Supporting Information

Tetrabromoethane as σ-hole donor toward bromide ligands: halogen bonding between $C_2H_2Br_4$ and bromide dialkylcyanamide platinum(II) complexes

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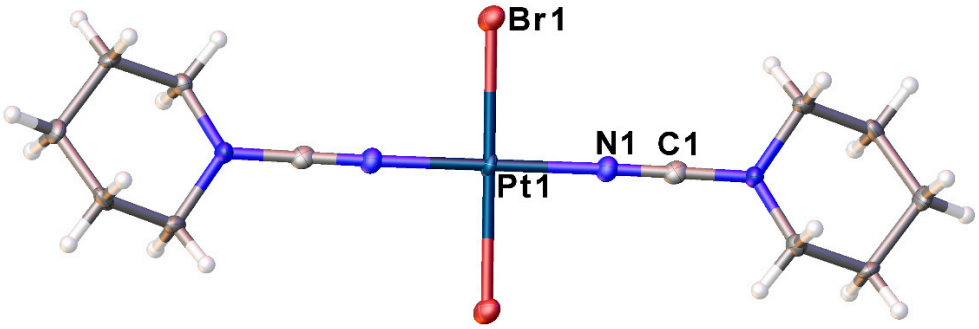

Figure S1. Structure of complex *trans*-[$PtBr_2(NCN(CH_2)_5)_2$]

