Electronic Supplementary Information

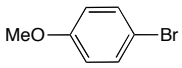
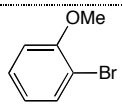
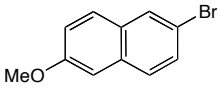
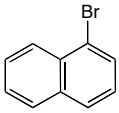
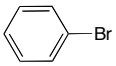
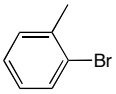
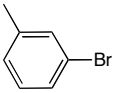
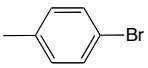
Resorcin[4]arene-derived mono-, bis- and tetra-imidazolium salts as ligand precursors for Suzuki-Miyaura cross-coupling

Hani El Moll,[a] David Sémeril,*[a] Dominique Matt,*[a] Loïc Toupet,[b] and Jean-Jacques Harrowfield[c]

[a]*Laboratoire de Chimie Inorganique et Catalyse, Institut de Chimie UMR 7177 CNRS, Université de Strasbourg, 67008 Strasbourg Cedex (France)*
E-mail: dsemeril@unistra.fr; dmatt@unistra.fr
[b]*Institut de Physique de Rennes, UMR 6251, Université de Rennes 1, Campus de Beaulieu, 35042, Rennes cedex, France*
[c] *Université de Strasbourg, ISIS, UMR 7006 CNRS, Université de Strasbourg, 8 allée Gaspard Monge, BP 70028, F-67083, Strasbourg cedex, France*

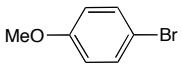
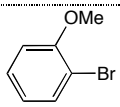
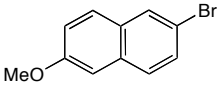
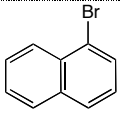
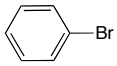
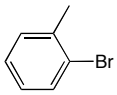
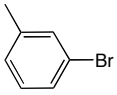
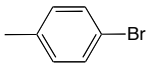
Contents

Table S-1. Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid using $[Pd(OAc)_2]$ and a mono-imidazolium salt.[a]

Entry	ArBr		Mono-imidazolium salt		
			2	**3**	**4**
1		conv. (%)	5.7	10.5	13.4
		PhPh:ArPh (%)	6.3	7.0	0.5
2		conv. (%)	7.9	12.4	14.8
		PhPh:ArPh (%)	5.4	7.6	4.4
3		conv. (%)	50.2	38.1	51.7
		PhPh:ArPh (%)	0.9	1.8	1.3
4		conv. (%)	39.1	45.3	53.4
		PhPh:ArPh (%)	3.2	2.3	1.0
5		conv. (%)	6.5	13.0	9.1
		PhPh:ArPh (%)	2.8	3.7	2.2
6		conv. (%)	10.6	8.2	5.2
		PhPh:ArPh (%)	3.1	6.2	0.2
7		conv. (%)	4.4	7.0	4.8
		PhPh:ArPh (%)	4.6	4.9	0.9
8		conv. (%)	7.5	7.9	11.2
		PhPh:ArPh (%)	3.7	4.1	1.1

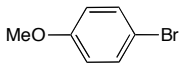
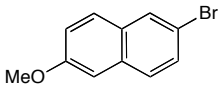
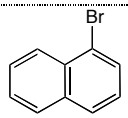
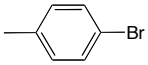
[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol %), mono-imidazolium salt (1×10^{-4} mmol, 2 equiv. / Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

Table S-2. Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid using $[Pd(OAc)_2]$ and a mono-imidazolium salt – increasing the palladium loading or the reaction time.[a]

Entry	ArBr	Imidazolium salt	$[Pd(OAc)_2]$ (mol %)	Time (h)	Conversion (%)	PhPh:ArPh (%)
1		**4**	0.1	2	92.8	1.1
2			0.01	16	94.9	0.8
3		**4**	0.1	2	89.3	4.8
4			0.01	16	95.7	5.2
5		**4**	0.1	1	98.6	2.2
6			0.01	3	98.5	1.7
7		**4**	0.1	1	99.1	3.1
8			0.01	3	97.6	2.4
9		**3**	0.1	2	93.7	2.7
10			0.01	16	94.8	3.3
11		**2**	0.1	2	87.9	0.6
12			0.01	16	91.6	1.1
13		**3**	0.1	2	81,6	2.1
14			0.01	16	76.7	1.8
15		**4**	0.1	2	90.3	0.9
16			0.01	16	89.1	1.6

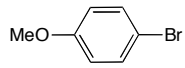
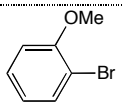
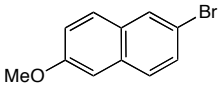
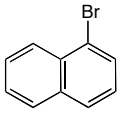
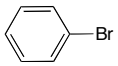
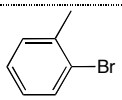
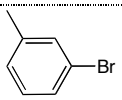
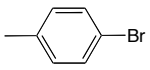
[a] Conditions: $[Pd(OAc)_2]$, mono-imidazolium salt (2 equiv. / Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

Table S-3. Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid using $[Pd(OAc)_2]$ and mono-imidazolium salts **3** and **16**.[a]

Entry	ArBr		Mono-imidazolium salt	
			3	**16**
1		conv. (%)	10.5	13.6
		PhPh:ArPh (%)	7.0	5.0
2		conv. (%)	38.1	48.5
		PhPh:ArPh (%)	1.8	3.2
3		conv. (%)	45.3	51.6
		PhPh:ArPh (%)	2.3	3.2
4		conv. (%)	7.9	10.1
		PhPh:ArPh (%)	4.1	6.8

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol %), mono-imidazolium salt (1×10^{-4} mmol, 2 equiv. / Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

