Instability of Metal 1,3-Benzodi(thiophosphinoyl)methandiide Complexes: Formation of Hafnium, Tin and Zirconium Complexes of 1,3-Benzodi(thiophosphinoyl)thioketone Dianionic Ligand [1,3-$C_6H_4(PhPS)_2C(S)^{2-}$]

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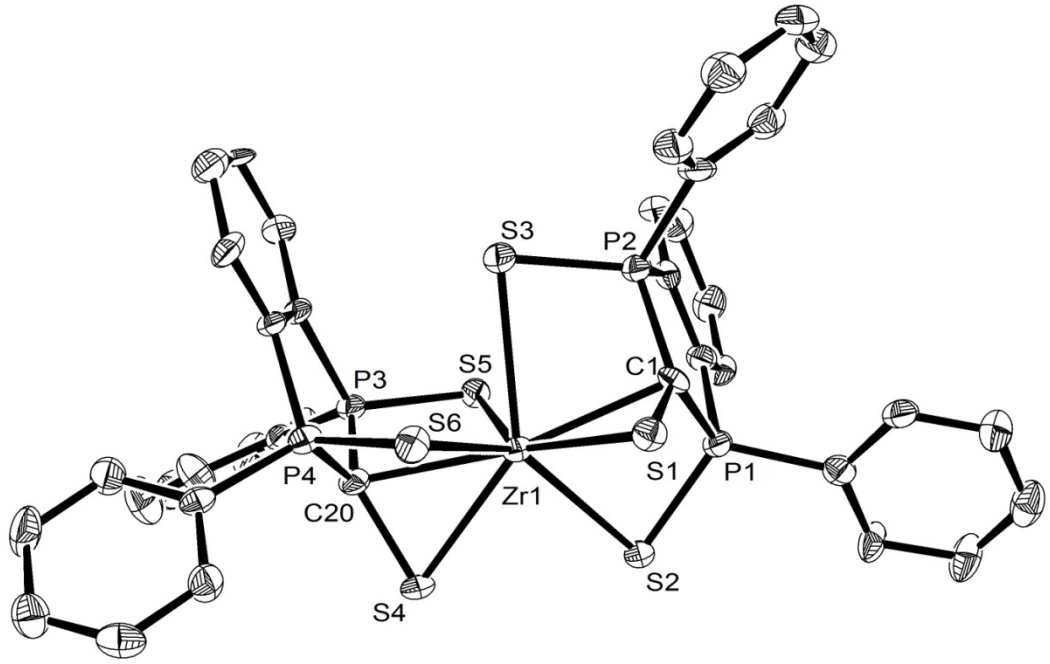
Supporting Information

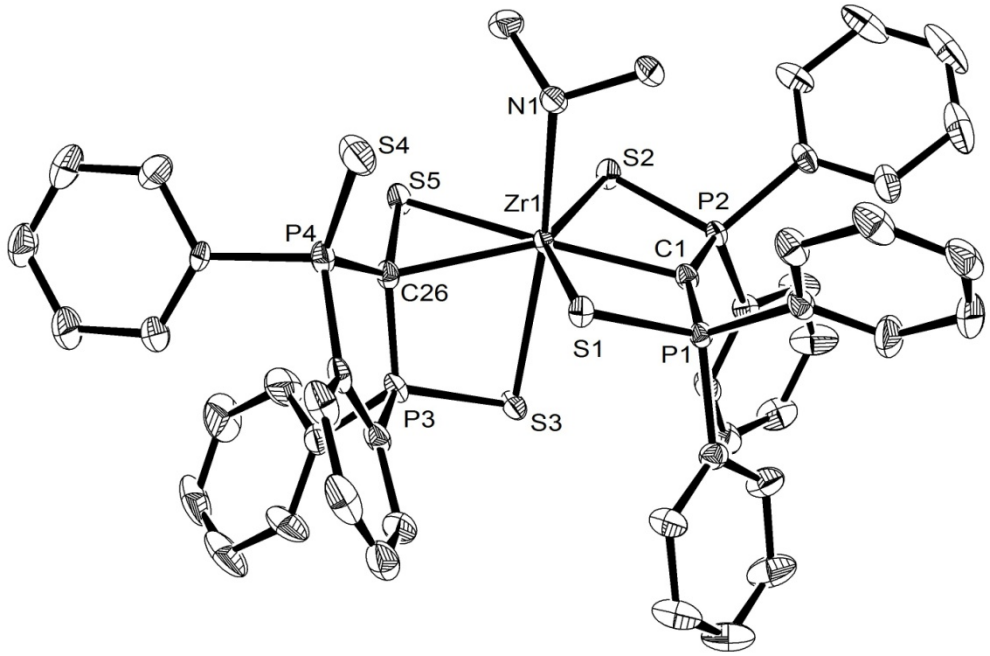
Table of Content

1. **Figure S1.** Molecular structure of **3** with thermal ellipsoids at the 50% probability level.



Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1-C1 2.431(5), Zr1-C20 2.446(5), Zr1-S1 2.526(2), Zr1-S2 2.722(2), Zr1-S3 2.741(2), Zr1-S4 2.511(2), Zr1-S5 2.810(2), Zr1-S6 2.690(2), C1-P1 1.748(5), C1-P2 1.740(5), P1-S2 1.9947(19), P2-S3 2.001(2), C20-P3 1.740(5), C20-P4 1.742(5), P3-S5 1.997(2), P4-S6 1.995(2), C1-S1 1.753(5), C20-S4 1.771(5), P2-C1-P1 115.0(3), C1-P1-S2 106.79(18), P1-S2-Zr1 81.24(6), C1-P2-S3 107.18(18), P2-S3-Zr1 80.39(6), C1-S1-Zr1 66.44(17), S1-C1-Zr1 72.19(17), S1-Zr1-C1 41.37(12).

2. **Figure S2.** Molecular structure of **5** with thermal ellipsoids at the 50% probability level.



Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1-N1 2.3766(13), Zr1-C1 2.2243(15), Zr1-C26 2.4126(15), Zr1-S1 2.6280(4), Zr1-S2 2.6151(4), Zr1-S3 2.7133(4), Zr1-S5 2.5275(4), C1-P1 1.6718(14), C1-P2 1.6639(15), C26-P3 1.7551(16), C26-P4 1.7715(15), C26-S5 1.7690(15), C26-Zr1-S5 41.89(3), Zr1-S5-C26 65.58(5), S5-C26-Zr1 72.54(5), P3-C26-P4 110.82(8), P3-C26-Zr1 96.46(7), P4-C26-Zr1 124.12(7), P1-C1-P2 156.25(10), P1-C1-Zr1 100.98(7), P2-C1-Zr1 102.77(7), C1-P1-S1 104.05(6), C1-P2-S2 102.76(5), C1-Zr1-S1 73.82(4), C1-Zr1-S2 73.27(4), C26-Zr1-N1 99.78(5), C1-Zr1-N1 99.10(5).

3. **Table S1.** Crystallographic data of **2**, **3**, **5**, **6** and **8**.

	2	**3**	**5**	**6**	**8**
formula	$C_{38}H_{28}HfP_4S_6$	$C_{38}H_{28}P_4S_6Zr$	$C_{53}H_{49}HfNP_4S_5$	$C_{53}H_{49}NP_4S_5Zr$	$C_{40}H_{32}Cl_4P_4S_6Sn$
formula weight	979.33	892.06	1162.60	1075.33	1089.38
color	yellow	yellow	yellow	yellow	red
crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*-1	*P*-1	*P*2(1)/*n*
a / Å	12.6474(2)	12.6708(13)	10.2767(4)	10.2451(2)	11.9643(5)
b / Å	20.4070(3)	20.4641(17)	14.8249(6)	14.8428(3)	12.8350(6)
c / Å	15.6269(2)	15.6111(15)	16.7593(7)	16.7675(3)	14.6553(5)
α / deg	90	90	82.255(3)	82.3140(10)	90
β / deg	113.0550(10)	112.891(6)	85.970(2)	86.1890(10)	90.804(2)
γ / deg	90	90	86.652(2)	86.6900(10)	90
V / Å^3	3711.09(9)	3729.1(6)	2520.66(18)	2518.19(8)	2250.27(16)
Z	4	4	2	2	2
d_{calcd} /mg cm^{-3}	1.753	1.589	1.532	1.418	1.608
μ / mm^{-1}	3.351	0.832	2.441	0.590	1.256
F(000)	1936	1808	1172	1108	1092
crystal size / mm^3	0.20 x 0.16 x 0.10	0.04 x 0.02 x 0.02	0.30 x 0.14 x 0.10	0.40 x 0.40 x 0.30	0.18 x 0.20 x 0.22
Index ranges	$-18 \le h \le 18$	$-17 \le h \le 17$	$-14 \le h \le 11$	$-16 \le h \le 17$	$-14 \le h \le 14$
	$-29 \le k \le 28$	$-28 \le k \le 23$	$-20 \le k \le 20$	$-23 \le k \le 24$	$-16 \le k \le 16$
	$-22 \le l \le 22$	$-19 \le l \le 21$	$-23 \le l \le 23$	$-28 \le l \le 24$	$-18 \le l \le 13$
no. of rflns collected	81778	39502	55479	52967	24725
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0210, 0.0485	0.0663, 0.0953	0.0587, 0.1029	0.0430, 0.0943	0.0290, 0.0659
*R*1, *wR*2 (all data)	0.0238, 0.0497	0.1904, 0.1281	0.1054, 0.1200	0.0644, 0.1044	0.0363, 0.0698
goodness of fit., F^2	1.131	0.938	1.027	1.014	1.037
no. of data / restraints / params	11921/0/442	10454/0/442	14359/824/705	23545/1174/759	4602/238/307
largest diff peak, hole / eÅ^{-3}	1.472, -0.953	0.749, -0.724	1.856, -2.115	0.791, -0.749	0.543, -0.365