Equations Supplementary Information

$$\underset{\mathbf{9}}{[Pd(PP_3)_2]Cl_2} + AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \underset{\mathbf{I}}{[PdAg(NO_3)(PP_3)_2]Cl_2} \quad (S1)$$

$$3\ \underset{\mathbf{12}}{[Pt(PP_3)_2]Cl_2} + 3\ AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \rightarrow\ 2\ \underset{\mathbf{12}}{[Pt(PP_3)_2]Cl_2} + \underset{\mathbf{I}}{[PtAg(NO_3)(PP_3)_2](NO_3)_2} + 2\ AgCl\downarrow \quad (S2)$$

$$2\ \underset{\mathbf{9/12}}{[M(PP_3)_2]Cl_2} + 4\ AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \rightarrow \underset{\mathbf{I}}{[MAgCl(PP_3)_2]Cl_2} + \underset{\mathbf{III}}{[MAg_2(NO_3)_4(PP_3)_2]} + AgCl\downarrow \quad (S3)$$

$$2\underset{\mathbf{9}}{[Pd(PP_3)_2]Cl_2} + 6AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \rightarrow \underset{\mathbf{II}}{[PdAg_2(NO_3)_2(PP_3)_2]Cl_2} + \underset{\mathbf{III}}{[PdAg_2(NO_3)_4(PP_3)_2]} + 2\ AgCl\downarrow \quad (S4)$$

$$2\underset{\mathbf{9}}{[Pd(PP_3)_2]Cl_2} + 8AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \rightarrow \underset{\mathbf{II}}{[PdAg_2(NO_3)_2(PP_3)_2](NO_3)_2} + \underset{\mathbf{III}}{[PdAg_2(NO_3)_4(PP_3)_2]} + 4AgCl\downarrow \quad (S5)$$

$$\underset{\mathbf{12}}{[Pt(PP_3)_2]Cl_2} + 3\ AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \underset{\mathbf{III}}{[PtAg_2Cl(NO_3)_3\ (PP_3)_2]} + AgCl\downarrow \quad (S6)$$

$$\underset{\mathbf{12}}{[Pt(PP_3)_2]Cl_2} + 4\ AgNO_3 \xrightarrow{DMSO\text{-}d_6+CD_3OD} \underset{\mathbf{III}}{[PtAg_2(NO_3)_4(PP_3)_2]} + 2\ AgCl\downarrow \quad (S7)$$

Table S1. $^{31}P\{^{1}H\}$ NMR data at room temperature for reactions of **1**, **2** and **5** with ligand

Reaction[a]	δP^A , δP^B, δP^C	δP for **1/2/5**	$\delta P^L/(P^T,P^M)$	$^1J(^{31}P,^{195}Pt)$	Solvent
1 + 1 eq NP_3	17.6s, -20.7s	35.0m, 23.1s (**1**)	-19.5		CD_3OD $+CD_2Cl_2$
1 + 2 eq NP_3	17.5s, -20.5s	36.0m, 23.5br (**1**)	-19.3s		
2 + 1 eq PP_3	56.0s, 52.1br, -14.6br	134.0s, 29.4s (**2**)	- 14.8d, -19.1q		$CDCl_3$
2 + 2 eq PP_3	56.1s, 52.2br, -14.6br	134.0s, 29.4s (**2**)	- 14.8d, -19.1q		
5 + 1 eq PP_3	47.9s[b], -12.0br, - 12.0br	118.3s[c], 25.0s[d] (**5**)	- 14.6d	2259[b],2503[c], 2591[d]	$CDCl_3$
5 + 1.5 eq PP_3	47.9s[b], -12.5br, - 12.5br		- 14.6d, -19.1q	2258[b]	

[a] See Scheme 1 for labels in P atoms. The underlined broad signals include P^B and P^c

Table S2 $^{31}P\{^{1}H\}$ NMR data at room temperature for reactions of **15** and **16** with ligand in $CDCl_3$

