Chalcogen-chalcogen Bonds in Edge-sharing Square-planar d^8 Complexes. Are They Possible?

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Supporting Material

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Table S1. Experimental and theoretical parameters[a] for the trinuclear and tetranuclear compounds with $Pd_n(\mu\text{-}S)_2$ cores.

Compound	Pd···Pd	S···S	Pd-S	Pd-L[b]	L-Pd-L	S-Pd-S	Δ[c]	
Experimental								Refcode
$[Pd_3(\mu\text{-}S)_2Cl_2(dppf)_2]$	3.127	2.927	2.324	2.304	97.7	78.0	120.0(15)	BAKWOZ
$[Pd_3(\mu\text{-}S)_2Cl(PPh_3)(dppf)_2]^+$	3.118	2.977	2.336	2.314	98.1	79.2	120.0(40)	BAKXUG
$[Pd_3(\mu\text{-}S)_2Cl(PPh_3)(dppf)_2]^+$	3.139	2.952	2.338	2.322	96.4	78.3	120.0(45)	BAKYAN
$[Pd_3(\mu\text{-}S)_2(dppe)_3]^{2+}$	3.061	3.103	2.352	2.267	85.8	82.6	120.0(01)	BAZQEY
$[Pd_3(\mu\text{-}S)_2(dpae)_3]^{2+}$	3.041	3.082	2.337	-	84.9	82.5	120.0(51)	CORJUO
$[\{Pd_3(\mu\text{-}S)_2(\{EtO\}_2PS_2)_2(Ph_3P)_2\}_2(\mu\text{-}SH)_2]$	3.128	2.916	2.322	2.290	90.8	77.8	120.0(56)	DETFAJ
$[Pd_3(\mu\text{-}S)_2(O_2C_2S_2)(PPh_3)_4]$	3.117	3.029	2.353	2.296	97.4	80.1	120.0(42)	FEBSAG
$[Pd_3(\mu\text{-}S)_2(PMe_3)_6]^{2+}$	3.110	2.979	2.334	2.280	97.4	79.3	120.0(62)	THIOPD
$[Pd_3(\mu\text{-}S)_2(\{EtO\}_2PS_2)_2(PPh_3)_2]$	3.102	2.912	2.312	2.311	89.6	78.1	120.0(91)	VAQDEW
$[Pd_3(\mu\text{-}S)_2Cl_2(PPh_3)_4]$	3.122	2.930	2.323	2.320	97.1	78.2	120.0(45)	VEHSAC
mean	*3.107*	*2.981*	*2.333*	*2.301*	*93.5*	*79.4*	*120.0*	
Calculated								E_{rel}
$[Pd_3(\mu\text{-}S)_2(PH_3)_6]^{2+}$	3.747	2.200 [d]	2.427	2.407	97.9	53.9	120.0	
	3.229	3.059	2.411	2.375	94.7	78.7	120.0	-26.0
$[Pd_4(\mu\text{-}S)_2(PH_3P)_8]^{4+}$	3.300	2.200 [d]	2.599	2.385	92.1	50.1	120.0	
	3.058	2.928	2.574	2.367	89.5	72.9	120.0	-26.2

[a] Distances in Å, angles in degrees, energies in kcal·mol^{-1}. [b] Only phosphine donors as L are considered. [c] Standard deviation of Δ is included as indicative of the loosing ideal trigonal symmetry. [d] Not a minimum, calculated with fixed S-S distance.

Table S2. Theoretically optimized structures of $[Pd_2X_2(PH_3)_4]$ complexes (X = O, S, Se and Te) adding an extra *f*-polarization function on palladium atoms. In parenthesis, values without polarization function (see Table 3).

Compound	Isomer	Pd···Pd	X···X	Pd-X	Pd-P	P·Pd·P	□	$E_{rel.}$
$[(H_3P)_4Pd_2O_2]$	**1b**	4.114 (4.127)	1.408 (1.406)	2.174 (2.180)	2.358 (2.362)	109.7 (109.9)	180.0 (180.0)	
	1a [b]	2.967 (2.976)	2.649 (2.662)	1.989 (1.996)	2.340 (2.347)	100.9 (101.2)	180.0 (180.0)	-11.3 (-8.3)
	1a	2.856 (2.861)	2.605 (2.616)	1.989 (1.997)	2.338 (2.344)	101.8 (102.2)	143.5 (142.7)	-12.6 (-9.7)
$[(H_3P)_4Pd_2S_2]$	**1b**	4.407 (4.424)	2.197 (2.193)	2.462 (2.469)	2.376 (2.379)	108.9 (109.1)	180.0 (180.0)	
	1a [b]	3.621 (3.636)	3.059 (3.052)	2.370 (2.373)	2.370 (2.375)	100.1 (100.3)	180.0 (180.0)	-1.6 (-0.7)
	1a	3.466 (3.468)	3.096 (3.090)	2.370 (2.374)	2.368 (2.373)	99.8 (100.1)	149.8 (150.5)	-1.8 (-0.8)
$[(H_3P)_4Pd_2Se_2]$	**1b** [c]	4.220 (4.331)	2.723 (2.621)	2.511 (2.531)	2.383 (2.384)	103.8 (105.4)	180.0 (180.0)	
$[(H_3P)_4Pd_2Te_2]$	**1b** [c]	4.474 (4.487)	2.996 (2.988)	2.692 (2.696)	2.384 (2.386)	104.1 (104.3)	180.0 (180.0)	

[a] Distances in Å, angles in degrees, energies in kcal·mol^{-1}. [b] Not a minimum, calculated with bending angle fixed at 180°. [c] Only one isomer has been found.