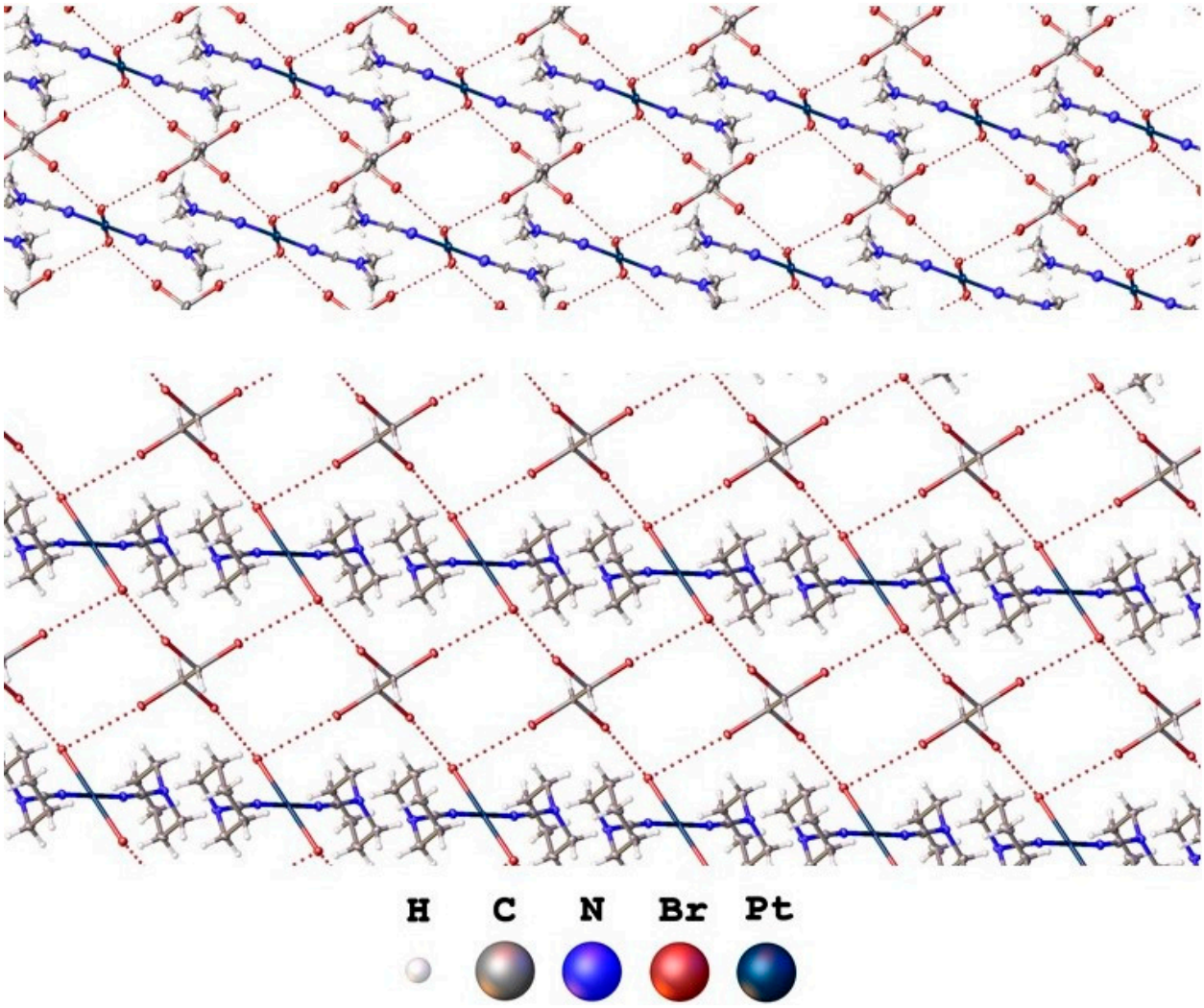

Figure S2. Formation of 2D polymer networks in adducts **1**·**tbe** (top) and **2**·**tbe** (bottom).

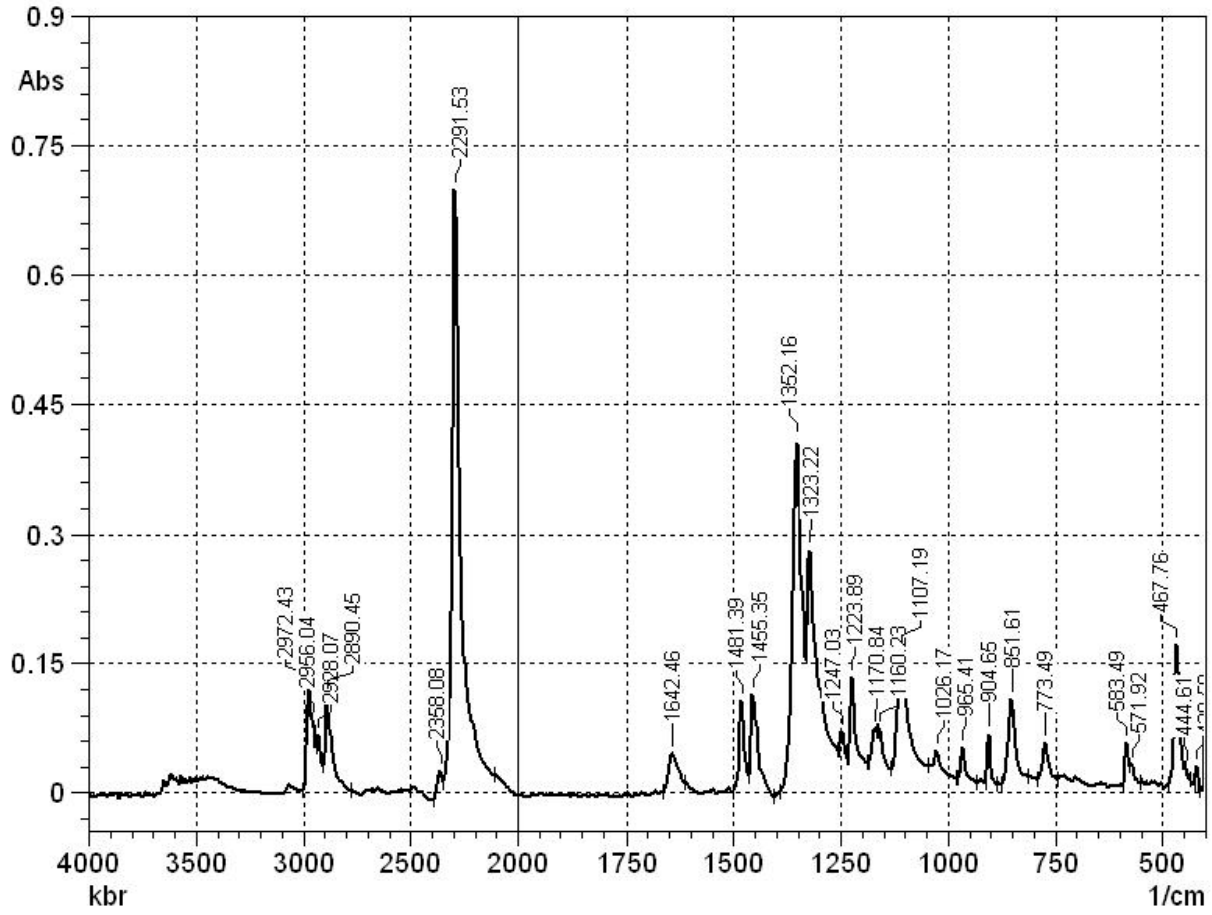

Figure S3. IR-spectra of complex *trans*-[$PtBr_2(NCN(CH_2)_5)_2$]: 2944 (w), 2852 (w), *ν*(C−H); 2291 (s), *ν*(C≡N); 1170 (w), 1107 (w), *ν*(C−N); 467 (m), *ν*(Pt−N).

