Supporting Information

Peri-substituted phosphorus-tellurium systems – an experimental and theoretical investigation of the P···Te through-space interaction.

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I. Experimental Section

A. Materials and Methods

A.1 NMR Spectroscopy

NMR spectra were recorded using a *JEOL DELTA EX 270* a *Bruker Avance 360* spectrometer, a *BRUKER Avance II 400* spectrometer, a *BRUKER Avance 500* or a *BRUKER Avance III 500* spectrometer. ^{1}H, ^{13}C, ^{31}P{^{1}H}, ^{77}Se{^{1}H}, ^{195}Pt{^{1}H} and ^{123}Te{^{1}H} as well as ^{125}Te{^{1}H} NMR spectra were measured in deuterated solvents or using the reaction mixture and capillaries filled with C_6D_6 at 25 °C. TMS was used as an internal standard for ^{1}H and ^{13}C NMR. 85 % H_3PO_4 was used as an external standard for ^{31}P{^{1}H} NMR spectra, Ph_2Te_2 or Me_2Te for ^{123}Te{^{1}H} and ^{125}Te{^{1}H} NMR spectra, Me_2Se for ^{77}Se{^{1}H} NMR spectra as well as Na_2PtCl_6 for ^{195}Pt{^{1}H} NMR spectra. As secondary references diphenyldiselenide in $CDCl_3$ and hexahydroxytelluride in D_2O was used. All ^{77}Se{^{1}H}, ^{123}Te{^{1}H}, ^{125}Te{^{1}H}, ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR spectra are reported as ^{77}Se, ^{123}Te, ^{125}Te, ^{195}Pt and ^{31}P NMR spectra in the experimental part. Chemical shifts (δ) are given in parts per million (ppm) relative to the solvent peaks.[1] Coupling constants (J) are given in Hertz (Hz).

^{31}P solid-state NMR spectra were acquired using a *Bruker AMX 300*, a *400 MHz Bruker Avance III* or a *Bruker Avance III 600 MHz* spectrometer operating at magnetic field strength of 7.05 T, 9.4 T and 14.1 T, corresponding to Larmor frequencies of 121.5, 161.9 and 242.9 MHz, respectively. Experiments were carried out using either *Bruker* 4 mm or 1.9 mm (outside diameter) zirconia rotors, with MAS rates between 10 and 40 kHz. The pulse sequence used was either cross-polarisation magic-angle spinning (CP MAS) or conventional magic-angle spinning. Chemical shifts are referenced to 85 % H_3PO_4 at 0 ppm using the isotropic resonance of solid BPO_4 at −29.6 ppm and solid $NH_4H_2PO_4$ at 0.8 ppm as a secondary reference. ^{31}P spectra were acquired using a $\pi/2$ pulse lengths of 2.1 μs (14.1 T) and 3.1 μs (9.4 T), with between 40 and 80 transients separated by recycle intervals of between 10 and 60 s, depending on the individual samples. For all spectra, the position of the isotropic resonances within the spinning sideband patterns was unambiguously determined by recording a second spectrum at a higher MAS rate.

^{125}Te solid-state NMR spectra were acquired using *Bruker Avance III* spectrometers operating at magnetic field strength of 9.4 T, corresponding to a Larmor frequency of 126.2 MHz. Experiments were carried out using conventional 4 mm zirconia rotors, with a MAS rate of 10.5 kHz. Chemical shifts are referenced relative to $(CH_3)_2Te$ at 0 ppm, using the isotropic resonance of solid $Te(OH)_6$ (site 1) at 692.2 ppm as a secondary reference. Transverse magnetisation was obtained by CP from ^{1}H using an optimized contact pulse duration of 8 ms, and two-pulse phase modulation (TPPM) ^{1}H decoupling during acquisition. Spectra were acquired with 8192 transients separated by recycle intervals of 3 s. The position of isotropic resonances within the spinning sideband patterns was

unambiguously determined by recording a second spectrum at a different MAS rate. Experimental ^{125}Te NMR parameters were determined by line shape analysis using *Bruker Topspin* software.

