Supporting Information pertaining to:

The role of the dendritic support in the catalytic performance of peripheral pincer Pd-complexes

Niels J. M. Pijnenburg,[a] Martin Lutz,[b] Maxime A. Siegler,[b] Anthony Spek,[b] Gerard van Koten,[a] Robertus J. M. Klein Gebbink*[a]

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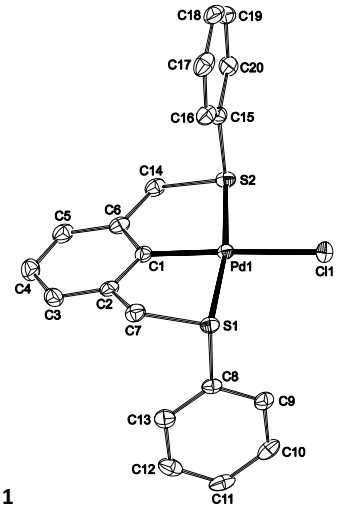
*X-ray structures of **1**, **13** and **2***

Single crystals of **2** and the bromide analogues of **1** and **13** suitable for X-ray crystal structure determinations were obtained by slow vapor diffusion of diethylether into dichloromethane solutions at room temperature. In the crystal structures of **1** and **13** occupational disorder between bromine and chlorine was found on the halogen positions. The bromine of the metal complex has been partially exchanged by chlorine from the dichloromethane solvent. This exchange has been reported before, by among others Kruithof[1] and Bergbreiter.[2] The molecular structures of **1**, **13**, and **2** are displayed in Figure 1 and typical bond lengths and angles are shown in Table 1. The Pd-center is found in a typical pincer-type distorted square planar geometry in all structures: S(1)–Pd(1)–S(2) was found to be 170.56(3)° for **1**, 168.26(3) for $\mathbf{13_{Br}}$, and 168.17(3)° for **2**. The observed Pd-C1 bond length for **1**, $\mathbf{13_{Br}}$ and **2** (1.981(3), 1.972(3) and 1.986(3) Å. respectively) was found to be equidistant to those in earlier published complexes and also other bond lengths and angles are very close to the corresponding bond lengths and angles for earlier published SCS-pincer Pd-complexes.[1-5] The five-membered palladacycles in these complexes are puckered in opposite directions with torsion angles Pd(1)–S(1)–C(7)–C(2) and Pd(1)– S(2)–C(14)–C(6) of 31.75(19)° and 14.05(19)° for **1**, -20.2(3)° and 2.5(3)° for $\mathbf{13_{Br}}$ and 29.31(19)° and 25.8(2)° for **2**, respectively. The orientation of the phenyl ring on S(2) for $\mathbf{13_{Br}}$ is almost parallel to the local C2 axis, whereas that on S(1) is perpendicular to it. For complex **1** and **2** the orientation of both phenyl rings is approximately perpendicular towards the local axis of symmetry. In **2** the N-H of the amide moiety acts as hydrogen bond donor with the metal-coordinated chlorine as acceptor. This hydrogen bonding results in a one-dimensional chain along the crystallographic b axis (not shown), comparable to *para*-OH functionalized SCS-pincer Pd-complexes by Mehendale.[5]



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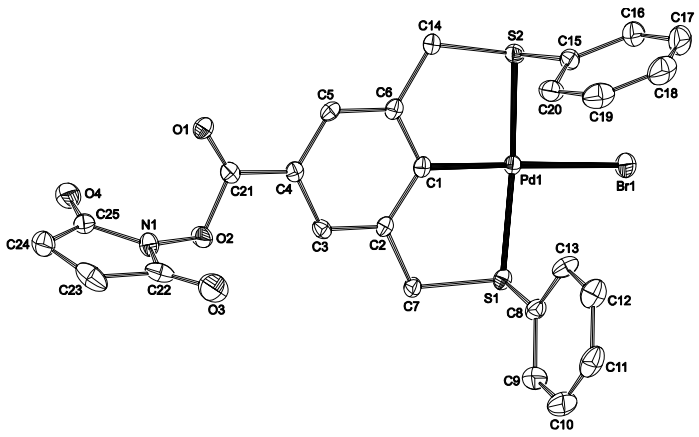