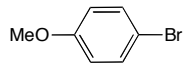
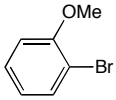
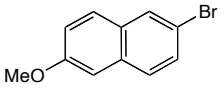
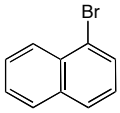
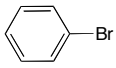
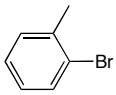
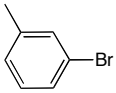
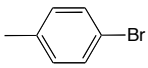
Table S-4. Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid using $[Pd(OAc)_2]$ and a bis-imidazolium salt.[a]

Entry	ArBr		Bis-imidazolium salt 6	7	8	9
1		conv. (%)	14.7	10.9	12.5	11.6
		PhPh:ArPh (%)	2.3	7.3	3.6	5.0
2		conv. (%)	4.2	12.0	17.5	13.5
		PhPh:ArPh (%)	6.4	6.8	4.8	2.7
3		conv. (%)	76.9	51.5	61.1	40.5
		PhPh:ArPh (%)	4.0	3.2	1.8	2.8
4		conv. (%)	52.4	91.3	96.6	41.9
		PhPh:ArPh (%)	5.2	3.1	2.4	4.5
5[b]		conv. (%)		37.2	41.6	
		PhPh:ArPh (%)		3.3	2.6	
6		conv. (%)	7.9	26.6	43.3	32.6
		PhPh:ArPh (%)	6.0	5.1	4.8	5.2
7		conv. (%)	6.1	29.6	22.4	14.1
		PhPh:ArPh (%)	2.2	2.1	2.5	2.1
8		conv. (%)	7.9	6.1	17.9	22.9
		PhPh:ArPh (%)	5.4	8.4	5.7	4.9
9		conv. (%)	15.9	39.6	54.4	57.3
		PhPh:ArPh (%)	5.4	3.8	2.0	4.3

[a] Conditions: $[Pd(OAc)_2]$ (5×10^{-5} mmol, 1×10^{-2} mol %), bis-imidazolium salt (5×10^{-5} mmol, 1 equiv. / Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

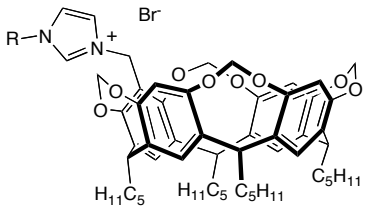
[b] $[Pd(OAc)_2]$ (5×10^{-6} mmol, 1×10^{-3} mol %), bis-imidazolium salt (5×10^{-6} mmol, 1 equiv. / Pd).

Table S-5. Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid using $[Pd(OAc)_2]$ and a tetra-imidazolium salt.[a]

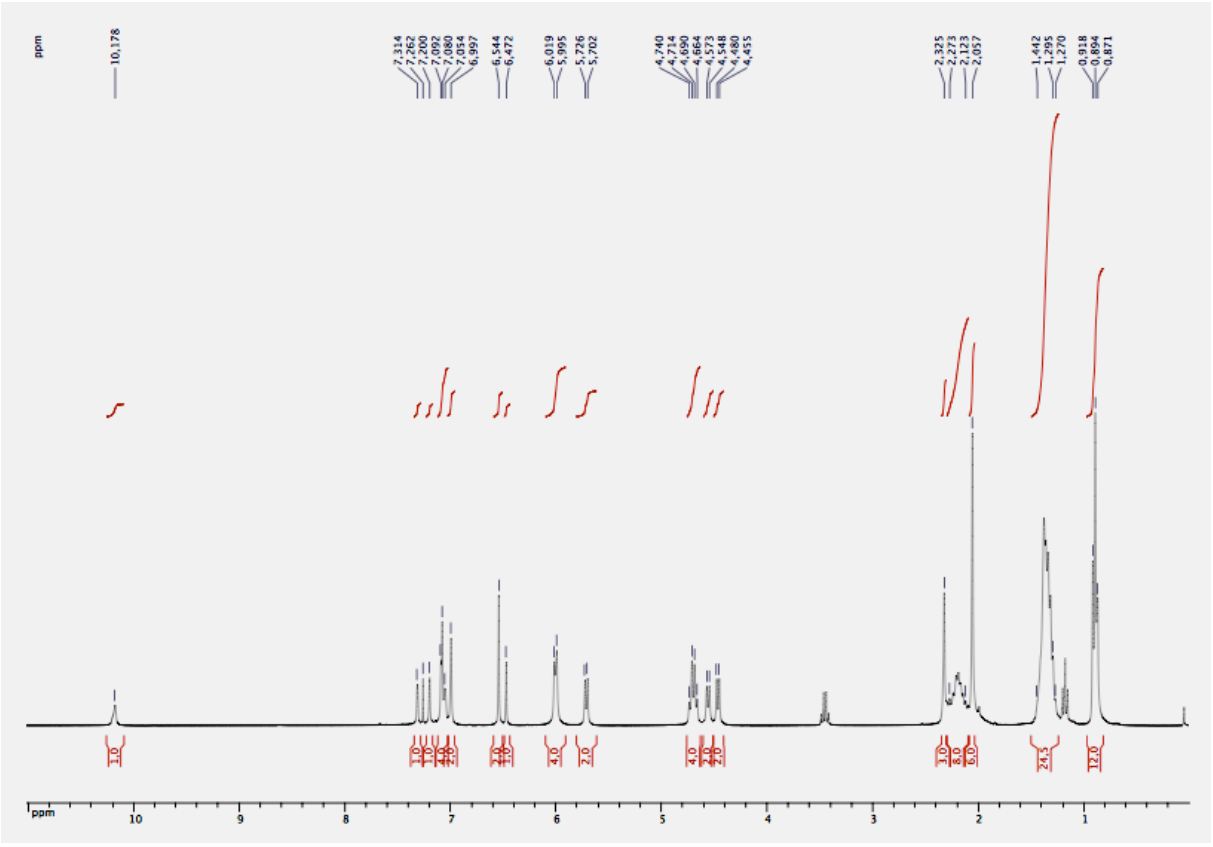
Entry	ArBr		Tetra-imidazolium salt			
			11	**12**	**13**	**14**
1		conv. (%)	14.1	11.3	26.1	23.8
		PhPh:ArPh (%)	1.6	0.3	0.1	1.3
2		conv. (%)	8.8	2.1	20.8	23.4
		PhPh:ArPh (%)	0.9	2.7	0.2	0.7
3		conv. (%)	32.3	30.9	61.9	35.1
		PhPh:ArPh (%)	0.7	0.2	0.2	0.3
4		conv. (%)	50.4	58.4	77.1	57.7
		PhPh:ArPh (%)	0.3	0.2	0.1	0.3
5		conv. (%)	25.8	26.9	30.7	28.9
		PhPh:ArPh (%)	1.1	0.7	0.2	0.3
6		conv. (%)	6.6	5.4	12.6	23.5
		PhPh:ArPh (%)	0.4	1.0	0.2	0.4
7		conv. (%)	8.5	5.3	15.1	31.1
		PhPh:ArPh (%)	0.5	0.9	0.3	0.8
8		conv. (%)	11.2	21.9	21.7	32.0
		PhPh:ArPh (%)	0.8	0.2	0.1	0.2

