Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Insertion of alkynes into Pt-X bonds of square planar [PtX$_2$(*N*^*N*)] (X = Cl, Br, I) complexes

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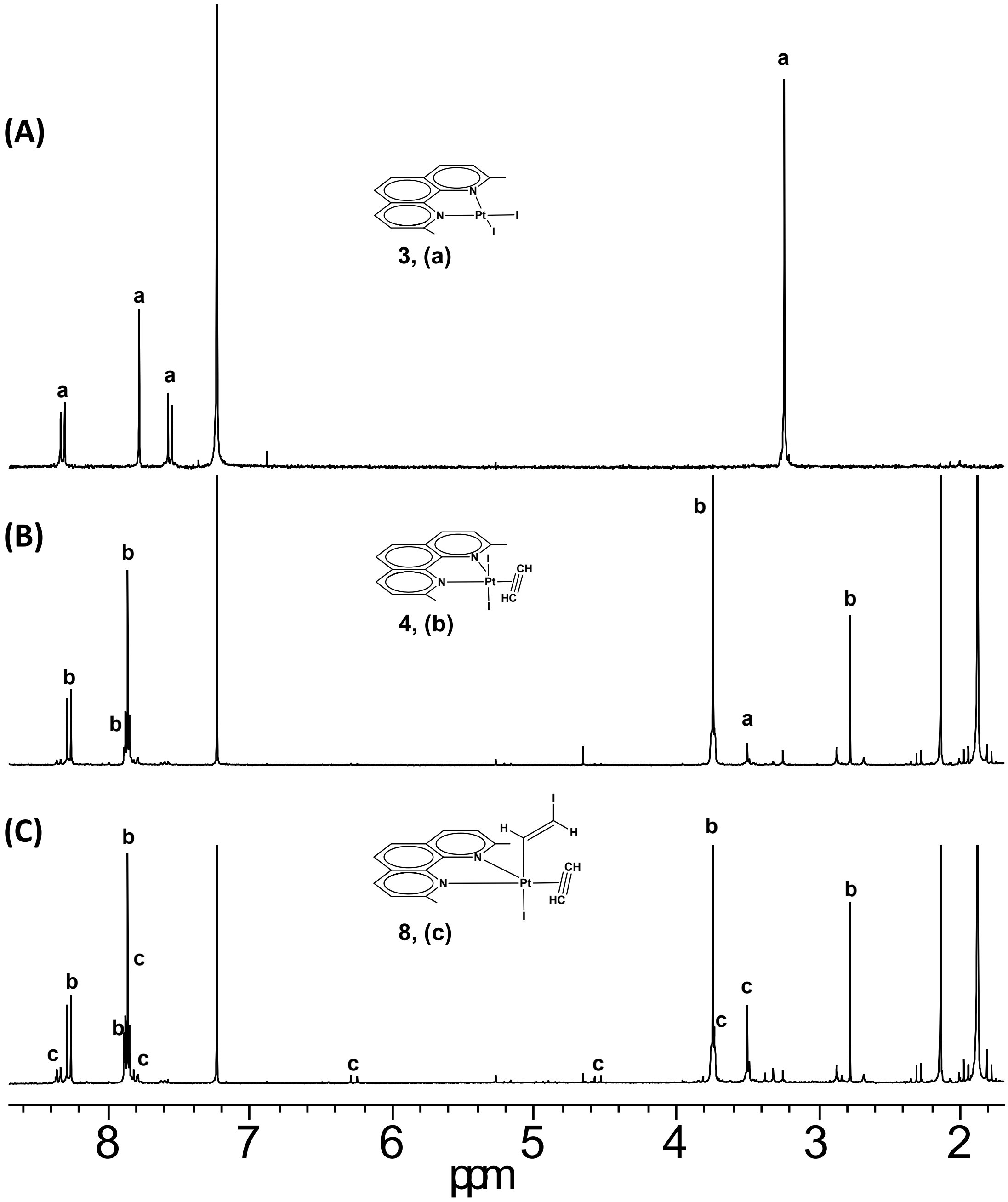

Figure 1S. (A) ^{1}H NMR spectrum ($CDCl_3$ solution) of complex $[PtI_2(Me_2phen)]$, **3**, signals (**a**). **(B)** Previous solution treated with excess acetylene and leading to formation of complex $[PtI_2(\eta^2\text{-}CH{\equiv}CH)(Me_2phen)]$ (**4**), signals (**b**). **(C)** Previous solution after 1.5 h showing formation of $[PtBr(\eta^1\text{-}E\text{-}CH{=}CHI)(\eta^2\text{-}CH{\equiv}CH)(Me_2phen)]$ (**8**), signals (**d**).

