Supplementary Information

Table S1: Crystallographic data and refinement parameters

Compound	***1***	***2***
Formuka	$C_{48}H_{36}P^+$, $N(CN)_2^-$	$2(C_{48}H_{36}P^+)$ $2(Br^-)$, $2(CH_3CN)$, H_2O
Empirical formula	$C_{50}H_{36}N_3P$	$C_{100}H_{80}Br_2N_2OP_2$
Formula weight /g mol^{-1}	709.79	1547.42
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a /Å	11.9466(7)	12.6244(5)
b /Å	12.1287(7)	12.7476(5)
c /Å	14.3527(9)	13.8190(5)
α /°	79.239(5)	78.115(3)
β /°	66.796(6)	65.545(4)
γ /°	89.851(5)	87.063(3)
V /Å^3	1872.01(2)	1979.55(15)
Z	2	1
D_c /g cm^{-3}	1.259	1.298
μ /mm^{-1}	0.114	2.074
F_{000}	744	802
Crystal size (mm^3)	0.27x0.18x0.08	0.14x0.13x0.13
θ range for data collection (°)	2.081 to 26.730	3.546 to 64.996
Miller index ranges	-15 ≤ h ≤ 15 -15 ≤ k ≤ 15 -18 ≤ l ≤ 18	-14 ≤ h ≤ 14 -14 ≤ k ≤ 14 -16 ≤ l ≤ 16
Completeness to θ_{max} (%)	99.9	99.3
Reflections (collected)	32127	21674
Min. and max. transmission	0.88707 and 1.0	0.96273 and 1.0
$2\theta_{max}$ /°	53.46	130.0
Reflections (collected)	27557	21699
R_{int}	0.0506	0.0396
Data / restraints / parameters	7953 / 0 / 497	6689 /41/ 510
Reflections ($I > 2\sigma(I)$)	5672	4357
Final GooF	1.000	1.000
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0490, wR2 = 0.1003	R1 = 0.0364, wR2 = 0.0777
R indices (all data)	R1 = 0.0773, wR2 = 0.1159	R1 = 0.0598, wR2 = 0.0812
Largest diff. peak and hole (e Å^{-3})	0.337 and -0.333	0.379 and -0.521
CCDC number	2211649	2211650

Table S2: Relevant geometrical parameters.

	Compound 1	**Compound 2**
C-P-C bond angles /°		
C(101)–P–C(201)	109.10(9)	108.40(11)
C(101)–P–C(301)	108.33(9)	108.59(12)
C(101)–P–C(401)	110.71(9)	111.69(12)
C(201)–P–C(301)	110.07(9)	109.07(11)
C(201)–P–C(401)	108.47(8)	109.65(12)
C(301)–P–C(401)	110.15(9)	109.39(12)
Interplanar angles /°		
ring 1a/ring 1b	36.83(9)	37.62(11)
ring 2a/ring 2b	27.36(10)	35.18(12)
ring 3a/ring 3b	27.48(7)	30.47(10)
ring 4a/ring 4b	34.32(8)	34.43(10)

Table S3: Selected hydrogen-bond geometry (Å, º) for Compound **2**.

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O1W-H1W*A*···Br1	0.84	2.51	3.349(3)	177
O1W-H1W*A*···Br2	0.84	2.27	3.067(6)	159
O1W-H1W*B*···N1	0.84	2.35	3.18(2)	174
C102-H102...O1W^{i}	0.95	2.63	3.440(4)	143
C402-H402...O1W^{ii}	0.95	2.58	3.270(4)	129
C02-H02*C*···Br1	0.98	2.66	3.539(15)	159
C02-H02*E*···Br2	0.98	2.38	2.957(17)	112

Symmetry codes: (i) –*x*+1, –*y*+1, –*z*+1; (ii) *x*–1, *y*, *z*; (iii) *x*+1, *y*, *z*