Supplementary information

Novel carbon-centred reactivity of $[(H)C(PPh_2Se)_2]^-$ in the formation of structurally diverse Sn(IV), Te(IV) and Hg(II) complexes of the triseleno ligand $[(Se)C(PPh_2Se)_2]^{2-}$

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General Procedures. All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. The compounds H₂C(PPh₂)₂ (Aldrich, 97%), TMEDA (Aldrich, 99%), TMTU (tetramethyl thiourea, Aldrich, 98%), MeLi (Aldrich, 1.6 M sol. in Et₂O), SnCl₂ (Aldrich, 99.99%), TeO₂ (Alfa Aeasar, 99.99%) and HgCl₂ (Strem Chemicals, 99+%) were used as received. TMEDA·Li[(H)C(PPh₂)₂] was prepared by the reaction between H₂C(PPh₂)₂ and MeLi in the presence of TMEDA in Et₂O,¹ and TMEDA·Li[(H)C(PPh₂Se)₂] was produced by oxidative addition of elemental selenium to the anion [(H)C(PPh₂)₂]⁻² The compounds Hg[(H)C(PPh₂Se)₂]₂ ² and TMTU·TeCl₂ ³ were synthesized by following literature procedures. The solvents *n*-hexane, toluene, Et₂O and THF were dried by distillation over Na/benzophenone under an argon atmosphere prior to use. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary.

Spectroscopic Methods. The ¹H, ¹³C{¹H}, ³¹P{¹H} and ⁷⁷Se{¹H} NMR spectra were obtained in d₈-THF, d₆-DMSO and CD₂Cl₂ at 23 °C on a Bruker DRX 400 spectrometer operating at 399.46, 100.46, 161.71 and 76.17 MHz, respectively. ¹H and ¹³C spectra are referenced to the solvent signal and the chemical shifts are reported relative to $(CH_3)_4Si$. ³¹P{¹H} and ⁷⁷Se{¹H} NMR spectra are referenced externally and the chemical shifts are reported relative to an 85% solution of H₃PO₄ and to neat Me₂Se, respectively.

X-ray Crystallography. The crystals of $\{Sn[(Se)C(PPh_2Se)_2]_2 \cdot (C_7H_8)_2\}$ (6·(C₇H₈)₂), $\{Te[(Se)C(PPh_2Se)_2]_2 \cdot (C_7H_8)\}$ (7·(C₇H₈)) and $\{Hg[(Se)C(PPh_2Se)_2] \cdot (THF)\}_2$ (8·(THF)₂) were coated with Paratone 8277 oil and mounted on a glass fiber. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated MoK_{α} radiation ($\lambda = 0.71073$ Å) (6·(C₇H₈)₂) and on a Bruker AXS APEX2 CCD diffractometer using monochromated CuK_{α} radiation ($\lambda = 1.54180$ Å) (7·(C₇H₈) and 8·(THF)₂) at -100 °C. The data sets were corrected for Lorentz and polarization effects, and empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97 ⁴ and refined using SHELXL-97.⁵ After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (C-H = 0.98 Å for -CH₃, 0.95 Å for phenyl and 0.99 Å for -CH₂ hydrogens). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times to that of the corresponding carbon for phenyl and -CH₂ hydrogens, and 1.5 times for -CH₃ hydrogens. In the final refinement the hydrogen atoms were riding on their respective carbon atoms. The structure of 7·(C₇H₈) shows two independent {Te[(Se)C(PPh₂Se)₂]₂} molecules in which one of selenium atoms (molecule 2, Se9A/Se9B) exhibits positional disorder with site occupancy factors of *ca.* 0.6:0.4 in the final refinement. Crystallographic data are summarized in Table S1.

Attempted Synthesis of {Sn[(H)C(PPh₂Se)₂]₂} (5c).

A suspension of SnCl₂ (0.038 g, 0.20 mmol) in 10 mL of toluene was cooled to -80 °C and a solution of TMEDA·Li[(H)C(PPh₂Se)₂] (0.266 g, 0.40 mmol) in 20 mL of toluene was added via cannula. The reaction mixture was stirred for ½ h at -80 °C and 1 h at 23 °C. Small amount of red powder (0.020 g) was allowed to settle the solution was decanted via cannula (through a PTFE-filter). Solvent evaporation resulted in an orange-yellow, amorphous powder (0.156 g), which contained a mixture of **6** and the neutral $[(H_2)C(PPh_2)(PPh_2Se)]$ (³¹P NMR: δ 31.2 [d, ²J(³¹P,³¹P) = 82.8 Hz, ¹J(³¹P,⁷⁷Se) = 752 Hz], -25.3 [d, ²J(³¹P,³¹P) = 82.8 Hz]⁶).