[a] Conditions: $[Pd(OAc)_2]$ (5 x 10^{-5} mmol, 1 x 10^{-2} mol %), tetra-imidazolium salt (5 x 10^{-5} mmol, 1 equiv. / Pd), ArBr (0.5 mmol), $PhB(OH)_2$ (0.122 g, 1.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol), decane (0.05 mL), DMF (1.5 mL), 130°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

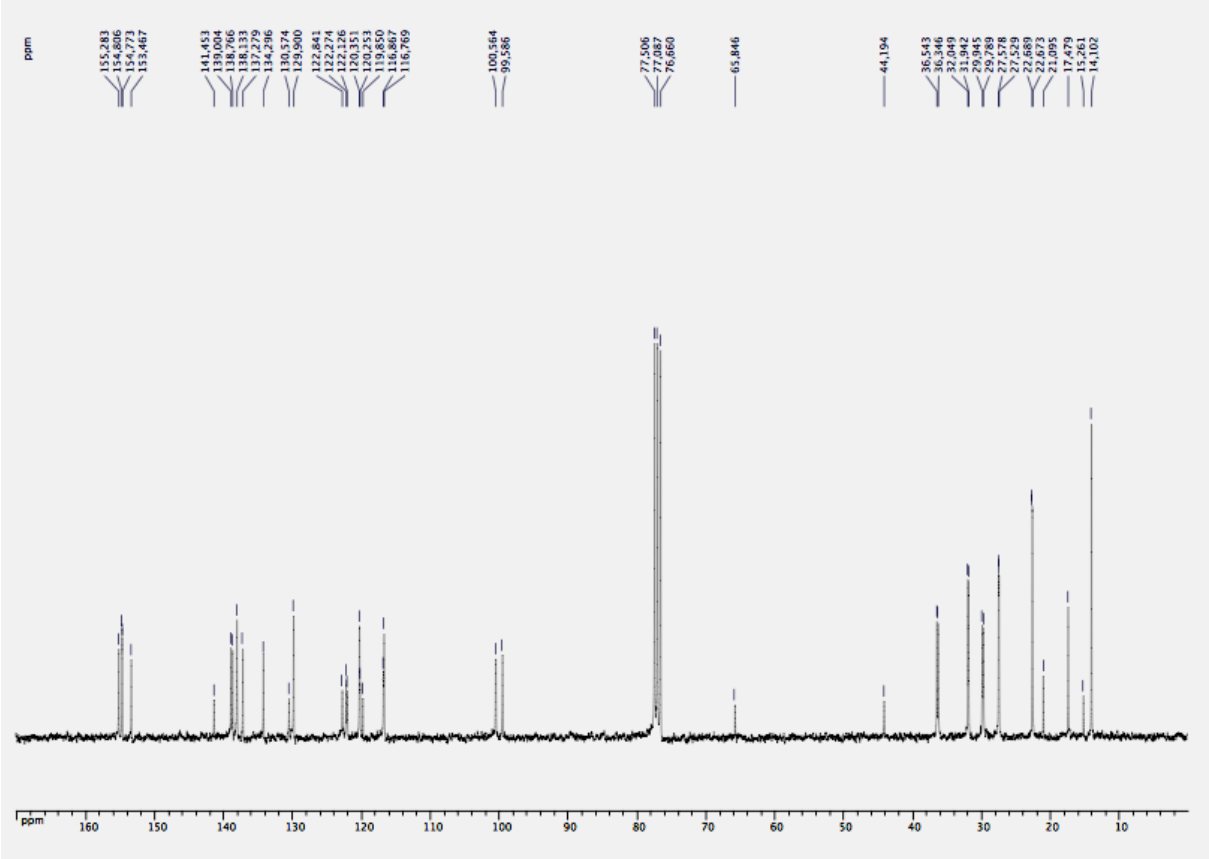
Example of characterising data for a mono-imidazolium salt