Compound[a]	δP^A, δP^B, δP^c	δPHomo[b]	$^1J(^{31}P\text{-}^{195}Pt)$	$^1J(^{31}P\text{-}^{107/109}Ag)$
15+1eqPP$_3$	58.5br, 13.6 d[e] 8.9br (**15***)			528[e]
15+2eqPP$_3$	61.0br, 31.9br, -11.9br (**17**)	16.2d[e], 8.1br, 0.4d[e],-0.5br		376[e] ,176[e]
15+3eqPP$_3$	60.9s, 32.2br, -7.2br (**17**)	16.1d[e],0.5d[e], -4.3br		384[e] ,202[e]
16+1eqPP$_3$	56.6s[c], 14.4 brd[e], 14.4 br (**16***)		2280[c]	496[e]
16+2eqPP$_3$	56.8s[c], 13.0br, -7.1br (**18**)	19.8d[e],13.0d[e] 5.3d,1.0b	2284[c]	378[e] ,369[e]

[a] See Scheme 1 for labels in P atoms. The underlined broad peaks include two resonances. [b] δPHomo = δP for the homonuclear complex $[Ag_2(\mu\text{-}PP_3)_2](NO_3)_2$

Table S3. $^{31}P\{^{1}H\}$ NMR data at room temperature for reactions of **9** and **12** with Cu(I), Ag(I) and Au(I).

Reaction[a]	$\delta P^D/P^H/P^P/P^S$	$\delta P^U/P^Q/P^I/P^E$	$\delta P^F/P^J/P^K$	$\delta P^G/P^N/P^R$	$\delta P^V/P^Y/P^X/P^Z$	$^1J(^{31}P,^{195}Pt)$	$^1J(^{31}P,^{107/109}Ag)$	Solvent
9+1eqCuCl→I	138.0br	37.4br	-6.9br	14.5br				DMSO-d_6
9+2eqCuCl→II	128.0br	50.0br	15.0br	-4.9br				
12+1eqCuCl→I	129.2s[b]	34.3s[c]	-6.0br	14.9br		2487[b]/2565[c]		DMSO-d_6
12+2eqCuCl→III	61.3m[b]	58.6m[d,e]		-5.3br		2169[b]/2272[d]		
9+1eqAgCl→I+III	142.6br,66.0m	66.0m,37.5br	3.3br[f]	10.0d[g]			4 23[g]	DMSO-d_6
9+2eqAgCl→II	127.4br	65.0br	7.6brd[g]	10.4br			160[g]	
12+1eqAgCl→I+III	135.0 br,57.0m	57.0m[d],34.3s[c]	5.1br[f]	9.8d[g]		2573[c],2315[d]	423[g]	DMSO-d_6
12+2eqAgCl→II	84.0 br	57.8br[h]	10.3br[i]			2310[h]		
9+1eqAgNO$_3$→I	143.0br	37.4s	6.6br[e, f, g]				335[g]	DMSO-d_6 +CD_3OD
9+2eqAgNO$_3$→I+III	143.0br,66.4m	66.4m,37.6br	5.4brd[f, g]	10.9d[g]			334[g],434[g]	
9+3eqAgNO$_3$→II+III	123.0br,67.0m	67.0m,52.3br	7.1br[g, i]	13.6br			218[g]	
12+1eqAgNO$_3$→I[j]	129.1s[b]	34.2s[c]	5.1br[f]			2398[b]/2570[c]		DMSO-d_6 +CD_3OD
12+2eqAgNO$_3$→I+III	128.0br,58.1s[e]	57.2s[d],34.1s[c]	5.1br[f]	10.6d[g]		2578[c], 2255[d]	428[g]	
12+3eqAgNO$_3$→III	58.2br[b,e]	57.4br		13.0br		2103[b]		
12+4eqAgNO$_3$→III	58.4br[b,e]	57.4br		14.5d[g]		2266[b]	482[g]	
9+1eqAuCl(tdg)→ →II'+IV	123.0br, 78.0br	78.0br,53.0br			40.1br[k], 39.1br[l]			DMSO-d_6 +CD_3OD
9+2eqAuCl(tdg)→IV	90.2br	74.3s			38.0m[e, m], 36.0s[n]			
12+1eqAuCl(tdg)→ → II'+IV	96.5s[p],62.9br[q]	51.0s[r],49.0s[s]			39.0br[e, k], 37.0s[l]	2963 [p],3389 [q] 3660[r], 2507 [s]		DMSO-d_6 +CD_3OD
12+2eqAuCl(tdg)→IV	63.0br [q]	51.0s [r]			39.0s[m]37.0s[n]	3378[q], 3641[r]		

[a] See Scheme 3 for structures **I -IV**. The underlined signals include 2 or more resonances. [e] $J(^{31}P,^{31}P)$ in Hz: 126 [**I** (P^F,P^G)], 281 [**III** (P^P,P^Q)], 157 [**III** (P^P,P^R)], 53 [**IV** (P^X,P^Y) . [f] P^F and P^G . [i] P^J, P^K and P^N. [j] **I** is coexisting with unreacted complex **12** [δ 56.7($^1J(^{31}P, ^{195}Pt)$ = 2168 Hz), 37.2, 12.0]. [k] P^N, P^V and P^Y. [l] P^J, P^K, P^X and P^Z. [m] P^V and P^Y. [n] P^X and P^Z.

