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 $H_2C(PPh_2)_2$ (Aldrich, 97%), TMEDA (Aldrich, 99%), TMTU (tetramethyl thiourea, Aldrich, 98%), MeLi (Aldrich, 1.6 M sol. in Et_2O), $SnCl_2$ (Aldrich, 99.99%), TeO_2 (Alfa Aeasar, 99.99%) and $HgCl_2$ (Strem Chemicals, 99+%) were used as received. TMEDA·Li$[(H)C(PPh_2)_2]$ was prepared by the reaction between $H_2C(PPh_2)_2$ and MeLi in the presence of TMEDA in Et_2O,[1] and TMEDA·Li$[(H)C(PPh_2Se)_2]$ was produced by oxidative addition of elemental selenium to the anion $[(H)C(PPh_2)_2]^-$.[2] The compounds $Hg[(H)C(PPh_2Se)_2]_2$ [2] and TMTU·$TeCl_2$ [3] were synthesized by following literature procedures. The solvents *n*-hexane, toluene, Et_2O 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, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were obtained in d_8-THF, d_6-DMSO and CD_2Cl_2 at 23 ºC on a Bruker DRX 400 spectrometer operating at 399.46, 100.46, 161.71 and 76.17 MHz, respectively. ^1H and ^{13}C spectra are referenced to the solvent signal and the chemical shifts are reported relative to $(CH_3)_4Si$. $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra are referenced externally and the chemical shifts are reported relative to an 85% solution of H_3PO_4 and to neat Me_2Se, respectively.

X-ray Crystallography. The crystals of $\{Sn[(Se)C(PPh_2Se)_2]_2\cdot(C_7H_8)_2\}$ (**6**·$(C_7H_8)_2$), $\{Te[(Se)C(PPh_2Se)_2]_2\cdot(C_7H_8)\}$ (**7**·(C_7H_8)) 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 (λ = 0.71073 Å) (**6**·$(C_7H_8)_2$) and on a Bruker AXS APEX2 CCD diffractometer using monochromated CuK_α

radiation (λ = 1.54180 Å) (**7**·(C_7H_8) 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 -CH_3, 0.95 Å for phenyl and 0.99 Å for -CH_2 hydrogens). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times to that of the corresponding carbon for phenyl and -CH_2 hydrogens, and 1.5 times for -CH_3 hydrogens. In the final refinement the hydrogen atoms were riding on their respective carbon atoms. The structure of **7**·(C_7H_8) shows two independent {Te[(Se)C(PPh_2Se)$_2$]$_2$} 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(PPh_2Se)$_2$]$_2$} (5c).

A suspension of $SnCl_2$ (0.038 g, 0.20 mmol) in 10 mL of toluene was cooled to -80 °C and a solution of TMEDA·Li[(H)C(PPh_2Se)$_2$] (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)] (^{31}P NMR: δ 31.2 [d, $^2J(^{31}P,^{31}P)$ = 82.8 Hz, $^1J(^{31}P,^{77}Se)$ = 752 Hz], -25.3 [d, $^2J(^{31}P,^{31}P)$ = 82.8 Hz][6]).

NMR data for {Sn[(H)C(PPh_2Se)$_2$]$_2$} (**5c**): ^{1}H NMR (d_8-THF, 23 °C): δ 7.20-7.95 [m, 40H, C_6H_5], 2.44 [s, 2H, -C*H* of the PCP carbon]. ^{31}P NMR (23 °C): δ 26.2 [s, $^1J(^{31}P,^{77}Se)$ = 532 Hz, $^2J(^{31}P,^{31}P)$ = 23.1 Hz, $^2J(^{31}P,^{117/119}Sn)$ = 128.0 Hz]. ^{77}Se NMR (23 °C): δ -51.2 [d, $^1J(^{77}Se,^{31}P)$ = 534 Hz]. ^{119}Sn NMR (23 °C): δ -94.7 (s, br). Repeated attempts to crystallize **5c** resulted in the formation red crystals of {Sn[(Se)C(PPh_2Se)$_2$]$_2$} (**6**) as proven by unit cell measurements as well as a full data collection.