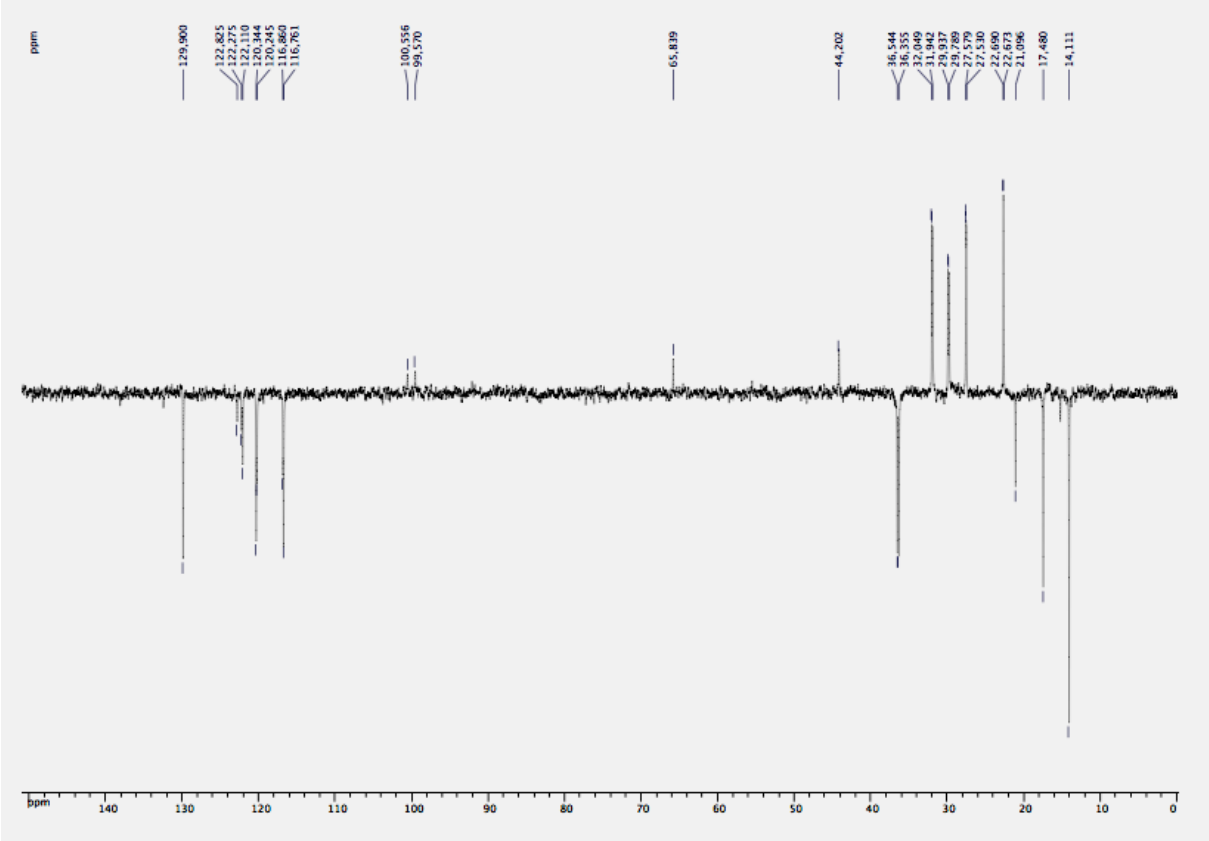
R = Mes (**3**)



^{1}H NMR spectrum of **3** ($CDCl_3$)

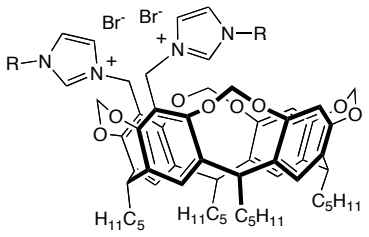


$^{13}C\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$)

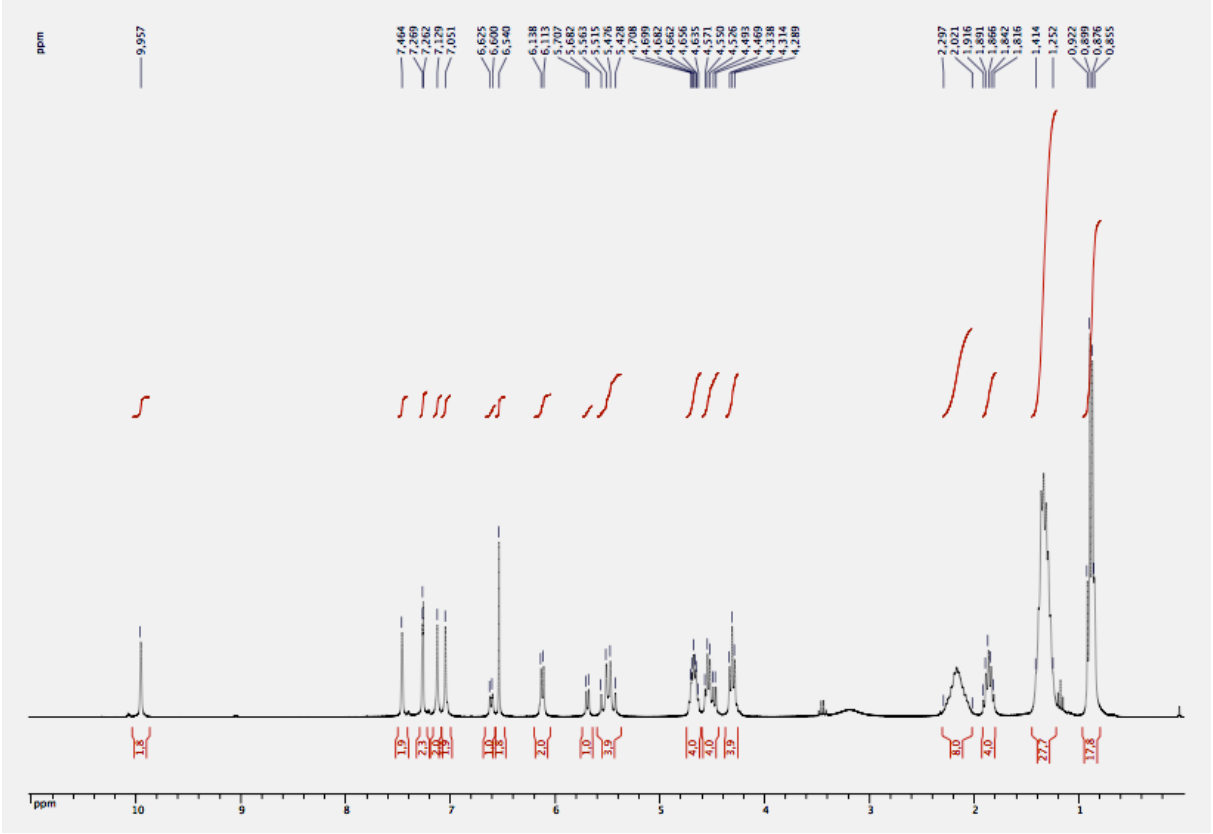


DEPT 135 NMR spectrum of **3** ($CDCl_3$)

