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## General cooperative effects of single atom ligands on a metal: a $^{195}\text{Pt}$ NMR chemical shift as a function of coordinated halido ligands' ionic radii overall sum

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An inverse linear relationship between the experimentally observed  $^{195}\text{Pt}$  NMR signals and the overall sum of coordinated halido ligands' ionic radii was discovered in Pt(II) and Pt(IV) complexes. The reduction of  $^{195}\text{Pt}$  NMR frequencies parallels the increase of coordinated halido ligands' ionic radii sum. This suggests that each halido ligand may act as a conducting ring whose induced electric current shields the  $^{195}\text{Pt}$  NMR signals proportionally to the ionic radius of the coordinated halido ligand.

In previous studies we analyzed the NMR properties of penta-coordinate complexes, formed by the interaction of Zeise's anion,  $[\text{PtCl}_3(\eta^2\text{-CH}_2=\text{CH}_2)]^-$ , with *N,N*-chelate ligands.<sup>1–14</sup> These specific complexes are generally considered to be interesting since platinum bonded unsaturated ligands are useful models in the study of the interaction of alkenes and alkynes with metals.<sup>14–22</sup> In particular, in the study of the single crystal X-ray structures and NMR signals of the symmetric penta-coordinate complexes  $[\text{PtX}_2(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  ( $\text{X} = \text{Cl}$ ,

$\text{Br}$ ,  $\text{I}$ ;  $\text{Me}_2\text{phen} = 2,9$ -dimethyl-1,10-phenanthroline), we described the evidence of pseudo-ring currents circulating around the Pt–X axes, Fig. 1 and 2. These currents seemed to be modulated by the ionic radii of the halido ligands coordinated at *trans* positions, above and below the trigonal equatorial plane. Indeed, in these complexes, characterized by negligible Pt– $\eta^2$ -ethene and Pt–N bond length variations in the trigonal plane, the two *trans*-axial halido ligands clearly influence the observed  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{195}\text{Pt}$  NMR chemical shifts of neighbour atoms.<sup>20</sup> Platinum chemical shift correlations with other parameters such as coordinated halido ligands electronegativity were previously reported.<sup>23,24</sup> Nevertheless recently we could evidence the existence of a linear relationship between the ionic radii of coordinated halido ligands and the  $^{195}\text{Pt}$  NMR chemical shifts.<sup>20</sup>

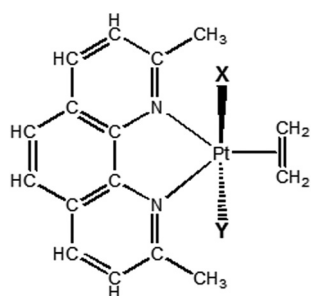


Fig. 1 Schematic representation of the structure of penta-coordinate complexes of the type  $[\text{PtXY}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$ , ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{Me}_2\text{phen} = 2,9$ -dimethyl-1,10-phenanthroline).

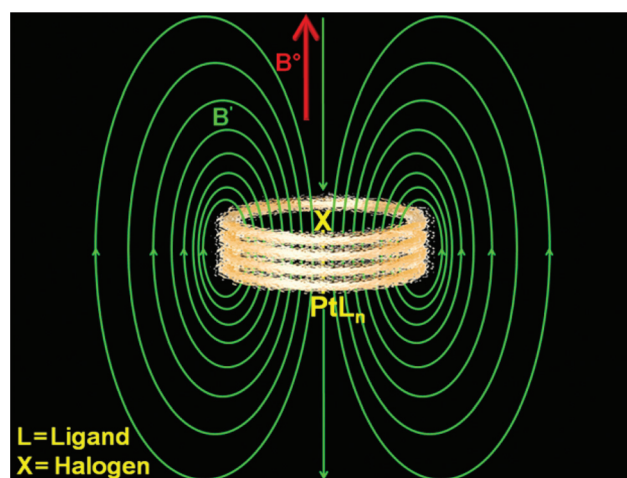


Fig. 2 Schematic representation of hypothesized pseudoring currents induced by an applied external magnetic field ( $B^0$ ) on a platinum coordinated  $\text{X}^-$  halido ligand, explaining the reduction of  $^{195}\text{Pt}$  NMR frequency, observed in platinum complexes, which parallels the increase of ionic radius of a coordinated halido ligand.

