Supplementary Material

Reactions of Trinuclear Platinum Clusters with Electrophiles: An Example of Ionisation Isomerism with $[Pt_3(\mu\text{-}I)(\mu\text{-}PPh_2)_2(PPh_3)_3]I$ and $[Pt_3(\mu\text{-}PPh_2)_2I_2(PPh_3)_3]$. Molecular Structures of $[Pt_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(PPh_3)_3]PF_6$, $[Pt_3(\mu\text{-}PPh_2)_2I_2(PPh_3)_3]\cdot C_6H_5Cl$ and of the Mixed-Metal Pt-Ag Cluster $[Pt_3\{\mu_3\text{-}AgBF_4\}(\mu\text{-}I)(\mu\text{-}PPh_2)_2(PPh_3)_3]BF_4$.†

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Table S-1. Summary of Crystal Data and Intensity Collection of $[Pt_3(\mu_2\text{-}Cl)(\mu\text{-}PPh_2)_2(PPh_3)_3]PF_6$ (**4**(PF_6))

Formula	$C_{78}H_{65}ClF_6P_6Pt_3$
fw	1922.41
crystal syst	Monoclinic
space group	$P2_1/c$
cryst. dimens, mm	0.1 x 0.1 x 0.13
a, Å	15.185(1)
b, Å	16.940(3)
c, Å	27.518(3)
β	□□□□□(□)
V, Å	7067.6
Z	4
ρ, g/cm3	1.79
F(000), e	3843.57
Temp, °C	20
diffractometer	Enraf Nonius CAD4 4F
radiation (graphite monochromator)	Mo Kα1 (λ = 0.70930 Å)
linear absorption coeff, cm-1	64.2
scan width, deg	1 + 0.35 tg□
step width, deg	0.04
scan θ/scan ω	2
scan speed deg/s	0.083
sinθ/λmax Å-1	0.66188
2θ limits deg	1 28
octants collected	±h +k +l
no of data collected	14309
no of unique data used	5804 ($I > 2\sigma(I)$)
$R = \sum \| \|F_o\| - \|F_o\| \| / \sum \|F_o\|$	0. 0621
$Rw = \|\sum w (\|F_o\| - \|F_e\|)^2 / \sum w \|F_o\|^2]^{1/2}$	0. 0733
Sdt error in an observn of unit wt, e	1.4
largest shift/esd, final cycle	3.0
largest peak in final diff map, e/Å3	1.1

Table S-2. Table of least-squares planes in $[Pt_3(\mu_2\text{-}Cl)(\mu\text{-}PPh_2)_2(PPh_3)_3]PF_6$ (**4**(PF_6))

Table of least-squares planes the equation of the plane is of the form :

Ax + By + Cz - D = 0 where A, B, C and D are constants and x, y, z are orthogonalized coordinates.

Plane n°1 : Pt1, Pt2, Pt3

0.0837	-0.9935	-0.0769	+12.2348

Others atoms

Cl1	0.226(9)	P1	-0.173(5)	P2	-0.138(5)
P3	-0.412(6)	P4	0.095(5)	P5	-0.168(5)

Plane n°2 : Pt1, Pt3, Cl1

0.0488	-0.9808	-0.1889	+12.9148

Plane n°3 : Pt1, Pt2, P4

0.0444	-0.9984	-0.0363	+12.3583

Plane n°4 : Pt2, Pt3, P5

-0.0125	-0.9951	-0.0977	+12.8030

Dihedral angles between planes

1 - 2	6.76(42)
1 - 4	5.64(16)
1 - 3	3.25(33)

Table S-3. Summary of Crystal Data and Intensity Collection of $[Pt_3(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(PPh_3)_3]OH$