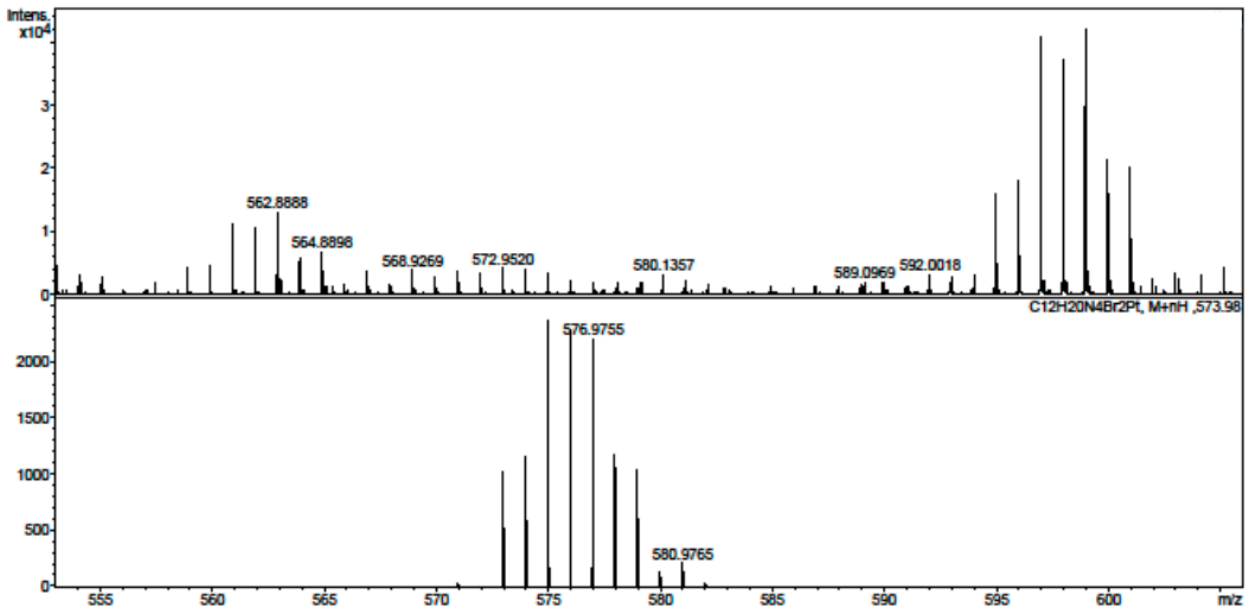

Figure S4. Mass spectrum of complex *trans*-[$PtBr_2(NCN(CH_2)_5)_2$]