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The problem of understanding the phenomena influencing the NMR signal frequencies, which can also be related to the physical properties of a molecule, has deserved particular attention in the recent literature.<sup>23–28</sup> In this work, we evaluated the NMR shielding properties of coordinated halido ligands in trigonal-bipyramidal Pt(II) and octahedral Pt(IV) complexes (Fig. 1 and 3). <sup>195</sup>Pt NMR data for pentacoordinate Pt(II) complexes of the type [PtXY(η<sup>2</sup>-CH<sub>2</sub>=CH<sub>2</sub>)(Me<sub>2</sub>phen)] (X≠Y = Cl, Br, I), where two non-equivalent axial halido ligands are bonded to the metal (Fig. 1), have been collected

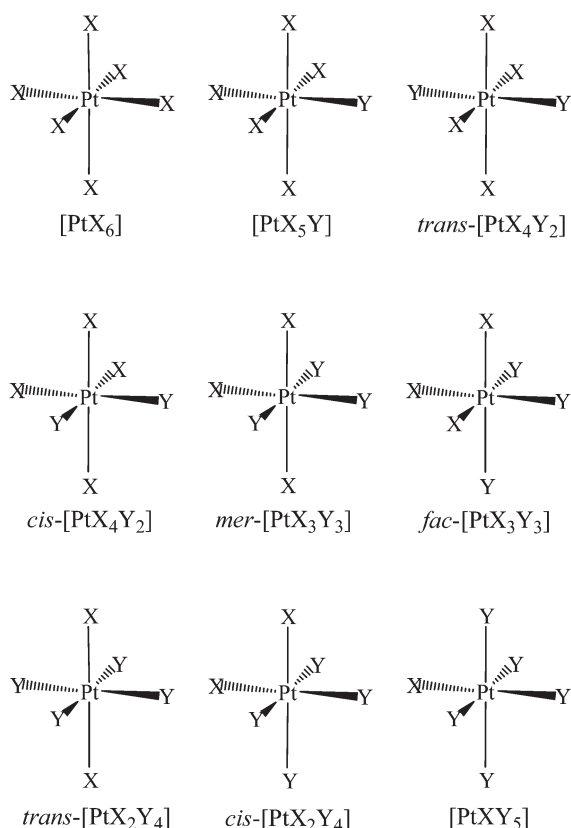


Fig. 3 Representation of the general structures of octahedral complexes [PtX<sub>n</sub>Y<sub>6-n</sub>]<sup>2-</sup> (1 ≤ n ≤ 6; X, Y = F, Cl, Br, I).

Table 1 Experimental <sup>195</sup>Pt NMR chemical shifts of pentacoordinate platinum(II) complexes of the type [PtXY(Me<sub>2</sub>phen)(η<sup>2</sup>-ethene)] (X, Y = Cl, Br, I)

Complex	<sup>195</sup> Pt δ (ppm)	Ref.
[PtCl <sub>2</sub> (η <sup>2</sup> -CH <sub>2</sub> =CH <sub>2</sub> )(Me <sub>2</sub> phen)]	-2169	20
[PtBrCl(η <sup>2</sup> -CH <sub>2</sub> =CH <sub>2</sub> )(Me <sub>2</sub> phen)]	-2456	<sup>a</sup>
[PtBr <sub>2</sub> (η <sup>2</sup> -CH <sub>2</sub> =CH <sub>2</sub> )(Me <sub>2</sub> phen)]	-2886	20
[PtClI(η <sup>2</sup> -CH <sub>2</sub> =CH <sub>2</sub> )(Me <sub>2</sub> phen)]	-3087	<sup>a</sup>
[PtBrI(η <sup>2</sup> -CH <sub>2</sub> =CH <sub>2</sub> )(Me <sub>2</sub> phen)]	-3426	<sup>a</sup>
[PtI <sub>2</sub> (η <sup>2</sup> -CH <sub>2</sub> =CH <sub>2</sub> )(Me <sub>2</sub> phen)]	-4041	20

<sup>a</sup> This work.

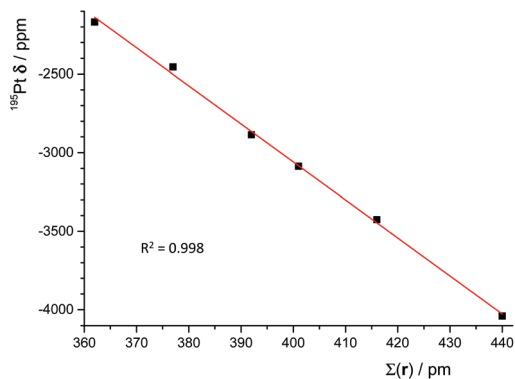
together with those of the previously reported symmetrical analogues (X = Y = Cl, Br, I), Table 1.<sup>20</sup> In a further step, octahedral Pt(IV) complexes of the type [PtX<sub>n</sub>Y<sub>6-n</sub>]<sup>2-</sup> (1 ≤ n ≤ 6; X, Y = F, Cl, Br, I) were also studied by <sup>195</sup>Pt NMR spectroscopy, in order to analyse the effect of changing the oxidation state and the coordination number and geometry of the metal which also includes *cis*, *trans*, *fac* and *mer* isomers, Table 2.