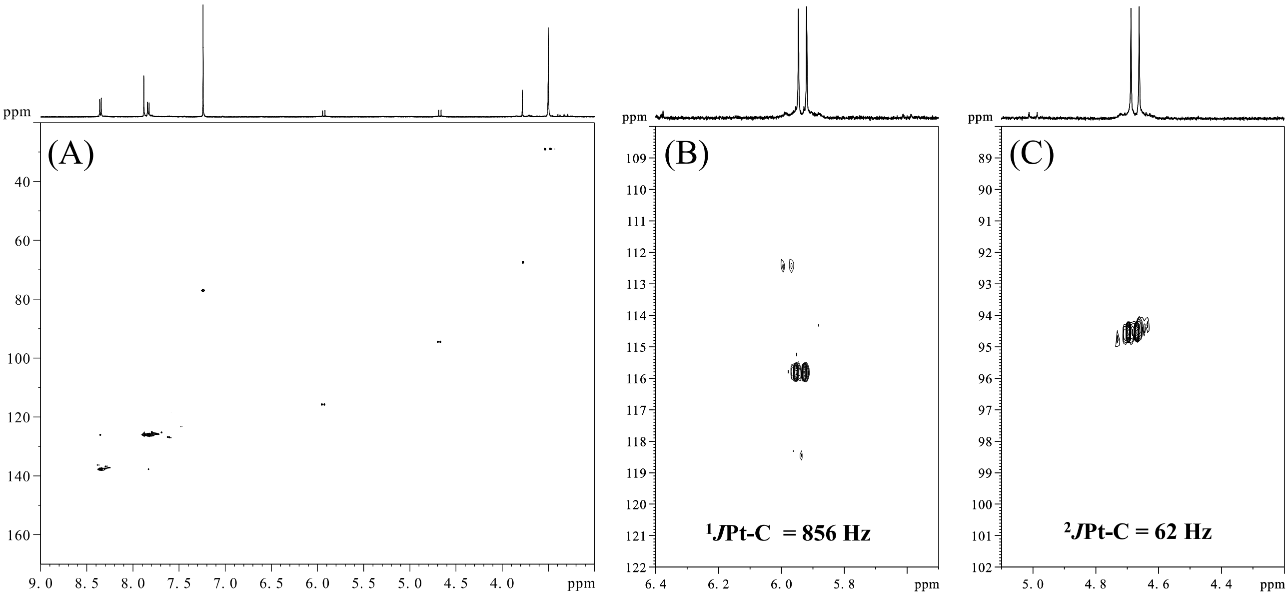

Figure 2S. 2D [^{1}H,^{13}C]-HETCOR NMR spectrum, in $CDCl_3$, of complex [PtBr(η^1-*E*-CH=CHBr)(η^2-CH≡CH)(Me_2phen)] (**6**), obtained by reacting [$PtBr_2(Me_2phen)$] (**2**), with a large excess of acetylene at room temperature **(A)**. Enlargement of the cross peaks formed in the vinylic region **(B-C)**.