A.2 MASS SPECTROMETRY

Mass spectrometry was performed on a *MICROMASS LCT* (ESI) and *MICROMAS GCT* (EI, CI) device by the University of St Andrews Mass Spectrometry Service. Air sensitive compounds were run on a *Finnigan MAT 95 XP,* an *Agilent 5975C Inert XL GC/MSD* or a *Thermofisher LTQ Orbitrap XL* at the EPSRC UK National MS Facility in Swansea.

Electron impact mass spectroscopy (EIMS) for the compounds **4b**, **6b** and **7b** was carried out using a *Finnigan MAT 95*. The ESI MS spectra were obtained with a *Bruker Esquire-LC MS*.

A.3 ELEMENTAL ANALYSIS AND MELTING POINTS

Elemental analysis was performed on a CARBO ERBA CHNS analyser or at the Elemental Analysis Service of the London Metropolitan University (by Mr. S. Boyer). The determined values are given in percent (%). Melting or decomposition points were determined by sealing the sample in capillaries and heating using a *Stuart SMP 30* melting point apparatus, a *Büchi Melting point B-540* or a *Laboratory Devices Inc. MEL-TEMP*, Model 1001.

A.4 X-RAY CRYSTALLOGRAPHY

The crystallographic data was collected using the St Andrews Robotic diffractometer (*Rigaku Saturn724 CCD*, graphite monochromator) at −148(1) °C, or a *Rigaku Mo MM007* high brilliance generator with Mercury CCD detector, rotating anode/confocal optics at −100(1) °C, or a *Rigaku FR-X* (dual-port) Ultrahigh brilliance Microfocus RA generator/confocal optics and *Rigaku XtaLAB P200* system at either−180 °C or −100 °C, or a *Bruker-Nonius Kappa CCD* diffractometer at −100 °C. All data were collected with Mo-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarisation effects. The data for all of the compounds were collected and processed using *CrystalClear* (*Rigaku*),[2] or *XSCANS* (*Siemens*).[3]

The crystal structures were solved using direct methods,[4, 5, 6] or heavy-atom Patterson methods[7] and expanded using Fourier techniques.[8] The structures were refined by full-matrix least-squares against F^2.[6] The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using either *CrystalStructure*[9] or WinGX.[10]

A.5 GENERAL SYNTHETIC CONSIDERATIONS

All synthetic manipulations were performed under an atmosphere of dry argon using standard Schlenk-line techniques and/or a Saffron glovebox running with argon unless otherwise stated. All glass apparatus were stored in a drying oven (120 °C) and flame dried *in vacuo* (10^{-3} mbar) before use. Dry solvents were collected from an *MBraun* solvent purification system under a nitrogen atmosphere and stored in Schlenk flasks over 4 Å molecular sieves or were dried and purified using

common procedures.[11] All chemicals were purchased from *Sigma Aldrich, ABCR, Acros Organics* and *Strem Chemicals Inc.* or were taken from inventory of the laboratories and used without further purification as long as not otherwise stated. The products were stored in a glove box under argon atmosphere or argon fluted Schlenk- or J. Young tubes or flasks. The cooling bath temperature of −78 °C was gained by using an acetone/dry ice bath, the temperature of −40 °C by using an acetonitrile/dry ice bath.

B. Experimental Procedures

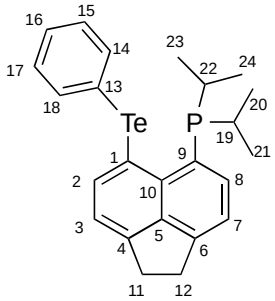
In the following reactions 5-Bromo-6-diisopropylphosphinoacenaphthene (abb. (^{i}Pr)$_2$P–Ace–Br)[12] or 5-Bromo-6-diphenylphosphinoacenaphthene (abb. Ph$_2$P–Ace–Br)[13] was used as a starting material, synthesized according to literature procedures. The ditellurides used were also prepared following literature procedures.[14]

B.0 General Reaction of (R)$_2$P–Acenap–Br with Ditellurides

To a cooled (−78 °C), rapidly stirring solution of (^{i}Pr)$_2$P–Acenap–Br (**P-5**) (500 mg, 1.43 mmol) in THF (15 ml) *n*-butyllithium (0.57 ml of 2.5 M solution in *n*-hexane, 1.43 mmol) was added dropwise over 10 min, and the mixture was left to stir for one hour at the same temperature.