The general structure of the considered pentacoordinate complexes is reported in Fig. 1. The <sup>195</sup>Pt NMR chemical shifts of these pentacoordinate species are reported in Table 1. A clear inverse linear relationship between <sup>195</sup>Pt NMR frequencies and the overall sum of coordinated halido ligands' ionic radii ( $R^2 = 0.998$ ) can be observed in the plot of <sup>195</sup>Pt NMR data (Table 1) as a function of coordinated halido ligands' ionic radii sum (Fig. 4). This means that in [PtXY(η<sup>2</sup>-

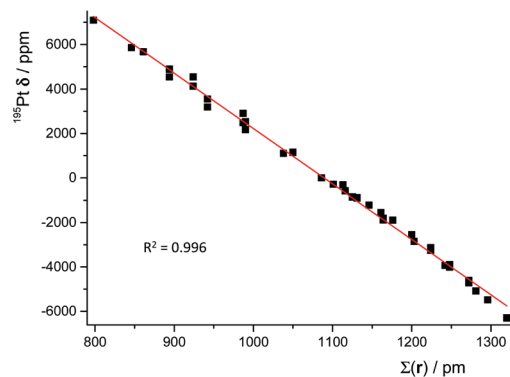
Table 2 Experimental <sup>195</sup>Pt NMR chemical shifts of octahedral platinum(IV) complexes of the type [PtX<sub>n</sub>Y<sub>6-n</sub>]<sup>2-</sup> (1 ≤ n ≤ 6; X, Y = F, Cl, Br, I)