Formula	$C_{78}H_{66}BrOP_5Pt_3$
fw	1838.9
crystal syst	Monoclinic
space group	$P2_1/c$
cryst. dimens, mm	0.1 x 0.08 x 0.11
a, Å	15.206(1)
b, Å	16.924(8)
c, Å	27.553(2)
β	92.825(7)
V, Å^3	7082.1
Z	4
ρ, g/cm^3	1.725
F(000), e	3546
Temp, °C	20
diffractometer	Enraf Nonius CAD4 4F
radiation (graphite monochromator)	Mo Kα_1 (λ = 0.70930 Å)
linear absorption coeff, cm^{-1}	69.74
scan width, deg	1 + 0.35 tgθ
step width, deg	0.04
scan θ/scan ω	2
scan speed deg/s	0.083
sinθ/λmax Å^{-1}	0.59582
2θ limits deg	1 25
octants collected	+h +k ±l
no of data collected	10025
no of unique data used	6864 ($I < 6\sigma(I)$)
$R = \sum \| \|F_o\| - \|F_o\| \| / \sum \|F_o\|$	0. 0499
$Rw = \|\sum w (\|F_o\| - \|F_e\|)^2 / \sum w \|F_o\|^2]^{1/2}$	0. 0455
Sdt error in an observn of unit wt, e	1.2
largest shift/esd, final cycle	3.8 (Y C(64))
largest peak in final diff map, e/Å^3	1.5

Table S-4. Table of least-squares planes for $[Pt_3(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(PPh_3)_3]OH$

The equation of the planes is of the form :

Ax + By + Cz - D = 0 where A, B, C and D are constants and x, y, z are orthogonalized coordinates.

Plane n°1 Pt1, Pt2, Pt3

-1.2105	16.8076	-2.2578	-3.3143

Others atoms

Br	0.240(2)	P1	-0.197(4)	P2	-0.135(4)
P3	-0.413(4)	P4	0.070(4)	P5	-0.178(4)

Plane n°2 Pt1, Pt3, Br

0.6813	16.5764	-5.3513	-2.9454

Plane n°3 Pt1, Pt2, P4

0.7766	16.8756	-1.4702	-3.7243

Plane n°4 Pt2, Pt3, P5

0.3529	16.8191	-3.0269	-4.2941

Dihedral angles between planes :

1 - 2	6.70
1 - 4	5.04
1 - 3	2.38

Table S-5. Selected Interatomic Distances and Angles for $[Pt_3(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(PPh_3)_3]OH$

		Bond lengths	
Pt(1) - Pt(2)	2.9180(7)	Pt(1) - Pt(3)	2.8813(7)
Pt(2) - Pt(3)	2.9207(8)	Pt(1) - Br	2.508(2)
Pt(3) - Br	2.515(2)	Pt(1) - P(1)	2.246(4)
Pt(1) - P(4)	2.208(4)	Pt(2) - P(4)	2.258(4)
Pt(2) - P(2)	2.271(4)	Pt(2) - P(5)	2.277(3)
Pt(3) - P(5)	2.202(3)	Pt(3) - P(3)	2.242(4)
		Bond Angles (deg)	
Pt(2) - Pt(1) - Pt(3)	60.48(2)	Pt(1) - Pt(2) - Pt(3)	59.14(2)
Pt(1) - Pt(3) - Pt(2)	60.38(1)	Pt(1) - Cl(1) - Pt(3)	70.01(5)
Pt(1) - P(4) - Pt(2)	81.6(1)	Pt(2) - P(5) - Pt(3)	81.4(1)
Pt(1) - Pt(3) - Br	54.89(3)	Pt(3) - Pt(1) - Br	55.10(4)
Pt(1) - Pt(2) - P(4)	48.45(9)	Pt(2) - Pt(1) - P(4)	50.0(1)
Pt(2) - Pt(3) - P(5)	50.44(9)	Pt(3) - Pt(2) - P(5)	48.19(9)
Br - Pt(1) - P(1)	91.2(1)	P(4) - Pt(1) - P(1)	104.1(1)
Br - Pt(3) - P(3)	91.2(1)	P(5) - Pt(3) - P(3)	103.3(1)
P(4) - Pt(2) - P(2)	105.7(1)	P(5) - Pt(2) - P(2)	98.5(1)
Pt(3) - Pt(1) - P(1)	145.3(1)	Pt(2) - Pt(1) - P(1)	153.5(1)
Pt(1) - Pt(2) - P(2)	153.86(9)	Pt(3) - Pt(2) - P(2)	146.64(9)
Pt(1) - Pt(3) - P(3)	143.5(1)	Pt(2) - Pt(3) - P(3)	152.7(1)
Br - Pt(1) - P(4)	163.6(1)	P(4) - Pt(2) - P(5)	155.5(1)
P5 - Pt(3) - Br	165.41(9)		