The ditelluride (0.72 mmol, 1 eq. RTe) was dissolved in THF (10 mL) in another Schlenk flask and an iodine solution (182 mg, 0.72 mmol, 1 eq. I) in THF (10 mL) was added by syringe. After 30 min of stirring, the mixture containing the RTeI was cooled to −78 °C and then added *via* cannula to the rapidly stirred and cooled solution of (^{i}Pr)$_2$P–Acenap–Li. The reaction mixture was left to stir and warm up to room temperature overnight. The THF was removed under vacuum, DCM (30 mL) was added to the resulting oil/solid and the suspension filtered to remove LiI. After the removal of DCM under vacuum, *n*-hexane (20 mL) was added and the mixture stirred for 30 min. The mixture was cooled to 0 °C and the solid was filtered off using a Schlenk frit. The solid was dried under vacuum for about 3 h. Recrystallization from DCM at −35 °C to −40 °C for about two days afforded crystals that were filtered off and dried *in vacuo*. *(Note: All compounds show low solubility in n-hexane – The procedure as described above is the best to afford pure material; However higher yields can be gained by leaving the n-hexane washing out of the procedure).*

B.1 SYNTHESIS OF PHTE–ACENAP–P(^{i}PR)$_2$ (1)



Synthesis according to the general procedure: Diphenyl ditelluride (PhTeTePh) (293 mg, 0.72 mmol, 0.5 eq) was used as a starting material and was reacted with iodine (182 mg, 0.72 mmol, 0.5 eq.). (Yield 14 %)

M.p. 78 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 7.94 (m, 2H, H16, Ph*H*), 7.72 (d, 1H, ^{3}J(H,P) = 4.0 Hz, ^{3}J(H,H) = 7.1 Hz, H8, Acenap*H*), 7.41 (m, H15+17, Ph*H*), 7.38 (d, ^{3}J(H,H) = 7.4 Hz, H2, Acenap*H*), 7.36-7.33 (m, H14+18//H7, Ph*H* and Acenap*H*), 6.97 (d, 1H, ^{3}J(H,H) = 7.4 Hz, H3, Acenap*H*), 3.32 (m, 2H, H12, AcenapCH_2), 3.28 (m, 2H, H11, AcenapCH_2) 2.20 (m, 2H, H19+22, C*H*), 1.20 (dd, 6H, ^{3}J(H,P) = 15.5 Hz, ^{3}J(H,H) = 6.9 Hz, H21/23/20/24 CH_3), 0.99 (dd, 6H, ^{3}J(H,P) = 12.7 Hz, ^{3}J(H,H) = 7.0 Hz, H21/23/20/24, CH_3).

^{13}C NMR (125.71 MHz, $CDCl_3$): δ [ppm] = 149.1 (s, qC, C6), 145.1 (d, qC, ^{4}J(C,P) = 1.7 Hz, C4), 140.2 (d, qC, ^{3}J(C,P) = 7.9 Hz, C5), 139.9 (s, CH, C16), 139.5 (d, qC, ^{2}J(C,P) = 26.7 Hz, C10), 135.5 (s, CH, C2), 134.2 (d, CH, ^{2}J(C,P) = 2.9 Hz, C8), 131.4 (s, qC, J(C,P) = 103.6 Hz, C13), 129.5 (d, 2xCH, ^{4}J(C,P) = 4.1 Hz, C14+C18), 129.1 (qC, ^{3}J(C,P) = 13.1 Hz, C9), 127.8 (s, 2xCH, C15+C17), 120.7 (s, CH, C3), 119.0 (s, CH, C7), 113.6 (d, qC, ^{3}J(C,P) = 6.5 Hz, C1), 30.4 (s, CH_2, C12), 29.5 (s, CH_2, C11), 25.8 (d, CH, ^{1}J(C,P) = 12.4 Hz, C19+C22), 20.3 (d, CH_3, ^{2}J(C,P) = 16.8 Hz, C20/21/23/24), 19.7 (d, CH_3, ^{2}J(C,P) = 8.3 Hz, C20/21/23/24).

