(Pt3)(Ni3) ↔ 2-(Pt3)(Pt3) + 3-(Pt3)(Ni3)

2-(Pt3)(Pt3) + 4-(Pt2Ni)(PtNi2) ↔ 2-(Pt3)(Pt3) + 7-(Pt3)(PtNi2)

2-(Pt3)(Pt3) + 5-(Pt2Ni)(Pt2Ni) ↔ 2-(Pt3)(Pt3) + 9-(Pt3)(Pt2Ni)

S52
Figure S53

Isomerization by CO migration of [Pt_{6-x}Ni_x(CO)_{12}]^{2-} (x = 2 – 4): General mechanism for [Pt_3Ni_3(CO)_{12}]^{2-}, [Pt_4Ni_2(CO)_{12}]^{2-} and [Pt_2Ni_4(CO)_{12}]^{2-} (only μ-CO are represented).

(a) 3-(Pt_3)(Ni_3) 4-(Pt_2Ni)(Ni_2)

(b) 5-(Pt_2Ni)(Pt_2Ni) 7-(Pt_3)(PtNi)

(c) 6-(PtNi_2)(PtNi_2) 8-(Ni_3)(Pt_2Ni)
Figure S54
Isomerization by CO migration of $[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]^{2-}$ ($x = 2 - 4$): Schematic representation for $[\text{Pt}_3\text{Ni}_3(\text{CO})_{12}]^{2-}$, $[\text{Pt}_4\text{Ni}_2(\text{CO})_{12}]^{2-}$ and $[\text{Pt}_2\text{Ni}_4(\text{CO})_{12}]^{2-}$ (all CO ligands are omitted).

(a) $3-(\text{Pt}_3)(\text{Ni}_3)$ $\leftrightarrow$ $4-(\text{Pt}_2\text{Ni})(\text{PtNi}_2)$

(b) $5-(\text{Pt}_2\text{Ni})(\text{Pt}_2\text{Ni})$ $\leftrightarrow$ $7-(\text{Pt}_3)(\text{PtNi}_2)$

(c) $6-(\text{PtNi}_2)(\text{PtNi}_2)$ $\leftrightarrow$ $8-(\text{Ni}_3)(\text{Pt}_2\text{Ni})$
Figure S55
Isomerization by triangle rotation of $[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]^{2-}$ ($x = 2 - 4$).

4'-(Pt$_2$Ni)(PtNi$_2$) \quad 4-(Pt$_2^\text{Ni}$)(PtNi$_2$)

5-(Pt$_2$Ni)(Pt$_2$Ni) \quad 5'-(Pt$_2$Ni)(Pt$_2$Ni)

6-(PtNi$_2$)(PtNi$_2$) \quad 6'-(PtNi$_2$)(PtNi$_2$)
X-ray Crystallographic Study

Crystal data and collection details for \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 1.25\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 3.24\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 4.15\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 4.16\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 4.41\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 5.78\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 5.90\)), \([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}][\text{Cl}_{1.77}\text{Br}_{0.23}]\) (\(x = 2.53\)), \([\text{NBu}_4]_2[\text{Pt}_{6}(\text{CO})_{12}]\cdot\text{thf}\), and \([\text{NBu}_4]_2[\text{Pt}_{6}(\text{CO})_{12}]\) are reported in Table S5. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo–K\(\alpha\) radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS). Structures were solved by direct methods and refined by full-matrix least-squares based on all data using \(F^2\). Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated.

\([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 1.25\)): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre) and one \([\text{NBu}_4]^+\) cation (located on a general position). The positions occupied by M(1), M(2) and M(3) are disordered Pt/Ni. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factors: M(1) = 0.839(4) Pt and 0.161(4) Ni; M(2) = 0.810(4) Pt and 0.190(4) Ni; M(3) = 0.723(4) Pt and 0.277(4) Ni.

\([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 3.24\)): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre) and one \([\text{NBu}_4]^+\) cation (located on a general position). The positions occupied by M(1), M(2) and M(3) are disordered Pt/Ni. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factors: M(1) = 0.532(4) Pt and 0.468(4) Ni; M(2) = 0.484(4) Pt and 0.516(4) Ni; M(3) = 0.367(4) Pt and 0.633(4) Ni.

\([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 4.15\)): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre) and one \([\text{NBu}_4]^+\) cation (located on a general position). The positions occupied by M(1), M(2) and M(3) are disordered Pt/Ni. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factors: M(1) = 0.372(4) Pt and 0.627(4) Ni; M(2) = 0.356(3) Pt and 0.643(3) Ni; M(3) = 0.197(2) Pt and 0.802(2) Ni.