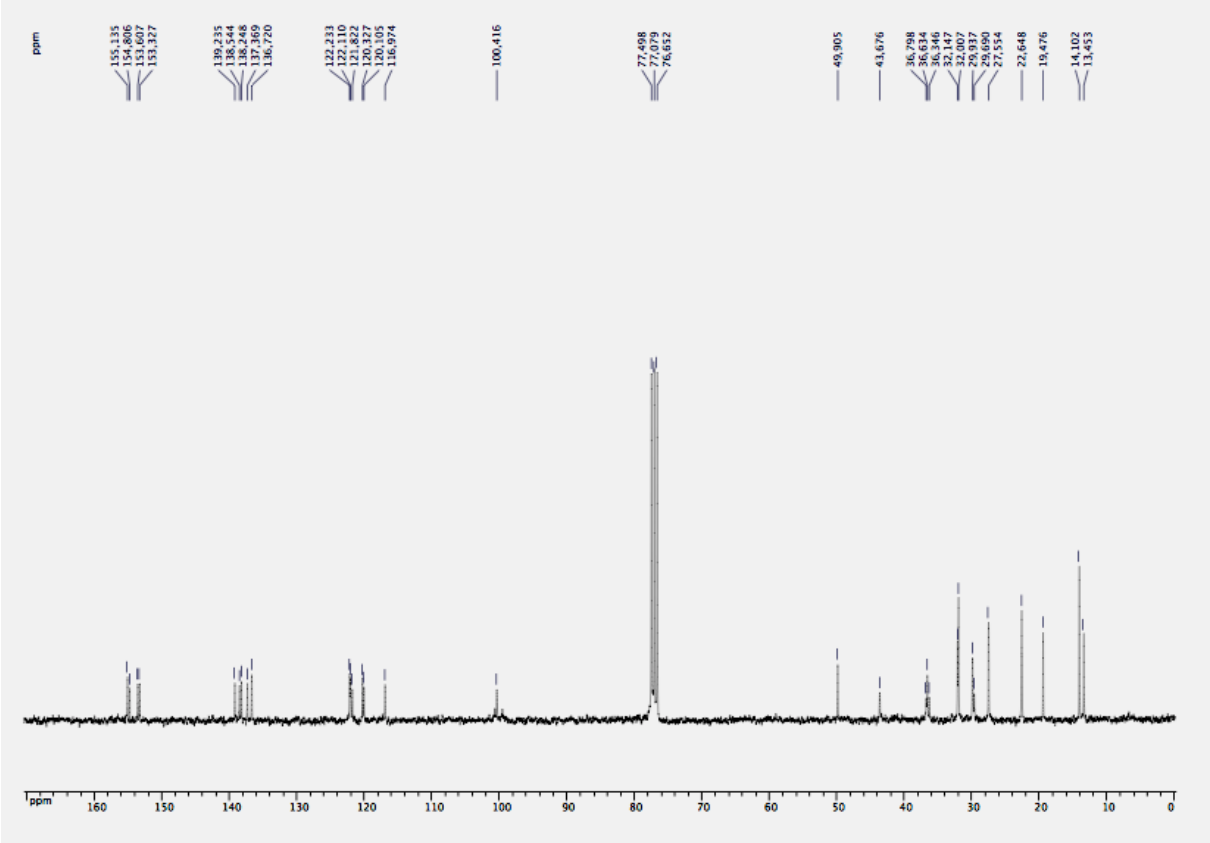
Example of characterising data for a bis-imidazolium salt