NMR data for {Sn[(H)C(PPh₂Se)₂]₂} (**5c**): ¹H NMR (d₈-THF, 23 °C): δ 7.20-7.95 [m, 40H, C₆H₅], 2.44 [s, 2H, -CH of the PCP carbon]. ³¹P NMR (23 °C): δ 26.2 [s, ¹J(³¹P,⁷⁷Se) = 532 Hz, ²J(³¹P,³¹P) = 23.1 Hz, ²J(³¹P,^{117/119}Sn) = 128.0 Hz]. ⁷⁷Se NMR (23 °C): δ -51.2 [d, ¹J(⁷⁷Se,³¹P) = 534 Hz]. ¹¹⁹Sn NMR (23 °C): δ -94.7 (s, br). Repeated attempts to crystallize **5c** resulted in the formation red crystals of {Sn[(Se)C(PPh₂Se)₂]₂} (**6**) as proven by unit cell measurements as well as a full data collection.

Synthesis of $\{Sn[(Se)C(PPh_2Se)_2]_2 \cdot (C_7H_8)_2\}$ (6·(C₇H₈)₂).

A suspension of $SnCl_2$ (0.076 g, 0.40 mmol) in 10 mL of toluene was cooled to -80 °C and a solution of TMEDA·Li[(H)C(PPh_2Se)_2] (0.532 g, 0.80 mmol) in 50 mL of toluene was added via cannula. The reaction mixture was stirred for $\frac{1}{2}$ h at -80 °C and 6 h at 55 °C. The red powder was

allowed to settle and the solution was decanted via cannula. The product was dissolved to 60 mL of CH₂Cl₂ followed by filtration through a PTFE-disk. The solvent was evaporated and the product was washed with toluene to afford $6 \cdot (C_7H_8)_2$ as a red powder (0.157 g, 51%, calculated by taking into account the selenium/hydrogen exchange and subsequent formation of the [(H₂)C(PPh₂)(PPh₂Se)] byproduct). Anal. Calcd for C₆₄H₅₆P₄Se₆Sn: C 49.87; H 3.66. Found: C 49.42; H 3.72. ¹H NMR (CD₂Cl₂, 23 °C): δ 6.86-8.23 [m, 40H, C₆H₅ of **6** and 10H, C₆H₅ of two toluene solvates], 2.33 [s, 6H, CH₃ of two toluene solvates]. ³¹P NMR (23 °C): δ 61.6 [s, ¹J(³¹P,⁷⁷Se) = 536 Hz, ²J(³¹P,³¹P) = 33.2 Hz]. X-ray quality crystals were obtained by layering toluene on top of a THF solution of $7 \cdot (C_7H_8)_2$ for 2 h at +5 °C.

Synthesis of $\{Te[(Se)C(PPh_2Se)_2]_2\}$ (7·(C₇H₈)).

A suspension of TMTU·TeCl₂ (0.132 g, 0.40 mmol) in 10 mL of toluene was cooled to -80 °C and a solution of TMEDA·Li[(H)C(PPh₂Se)₂] (0.532 g, 0.80 mmol) in 50 mL of toluene was added via cannula. The reaction mixture was stirred for $\frac{1}{2}$ h at -80 °C and 15 h at 23 °C. The solvent was removed by evaporation and the dark red, amorphous powder was dissolved to 60 mL of CH₂Cl₂. The solution was filtered through a PTFE-disk and the solvent was evaporated under vacuum. The product was washed with hexane and toluene to afford 7·(C₇H₈) as a brownish-red powder (0.137 g, 47%, calculated by taking into account the selenium/hydrogen exchange and subsequent formation of the [(H₂)C(PPh₂)(PPh₂Se)] byproduct). Anal. Calcd for C₅₀H₄₀P₄Se₆Te: C 43.96; H 2.95. Found: C 43.52; H 3.12. ¹H NMR (d₈-THF, -10 °C): δ 6.86-8.20 [m, 40H, C₆H₅ of 7 and 5H, C₆H₅ of a toluene solvate], 2.31 [s, 3H, CH₃ of a toluene solvate]. ³¹P NMR (-10 °C): δ 64.3 [d, ¹J(³¹P,⁷⁷Se) = 500 Hz, ²J(³¹P,³¹P) = 39.0 Hz], 53.3 [d, ¹J(³¹P,⁷⁷Se) = 679 Hz, ²J(³¹P,³¹P) = 39.0 Hz]. ⁷⁷Se NMR (-10 °C): δ 223.1 [d, ¹J(⁷⁷Se,³¹P) = 499 Hz], -195.3 [d, ¹J(⁷⁷Se,³¹P) = 678 Hz], -313.5 (s).