Supplementary Information

Equations S1-S7

Tables S1- S3

Figure Captions

Figure S1. $^{31}P\{^{1}H\}$NMR spectra at room temperature for : (a) **1** in CD_3OD; (b) or (c) **1**+ **1** or **2 eq NP_3** in CD_3OD+ CD_2Cl_2 affording **8** in coexistence with **1** (•) and free PP_3; (d) **5 + 1.5 eq PP_3** in $CDCl_3$ affording **12** in coexistence with free PP_3.

Figure S2. (a) ORTEP diagram for **10**; (b)View of the unit cell for **10**· $4CHCl_3$. Phenyl rings omitted for clarity.

Figure S3. (a) ORTEP diagram for **18**; (b)View of the unit cell for **18**· $2CHCl_3$. Phenyl rings omitted for clarity

Figure S4. $^{31}P\{^{1}H\}$NMR spectra (r.t) for : (a) **12+1 eq AgCl** in DMSO-d_6 affording **I+III** and (b) **9+1eq $AgNO_3$** in DMSO-d_6 + CD_3OD affording **I**.

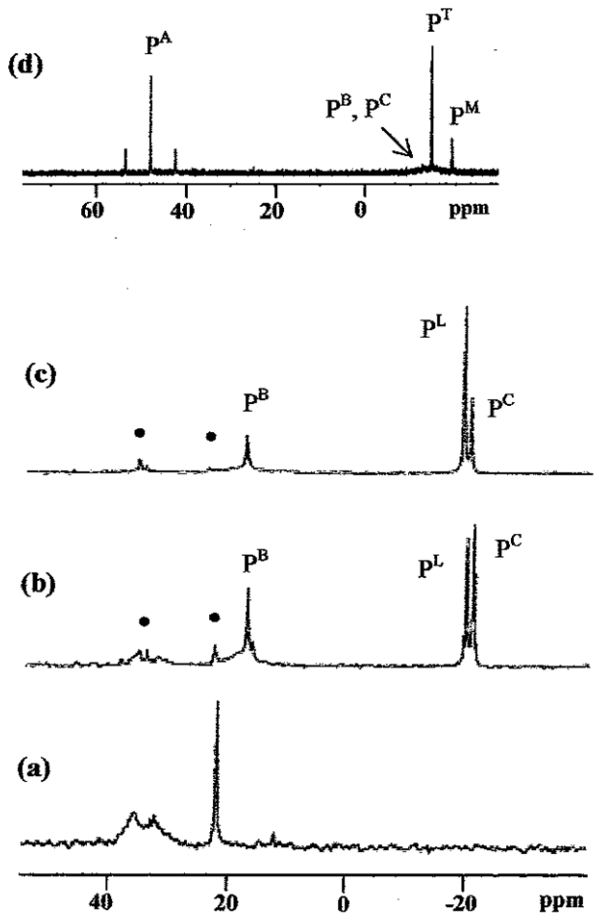
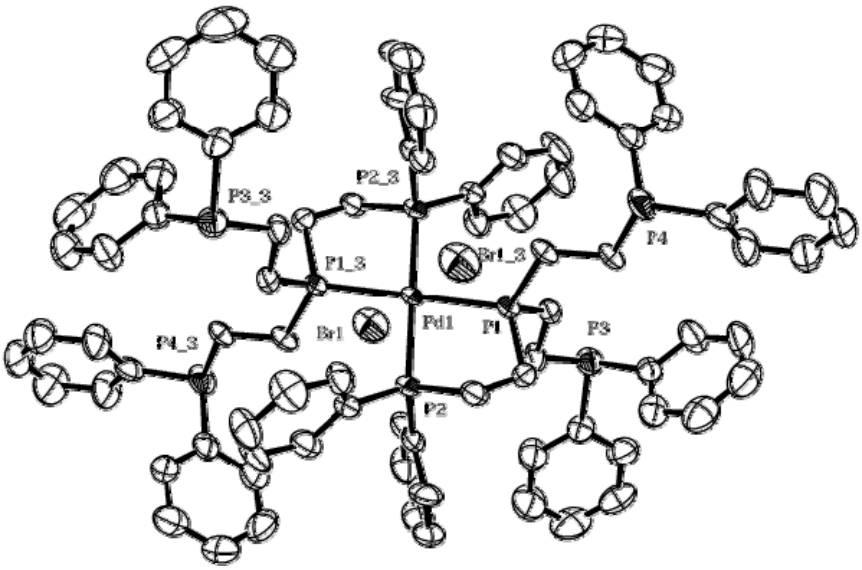
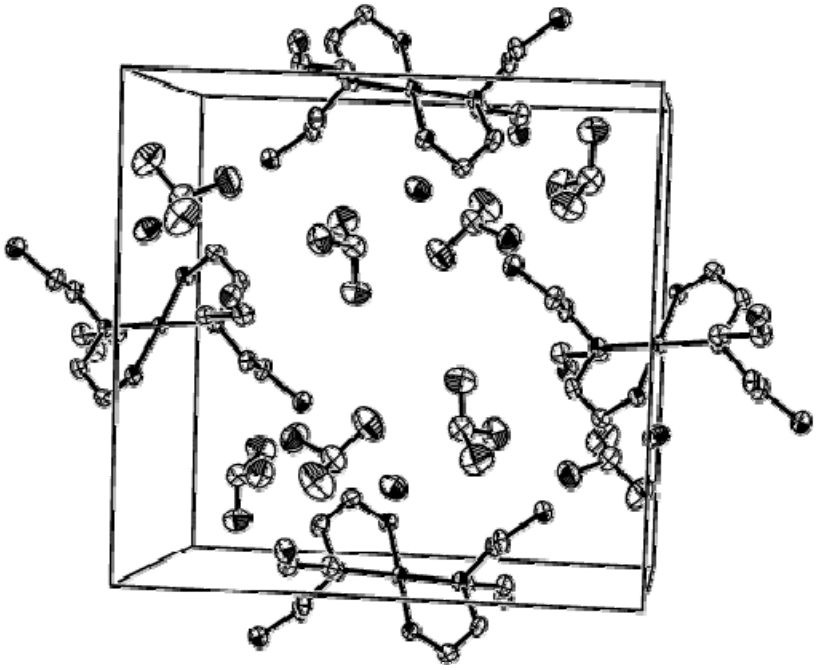