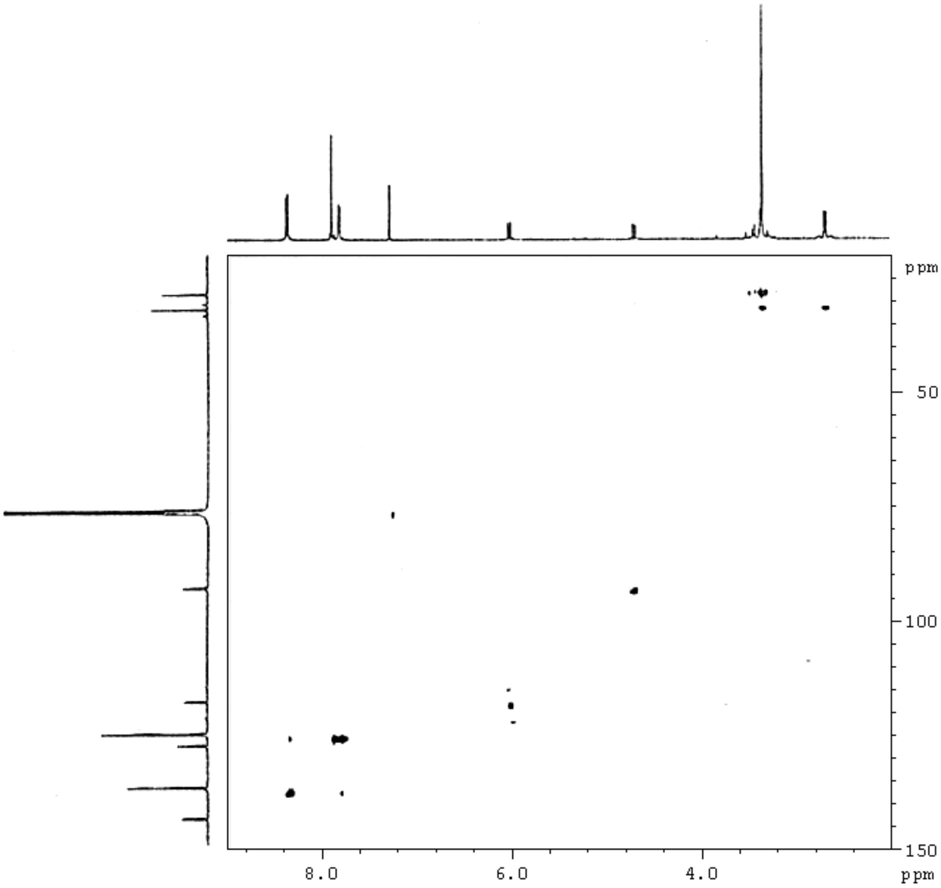

Figure 3S. 2D [^{1}H,^{13}C]-HSQC spectrum of complex [PtBr(η^1-*E*-CH=CHBr)(η^2-CH$_2$=CH$_2$)(Me$_2$phen)] (**7**).