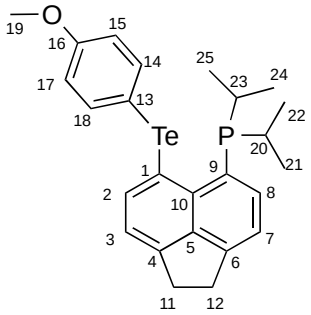
^{31}P NMR (109.37 MHz, [D_8]toluene): δ [ppm] = −20.8 (s, J(P,^{125}Te) = 1305.6 Hz, J(P,^{123}Te) = 1083.6 Hz, J(P,C) = 100.4 Hz).

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 597.4 (J(^{125}Te,P) = 1306.7 Hz).

HR-MS (ASAP, *m/z*), 477.0979 [M^++H] (calculated for $C_{24}H_{28}PTe$: 477.0987 [M^++H], 100%).

EA: Every sample was slightly contaminated, which prevented precise analysis.

B.2 SYNTHESIS OF *p*-AnTe–Acenap–P(^{i}Pr)$_2$ (2)



Synthesis according to the general procedure: Bis(4-methoxyphenyl)ditelluride (AnTeTepAn) (336 mg, 0.72 mmol, 0.5 eq) was used as the starting material. (Yield: 39 %)

M.p. 67 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 7.87 (dd, 2H, ^{3}J(H,H) = 8.6 Hz, J = 2.8 Hz, H14/18, An*H*), 7.71 (dd, 1H, J = 4.0 Hz, ^{3}J(H,H) = 7.1 Hz, H8, Acenap*H*), 7.34 (m, 2H, H2, Acenap*H*), 7.33 (m, 1H, ^{3}J(H,H) = 7.3 Hz, H7, Acenap*H*), 6.97 (d, 1H, ^{3}J(H,H) = 7.4 Hz, H3, Acenap*H*), 6.90 (m, 1H, ^{3}J(H,H) = 7.4 Hz, H15/17, An*H*), 3.88 (s, 3H, H19, AnCH_3), 3.39 (m, 2H, H12, AcenapCH_2), 3.32 (m, 2H, H11, AcenapCH_2), 2.23 (m, 2H, H20+23, C*H*), 1.23 (dd, 6H, ^{3}J(H,P) = 15.5 Hz, ^{3}J(H,H) = 7.0 Hz, H21/22/24/25, CH_3), 1.02 (dd, 6H, ^{3}J(H,P) = 12.6 Hz, ^{3}J(H,H) = 7.0 Hz, H21/22/24/25, CH_3).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ [ppm] = 159.6 (s, qC, C16), 149.0 (s, qC, C6), 145.0 (m, qC, C4), 141.7 (s, CH, C14/C18), 140.2 (d, qC, J(C,P) = 8.1 Hz, C5), 139.5 (d, qC, J(C,P) = 27.0 Hz, C10), 135.1 (s, CH, C2), 134.0 (d, CH, J(C,P) = 2.8 Hz, C8), 129.2 (d, qC, ^{1}J(C,P) = 13.7 Hz, C9), 120.9 (d, qC, J(C,P) = 103.3 Hz, C13), 120.6 (s, CH, C3), 118.9 (s, CH, C7), 115.4 (d, CH, J(C,P) = 4.3 Hz, C15+C17), 114.0 (d, qC, J(C,P) = 5.5 Hz, C1), 55.1 (s, CH_3, C19), 30.4 (s, CH_2, C12), 29.4 (s, CH_2, C11), 25.7 (d, CH, ^{1}J(C,P) = 12.6 Hz, C20+C23), 20.3 (d, CH_3, ^{2}J(C,P) = 17.0 Hz, C21/22/24/25, 19.7 (d, CH_3, ^{2}J(C,P) = 8.5 Hz, C21/22/24/25).

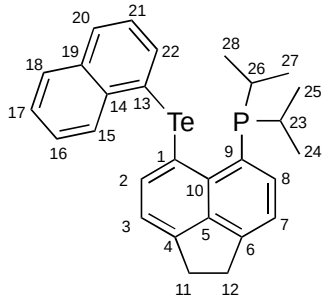
^{31}P NMR (109.37 MHz, [D_8]toluene): δ [ppm] = −20.4 (s, J(P,^{125}Te) = 1323.4 Hz; ^{1}J(P,^{123}Te) = 1096.3 Hz; J(P,C) = 100.4 Hz).

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 580.9 (J(^{125}Te,P) = 1323.4 Hz).