\([\text{NBu}_4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]\) (\(x = 4.16\)): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre) and one \([\text{NBu}_4]^+\) cation (located on a general position). The positions occupied by M(1), M(2) and M(3) are disordered Pt/Ni. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factors: M(1) = 0.372(4) Pt and 0.627(4) Ni; M(2) = 0.356(3) Pt and 0.643(3) Ni; M(3) = 0.197(2) Pt and 0.802(2) Ni.
occupancy factors: M(1) = 0.3670(17) Pt and 0.6330(17) Ni; M(2) = 0.3482(18) Pt and 0.6518(18) Ni; M(3) = 0.2039(15) Pt and 0.7961(15) Ni.

$[\text{NBu}4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]$ ($x = 4.41$): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre) and one $[\text{NBu}4]^+$ cation (located on a general position). The positions occupied by M(1), M(2) and M(3) are disordered Pt/Ni. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factors: M(1) = 0.331(4) Pt and 0.669(4) Ni; M(2) = 0.315(4) Pt and 0.685(4) Ni; M(3) = 0.165(4) Pt and 0.835(4) Ni.

$[\text{NBu}4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}]$ ($x = 5.78$): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre) and one $[\text{NBu}4]^+$ cation (located on a general position). The positions occupied by M(1), M(2) and M(3) are disordered Pt/Ni. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factors: M(1) = 0.063(14) Pt and 0.9370(14) Ni; M(2) = 0.0385(14) Pt and 0.9615(13) Ni; M(3) = 0.0049(13) Pt and 0.9951(13) Ni.

$[\text{NBu}4]_2[\text{Pt}_{6-x}\text{Ni}_x(\text{CO})_{12}][\text{Cl}_{1.77}\text{Br}_{0.23}]$ ($x = 2.53$): The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion centre), two $[\text{NBu}4]^+$ cations and one X$^-$ anion (located on a general position). The positions occupied by M(1) and M(2) are disordered Pt/Ni, and the position occupied by X$^-$ is disordered Br/Cl. These have been refined applying dummy atoms constraints (EADP and EXYZ lines in SHLEXL) resulting in the following refined occupancy factor: M(1) = 0.661(3) Pt and 0.339(3) Ni; M(2) = 0.584(3) Pt and 0.416(3) Ni; M(3) = 0.492(3) Pt and 0.508(3) Ni; X = 0.112(4) Br and 0.888(4) Cl. All C, O and N atoms have been restrained to have similar $U$ parameters (SIMU line in SHELXL, s.u. 0.005) and isotropic like behaviour (ISOR line in SHELXL, s.u. 0.005).

$[\text{NBu}4]_2[\text{Pt}_9(\text{CO})_{18}]\cdot\text{thf}$: The asymmetric unit of the unit cell contains one cluster anion, two $[\text{NBu}4]^+$ cations and one thf molecule all located on general positions. Since this compound was obtained by the reaction of $[\text{NBu}4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ with $[\text{NBu}4]_2[\text{Ni}_6(\text{CO})_{12}]$, during the initial refinement all the M sites were tested for the possible presence of Pt/Ni disorder. Nonetheless, for all positions, the refinement pointed out the exclusive presence of Pt. Thus, in the final refinement, only Pt-atoms were included in the cluster. One $[\text{NBu}4]^+$ cation and one Bu-group in the other
cation are disordered and, therefore, they have been split into two positions and refined anisotropically employing one occupancy factor per disordered group. The [NBu₄]⁺ cations have been restrained to have similar thermal parameters (SIMU line in SHELXL, s.u. 0.01). The thf molecule has been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). Restraints to bond distances were applied as follow (s.u. 0.02): 1.47 Å for C–N and 1.53 Å for C–C in [NBu₄]⁺.