Figure S1

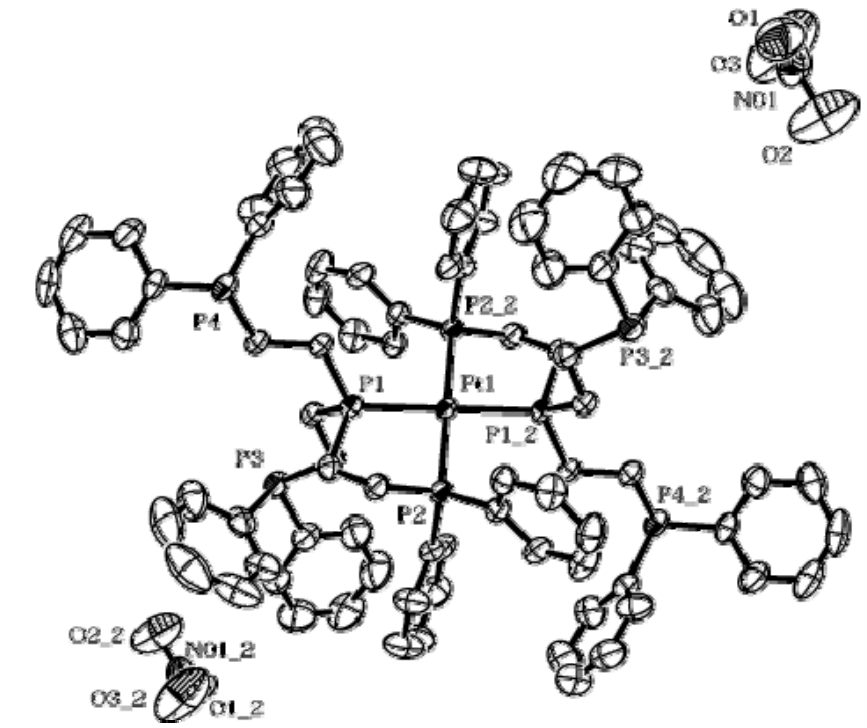


(a)