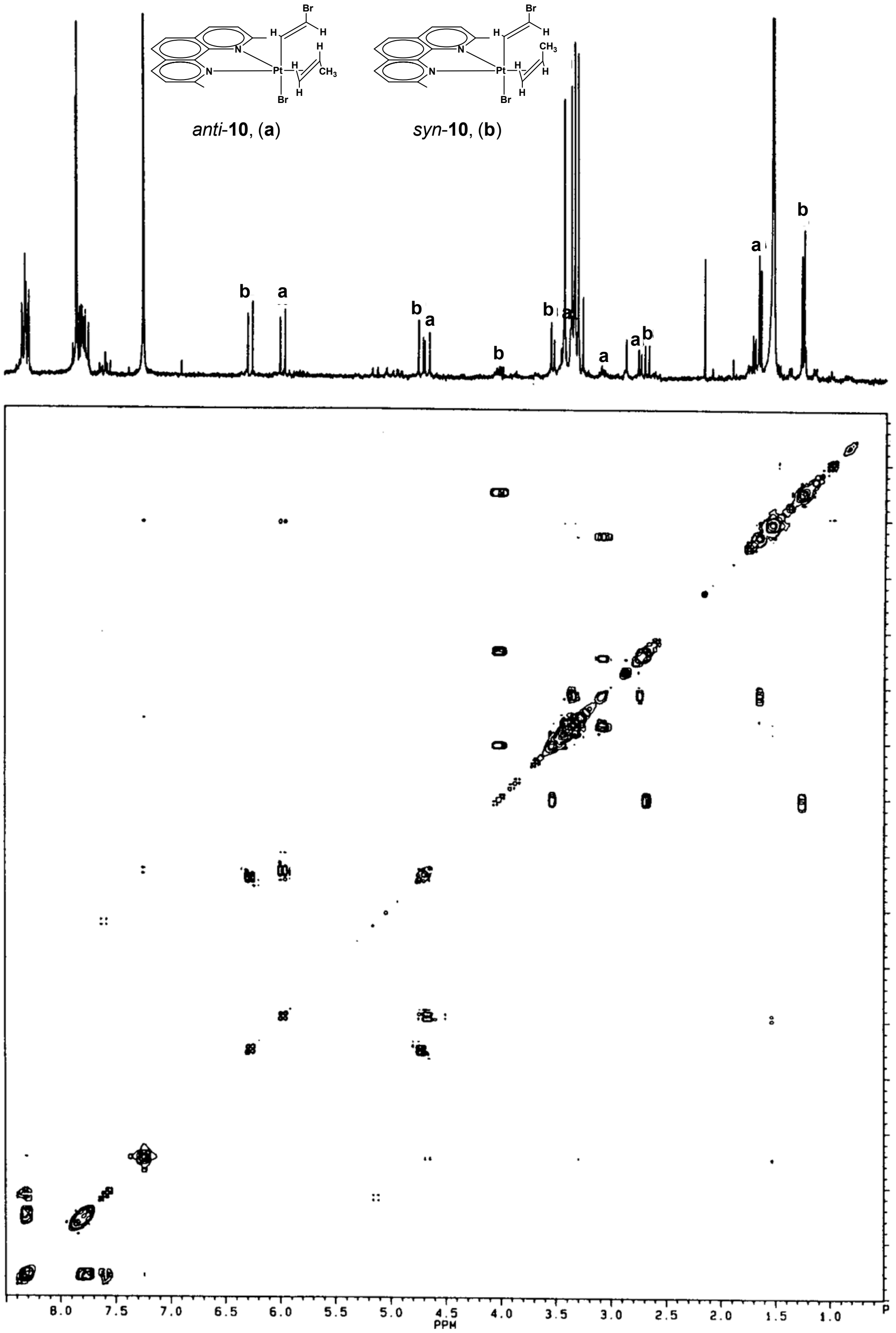

Figure 4S. 1D ^{1}H and 2D [^{1}H,^{1}H]-COSY NMR spectrum, in $CDCl_3$, of complex *syn* and *anti*-[PtBr(η^1-*E*-CH=CHBr)(η^2-propene)(Me_2phen)], *syn* and *anti*-**10**, obtained by reacting [PtBr(η^1-*E*-CH=CHBr)(η^2-CH≡CH)(Me_2phen)] (**6**), with a large excess of propene.