**[NBu₄]₂[Pt₆(CO)₁₂]:** The asymmetric unit of the unit cell contains half of a cluster anion (located on a 2-fold axis), and one [NBu₄]⁺ cation (located on a general position).

| Table S5 |
| --- |
| Crystal data and experimental details for [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 1.25), [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 3.24), [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 4.15), [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 4.16), [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 4.41), [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 5.78), [NBu₄]₂[Pt₆₋ₓNiₓ(CO)₁₂] (x = 5.90), [NBu₄]₄[Pt₆₋ₓNiₓ(CO)₁₂][Cl₁.77Br₀.23] (x = 2.53), [NBu₄]₂[Pt₉(CO)₁₈]·thf, and [NBu₄]₂[Pt₆(CO)₁₂] |  |
| **Formula** | C₄₄H₇₂N₂Ni₁.25O₁₂Pt₄.75 | C₄₄H₇₂N₂Ni₃.24O₁₂Pt₂.76 | C₄₄H₇₂N₂Ni₄.15O₁₂Pt₁.85 | C₄₄H₇₂N₂Ni₄.16O₁₂Pt₁.84 |
| **Fw** | 1820.41 | 1550.38 | 1425.59 | 1424.23 |
| **T, K** | 100(2) | 100(2) | 100(2) | 100(2) |
| **λ, Å** | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| **Crystal system** | Monoclinic | Monoclinic | Triclinic | Triclinic |
| **Space Group** | P₂₁/n | P₂₁/n | P₁ | P₁ |
| **a, Å** | 12.625(5) | 12.5005(59) | 11.0155(4) | 11.0219(3) |
| **b, Å** | 11.982(4) | 11.9264(8) | 11.8405(4) | 11.8581(3) |
| **c, Å** | 17.790(7) | 17.6604(13) | 11.9056(4) | 11.9028(3) |
| **α, °** | 90 | 90 | 89.9930(10) | 89.9820(10) |
| **β, °** | 91.427(18) | 91.724(3) | 64.9450(10) | 64.9860(10) |
| **γ, °** | 90 | 90 | 70.9870(10) | 70.9560(10) |
| **Cell Volume, Å³** | 2690.4(17) | 2631.7(3) | 1312.64(8) | 1315.29(6) |
| **Z** | 2 | 2 | 1 | 1 |
| **Dₐ, g cm⁻³** | 2.247 | 1.956 | 1.803 | 1.798 |
| **µ, mm⁻¹** | 12.775 | 8.510 | 6.424 | 6.388 |
| **F(000)** | 1702 | 1504 | 706 | 706 |
| **Crystal size, mm** | 0.18×0.15×0.12 | 0.18×0.16×0.14 | 0.21×0.18×0.15 | 0.19×0.16×0.14 |
| **θ limits, °** | 2.049–26.999 | 1.968–25.997 | 2.298–27.000 | 1.841–26.999 |
| Index ranges | \(-16 \leq h \leq 16\) | \(-15 \leq h \leq 15\) | \(-14 \leq h \leq 14\) | \(-14 \leq h \leq 14\) |
|--------------|-----------------|-----------------|-----------------|-----------------|
| \(-15 \leq k \leq 15\) | 36640 | 25908 | 20102 | 19229 |
| \(-22 \leq l \leq 22\) | 5871 \([R_{int} = 0.0371]\) | 5179 \([R_{int} = 0.0553]\) | 5720 \([R_{int} = 0.0374]\) | 5737 \([R_{int} = 0.0331]\) |