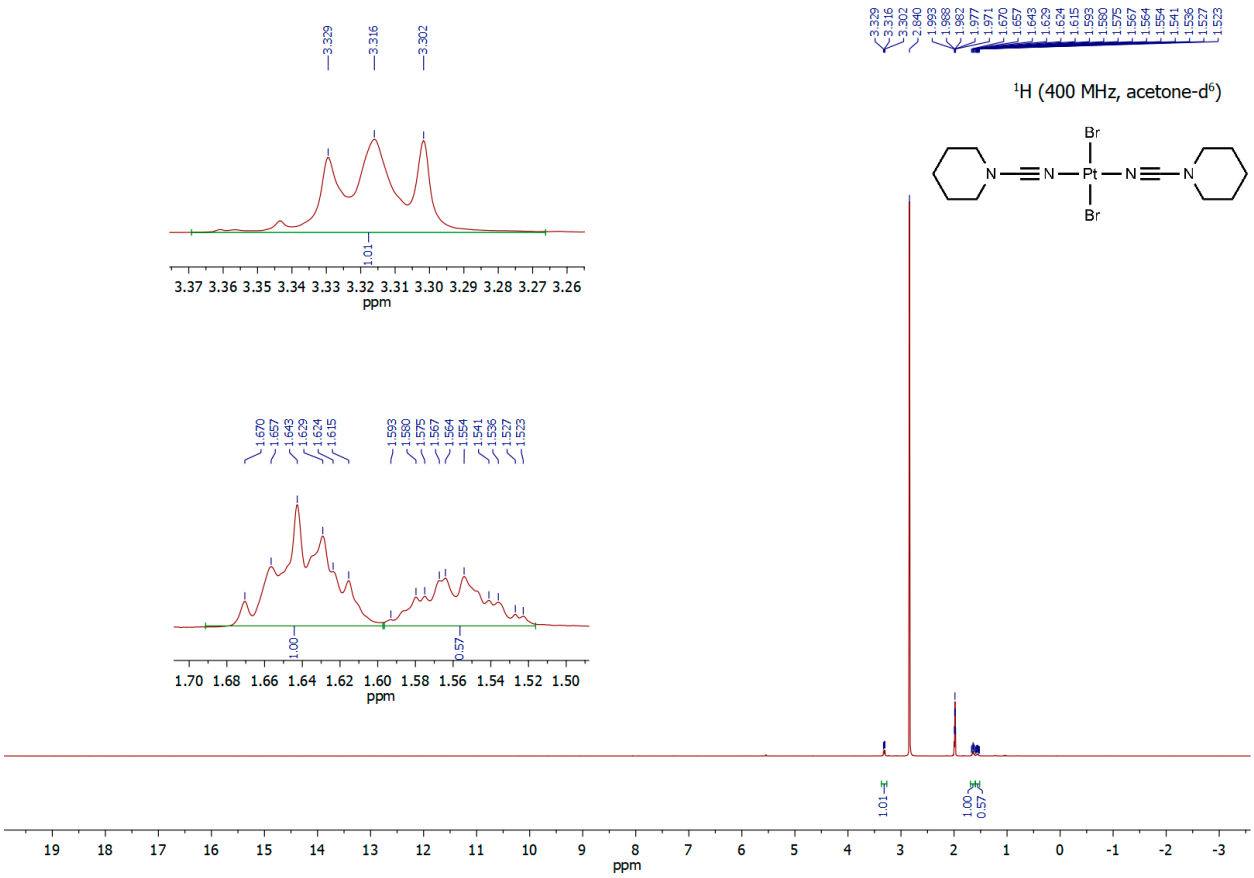

Figure S5. ^{1}H NMR spectrum of complex *trans*-[PtBr$_2$(NCN(CH$_2$)$_5$)$_2$]