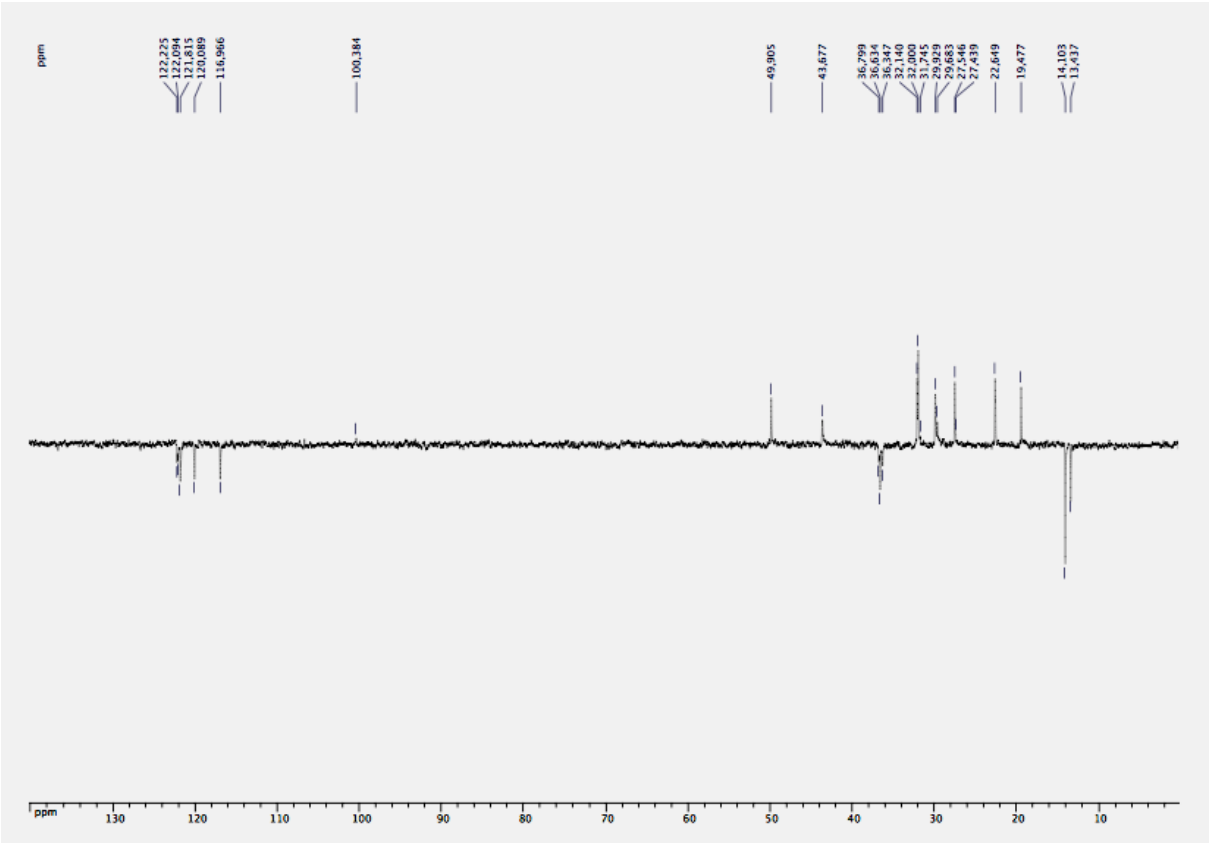
R = ^{n}Bu (**6**)



^{1}H NMR spectrum of **6** ($CDCl_3$)

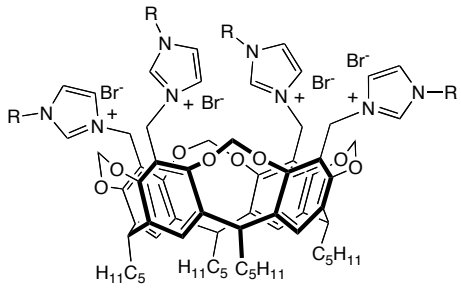


$^{13}C\{^{1}H\}$ NMR spectrum of **6** ($CDCl_3$)

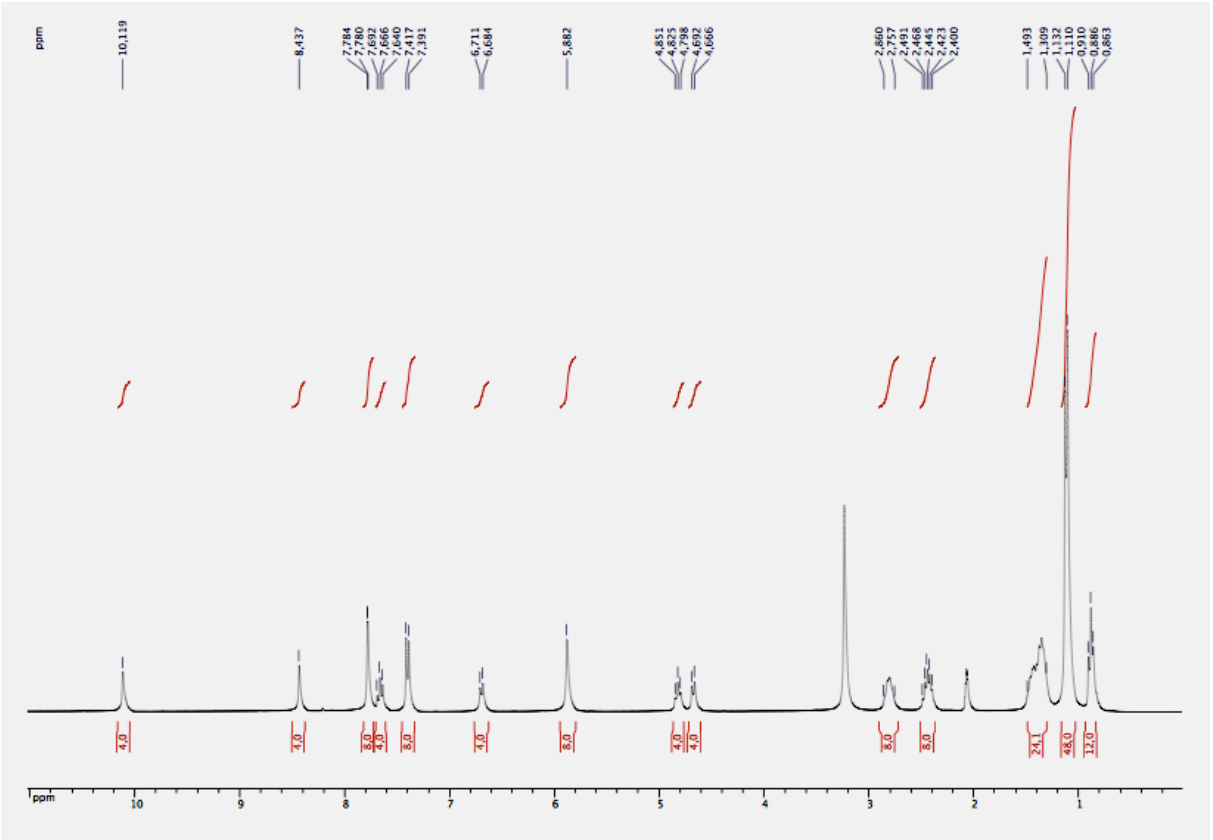


DEPT 135 NMR spectrum of **6** ($CDCl_3$)