| Reflections collected | 36640 | 25908 | 20102 | 19229 |
| Independent reflections | 5871 \([R_{int} = 0.0371]\) | 5179 \([R_{int} = 0.0553]\) | 5720 \([R_{int} = 0.0374]\) | 5737 \([R_{int} = 0.0331]\) |
| Completeness to \(\theta\) max | 99.9\% | 100.0\% | 99.9\% | 100.0\% |
| Data / restraints / parameters | 5871 / 0 / 305 | 5179 / 0 / 305 | 5720 / 1 / 305 | 5737 / 1 / 305 |
| Goodness on fit on \(F^2\) | 1.262 | 1.184 | 1.079 | 1.167 |
| \(R_1(1 > 2\sigma(I))\) | 0.0238 | 0.0411 | 0.0219 | 0.0275 |
| \(wR_2(\text{all data})\) | 0.0517 | 0.0840 | 0.0506 | 0.0535 |
| Largest diff. peak and hole, \(e \text{ Å}^{-3}\) | 1.199 / -0.959 | 1.371 / -1.057 | 0.658 / -0.845 | 0.704 / -1.016 |
| \([\text{NBu}_4]_2[\text{Pt}_6\text{Ni}_x(\text{CO})_{12}] (x = 4.41)\) | \(C_{44}H_{72}N_{2}\text{Ni}_{4.4}\text{O}_{12}\text{Pt}_{1.5}\) | \(C_{44}H_{72}N_{2}\text{Ni}_{5.78}\text{O}_{12}\text{Pt}_{0.2}\) | \(C_{44}H_{72}N_{2}\text{Ni}_{5.96}\text{O}_{12}\text{Pt}_{0.1}\) | \(C_{76}H_{144}\text{Br}_{0.23}\text{Cl}_{1.77}\text{N}_{4}\text{Ni}_{2.53}\text{O}_{12}\text{Pt}_{3}\) |
| Fw | 1390.14 | 1203.35 | 1186.93 | 2213.03 |
| T, K | 100(2) | 100(2) | 100(2) | 100(2) |
| \(\lambda\), Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic |
| Space Group | \(P\bar{1}\) | \(P\bar{1}\) | \(P\bar{1}\) | \(P2_1/n\) |
| a, Å | 11.015(5) | 10.9784(8) | 11.0218(7) | 12.0740(8) |
| b, Å | 11.819(5) | 11.7985(9) | 11.8443(7) | 31.835(2) |
| c, Å | 11.916(6) | 11.8483(9) | 11.8632(7) | 12.3924(8) |
| \(\alpha\), ° | 89.82(2) | 89.202(3) | 89.085(2) | 90 |
| \(\beta\), ° | 64.944(19) | 64.938(2) | 64.843(2) | 108.155(2) |
| \(\gamma\), ° | 70.764(18) | 70.309(2) | 70.214(2) | 90 |
| Cell Volume, Å\(^3\) | 1309.9(11) | 1293.90(17) | 1304.07(14) | 4526.2(5) |
| Z | 1 | 1 | 1 | 2 |
| $D_0$, g cm$^{-3}$ | 1.762 | 1.544 | 1.511 | 1.624 |
|-------------------|-------|-------|-------|-------|
| $\mu$, mm$^{-1}$  | 5.837 | 2.709 | 2.410 | 6.069 |
| F(000)            | 694   | 625   | 619   | 2208  |
| Crystal size, mm  | 0.15×0.13×0.10 | 0.16×0.13×0.11 | 0.18×0.16×0.14 | 0.22×0.16×0.14 |
| $\theta$ limits, ° | 1.849–26.000 | 1.919–26.999 | 1.848–26.999 | 1.844–27.999 |
| Index ranges      | -13 ≤ h ≤ 13  | -14 ≤ h ≤ 14  | -14 ≤ h ≤ 14  | -15 ≤ h ≤ 15  |
|                   | -14 ≤ k ≤ 14  | -15 ≤ k ≤ 15  | -15 ≤ h ≤ 15  | -42 ≤ h ≤ 42  |
|                   | -14 ≤ h ≤ 14  | -15 ≤ k ≤ 15  | -15 ≤ h ≤ 15  | -16 ≤ h ≤ 16  |
| Reflections       | 11021         | 17671         | 19609         | 73113         |
| collected         |               |               |               |               |
| Independent       | 5132 [Rint = 0.0592] | 5629 [Rint = 0.0414] | 5693 [Rint = 0.0266] | 10914 [Rint = 0.0502] |
| reflections       |               |               |               |               |
| Completeness to $\theta$ max | 99.7% | 99.9% | 100.0% | 100.0% |
| Data / restraints / parameters | 5132 / 1 / 305 | 5629 / 1 / 296 | 5693 / 1 / 295 | 10914 / 504 / 455 |
| Goodness on fit on F$^2$ | 1.088 | 1.128 | 1.142 | 1.223 |
| $R_1$ (I > 2σ(I)) | 0.0565 | 0.0334 | 0.0234 | 0.0350 |
| wR$^2$ (all data) | 0.1109 | 0.0764 | 0.0525 | 0.0734 |
| Largest diff. peak and hole, e Å$^{-3}$ | 1.291 / −1.295 | 0.621 / −0.695 | 0.357 / −0.395 | 1.758 / −1.545 |