Complex	<sup>195</sup> Pt δ (ppm)	Ref.
[PtF <sub>6</sub> ] <sup>2-</sup>	7090	25
[PtClF <sub>5</sub> ] <sup>2-</sup>	5856	25
[PtBrF <sub>5</sub> ] <sup>2-</sup>	5669	25
<i>trans</i> -[PtCl <sub>2</sub> F <sub>4</sub> ] <sup>2-</sup>	4887	25
<i>trans</i> -[PtBr <sub>2</sub> F <sub>4</sub> ] <sup>2-</sup>	4551	25
<i>cis</i> -[PtCl <sub>2</sub> F <sub>4</sub> ] <sup>2-</sup>	4547	25
<i>cis</i> -[PtBr <sub>2</sub> F <sub>4</sub> ] <sup>2-</sup>	4136	25
<i>mer</i> -[PtCl <sub>3</sub> F <sub>3</sub> ] <sup>2-</sup>	3551	25
<i>fac</i> -[PtCl <sub>3</sub> F <sub>3</sub> ] <sup>2-</sup>	3191	25
<i>mer</i> -[PtBr <sub>3</sub> F <sub>3</sub> ] <sup>2-</sup>	2907	25
<i>trans</i> -[PtCl <sub>4</sub> F <sub>2</sub> ] <sup>2-</sup>	2534	25
<i>fac</i> -[PtBr <sub>3</sub> F <sub>3</sub> ] <sup>2-</sup>	2487	25
<i>cis</i> -[PtCl <sub>4</sub> F <sub>2</sub> ] <sup>2-</sup>	2171	25
<i>trans</i> -[PtBr <sub>4</sub> F <sub>2</sub> ] <sup>2-</sup>	1157	25
<i>cis</i> -[PtBr <sub>4</sub> F <sub>2</sub> ] <sup>2-</sup>	1142	25
[PtCl <sub>5</sub> F] <sup>2-</sup>	1111	25
[PtCl <sub>6</sub> ] <sup>2-</sup>	0	23
[PtCl <sub>5</sub> Br] <sup>2-</sup>	-286	23
[PtBr <sub>5</sub> F] <sup>2-</sup>	-311	25
<i>cis</i> -[PtCl <sub>4</sub> Br <sub>2</sub> ] <sup>2-</sup>	-583	23
<i>trans</i> -[PtCl <sub>4</sub> Br <sub>2</sub> ] <sup>2-</sup>	-585	23
[PtCl <sub>5</sub> I] <sup>2-</sup>	-854	23
<i>fac</i> -[PtCl <sub>3</sub> Br <sub>3</sub> ] <sup>2-</sup>	-892	23
<i>mer</i> -[PtCl <sub>3</sub> Br <sub>3</sub> ] <sup>2-</sup>	-894	23
<i>cis</i> -[PtCl <sub>2</sub> Br <sub>4</sub> ] <sup>2-</sup>	-1213	23
<i>trans</i> -[PtCl <sub>2</sub> Br <sub>4</sub> ] <sup>2-</sup>	-1216	23
[PtClBr <sub>5</sub> ] <sup>2-</sup>	-1547	23
<i>cis</i> -[PtCl <sub>4</sub> I <sub>2</sub> ] <sup>2-</sup>	-1806	23
<i>trans</i> -[PtCl <sub>4</sub> I <sub>2</sub> ] <sup>2-</sup>	-1884	23
[PtBr <sub>6</sub> ] <sup>2-</sup>	-1891	23
[PtBr <sub>5</sub> I] <sup>2-</sup>	-2545	23
<i>fac</i> -[PtCl <sub>3</sub> I <sub>3</sub> ] <sup>2-</sup>	-2849	23
<i>mer</i> -[PtCl <sub>3</sub> I <sub>3</sub> ] <sup>2-</sup>	-2849	23
<i>trans</i> -[PtBr <sub>4</sub> I <sub>2</sub> ] <sup>2-</sup>	-3132	23
<i>cis</i> -[PtBr <sub>4</sub> I <sub>2</sub> ] <sup>2-</sup>	-3252	23
<i>mer</i> -[PtBr <sub>3</sub> I <sub>3</sub> ] <sup>2-</sup>	-3898	23
<i>cis</i> -[PtCl <sub>2</sub> I <sub>4</sub> ] <sup>2-</sup>	-3932	23
<i>trans</i> -[PtCl <sub>2</sub> I <sub>4</sub> ] <sup>2-</sup>	-3932	23
<i>fac</i> -[PtBr <sub>3</sub> I <sub>3</sub> ] <sup>2-</sup>	-4014	23
<i>trans</i> -[PtBr <sub>2</sub> I <sub>4</sub> ] <sup>2-</sup>	-4603	23
<i>cis</i> -[PtBr <sub>2</sub> I <sub>4</sub> ] <sup>2-</sup>	-4719	23
[PtClI <sub>5</sub> ] <sup>2-</sup>	-5081	23
[PtBrI <sub>5</sub> ] <sup>2-</sup>	-5483	23
[PtI <sub>6</sub> ] <sup>2-</sup>	-6293	23





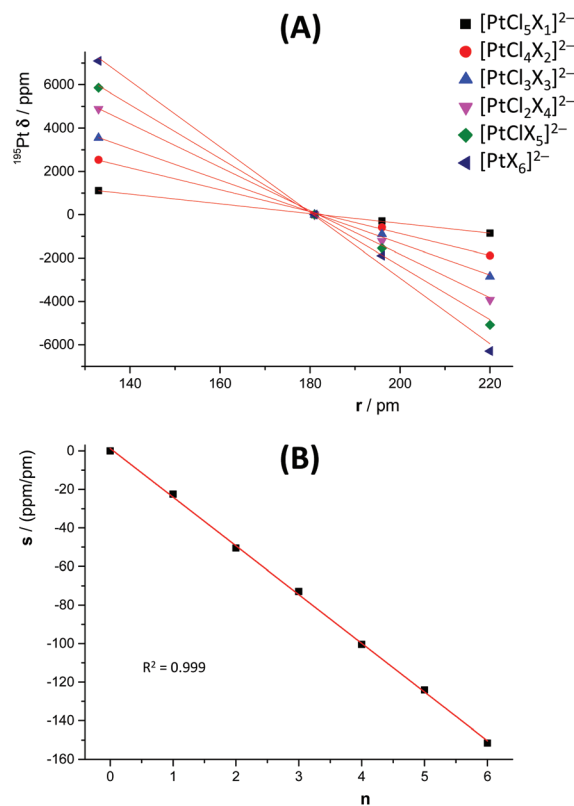
**Fig. 4**  $^{195}\text{Pt}$  NMR chemical shifts ( $\delta$ ) of pentacoordinate complexes  $[\text{PtXY}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  ( $\text{Me}_2\text{phen}$  = 2,9-dimethyl-1,10-phenanthroline;  $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$ ), as a function of the sum of coordinated halido ligands' ionic radii,  $\Sigma(r)$ . The interpolating line is also shown in red.