Synthesis of {Hg[(Se)C(PPh₂Se)₂]}₂ (8).

Method A. A solution of $\{Hg[(H)C(PPh_2Se)_2]_2\}$ (0.257 g, 0.20 mmol) in 35 mL of toluene (or THF) was heated to 65 °C for 48 hours resulting in a yellow powder and an off-white solution. The powder was allowed to settle and the solution was decanted via a cannula. The product was washed with THF (to remove $[(H_2)C(PPh_2)(PPh_2Se)]$ byproduct) to afford **8** as a yellow powder (0.113 g, 69%). Anal. Calcd for $C_{50}H_{40}P_4Se_6Hg_2$: C 36.62; H 2.46. Found: C 36.46; H 2.56. ¹H NMR (d₆-DMSO, 70 °C): δ 6.94-8.20 [m, 40H, C₆H₅]. ³¹P NMR (70 °C): δ 52.5 (s, br, weak). **Method B.** A mixture of $\{Hg[(H)C(PPh_2Se)_2]_2\}$ (0.257 g, 0.20 mmol) and elemental selenium (0.016 g, 0.20 mmol) in 35 mL of toluene was heated to 65 °C for 20 hours resulting in a yellow powder and an off-white solution. The powder was allowed to settle and the solution was decanted via a cannula. The product was washed with THF (to remove $[(H_2)C(PPh_2Se)_2]$ byproduct) to afford **8** as a yellow powder (0.139 g, 85%).

X-ray quality crystals of $\{Hg[(Se)C(PPh_2Se)_2] \cdot (THF)\}_2$ (8·(THF)₂) were obtained by keeping a solution of $\{Hg[(H)C(PPh_2Se)_2]_2\}$ in THF at 100 °C undisturbed for 24 hours.

References

- (1) D. J. Brauer, S. Hietkamp and O. Stelzer, J. Organomet. Chem., 1986, 299, 137.
- (2) J. Konu, H. M. Tuononen and T. Chivers, *Inorg. Chem.*, 2009, 48, 11788.
- (3) O. Foss and W. Johannessen, *Acta Chem. Scand.*, 1961, **15**, 1940.
- (4) Sheldrick, G. M. SHELXS-97, *Program for Crystal Structure Determination*, University of Göttingen, Germany, 1997.
- (5) Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.
- (6) S. O. Grim and E. D. Walton, *Inorg. Chem.*, 1980, **19**, 1982.

	$6 \cdot (\mathbf{C}_7 \mathbf{H}_8)_2 \overset{a}{}$	$7 \cdot (\mathbf{C}_7 \mathbf{H}_8)^{b}$	$8 \cdot (\mathrm{C_4H_8O})_2 \ ^b$
emp. formula	$C_{64}H_{56}P_4Se_6Sn$	$C_{57}H_{48}P_4Se_6Te$	$C_{58}H_{56}Hg_2O_2P_4Se_6$
fw	1541.42	1458.19	1783.85
cryst. system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	P-1	$P2_1/n$
a, Å	15.803(3)	13.002(3)	16.115(3)
b, Å	11.518(2)	17.066(3)	11.323(2)
<i>c</i> , Å	16.376(3)	24.900(5)	16.189(3)
α, deg.	90.00	79.57(3)	90.00
β, deg.	91.70	87.46(3)	94.99(3)
γ, deg.	90.00	85.93(3)	90.00
<i>V</i> , Å ³	2979.4(9)	5417(2)	2943(1)
Ζ	2	4	2
T, ⁰C	-100	-100	-100
$\rho_{calcd}, g/cm^3$	1.718	1.788	2.013
μ , mm ⁻¹	4.241 ^c	10.351 ^{<i>d</i>}	14.814^d
crystal size, mm ³	0.24×0.12×0.02	0.23×0.20×0.12	0.06×0.04×0.02
<i>F</i> (000)	1508	2824	1688
Θ range, deg	2.50-25.03	1.80-68.04	3.71-68.13
reflns collected	9927	65323	19188
unique reflns	5232	18963	5278
R _{int}	0.0289	0.0711	0.0312
reflns [$I > 2\sigma(I)$]	4479	13674	4821
$R_1 [I > 2\sigma(I)]$	0.0488	0.0478	0.0230
wR_2 (all data)	0.1287	0.1141	0.0545
GOF on F^2	1.076	1.032	1.052
completeness	0.995	0.959	0.980