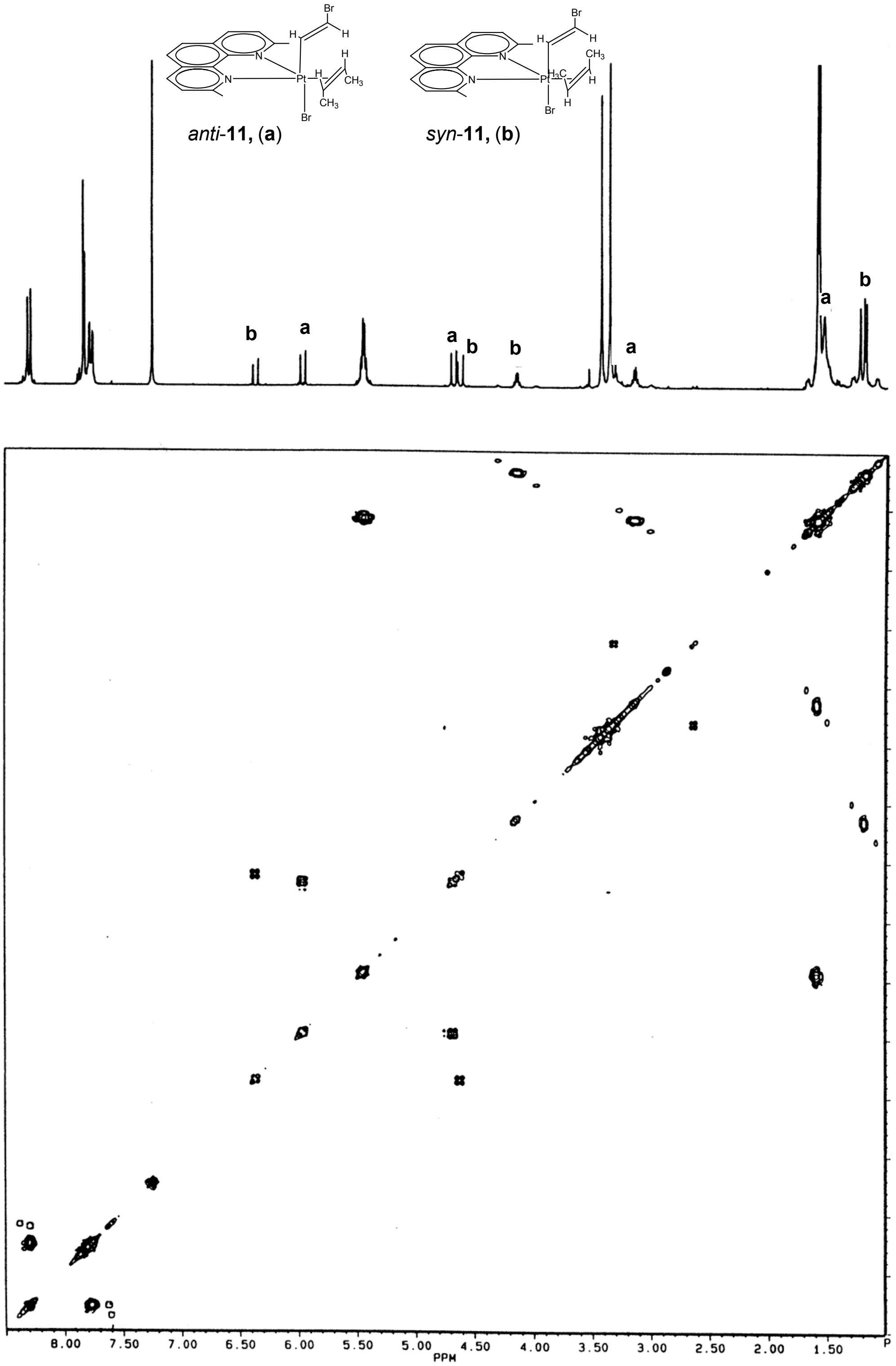

Figure 5S. 1D ^{1}H and 2D [^{1}H,^{1}H]-COSY NMR spectrum, in $CDCl_3$, of complex *syn* and *anti*-[PtBr(η^1-κ-*E*-CH=CHBr)(η^2-*cis*-2-butene)(Me_2phen)], *syn* and *anti*-**11**, obtained by reacting [PtBr(η^1-*E*-CH=CHBr)(η^2-CH≡CH)(Me_2phen)] (**6**), with a large excess *cis*-2-butene.

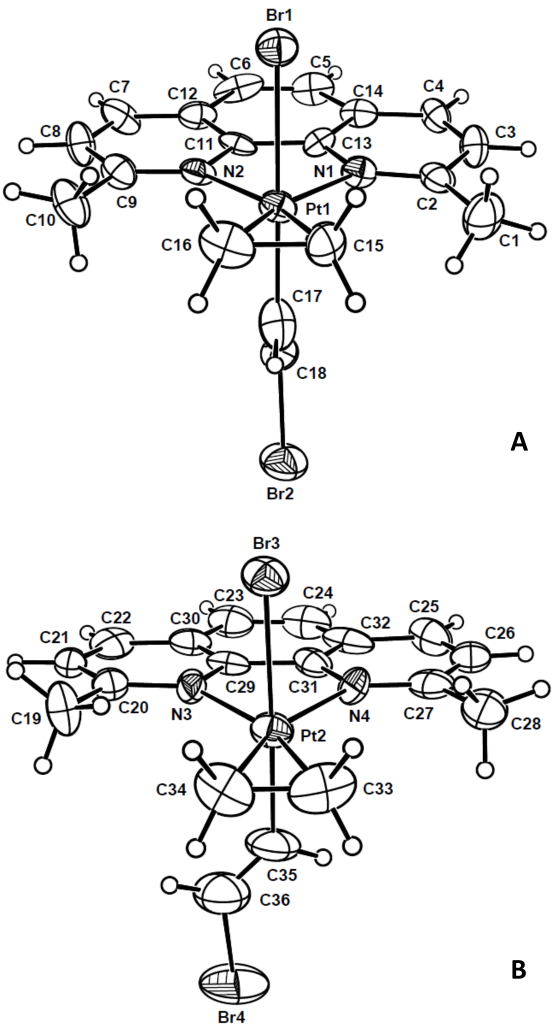

Figure 6S. Ortep drawing for the molecular structure and atomic numbering scheme for complex [PtBr(η^1-*E*-CH=CHBr)(η^2-CH_2=CH_2)(Me_2phen)] (**7**). Two non equivalent molecules (**A** and **B**) are present in the asymmetric unit. Thermal ellipsoids are drawn at 30% probability level.