**Fig. 5**  $^{195}\text{Pt}$  NMR chemical shifts ( $\delta$ ) of octahedral complexes  $[\text{PtX}_n\text{Y}_{6-n}]^{2-}$  ( $1 \leq n \leq 6$ ;  $\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), as a function of the sum of coordinated halido ligands' ionic radii,  $\Sigma(r)$ . The interpolating line is also shown in red.

$\text{CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  complexes the shielding produced by each halido ligand on the observed  $^{195}\text{Pt}$  NMR signal frequency, depends in first approximation only on its ionic radius, as previously stated for the symmetric species  $[\text{PtX}_2(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$ .<sup>20</sup> On the other hand, it appears that the  $^{195}\text{Pt}$  NMR shielding is not directly related to the mutual *trans* influence of the axial  $\text{X}^-$  ligands, potentially able to affect the Pt-X(Y) bond lengths in  $[\text{PtXY}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  complexes.

The correlation of  $^{195}\text{Pt}$  NMR frequencies, with the overall sum of coordinated halido ligands' ionic radii, also in platinum complexes with a different oxidation state, coordination number and geometry was therefore investigated. We studied with a similar approach the  $^{195}\text{Pt}$  NMR frequency variation observed in octahedral Pt(IV) complexes of the type  $[\text{PtX}_n\text{Y}_{6-n}]^{2-}$  ( $1 \leq n \leq 6$ ;  $\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), Fig. 3. The  $^{195}\text{Pt}$  NMR signals of the investigated Pt(IV) model complexes are reported in Table 2. Also for octahedral Pt(IV) complexes  $[\text{PtX}_n\text{Y}_{6-n}]^{2-}$  a clear inverse linear relationship between  $^{195}\text{Pt}$  NMR frequencies and the overall sum of coordinated halido ligands' ionic radii was found. This is evident in the linear plot ( $R^2 = 0.996$ ) of  $^{195}\text{Pt}$  NMR data, as a function of coordinated halido ligands' ionic radii sum, reported in Fig. 5. The pure additional effect of halido ligands' ionic radii on  $^{195}\text{Pt}$  NMR frequencies, in the studied Pt(IV) species, is further evidenced in Fig. 6, where the  $^{195}\text{Pt}$  chemical shifts are reported as a function of the  $\text{X}^-$  halido ligand ionic radius, for six different groups of complexes of the type  $[\text{PtCl}_n\text{X}_{6-n}]^{2-}$ . In each group, the platinum complexes bear a specific number ( $n$ ;  $0 \leq n \leq 5$ ) of chlorido ligands and a variable  $\text{X}^-$  halido ligand for the remaining  $6 - n$  coordination sites. Six different lines interpolating the  $^{195}\text{Pt}$  NMR chemical shifts, as a function of the remaining specific  $\text{X}^-$  ionic radius, in  $[\text{PtCl}_n\text{X}_{6-n}]^{2-}$  complexes, are reported in Fig. 6A. Interestingly, each unit increase of the chlorido ligand number ( $n$ ), which results in a nearly constant increase of the slope of the specific interpolating line. The linear relationship between the slopes of the six



**Fig. 6** (A)  $^{195}\text{Pt}$  NMR chemical shifts ( $\delta$ ) of octahedral complexes  $[\text{PtX}_n\text{Y}_{6-n}]^{2-}$  ( $0 \leq n \leq 5$ ;  $\text{X}, \text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), as a function of the variable ionic radius of the coordinated  $\text{X}^-$  halido ligands,  $r$ . (B) Slopes ( $s$ ) of the interpolating lines reported in (A), represented as a function of the number of variable  $\text{X}^-$  halido ligands,  $n$ . In (A) and (B) the interpolating lines are also shown in red.

lines in Fig. 6A and the chlorido ligand number ( $n$ ) ( $R^2 = 0.999$ ) is reported in Fig. 6B. It is also noteworthy that all the six interpolating lines of Fig. 6A pass exactly through the data



point representing in the graph the  $^{195}\text{Pt}$  NMR chemical shift of the  $[\text{PtCl}_6]^{2-}$  complex, the only one that belongs to all the six groups of model complexes. These results further confirm the regular trend of the observed correlation. Consistently, similar trends are observed in the analogue  $[\text{PtF}_n\text{X}_{6-n}]^{2-}$ ,  $[\text{PtBr}_n\text{X}_{6-n}]^{2-}$  and  $[\text{PtI}_n\text{X}_{6-n}]^{2-}$  series of complexes.