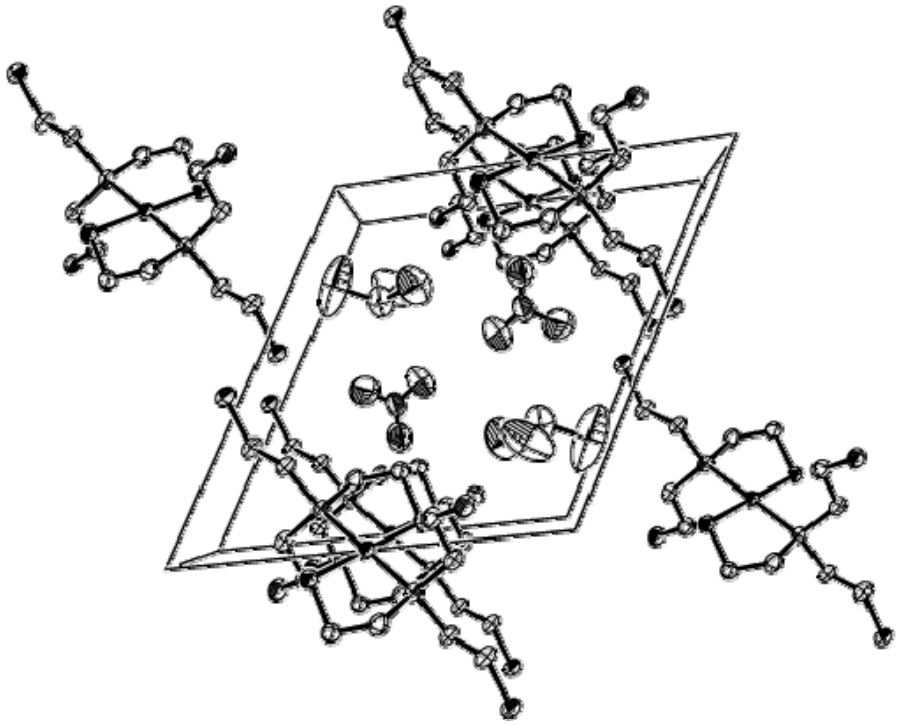


(b)

Figure S2



(a)



(b)

Figure S3

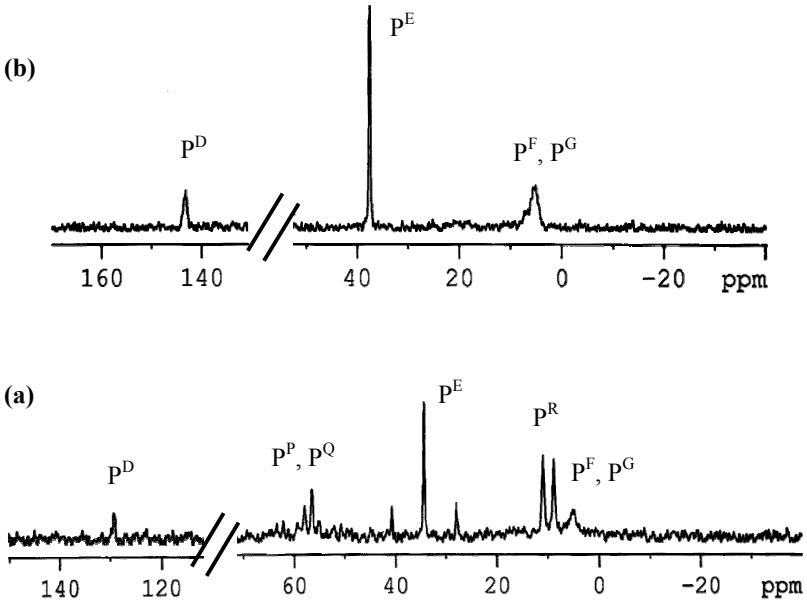

(b)
P^E
P^D
P^F, P^G
160
140
40
20
0
-20
ppm
(a)
P^E
P^R
P^P, P^Q
P^D
P^F, P^G
140
120
60
40
20
0
-20
ppm

Figure S4