Table S-6. Comparison between selected bond distances (Å) and angles (°) in the clusters $[Pt_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(PPh_3)_3]BF_4$ (**4**·BF_4) and $[Pt_3(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(PPh_3)_3]OH$

	4·BF_4	$[Pt_3(\mu\text{-}Br)(\mu\text{-}PPh_2)_2(PPh_3)_3]OH$
Pt(1) – Pt(2)	2.904(1)	2.9180(7)
Pt(1) – Pt(3)	2.825(1)	2.8813(7)
Pt(2) – Pt(3)	2.901(1)	2.9207(8)
Pt(1) – X	2.366(8)	2.508(2)
Pt(3) – X	2.364(8)	2.515(2)
Pt(1) – P(1)	2.254(5)	2.246(4)
Pt(1) – P(4)	2.184(6)	2.208(4)
Pt(2) – P(4)	2.260(5)	2.258(4)
Pt(2) – P(2)	2.255(6)	2.271(4)
Pt(2) – P(5)	2.288(5)	2.277(3)
Pt(3) – P(5)	2.194(5)	2.202(3)
Pt(3) – P(3)	2.230(6)	2.242(4)
Pt(2) – Pt(1) – Pt(3)	60.8(0)	60.48(2)
Pt(1) – Pt(2) – Pt(3)	58.2(0)	59.14(2)
Pt(1) – Pt(3) – Pt(2)	60.9(0)	60.38(1)
Pt(1) – X – Pt(3)	72.8(2)	70.01(5)
Pt(1) – P(4) – Pt(2)	81.6(2)	81.6(1)
Pt(2) – P(5) – Pt(3)	80.7(2)	81.4(1)
Pt(1) – Pt(3) – X	53.1(2)	54.89(3)
Pt(3) – Pt(1) – X	54.0(1)	55.10(4)
Pt(1) – Pt(2) – P(4)	48.1(1)	48.45(9)
Pt(2) – Pt(1) – P(4)	50.3(1)	50.0(1)
Pt(2) – Pt(3) – P(5)	51.1(1)	50.44(9)
Pt(3) – Pt(2) – P(5)	48.3(1)	48.19(9)
X – Pt(1) – P(1)	90.4(2)	91.2(1)
P(4) – Pt(1) – P(1)	105.2(2)	104.1(1)
X – Pt(3) – P(3)	91.4(2)	91.2(1)
P(5) – Pt(3) – P(3)	103.6(2)	103.3(1)

P(4) – Pt(2) – P(2)	106.8(2)	105.7(1)
P(5) – Pt(2) – P(2)	98.6(2)	98.5(1)
Pt(3) – Pt(1) – P(1)	143.6(2)	145.3(1)
Pt(2) – Pt(1) – P(1)	155.0(2)	153.5(1)
Pt(1) – Pt(2) – P(2)	154.5(1)	153.86(9)
Pt(3) – Pt(2) – P(2)	146.9(1)	146.64(9)
Pt(1) – Pt(3) – P(3)	142.1(2)	143.5(1)
Pt(2) – Pt(3) – P(3)	153.6(2)	152.7(1)
X – Pt(1) – P(4)	163.0(2)	163.6(1)
P(4) – Pt(2) – P(5)	154.4(2)	155.5(1)
P(5) – Pt(3) – X	163.8(2)	165.41(9)