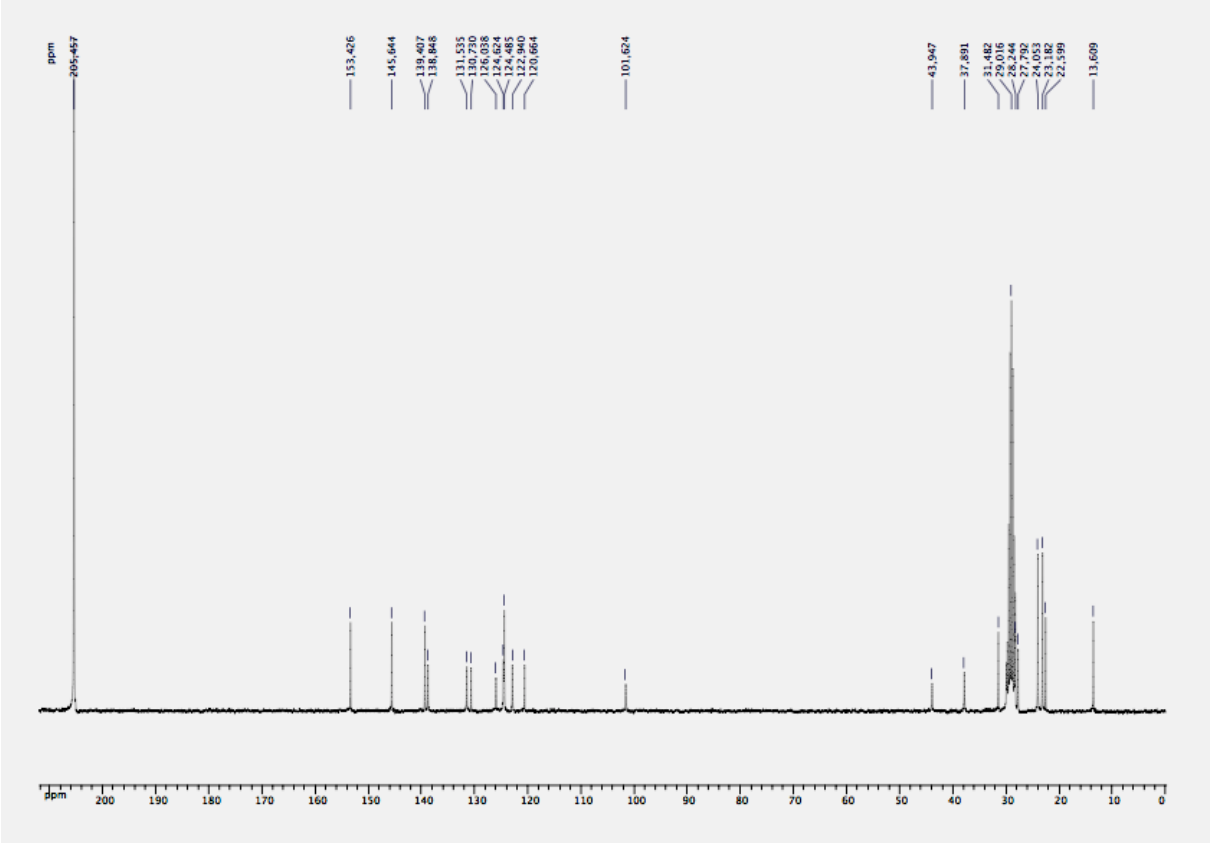
Example of characterising data for a tetra-imidazolium salt



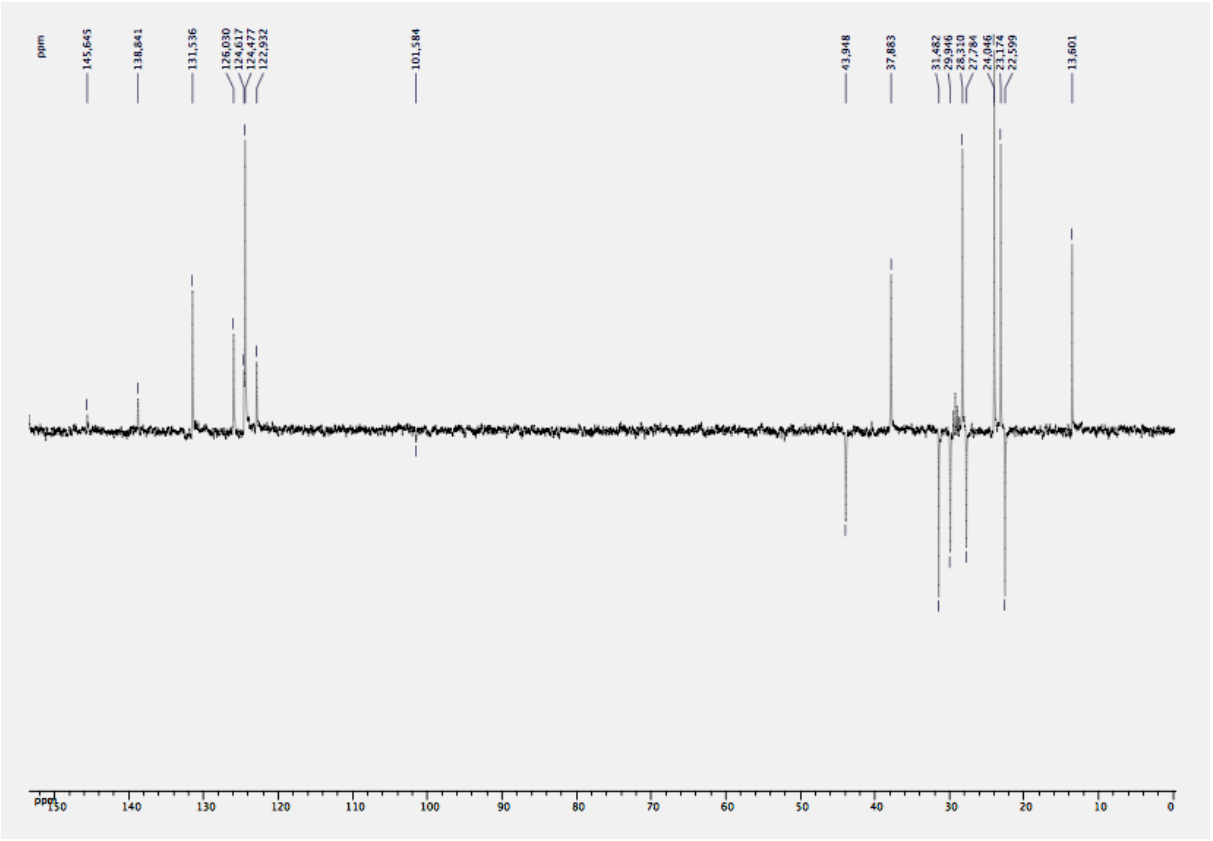
R = $^{i}Pr_2C_6H_3$ (**14**)



