

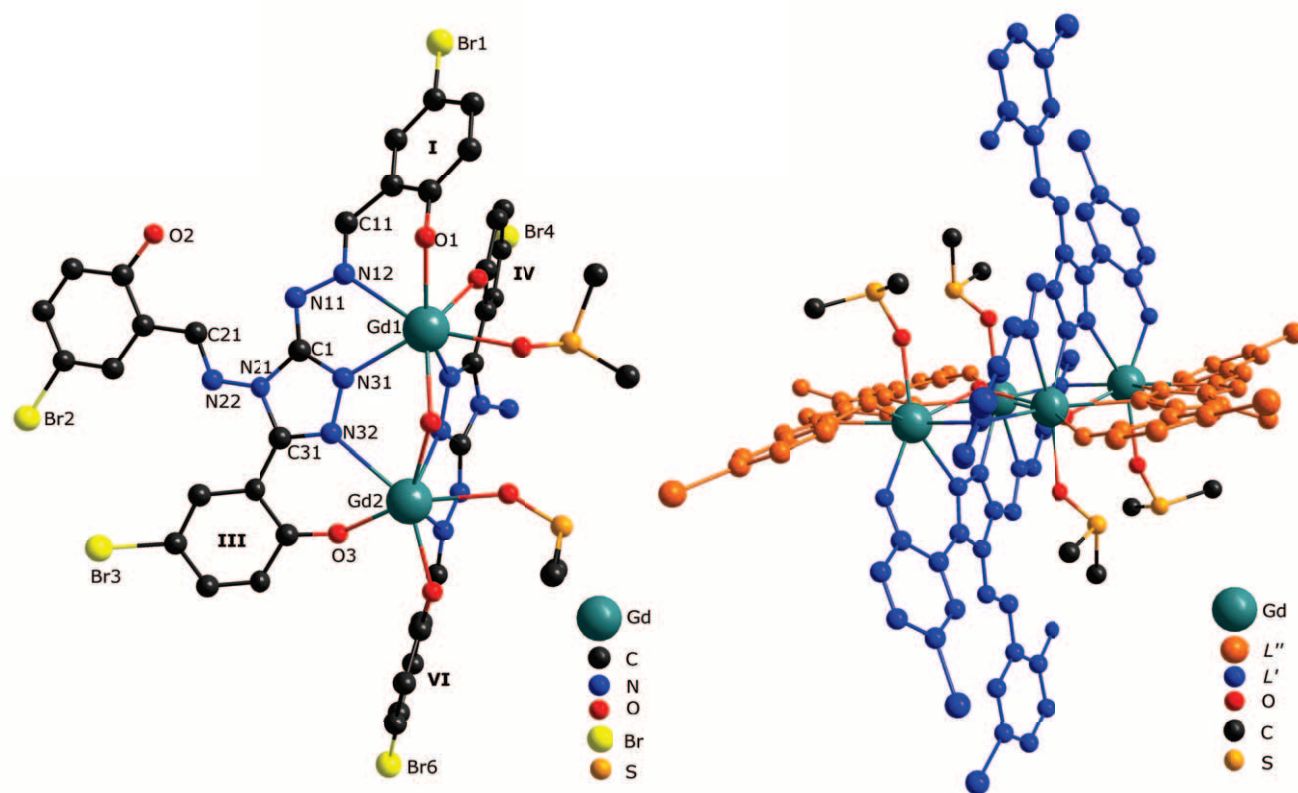
# Intramolecular Triazole Formation - Supporting Information

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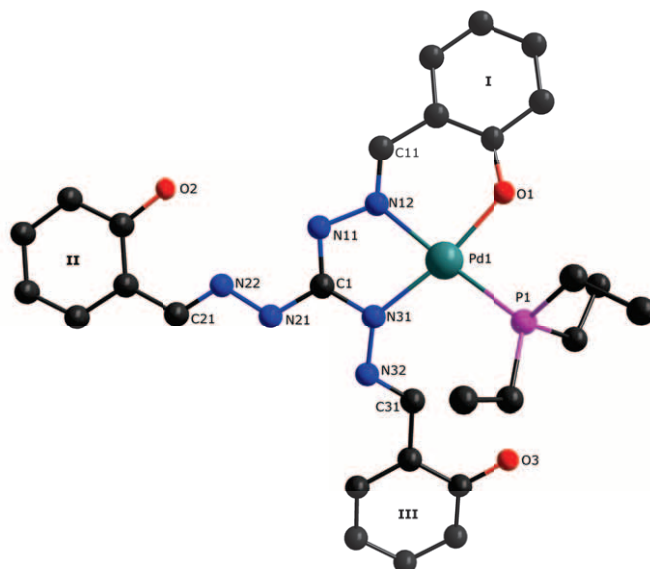
## 1 Moleculare Structures

Chelation of Gd(III)-ions by **2** in the presence of  $\text{NEt}_3$  in DMSO results within four months to formation of orange crystals of  $[\{\{\text{Gd}(\text{DMSO})\}_2(\text{HBr}_3\text{L}')(\text{H}_3\text{Br}_2\text{L}'')\}_2(\mu\text{-OH})_2] \cdot 18\text{DMSO}$  **6** (Fig. 1).