13_{Br}

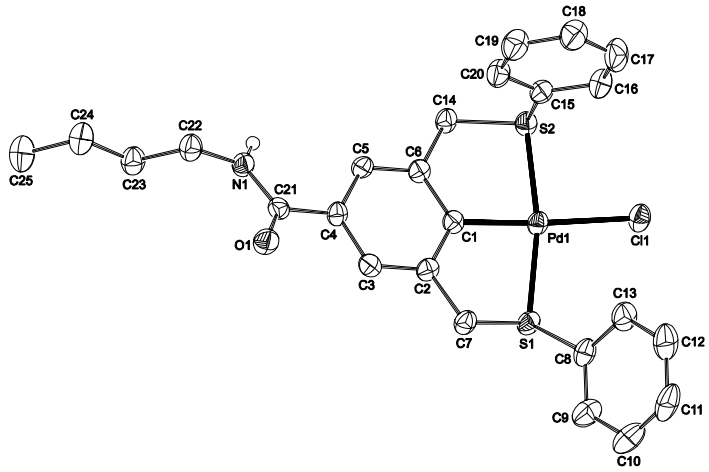

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Figure 1: ORTEP representations of the molecular structures of **1**, **13_{Br}**, and **2**. Displacement ellipsoids are drawn at the 50% probability level. C-H hydrogen atoms are omitted for clarity. Of the disordered halogen ligands in **1** and **13_{Br}** only the major form is shown.

Table 1: Selected bond lengths [Å], angles [°] and torsion angles [°] for crystal structures **1**, **13_{Br}** and **2**.

	1	**13_{Br}**	**2**
Pd1-C1	1.981(3)	1.972(3)	1.986(3)
Pd1-S1	2.3002(7)	2.2956(9)	2.2996(7)
Pd1-S2	2.2946(7)	2.2963(10)	2.2980(7)
C1-Pd1-S1	85.59(8)	86.04(11)	83.39(8)
C1-Pd1-S2	84.97(8)	85.83(11)	85.09(8)
S1-Pd1-S2	170.56(3)	168.26(3)	168.17(3)
Pd1-S1-C7-C2	31.75(19)	-20.2(3)	29.31(19)
Pd1-S2-C14-C6	14.05(19)	2.5(3)	25.8(2)
Pd1-S1-C8-C9	70.4(2)	178.2(3)	-172.5(2)
Pd1-S2-C15-C16	-9.3(2)	107.5(3)	82.4(2)

X-ray crystal structure determination of compounds 1, 13 and 2

X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. Integration was performed with EvalCCD[6] (compounds **1**, **13**) or HKL2000[7] (compound **2**). The structures were solved with automated Patterson methods using DIRDIF-08[8] (**1**, **13**) or Direct Methods using SHELXS-97[9] (**2**). Least squares refinement was performed with SHELXL-97[9] on F^2 of all reflections. Structure calculations and checking for higher symmetry was performed with PLATON.[10] Further details are given in Table 2.