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

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 ½ 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 CH_2Cl_2 followed by filtration through a PTFE-disk. The solvent was evaporated and the product was washed with toluene to afford **6**·$(C_7H_8)_2$ as a red powder (0.157 g, 51%, calculated by taking into account the selenium/hydrogen exchange and subsequent formation of the $[(H_2)C(PPh_2)(PPh_2Se)]$ byproduct). Anal. Calcd for $C_{64}H_{56}P_4Se_6Sn$: C 49.87; H 3.66. Found: C 49.42; H 3.72. ^{1}H NMR (CD_2Cl_2, 23 ^{o}C): δ 6.86-8.23 [m, 40H, C_6H_5 of **6** and 10H, C_6H_5 of two toluene solvates], 2.33 [s, 6H, CH_3 of two toluene solvates]. ^{31}P NMR (23 ^{o}C): δ 61.6 [s, $^1J(^{31}P,^{77}Se)$ = 536 Hz, $^2J(^{31}P,^{31}P)$ = 33.2 Hz]. X-ray quality crystals were obtained by layering toluene on top of a THF solution of **7**·$(C_7H_8)_2$ for 2 h at +5 ^{o}C.

Synthesis of {Te[(Se)C(PPh$_2$Se)$_2$]$_2$} (7·(C$_7$H$_8$)).

A suspension of TMTU·$TeCl_2$ (0.132 g, 0.40 mmol) in 10 mL of toluene was cooled to -80 ^{o}C and a solution of TMEDA·Li[(H)C(PPh$_2$Se)$_2$] (0.532 g, 0.80 mmol) in 50 mL of toluene was added via cannula. The reaction mixture was stirred for ½ h at -80 ^{o}C and 15 h at 23 ^{o}C. The solvent was removed by evaporation and the dark red, amorphous powder was dissolved to 60 mL of CH_2Cl_2. 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**·(C_7H_8) as a brownish-red powder (0.137 g, 47%, calculated by taking into account the selenium/hydrogen exchange and subsequent formation of the $[(H_2)C(PPh_2)(PPh_2Se)]$ byproduct). Anal. Calcd for $C_{50}H_{40}P_4Se_6Te$: C 43.96; H 2.95. Found: C 43.52; H 3.12. ^{1}H NMR (d_8-THF, -10 ^{o}C): δ 6.86-8.20 [m, 40H, C_6H_5 of **7** and 5H, C_6H_5 of a toluene solvate], 2.31 [s, 3H, CH_3 of a toluene solvate]. ^{31}P NMR (-10 ^{o}C): δ 64.3 [d, $^1J(^{31}P,^{77}Se)$ = 500 Hz, $^2J(^{31}P,^{31}P)$ = 39.0 Hz], 53.3 [d, $^1J(^{31}P,^{77}Se)$ = 679 Hz, $^2J(^{31}P,^{31}P)$ = 39.0 Hz]. ^{77}Se NMR (-10 ^{o}C): δ 223.1 [d, $^1J(^{77}Se,^{31}P)$ = 499 Hz], -195.3 [d, $^1J(^{77}Se,^{31}P)$ = 678 Hz], -313.5 (s).

Synthesis of {Hg[(Se)C(PPh$_2$Se)$_2$]}$_2$ (8).

Method A. A solution of {Hg[(H)C(PPh$_2$Se)$_2$]$_2$} (0.257 g, 0.20 mmol) in 35 mL of toluene (or THF) was heated to 65 ^{o}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. ^{1}H NMR (d_6-DMSO, 70 ^{o}C): δ 6.94-8.20 [m, 40H, C_6H_5]. ^{31}P NMR (70 ^{o}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 ^oC 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**$\cdot(THF)_2$) were obtained by keeping a solution of $\{Hg[(H)C(PPh_2Se)_2]_2\}$ in THF at 100 ^oC undisturbed for 24 hours.

References

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Table S1. Crystallographic data for $\{Sn[(Se)C(PPh_2Se)_2]_2\cdot(C_7H_8)_2\}$ (**6**·$(C_7H_8)_2$), $\{Te[(Se)C(PPh_2Se)_2]_2\cdot(C_7H_8)\}$ (**7**·(C_7H_8)) and $\{Hg[(Se)C(PPh_2Se)_2]\cdot THF\}_2$ (**8**·$(C_4H_8O)_2$).[a]

	6·$(C_7H_8)_2$ [a]	**7**·(C_7H_8) [b]	**8**·$(C_4H_8O)_2$ [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)
c, 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
V, $Å^3$	2979.4(9)	5417(2)	2943(1)
Z	2	4	2
T, °C	-100	-100	-100
ρ_{calcd}, g/cm^3	1.718	1.788	2.013
μ, mm^{-1}	4.241[c]	10.351[d]	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
F(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

[a] λ (MoKα) = 0.71073 Å. [b] λ (CuKα) = 1.54180 Å. [c] (MoKα). [d] (CuKα)

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

	6·$(C_7H_8)_2$	**7**·(C_7H_8)	**8**·$(C_4H_8O)_2$
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) [a]
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) [a]
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) [a]
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)

[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).