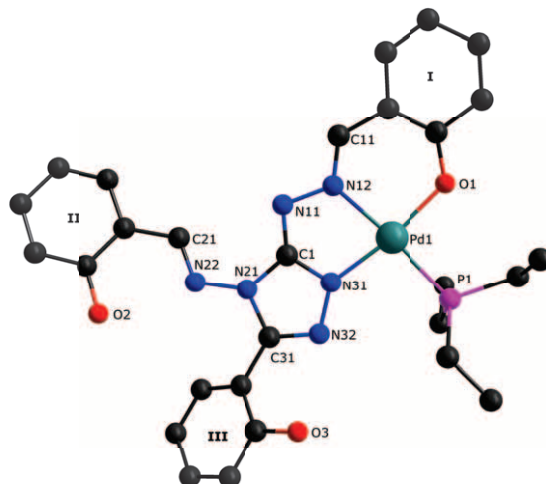
**Figure 1** Molecular structure of  $[\{\{\text{Gd}(\text{DMSO})\}_2(\text{HBr}_3\text{L}')(\text{H}_3\text{Br}_2\text{L}'')\}_2(\mu\text{-OH})_2] \cdot 18\text{DMSO}$  **6**: asymmetric unit (left) and visualisation of different triazole backbones in entire coordination (right). Hydrogen atoms and free solvent molecules have been omitted for clarity.

The reaction of **1** with  $[\text{PdCl}_2(\text{PEt}_3)_2]$  and 2 equiv. NaOH is performed under inert conditions in dry MeOH. Orange crystals of  $[\text{Pd}(\text{PEt}_3)(\text{H}_3\text{L})]$  **9** are obtained from redissolving in  $\text{Et}_2\text{O}$  and gentle solvent evaporation (Fig. 2).



**Figure 2** Molecular structure of  $[\text{Pd}(\text{PEt}_3)(\text{H}_3\text{L})]$  **9**. Hydrogen atoms and solvent molecules have been omitted for clarity.

Orange crystals of  $[\text{Pd}(\text{PEt}_3)(\text{H}_2\text{L}')]$  **11** are obtained from gentle NMR-solvent evaporation (Fig. 3).



**Figure 3** Molecular structure of  $[\text{Pd}(\text{PEt}_3)(\text{H}_2\text{L}')]$  **11**. Hydrogen atoms have been omitted for clarity.

## 2 Coordination pattern of Pd(II)-ions

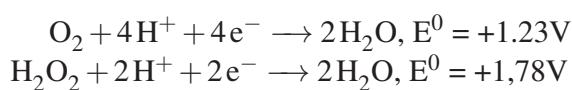
To compare the coordination geometry of Pd(II)-ions in **7**, **8** and **9**, the CSD database was used to look for similar coordination patterns. The bonding parameters are listed below (Tabl. 1).

CSD code	Pd-N <sub>am</sub>	Pd-P	Pd-N <sub>im</sub>	Pd-O
FECJUU	1.985	2.265	2.017	1.998
FECKAB	1.995	2.260	2.001	2.022
FECKAB	2.012	2.277	1.980	2.010
FECKAB	1.964	2.262	2.008	1.997
FECKAB	1.966	2.281	2.014	1.994
FECKEF	1.965	2.262	1.979	2.005
FECKIJ	1.976	2.269	2.033	1.984
FECKIJ	1.967	2.261	2.024	1.981
IZODAC	1.979	2.284	2.020	1.976
PUWTAC	1.976	2.332	1.998	1.995
TARMUW	1.965	2.280	2.014	2.008
median	1.976	2.269	2.014	1.997

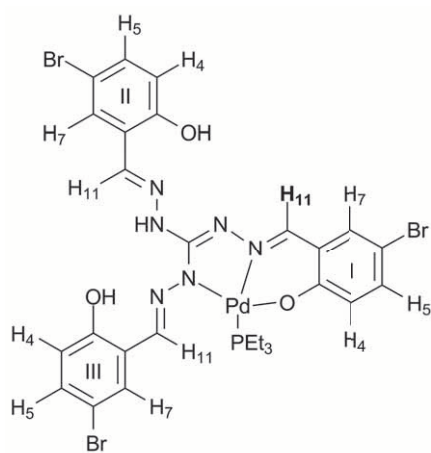
**Table 1** Bond distances of Pd-O-N-N coordination

## 3 Standard reduction potential

Standard reduction potentials at 298 K are taken from *Handbook of Physics and Chemistry*.  
W. M. Haynes, *Handbook of Chemistry and Physics*, **2012 – 2013**, 93<sup>rd</sup> edition.