HR-MS (APCI^{+}, *m/z*), 507.1093 [M^{+}+H] (calculated for $C_{25}H_{30}OPTe$: 507.1093 [M^{+}+H], 100%) $C_{25}H_{30}OP^{122}Te$: 499.1062 [M^{+}+H] (calculated for $C_{25}H_{30}OP^{122}Te$: 499.1059 [M^{+}+H]).

EA calcd (%) for $C_{25}H_{29}PTeO$: C 59.57, H 5.80, found: C 59.49, H 5.87.

B.3 SYNTHESIS OF NapTe–Acenap–P(^{i}Pr)$_2$ (3)



Synthesis according to the general procedure: $(NapTe)_2$ (365 mg, 0.72 mmol, 0.5 eq) was used as starting material. (Yield: 26 %)

M.p. 129 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = Signals for the Nap moiety appear between 8.4 and 7.1; 7.68 (dd, 1H, ^3J(H,P) = 3.9 Hz, ^3J(H,H) = 7.1 Hz H8, Acenap*H*), 7.28 (d, 1H, ^3J(H,H) = 7.3 Hz, H7, Acenap*H*), 7.10 (d, 1H, ^3J(H,H) = 7.4 Hz, H2, Acenap*H*), 6.64 (d, 1H, ^3J(H,H) = 7.4 Hz, H3, Acenap*H*), 3.25 (d, 2H, ^3J(H,H) = 6.7 Hz, H12, AcenapCH_2), 3.14 (d, 2H, ^3J(H,H) = 7.0 Hz, H11, AcenapCH_2), 2.22 (m, 2H, H23+26, C*H*), 1.24 (dd, 3H, ^3J(H,P) = 15.6 Hz, ^3J(H,H) = 7.0 Hz, H24 or 25+27 or 28, CH_3), 1.11 (dd, 3H, ^3J(H,P) = 15.1 Hz, ^3J(H,H) = 7.0 Hz, H24 or 25+27 or 28, CH_3), 1.03 (dd, 3H, ^3J(H,P) = 12.7 Hz, ^3J(H,H) = 6.9 Hz, H24 or 25+27 or 28, CH_3), 0.93 (dd, 3H, ^3J(H,P) = 11.7 Hz, ^3J(H,H) = 6.9 Hz, H24 or 25+27 or 28, CH_3).

^{13}C NMR (125.71 MHz, $CDCl_3$): δ [ppm] = Due to overlaps the C resonances of the Nap moiety could not reliably assigned; 149.1 (s, qC, C6), 144.9 (d, qC, ^4J(C,P) = 2.1 Hz, C4), 139.4 (d, qC, J(C,P) = 27.1 Hz, C10), 140.2 (s, qC, C5), 135.7 (s, CH, C2), 134.2 (d, CH, ^3J(C,P) = 2.3 Hz, C8), 128.7 (d, qC, ^1J(C,P) = 12.7 Hz, C9), 121.0 (s, CH, C3), 119.1 (d, CH, ^3J(C,P) = 9.1 Hz, C7), 113.1 (d, qC, ^3J(C,P) = 6.9 Hz, C1), 30.4 (s, CH_2, C12), 29.4 (s, CH_2, C11), 25.7 (d, CH, ^2J(C,P) = 12.6 Hz, C23/26), 23.4 (d, CH, ^2J(C,P) = 11.3 Hz, C23/26) 20.5 (d, CH_3, ^2J(C,P) = 18.4 Hz, C24 or 25+27 or 28), 20.4 (d, CH_3, ^2J(C,P) = 16.7 Hz, C24 or 25+27 or 28), 19.78 (d, CH_3, ^2J(C,P) = 8.1 Hz, C24 or 25+27 or 28), 19.01 (d, CH_3, ^2J(C,P) = 9.3 Hz, C24 or 25+27 or 28).

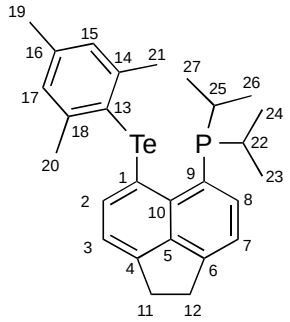
^{31}P NMR (109.37 MHz, [D_8]toluene): δ [ppm] = −21.4 (s, J(P,^{125}Te) = 1349.3 Hz; J(P,^{123}Te) = 1119.3 Hz; J(P,C) = 108.5 Hz).