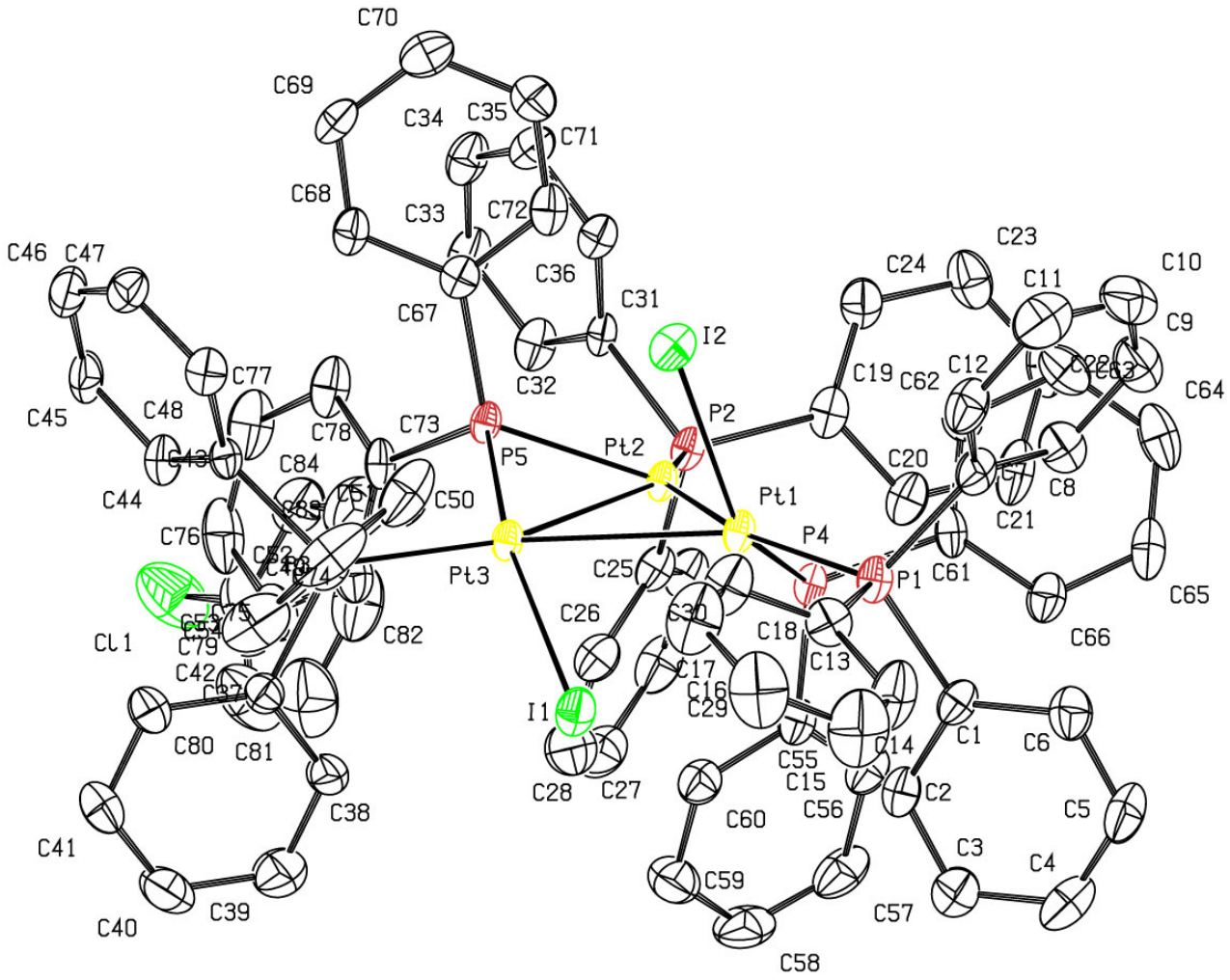

Figure S1. ORTEP view of $[Pt_3(\mu\text{-}PPh_2)_2I_2(PPh_3)_3]\cdot PhCl$ (**5**·PhCl) with complete numbering scheme (the PhCl solvent molecule is not shown).