Our hypothesis on the  $^{195}\text{Pt}$  NMR chemical shift linear dependence from the overall halido ligands' ionic radius sum therefore holds not only for Pt(II) trigonal-bipyramidal  $[\text{PtXY}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  but also for octahedral Pt(IV)  $[\text{PtX}_n\text{Y}_{6-n}]^{2-}$  (X, Y = halido ligand) complexes. As a further confirmation of the simple additional effect of the overall halido ligands' ionic radius sum, only slight variations of the  $^{195}\text{Pt}$  NMR frequency are observed here on passing from *cis* to *trans* and from *fac* to *mer* geometric isomers. Therefore, at least for the studied model complexes, it is also possible, based on the  $^{195}\text{Pt}$  NMR data for some complexes within a series, to easily predict the  $^{195}\text{Pt}$  NMR shifts for analogous complexes bearing a different combination of coordinated halido ligands.

## Experimental

All solvents and reagents, except otherwise stated, were purchased from Aldrich Chemical Company and used as received. The symmetric pentacoordinate complexes  $[\text{PtX}_2(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  (X = Cl, Br, I) were prepared with the previously reported methods.<sup>29</sup> These complexes  $[\text{PtXY}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  (X ≠ Y = Cl, Br, I) were obtained in equilibrium mixtures with symmetric species  $[\text{PtX}_2(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  (X = Cl, Br, I), following the previously reported procedures.<sup>29</sup> Alternatively, similar mixtures of complexes could be also obtained by direct reaction of symmetric  $[\text{PtX}_2(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  (X = Cl, Br) derivatives with KBr or KI. The asymmetric  $[\text{PtXY}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$  species, with mixed halido ligands, could be identified by  $^1\text{H}$  and  $^{195}\text{Pt}$  NMR spectroscopy. NMR ( $\text{CDCl}_3$ , 600 MHz ( $^1\text{H}$ ), 130 MHz ( $^{195}\text{Pt}$ ), 300 K):  $[\text{PtClBr}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$ .  $\delta(^1\text{H})$  3.48 (s, 6H,  $\text{CH}_3$ ); 3.68 (m, 2H, CH,  $\eta^2$ -ethene,  $^2J_{\text{Pt-H}} = 70$  Hz); 3.78 (m, 2H, CH,  $\eta^2$ -ethene,  $^2J_{\text{Pt-H}} = 70$  Hz); 7.79 (d, 2H, CH,  $^3J_{\text{H-H}} = 8$  Hz); 7.85 ppm (s, 2H, CH); 8.31 (d, 2H, CH,  $^3J_{\text{H-H}} = 8$  Hz).  $\delta(^{195}\text{Pt})$  -2456 ppm.  $[\text{PtClI}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$ .  $\delta(^1\text{H})$  3.47 (s, 6H,  $\text{CH}_3$ ); 3.68 (m, 2H, CH,  $\eta^2$ -ethene,  $^2J_{\text{Pt-H}} = 70$  Hz); 3.90 (m, 2H, CH,  $\eta^2$ -ethene,  $^2J_{\text{Pt-H}} = 70$  Hz); 7.79 (d, 2H, CH,  $^3J_{\text{H-H}} = 8$  Hz); 7.85 ppm (s, 2H, CH); 8.29 (d, 2H, CH,  $^3J_{\text{H-H}} = 8$  Hz).  $\delta(^{195}\text{Pt})$  -3087 ppm.  $[\text{PtBrI}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{Me}_2\text{phen})]$ .  $\delta(^1\text{H})$  3.46 (s, 6H,  $\text{CH}_3$ ); 3.68 (m, 2H, CH,  $\eta^2$ -ethene,  $^2J_{\text{Pt-H}} = 70$  Hz); 3.90 (m, 2H, CH,  $\eta^2$ -ethene,  $^2J_{\text{Pt-H}} = 70$  Hz); 7.79 (d, 2H, CH,  $^3J_{\text{H-H}} = 8$  Hz); 7.85 ppm (s, 2H, CH); 8.27 (d, 2H, CH,  $^3J_{\text{H-H}} = 8$  Hz).  $\delta(^{195}\text{Pt})$  -3426 ppm.

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