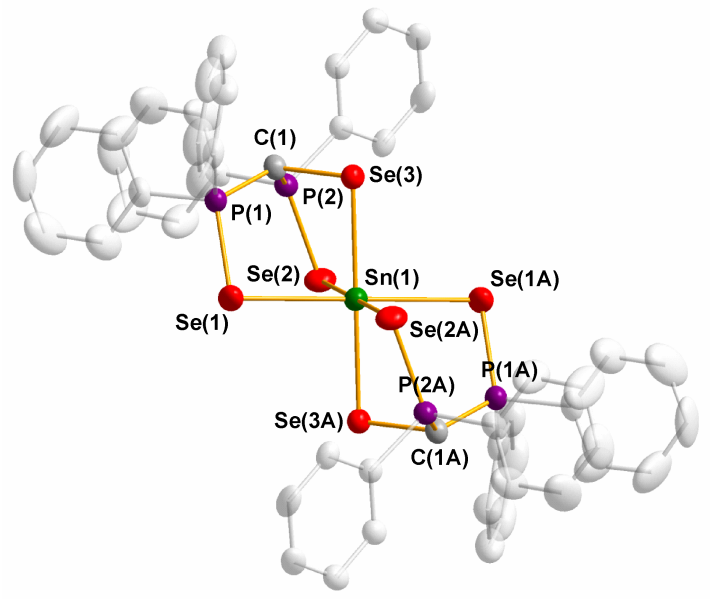

Figure S1. Crystal structure of **6**·$(C_7H_8)_2$ drawn with 50 % thermal ellipsoid. Hydrogen atoms and toluene solvates have been omitted for clarity. Symmetry operation (A): -x,1-y,-z.

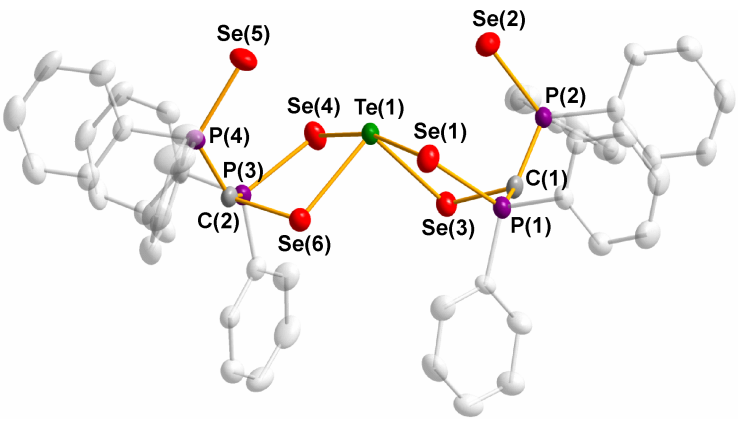

Figure S2. Molecular structure of **7**·(C_7H_8) drawn with 50% thermal ellipsoids. Hydrogen atoms and toluene solvate have been omitted for clarity.

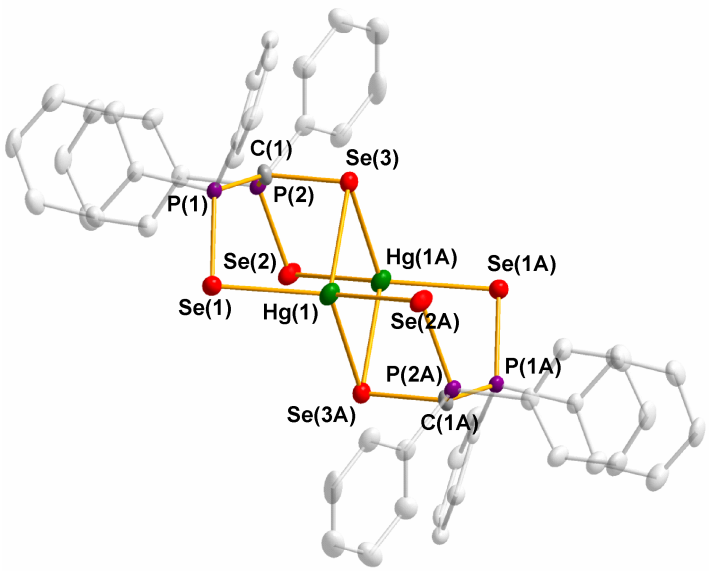

Figure S3. Molecular structure of **8**·$(THF)_2$ drawn with 50% thermal ellipsoids. Hydrogen atoms and THF solvate have been omitted for clarity. Symmetry operation (A): 1-x,1-y,-z