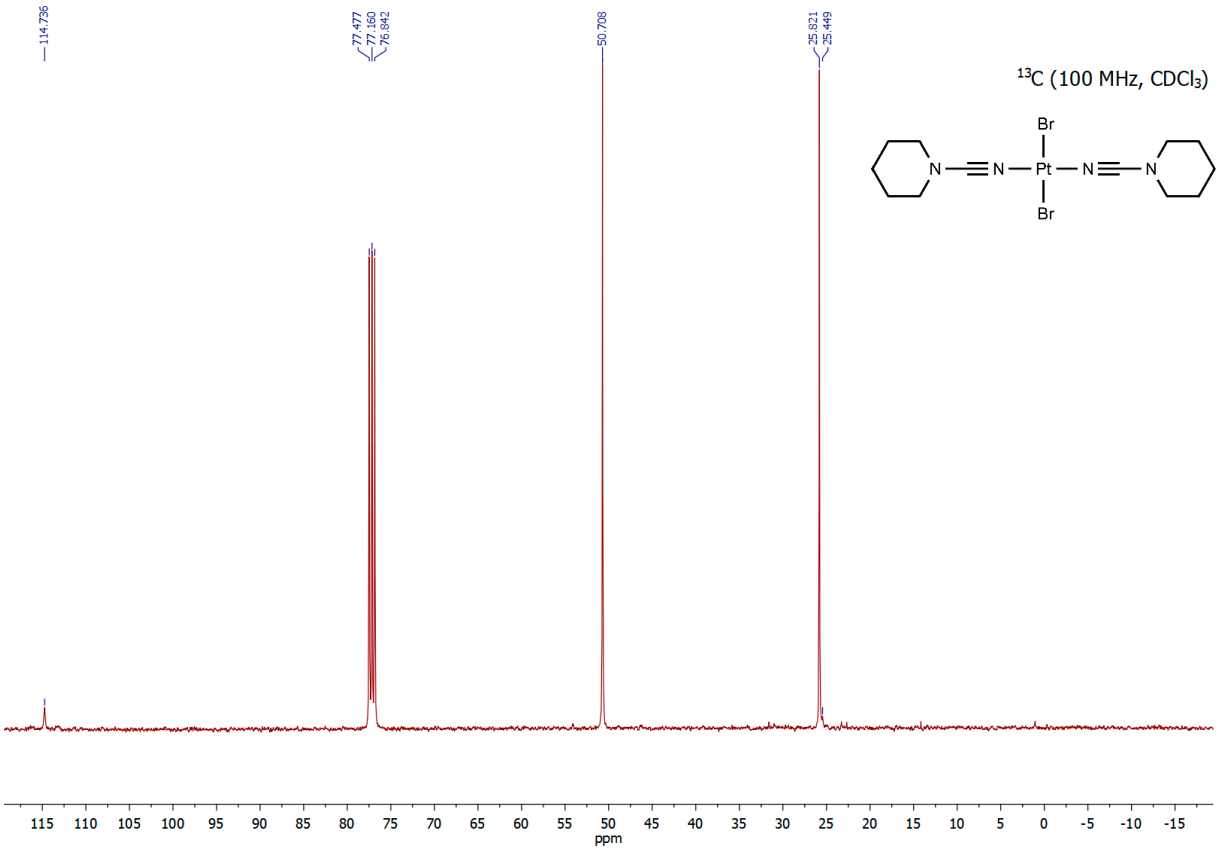

Figure S6. ^{13}C{^{1}H} NMR spectrum of complex *trans*-[PtBr$_2$(NCN(CH$_2$)$_5$)$_2$]