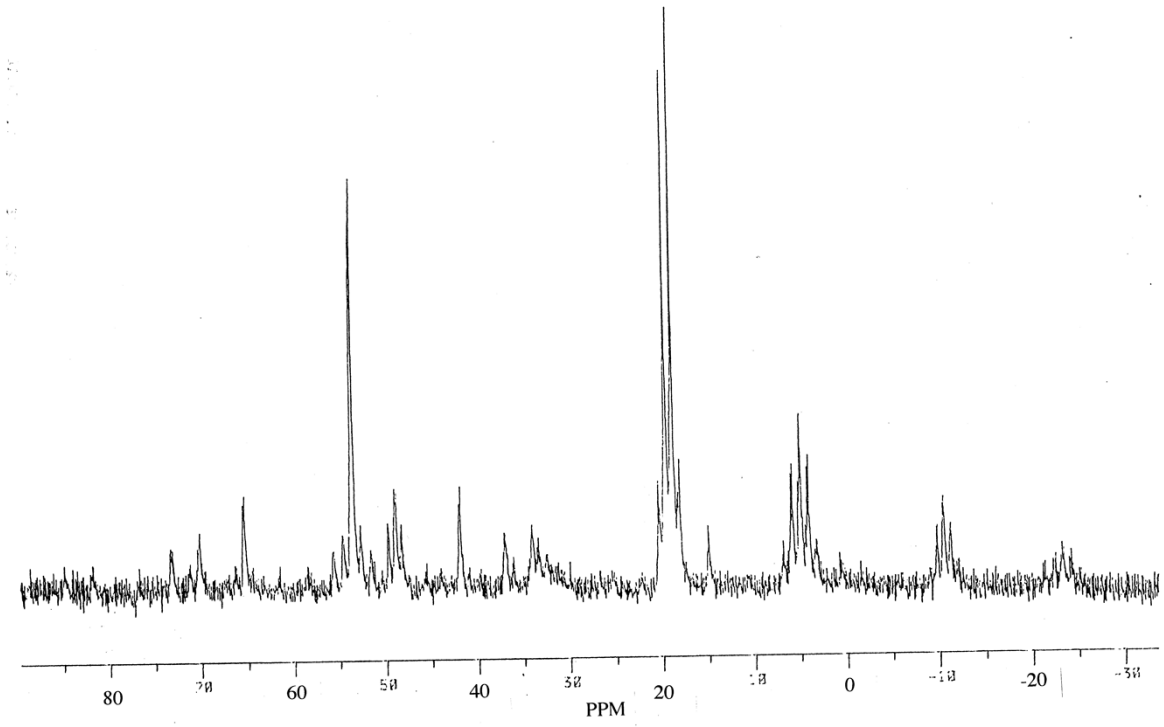

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum in CH_2Cl_2 of the cluster cation $[Pt_3(\mu_3\text{-}AgOTf)(\mu\text{-}OH)(\mu\text{-}PPh_2)_2(PPh_3)_3]^+$ (**9**) in **9**(BF_4).