Table	S1.	Crystallographic	data	for	$\{Sn[(Se)C(PPh_2Se)_2]_2 \cdot (C_7H_8)_2\}$	$(6 \cdot (C_7 H_8)_2),$
{Te[(Se)	C(PPh ₂ S	Se) ₂] ₂ ·(C ₇ H ₈)} (7·(C ₇	H ₈)) and	l {Hg[(Se)C(PPh ₂ Se) ₂]·THF} ₂ (8 ·(C ₄ H ₈ O) ₂)). ^{<i>a</i>}

 $\overline{}^{a} \lambda (MoK\alpha) = 0.71073 \text{ Å}. {}^{b} \lambda (CuK\alpha) = 1.54180 \text{ Å}. {}^{c} (MoK\alpha). {}^{d} (CuK\alpha)$

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	6 ·(C ₇ H ₈) ₂	$7 \cdot (C_7 H_8)$	$8 \cdot (C_4 H_8 O)_2$
M(1)-Se(1)	2.812(1)	2.744(1)	2.5682(8)
M(1)-Se(2)	2.810(1)	3.463(1)	2.5781(7) ^{<i>a</i>}
M(1)-Se(3)	2.637(1)	2.637(1)	2.8458(9)
P(1)-Se(1)	2.181(2)	2.226(2)	2.217(1)
P(2)-Se(2)	2.187(2)	2.133(2)	2.208(1)
C(1)-Se(3)	1.929(6)	1.890(5)	1.936(3)
P(1)-C(1)	1.749(6)	1.744(6)	1.729(3)
P(2)-C(1)	1.749(5)	1.760(6)	1.722(3)
Hg(1)-Se(3)	-		2.7271(6) ^b
Se(1)-M(1)-Se(2)	91.09(3)	-	-
Se(1)-M(1)-Se(3)	86.25(3)	87.34(4)	95.70(2)
Se(2)-M(1)-Se(3)	87.76(2)	-	95.78(2) ^{<i>a</i>}
Se(1)-M(1)-Se(2)'	88.91(3) ^c	167.21(3) ^d	138.92(2)
Se(1)-M(1)-Se(3)'	93.75(3) ^c	89.93(3) ^e	109.45(1)
Se(2)-M(1)-Se(3)'	92.24(2) ^c	-	104.19(2) ^{<i>a</i>}
Se(1)-M(1)-Se(1)'	180.0 ^c	-	-
Se(2)-M(1)-Se(2)'	180.0 ^c	-	-
Se(3)-M(1)-Se(3)'	180.0 ^c	93.82 ^e	-
M(1)-Se(1)-P(1)	94.61(5)	96.44(5)	92.05(3)
M(1)-Se(2)-P(2)	94.33(5)	-	92.23(3)
M(1)-Se(3)-C(1)	94.0(2)	100.9(2)	95.1(1)
C(1)-P(1)-Se(1)	114.0(2)	114.0(2)	118.3(1)
C(1)-P(2)-Se(2)	113.7(2)	116.1(2)	118.3(1)
P(1)-C(1)-P(2)	123.1(3)	123.7(3)	130.1(2)
P(1)-C(1)-Se(3)	108.4(3)	107.7(3)	110.6(2)
P(2)-C(1)-Se(3)	109.4(3)	110.4(3)	112.0(2)
Hg(1)-Se(3)-Hg(1A)	-	-	67.67(1)

Table S2. Selected bond lengths (Å) and angles (°) in $6 \cdot (C_7H_8)_2$, $7 \cdot (C_7H_8)$ and $8 \cdot (C_4H_8O)_2$.

 $\overline{}^{a}$ M =Hg(1A). Symmetry operation for the atom marked with single quote ('):^b 1-x,1-y,-z.^c -x,1-y,-z.

^{*d*} Se(2)' = Se(4).^{*e*} Se(3)' = Se(6).



Figure S1. Crystal structure of $6 \cdot (C_7H_8)_2$ drawn with 50 % thermal ellipsoid. Hydrogen atoms and toluene solvates have been omitted for clarity. Symmetry operation (A): -x,1-y,-z.



Figure S2. Molecular structure of $7 \cdot (C_7H_8)$ drawn with 50% thermal ellipsoids. Hydrogen atoms and toluene solvate have been omitted for clarity.



Figure S3. Molecular structure of $8 \cdot (THF)_2$ drawn with 50% thermal ellipsoids. Hydrogen atoms and THF solvate have been omitted for clarity. Symmetry operation (A): 1-x,1-y,-z