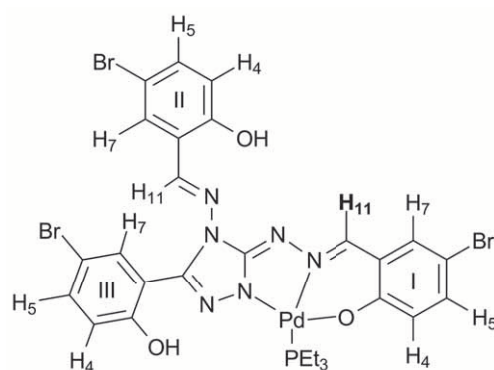
## 4 NMR data



[Pd(PEt<sub>3</sub>)(H<sub>3</sub>Br<sub>3</sub>L)] **8**

$\delta$ [ppm]	m	H	J [Hz]	int
1.20	dt	CH <sub>3</sub>	7.63 16.95	9
1.79	dq	CH <sub>2</sub>	7.66 10.02	6
6.89	d	7	8.6	1
6.91	d	7	8.8	1
6.92	d	7	8.7	1
7.27	dd	5	9.0 / 2.6	1
7.33	m	5, 4, 4	-	3
7.39	dd	5	8.7 / 2.4	1
7.45	d	4	2.6	1
7.82	s	11	-	1
7.98	s	11	-	1
<b>8.12</b>	<b>d</b>	<b>11</b>	<b>14.1</b>	<b>1</b>
8.27	s	OH	-	1
10.42	s	OH	-	1
11.33	s	NH	-	1

Table 2 <sup>1</sup>H-NMR assignment of **8**



[Pd(PEt<sub>3</sub>)(H<sub>2</sub>Br<sub>3</sub>L')] **10**

$\delta$ [ppm]	m	H	J [Hz]	int
1.30	dt	CH <sub>2</sub>	7.63 17.20	9
2.08	dq	CH <sub>3</sub>	7.62 10.96	6
6.94	d	7	8.8	1
6.97	d	7	8.8	1
7.00	d	7	9.0	1
7.30	dd	5	9.0 / 2.6	1
7.45	dd	5	8.8 / 2.4	1
7.49	dd	5	8.8 / 2.5	1
7.52	d	4	2.6	1
7.69	d	4	2.4	1
8.02	d	4	2.4	1
<b>8.39</b>	<b>d</b>	<b>11</b>	<b>13.7</b>	<b>1</b>
9.81	s	11	-	1
10.02	s	OH	-	1
10.04	s	OH	-	1

Table 3 <sup>1</sup>H-NMR assignment of **10**

## 5 ESI-MS

ESI-mass spectra for **5**, **6** could not be obtained as the compounds seemed to decompose after acidification of the samples. ESI-mass spectra of **8** and **9** could not be recorded as they underwent the oxidation process to the form triazoles **10** and **11** in solution too fast.

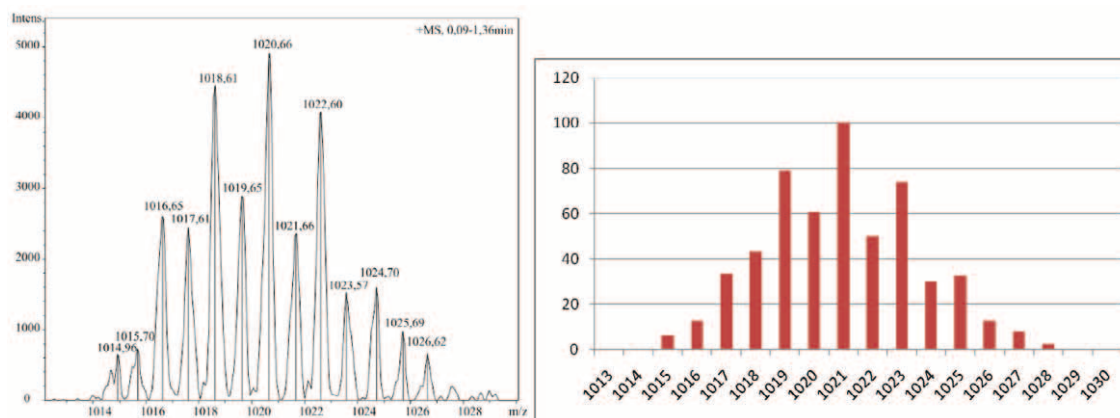


Figure 4 ESI(+) of  $[\text{Pd}(\text{PPh}_3)_3\text{H}_3\text{Br}_3\text{L}]$  **7**.