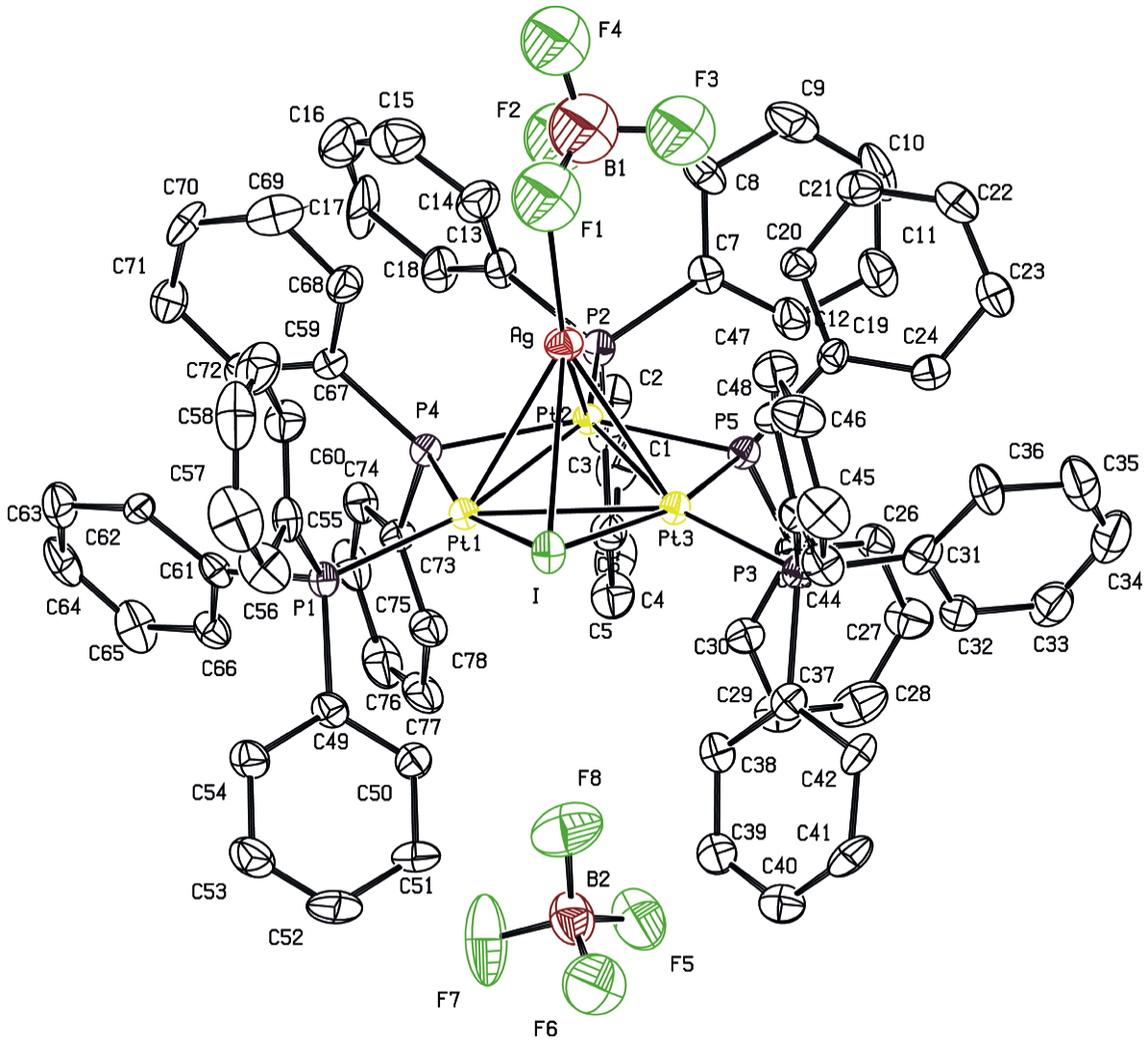

Figure S3. ORTEP view of $[Pt_3(\mu_3\text{-}AgBF_4)(\mu\text{-}PPh_2)_2(\mu\text{-}I)(PPh_3)_3]BF_4$ (**11**(BF_4)) with complete numbering scheme. Hydrogen atoms have been omitted for clarity.