^{1}H NMR spectrum of **14** (acetone-d_6)



$^{13}C\{^{1}H\}$ NMR spectrum of **14** (acetone-d_6)



DEPT 135 NMR spectrum of **14** (acetone-d_6)

Reaction of 9 with [Pd(OAc)$_2$].

A solution of [Pd(OAc)$_2$] (0.014 g, 0.061 mmol) in DMF (15 mL) was added to a stirred solution of **9** (0.079 g, 0.061 mmol) in DMF (15 mL) at room temperature. The reaction mixture was first heated at 50°C (2 h) then at 80°C (2 h) and finally at 130°C for 2 further hours. The resulting solution was concentrated to *ca*. 1 mL. Addition of hexane (100 mL) afforded a yellow precipitate, which was found to contain several complexes that could not be separated. The mass spectrum of the crude reaction mixture revealed an intense peak (ESI-TOF) at *m/z* 1563.54. This peak could be assigned either to the species [PdBr$_2$(bis-carbene)$_2$ + H$^+$] or its isomer [PdBr$_2$(monocarbene-monoimidazolium)]$^+$ (requiring 1563.53).

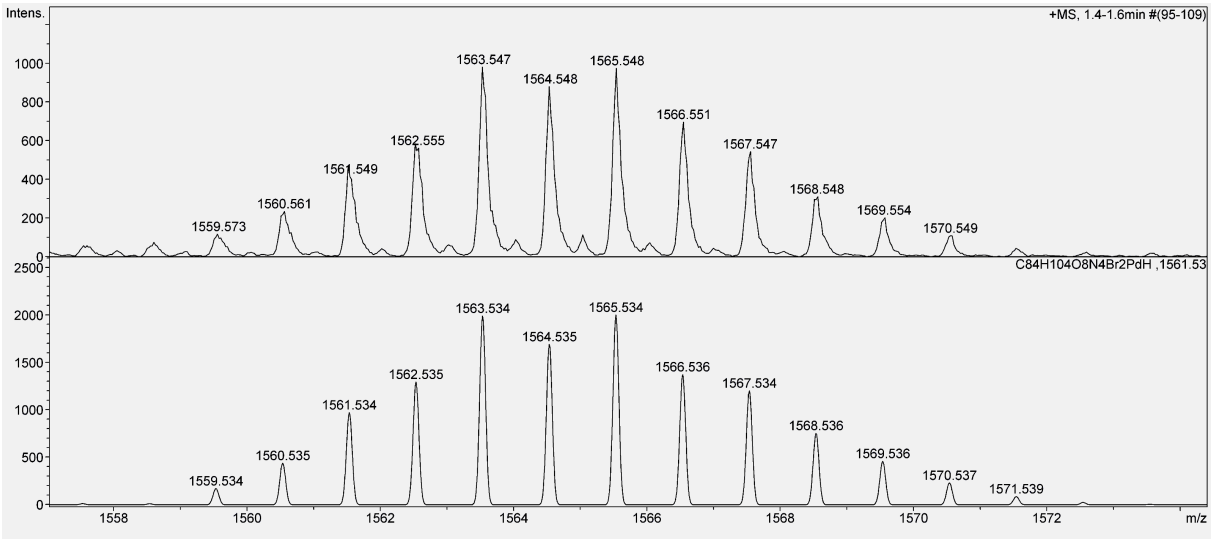


Fig. S-1. MS (ESI-TOF) of the palladium(II) complex derived from **9** (bottom: calculated spectrum).

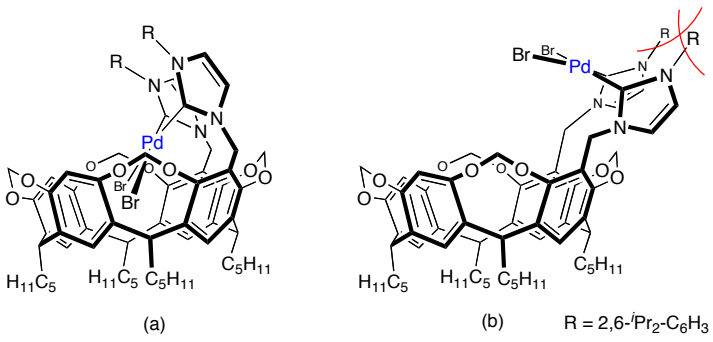


Fig. S-2. Possible "endo" (a) and "exo" (b) structures for the hypothetical chelate complex [PdBr$_2$•**9**]