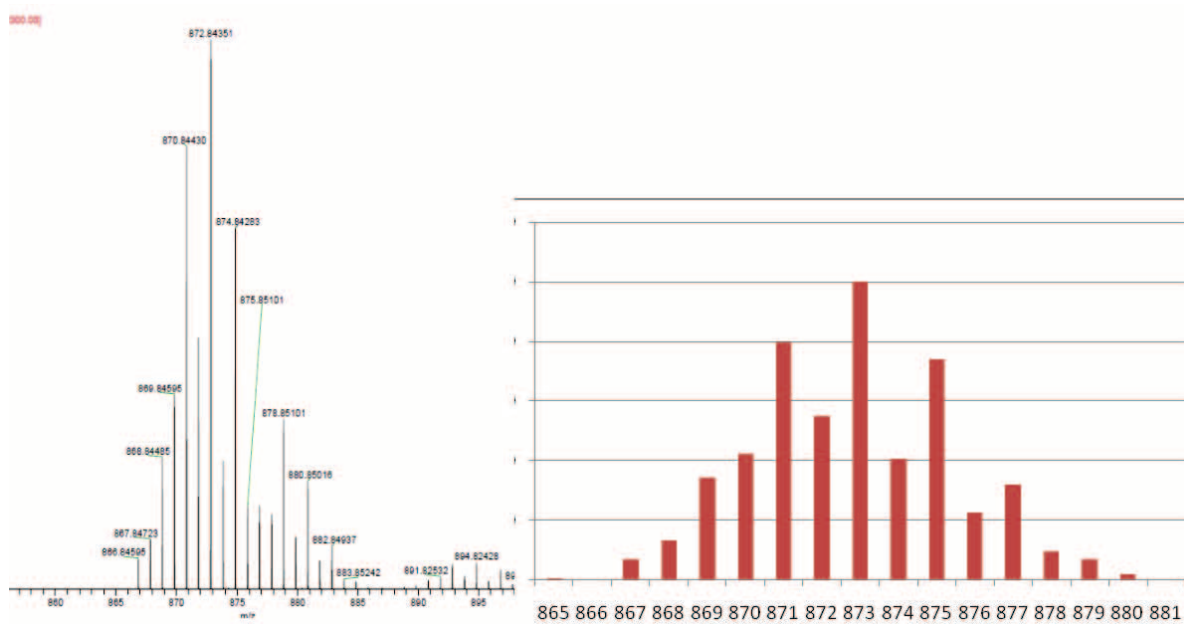


Figure 5 ESI-MS(-) of  $[\text{Pd}(\text{PEt}_3)(\text{H}_2\text{Br}_3\text{L}')]$  **10**.

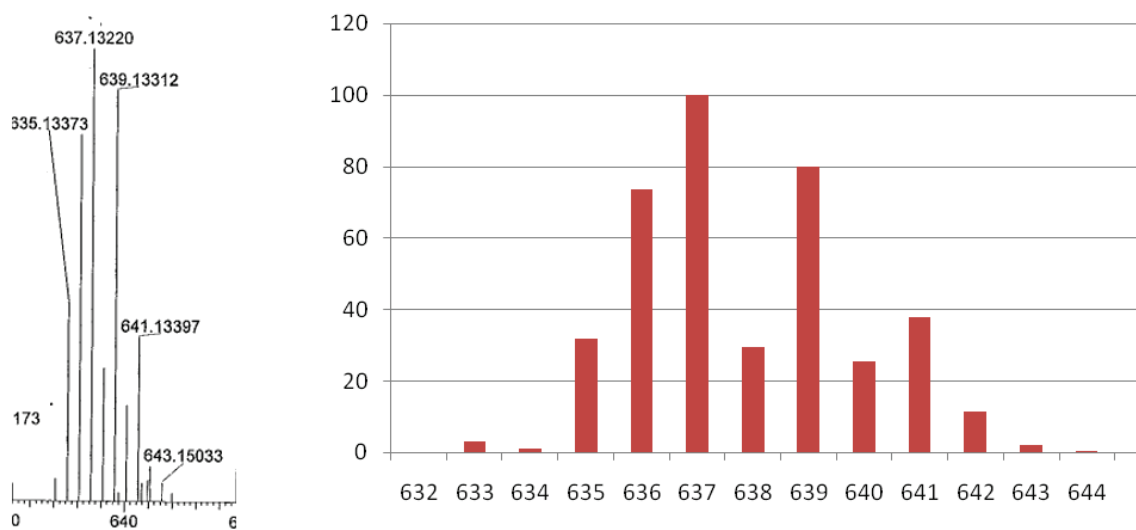


Figure 6 ESI-MS(+) of  $[\text{Pd}(\text{PEt}_3)(\text{H}_2\text{L}')]$  **11**.