Table 1S. Crystal Data and Structure Refinement parameters for [PtBr(Me_2phen)(η^1-*E*-CH=CHBr)(η^2-CH_2=CH_2)] (7). [40]

Empirical formula	$C_{18}H_{18}Br_2N_2Pt$
fw	617.25
temp/K	293(2)
wavelength/Å	0.71073
crystal system, space group	Monoclinic, *P2₁/n*
unit cell dimensions	
a/Å	12.288(5)
b/Å	21.385(5)
c/Å	15.250(5)
β	112.040(5)
V/Å^3	919.69(3)
Z	8
calcd density/Mg/m^3	2.207
abs coeff/mm^{-1}	11.858
F(000)	2304
crystal size/mm^3	0.250 x 0.200 x 02
θ range for data collcn/deg	2.03 to 27.58.
index ranges	0≤h≤15, 0≤k≤27, -19≤l≤18
reflections collected	8313
independent reflections	8313 [R(int) = 0.0255]
data/ restraints/params	8313 / 0 / 420
goodness-of-fit on F^2	0.894
final R indices [I>2sigma(I)]	R1 = 0.0685, wR2 = 0.1596

R indices (all data)	R1 = 0.1891, wR2 = 0.1564
largest diff. peak and hole	7.884 and -2.277 e.Å^{-3}

Table 2S. Selected Bond Lengths [Å] and Angles (deg) for [PtBr(Me_2phen)(η^1-*E*-CH=CHBr)(η^2-CH_2=CH_2)], **7**.

Pt1−N1	2.23(1)	N1−Pt1−Br1	87.8(3)
Pt1−N2	2.19(1)	C15−Pt1−C16	41.4(6)
Pt1−Br1	2.556(2)	C15−Pt1−N2	162.3(6)
Pt1−C15	2.06(2)	C16−Pt1−N2	121.0(7)
Pt1−C16	2.07(2)	C17−Pt1−N2	91.8(7)
Pt1−C17	1.98(2)	N2−Pt1−Br1	87.0(3)
Pt2−N3	2.19(1)	N3−Pt2−N4	75.0(5)
Pt2−N4	2.21(1)	N3−Pt2−C33	163.5(9)
Pt2−Br3	2.565(2)	N3−Pt2−C34	122.9(7)
Pt2−C33	2.08(2)	N3−Pt2−C35	88.6(7)
Pt2−C34	2.07(2)	N3−Pt2−Br3	89.1(4)
Pt2−C35	2.07(2)	C33−Pt2−C34	40.6(8)
N1−Pt1−N2	75.2(5)	C33−Pt2−N4	121.4(9)
N1−Pt1−C15	122.3(6)	C34−Pt2−N4	162.0(8)
N1−Pt1−C16	163.7(6)	C35−Pt2−N4	88.0(9)
N1−Pt1−C17	91.6(7)	N4−Pt2−Br3	91.7(4)

X-ray crystal structure determination

Red crystals of [PtBr(η^1-*E*-CH=CHBr)(η^2-CH_2=CH_2)(Me_2phen)] (**7**), were obtained from a chloroform/hexane solution. X-ray data were collected with a Siemens *P*3 automatic four circle diffractometer by using Mo-Ka radiation (λ = 0.71069 Å). A total of 8313 reflections were collected in the range $0 < h < 15$, $0 < k < 27$, $-19 < l < 18$; 3808 were the independent reflections. Three reflections were monitored during data collection after every 97 reflections. The full data set was corrected for Lorenz polarization effects. The absorption correction was performed via the ψ–scan technique. The structure was solved by using direct methods technique in the P 21/*n* space group. The model was refined by full-matrix least-square methods. Anisotropic thermal parameters were applied for all non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions and included in the full-matrix least-square cycles with isotropic thermal parameters (U) tied at the values of U of relative carbon or nitrogen atoms. All calculation and molecular graphics were carried out using SIR97, [44] SHELXL97, [45] PARST97, [46] and ORTEP-3 for Windows [47] packages.

References

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