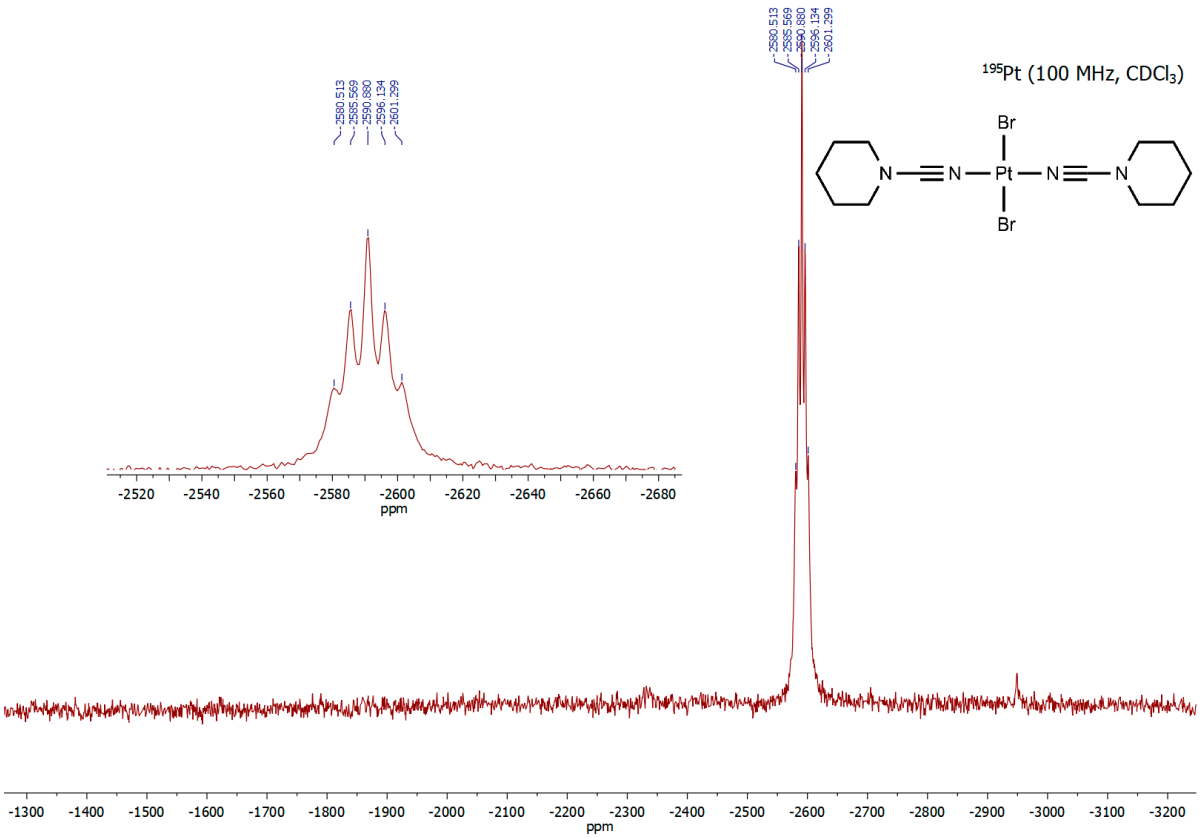

Figure S7. ^{195}Pt NMR spectrum of complex *trans*-[$PtBr_2(NCN(CH_2)_5)_2$]

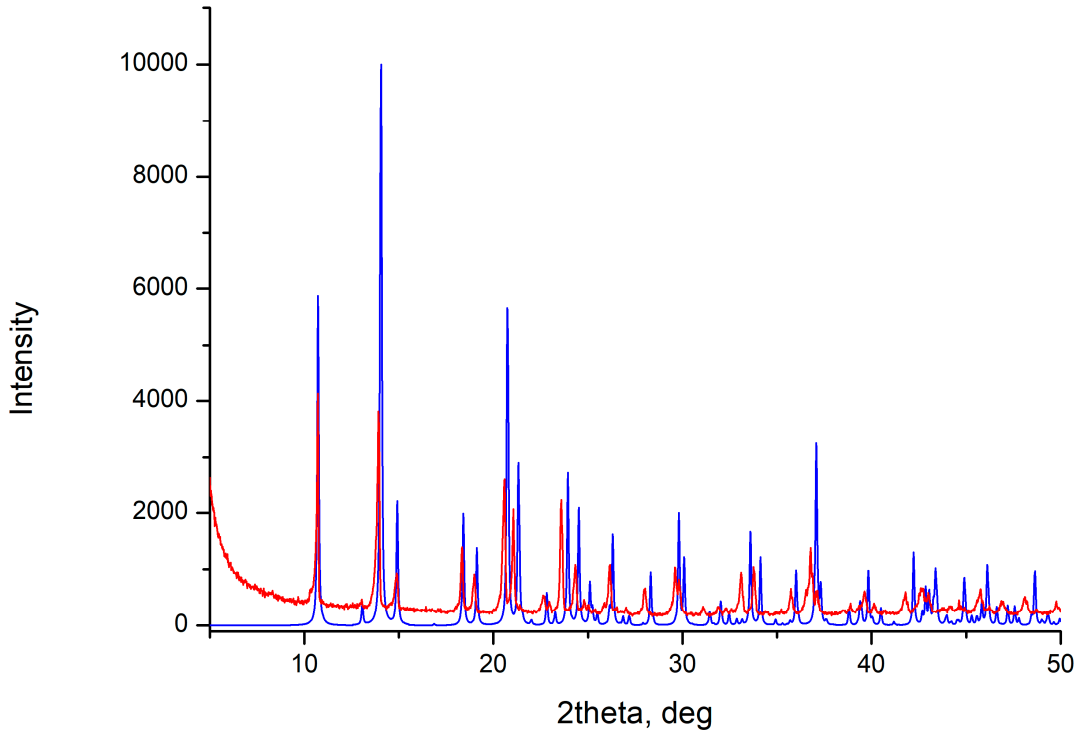

Figure S8. Comparison of PXRD (red line) and XRD (blue line) complex *trans*-[$PtBr_2(NCN(CH_2)_5)_2$]. The phases coincide, the difference is due to different experimental conditions (for PXRD - RT, for XRD - 100 K)

Table S1. Crystal data and structure refinement for **1·tbe**, **2** and **2·tbe** at 100 K