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 483.9 (J(^{125}Te,P) = 1350.2 Hz).

HR-MS (APCI$^+$, *m/z*), 527.1141 [M^++H] (calculated for $C_{28}H_{30}PTe$: 527.1144 [M^++H], 100%); 519.1111 [M^++H] (calculated for $C_{28}H_{30}P^{122}Te$: 519.1110 [M^++H], 100%).

EA calcd (%) for $C_{28}H_{29}PTe \bullet 0.5(CH_2Cl_2)$: C 60.42, H 5.34, found: C 59.34, H 5.46.

B.4 SYNTHESIS OF MesTe–Acenap–P(^{i}Pr)$_2$ (4a)



Synthesis according to the general procedure: Bis(2,4,6-trimethylphenyl)ditelluride (MesTeTeMes) (353 mg, 0.72 mmol, 0.5 eq) was used as starting material. (Yield: 87 %)

M.p. 155 °C (dec.).

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 7.72 (dd, 1H, ^{3}J(H,P) = 3.9 Hz, ^{3}J(H,H) = 7.1 Hz, H8, Acenap*H*), 7.34 (d, 1H, ^{3}J(H,H) = 7.1 Hz, H7, Acenap*H*), 7.19 (d, 1H, ^{3}J(H,H) = 7.3 Hz, H2, Acenap*H*), 7.05 (s, 2H, H15+17, Mes*H*), 6.92 (d, 1H, ^{3}J(H,H) = 7.4 Hz, H3, Acenap*H*), 3.39 (m, 2H, H12, AcenapCH_2), 3.31 (m, 2H, H11, AcenapCH_2), 2.58 (s, 6H, H20+21, 2xMesCH_3), 2.36 (s, 3H, H19, MesCH_3), 2.25 (m, 2H, H22+25, C*H*), 1.26 (dd, 6H, ^{3}J(H,P) = 15.4 Hz, ^{3}J(H,H) = 6.9 Hz, H23 or 24+26 or 27, CH_3), 1.04 (dd, 6H, ^{3}J(H,P) = 12.4 Hz, ^{3}J(H,H) = 6.9 Hz, H23 or 24+26 or 27, CH_3).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ [ppm] = 149.0 (s, qC, C6), 145.0 (s, qC, C14+C18), 144.8 (d, qC, ^{4}J(C,P) = 2.2 Hz, C4), 140.3 (d, qC, ^{3}J(C,P) = 7.8 Hz, C5), 139.6 (d, qC, ^{2}J(C,P) = 26.9 Hz, C10), 138.4 (s, qC, C16), 133.9 (d, CH, ^{3}J(C,P) = 2.8 Hz, C8), 133.8 (s, CH, C2), 133.3 (d, qC, J(C,P) = 91.8 Hz, C13), 129.2 (d, qC, ^{2}J(C,P) = 15.0 Hz, C9), 127.4 (d, CH, ^{7}J(C,P) = 4.9 Hz, C15+C17), 120.9 (s, CH, C3), 118.9 (s, CH, C7), 113.4 (d, qC, ^{3}J(C,P) = 6.2 Hz, C1), 30.4 (s, CH_2, C12), 29.5 (s, CH_2, C11), 28.7 (s, CH_3, C20+21), 25.7 (d, CH, ^{1}J(C,P) = 13.4 Hz, C22+C25), 21.2 (s, CH_3, C19), 20.3 (d, CH_3, ^{2}J(C,P) = 17.1 Hz, C23/24/26/27), 19.8 (d, CH_3, ^{2}J(C,P) = 8.7 Hz, C23/24/26/27).

^{31}P NMR (202.46 MHz, [D_8]toluene): δ [ppm] = −20.9 (s, J(P,^{125}Te) = 1332.2 Hz; J(P,^{123}Te) = 1105.4 Hz; J(P,C) = 93.1 Hz).

^{31}P NMR (242.99 MHz, *solid state*, 25 °C, MAS 40 kHz, NaH_2PO_4): δ [ppm] = −25.4 (s, J(P,^{125}Te) = 1336.4 Hz).