Table 2: Experimental details of the crystal structure determinations

	1	**13**	**2**
formula	$C_{20}H_{17}Br_{0.26}Cl_{0.74}PdS_2$	$C_{25}H_{20}Br_{0.66}Cl_{0.34}NO_4PdS_2$	$C_{25}H_{26}ClNOPdS_2$
fw	475.09	633.73	562.44
crystal size [mm^3]	0.40x0.08x0.08	0.37x0.25x0.06	0.30x0.15x0.04
crystal color	yellow	pale yellow	Yellow
T [K]	110(2)	110(2)	150(2)
crystal system	monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/c$ (no. 14)	$Pca2_1$ (no. 29)	$P2_1/c$ (no. 14)
a [Å]	9.8035(7)	8.6141(2)	15.8584(2)
b [Å]	18.0936(12)	12.4476(2)	9.8059(2)
c [Å]	10.0847(5)	22.2620(4)	16.2730(3)
β [°]	97.542(3)	-	113.3804(7)
V [$Å^3$]	1773.35(19)	2387.04(8)	2322.76(7)
Z	4	4	4
d_{calc} [g/cm^3]	1.779	1.763	1.608
μ [mm^{-1}]	1.988	2.129	0.841
abs. corr. type	analytical	multi-scan	multi-scan
abs. corr. range	0.53-0.91	0.70-0.88	0.84-1.12
refl. measured / unique	25006 / 4063	30099 / 5863	28291 / 5286
parameters / restraints	221 / 2	312 / 3	285 / 0
R1/wR2 [$I>2\sigma(I)$]	0.0271 / 0.0511	0.0296 / 0.0558	0.0350 / 0.0851
R1/wR2 [all refl.]	0.0452 / 0.0556	0.0374 / 0.0578	0.0493 / 0.0932
S	1.070	1.133	1.055
Flack x[11]	-	-0.011(10)	-
$\rho_{min/max}$ [$e/Å^3$]	-0.60 / 0.59	-0.50 / 0.69	-1.05 / 1.02

Compound **1.** The position of the halogen was partially occupied by bromine (26% occupancy) and chlorine (74% occupancy). The anisotropic displacement parameters of chlorine and bromine were constrained to the same values. The Pd-halogen distances were restrained to the expectation values of 2.4 Å (chlorine) and 2.5 Å (bromine). All hydrogen atoms were located in difference Fourier maps and refined with a riding model.

Compound **13.** The crystal was cracked with a 4.7° rotation about an arbitrary axis relating the two fragments. Refinement was performed on a HKLF5 file.[12] The position of the halogen was partially occupied by bromine (66% occupancy) and chlorine (34% occupancy). The anisotropic displacement parameters of chlorine and bromine were constrained to the same values. The Pd-halogen distances were restrained to the expectation values of 2.4 Å (chlorine) and 2.5 Å (bromine). All hydrogen atoms were located in difference Fourier maps and refined with a riding model.

Compound **2.** All hydrogen atoms were located in difference Fourier maps. The N-H hydrogen atom was refined freely with isotropic displacement parameters, C-H hydrogen atoms were refined with a riding model.

1. C. A. Kruithof, H. P. Dijkstra, M. Lutz, A. L. Spek, R. J. M. Klein Gebbink and G. van Koten, *Organometallics*, 2008, **27**, 4928-4937.
2. D. E. Bergbreiter, J. D. Frels, J. Rawson, J. Li and J. H. Reibenspies, *Inorg. Chim. Acta*, 2006, **359**, 1912-1922.
3. H. J. van Manen, K. Nakashima, S. Shinkai, H. Kooijman, A. L. Spek, F. C. J. M. van Veggel and D. N. Reinhoudt, *Eur. J. Inorg. Chem.*, 2000, 2533-2540.
4. R. Cervantes, S. Castillejos, S. J. Loeb, L. Ortiz-Frade, J. Tiburcio and H. Torrens, *Eur. J. Inorg. Chem.*, 2006, 1076-1083.
5. N. C. Mehendale, M. Lutz, A. L. Spek, R. J. M. K. Gebbink and G. van Koten, *J. Organomet. Chem.*, 2008, **693**, 2971-2981.
6. A. J. M. Duisenberg, L. M. J. Kroon-Batenburg and A. M. M. Schreurs, *J. Appl. Cryst.*, 2003, **36**, 220-229.
7. Z. Otwinowski and W. Minor, *Macromol. Cryst. A*, 1997, **276**, 307-326.
8. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, *The DIRDIF08 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands*, 2008
9. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
10. A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.
11. H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876-881.
12. R. Herbst-Irmer and G. M. Sheldrick, *Acta Cryst.*, 1998, **B54**, 443-449.