Identification code	**1·tbe**	**2**	**2·tbe**
CCDC number	**2094282**	**2094284**	**2094283**
Empirical formula	$C_8H_{14}Br_6N_4Pt$	$C_{12}H_{20}Br_2N_4Pt$	$C_{14}H_{22}Br_6N_4Pt$
Formula weight	840.78	575.23	920.90
Temperature/K	100(2)	100(2)	100(2)
Crystal system	triclinic	orthorhombic	triclinic
Space group	P-1	Pbca	P-1
a/Å	7.2697(4)	11.8704(11)	8.5098(4)
b/Å	7.9781(4)	8.3227(6)	8.6937(5)
c/Å	9.4586(3)	16.4831(12)	9.3226(4)
α/°	100.930(4)	90	112.221(5)
β/°	104.580(4)	90	91.242(4)
γ/°	110.313(5)	90	116.652(5)
Volume/Å^3	474.14(4)	1628.4(2)	555.17(6)
Z	1	4	1
P_{calc}g/cm^3	2.945	2.346	2.754
μ/mm^{-1}	28.603	13.517	24.527
F(000)	378.0	1072.0	422.0
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.148 to 140.63	6.018 to 51.986	10.536 to 152.364
Index ranges	-8 ≤ h ≤ 8, -6 ≤ k ≤ 9, -11 ≤ l ≤ 11	-14 ≤ h ≤ 11, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11
Reflections collected	3907	7919	9583
Independent reflections	1806 [R_{int} = 0.0386, R_{sigma} = 0.0502]	1593 [R_{int} = 0.0406, R_{sigma} = 0.0300]	2293 [R_{int} = 0.0499, R_{sigma} = 0.0347]
Data/restraints/parameters	1806/0/90	1593/0/88	2293/0/115
Goodness-of-fit on F^2	1.113	1.163	1.063
Final R indexes [I≥2σ (I)]	R_1 = 0.0409, wR_2 = 0.1102	R_1 = 0.0274, wR_2 = 0.0624	R_1 = 0.0261, wR_2 = 0.0641
Final R indexes [all data]	R_1 = 0.0469, wR_2 = 0.1135	R_1 = 0.0366, wR_2 = 0.0660	R_1 = 0.0282, wR_2 = 0.0654
Largest diff. peak/hole / e·Å^{-3}	1.40/-2.42	0.78/-1.44	1.53/-1.76

Table S2. Values of the Wiberg indices (WBI), Lagrangian kinetic energy G(r), potential energy density V(r), and energy density H(r) (Hartree) at the bond critical points (3, −1), corresponding to different noncovalent interactions in **1**·**tbe**.

Adduct	HB	Wiberg	sign($\lambda_2\rho$)	G(r)	V(r)	Energy density
(**1**)·(tbe) (type 1)	H2A···Br1A	0.00	-0.006	0.004	-0.003	0.001
(**1**)·(tbe) (type 1)	H2A···Br2A	0.00	-0.004	0.002	-0.002	0.000
(**1**)·(tbe) (type 1)	H1A···Br1	0.01	-0.011	0.006	-0.005	0.001
(**1**)·(tbe) (type 2)	H3B···Br2A	0.00	-0.004	0.002	-0.002	0.000
(**1**)·(tbe) (type 2)	H3C···Br1A	0.00	-0.005	0.003	-0.002	0.001
(**2**)·(tbe) (type 1)	H6B···Br1A	0.00	-0.007	0.004	-0.004	0.000
(**2**)·(tbe) (type 1)	H6B···Br2A	0.00	-0.005	0.003	-0.002	0.001
(**2**)·(tbe) (type 2)	H2A···Br2A	0.00	-0.005	0.003	-0.003	0.000
(**2**)·(tbe)(type 2)	H2B···Br1A	0.00	-0.005	0.003	-0.003	0.000