| [NBu$_4$]$_2$[Pt$_9$(CO)$_{18}$]thf | [NBu$_4$]$_2$[Pt$_6$(CO)$_{12}$] |
|------------------------------------|---------------------------------|
| **Formula** | C$_{54}$H$_{80}$N$_2$O$_{19}$Pt$_9$ | C$_{44}$H$_{72}$N$_2$O$_{12}$Pt$_6$ |
| **Fw** | 2817.01 | 1991.57 |
| **T, K** | 100(2) | 100(2) |
| **$\lambda$, Å** | 0.71073 | 0.71073 |
| **Crystal system** | Orthorhombic | Tetragonal |
| **Space Group** | Pbca | I4$_1$/a |
| **a, Å** | 18.4985(14) | 17.5967(7) |
| **b, Å** | 19.5823(13) | 17.5967(7) |
| **c, Å** | 37.554(3) | 35.3226(15) |
|               | Value 1 | Value 2 |
|---------------|---------|---------|
| $\alpha$, °  | 90      | 90      |
| $\beta$, °    | 90      | 90      |
| $\gamma$, °   | 90      | 90      |
| Cell Volume, Å$^3$ | 13603.8(17) | 10937.4(10) |
| $Z$           | 8       | 8       |
| $D_c$, g cm$^{-3}$ | 2.751    | 2.419   |
| $\mu$, mm$^{-1}$ | 18.496   | 15.344  |
| $F(000)$      | 10176   | 7312    |
| Crystal size, mm | 0.16×0.13×0.11 | 0.18×0.16×0.08 |
| $\theta$ limits, ° | 1.545–26.000 | 2.002–26.615 |
| Index ranges  | -22 ≤ h ≤ 22, -24 ≤ k ≤ 24, -46 ≤ l ≤ 46 | -22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -44 ≤ l ≤ 44 |
| Reflections collected | 175114 | 105705 |
| Independent reflections | 13352 [Rint = 0.1292] | 5748 [Rint = 0.1628] |
| Completeness to $\theta$ max | 99.9% | 100.0% |
| Data / restraints / parameters | 13352 / 752 / 813 | 5748 / 0 / 293 |
| Goodness on fit on $F^2$ | 1.202 | 1.072 |
| $R_1$ (I > 2$\sigma$(I)) | 0.0671 | 0.0382 |
| $wR_2$ (all data) | 0.1322 | 0.0678 |
| Largest diff. peak and hole, e Å$^{-3}$ | 2.240 / −2.345 | 1.804 / −1.369 |
Computational details with figures and tables

Full geometry optimizations, optimizations with selected constrained internal coordinates and single-point calculations were carried out *in vacuo* using the hybrid meta-GGA DFT functional TPSS0, with 25% HF exchange, in combination with Ahlrichs' def-2 TZVP basis set, with relativistic ECP for Pt. The “restricted” approach was used in all the cases. Calculations were performed with the ORCA 4.2.0 software. Cartesian coordinates of the DFT-optimized structures are collected in a separated .xyz file.

Figure S56

DFT-optimized (TPSS0/def2-TZVP) trigonal prismatic geometry of [Pt$_6$(CO)$_{12}$]$^{2-}$ (a) and octahedral geometry of [Ni$_6$(CO)$_{12}$]$^{2-}$ (b).
Relative energy variations of clusters 1 and 2 on changing the dihedral angle defining the relative position of the two \{M_3\} triangles. Solid line: single point calculations. Dashed line: geometry optimizations with constrained inter-triangular dihedral angles.
Figure S58
HOMOs of clusters 1-10, DFT-optimized octahedral structures. Surface isovalue = 0.025 a.u.

1-$(\text{Ni}_3)(\text{Ni}_3)$
2-$(\text{Pt}_3)(\text{Pt}_3)$
3-$(\text{Pt}_3)(\text{Ni}_3)$
4-$(\text{Pt}_2\text{Ni})(\text{PtNi}_2)$
4’-$(\text{Pt}_2\text{Ni})(\text{PtNi}_2)$
5-$(\text{Pt}_2\text{Ni})(\text{Pt}_2\text{Ni})$
5’-$(\text{Pt}_2\text{Ni})(\text{Pt}_2\text{Ni})$
6-$(\text{PtNi}_2)(\text{PtNi}_2)$
6’-$(\text{PtNi}_2)(\text{PtNi}_2)$
7-$(\text{Pt}_3)(\text{PtNi}_2)$
8-$(\text{Ni}_3)(\text{Pt}_2\text{Ni})$
9-$(\text{Pt}_3)(\text{Pt}_2\text{Ni})$
10-$(\text{Ni}_3)(\text{PtNi}_2)$
Figure S59
HOMOs of clusters 1-10, single point calculations on trigonal prismatic conformations. Surface isovalue = 0.025 a.u.
Figure S60
HOMO-1 and HOMO-2 orbitals of \([\text{Ni}_6(\text{CO})_{12}]^{2-}\) and \([\text{Pt}_6(\text{CO})_{12}]^{2-}\), DFT-optimized octahedral geometry. Surface isovalue = 0.025 a.u.
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