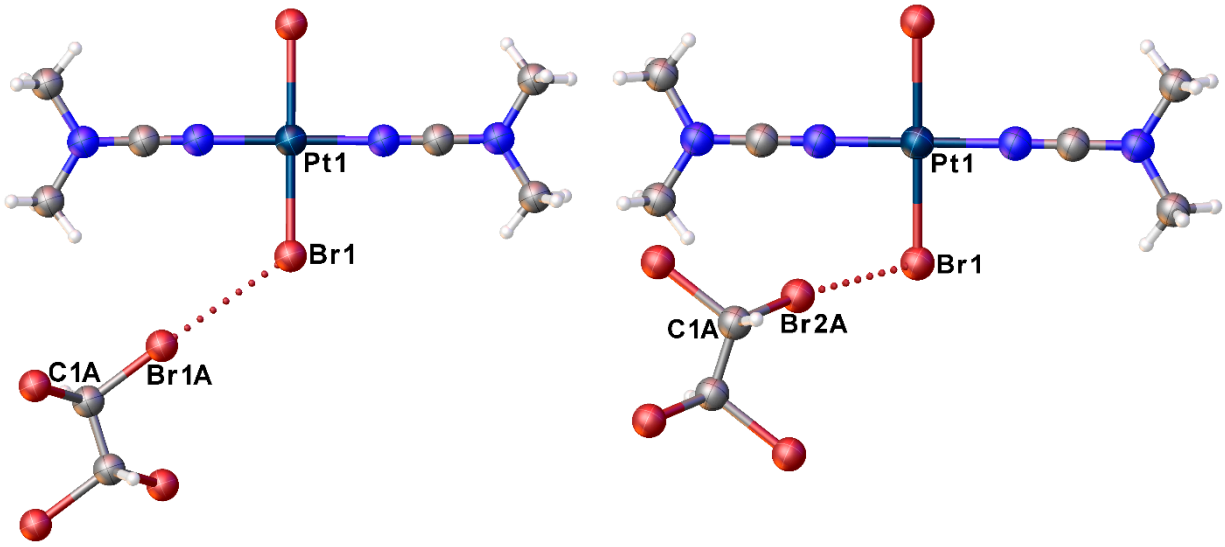

Figure S9. Structure of cluster **1**·**tbe** (halogen bonding)

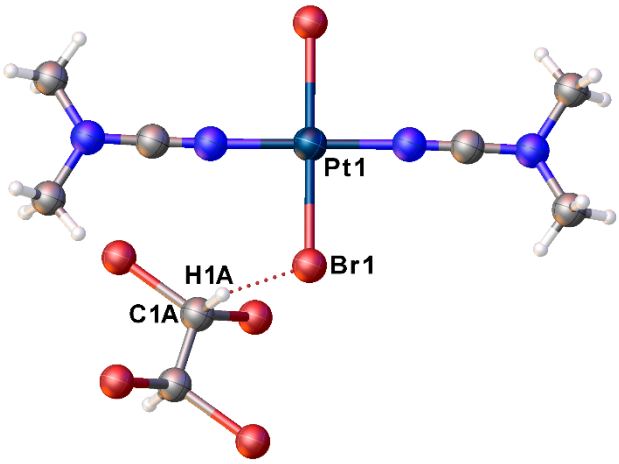

Figure S10. Structure of cluster **1**·**tbe** (hydrogen bonding)

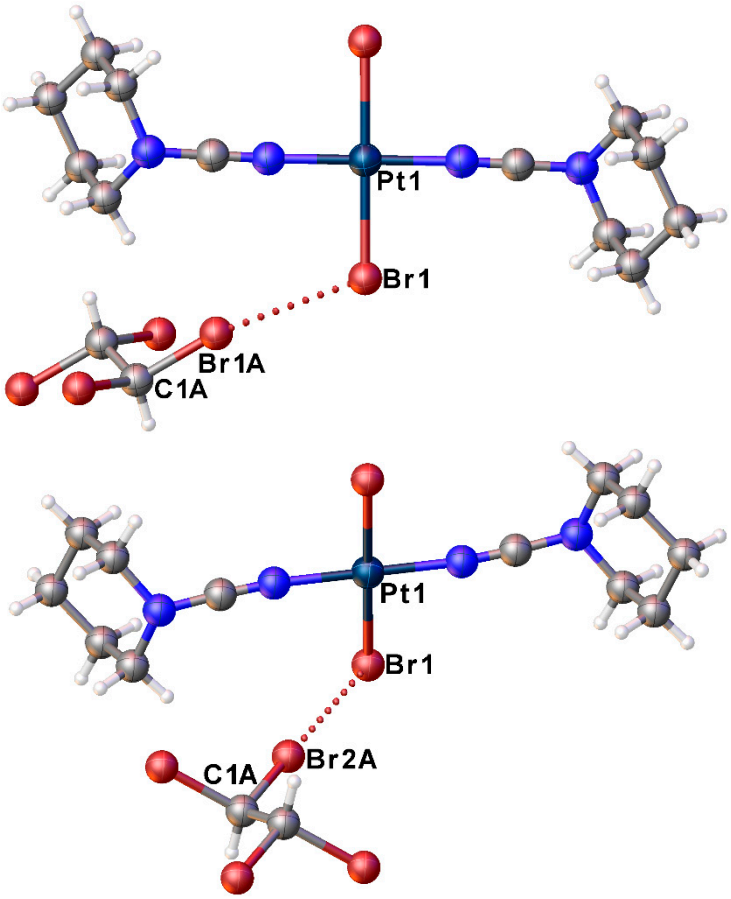

Figure S11. Structure of cluster **2**·**tbe** (halogen bonding)