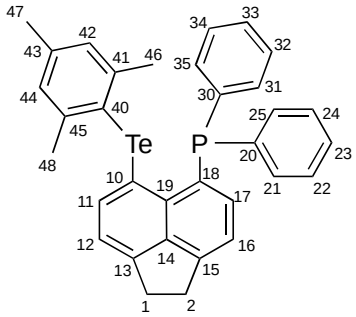
^{123}Te NMR (70.70 MHz, [D_8]toluene): δ [ppm] = 370.2 (J(^{123}Te,P) = 1105 Hz).

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 372.2 (J(^{125}Te,P) = 1337.4 Hz).

HR-MS (ESI$^+$, *m/z*), 519.1450 [M^++H] (calculated for $C_{27}H_{33}PTe$: 519.1457 [M^++H], 100%);
MS (EI$^+$, *m/z*), 518.0 [M^+] (calculated: 518.1 [M^+]).

EA calcd (%) for $C_{27}H_{33}PTe$: C 62.83, H 6.44, found: C 62.95, H 6.36.

B.5 SYNTHESIS OF MesTe–Acenap–PPh_2 (4b)



n-Butyllithium (1.20 mmol, 2.5 M in *n*-hexane) and N,N,N′,N′-tetra-methyl-ethylene-diamine (TMEDA; 0.14 g, 1.20 mmol) were added at −78°C to a suspension of 5-bromo-6-diphenyl-phosphino-acenaphthene (0.50 g, 1.20 mmol) in diethyl ether (5 ml) and stirred for 2 h at this temperature. The suspension was allowed to warm up to RT, stirred for 1 h and a freshly prepared solution of mesityltellurium iodide (by the reaction of dimesitylditelluride (0.30 g, 0.60 mmol) and iodine (0.15 g, 0.60 mmol) in toluene (5 ml) for 1 h) was added at RT and the reaction mixture was stirred overnight. Dichloromethane was added and after aqueous workup the solvent was removed by rotary evaporation. The yellow residue was recrystallized by dichloromethane and *n*-hexane to give yellow crystals of **4b** (0.31 g, 0.53 mmol, 44 %).

M.p. 197°C (dec.).

^{1}H NMR (360.32 MHz, $CDCl_3$): δ [ppm] = 7.54-7.45 (m, 5H), 7.41-7.36 (m, 6H), 7.30-7.28 (m, 2H), 7.04 (s, 2H, H15+H17, Mes*H*), 6.99 (d, 1H, ^{3}J(H,H) = 7.4 Hz, H3, Acenap*H*), 3.41-3.35 (m, 4H, H11+H12, 2xAcenapCH_2), 2.50 (s, 6H, H20+H21, 2xMesCH_3), 2.37 (s, 3H, H19, MesCH_3).

^{13}C NMR (90.60 MHz, $CDCl_3$): δ [ppm] = 149.8 (s, qC, C15), 145.2 (d, qC, ^{4}J(C,P) = 2.3 Hz, C13), 145.0 (s, qC, C41+C45), 140.4 (d, qC, ^{3}J(C,P) = 8.6 Hz, C14), 138.7 (s, qC, C43), 138.3 (d, qC, ^{2}J(C,P) = 29.9 Hz, C19), 138.0 (d, CH, ^{2}J(C,P) = 8.3 Hz, C17), 134.7 (d, CH, ^{4}J(C,P) = 1.3 Hz, C11), 133.4 (d, CH, ^{2}J(C,P) = 17.5 Hz, C21+C25+C31+C35), 132.4 (d, qC, ^{1}J(C,P) = 9.8 Hz, C18), 129.9 (d, qC, J(C,P) = 74.4 Hz, C40), 129.7 (d, qC, ^{1}J(C,P) = 11.1 Hz, C20+C30), 128.4 (d, CH, ^{3}J(C,P) = 6.8 Hz, C22+C24+C32+C34), 128.2 (s, CH, C23+C33), 127.5 (d, CH, J(C,P) = 4.0 Hz, C42+C44), 121.2 (s, CH, C12), 119.7 (s, CH, C16), 112.0 (d, qC, ^{3}J(P,C) = 4.6 Hz, C10), 30.3 (s, CH_2, C2), 29.6 (s, CH_2, C1), 28.7 (s, CH_3, C46+C48), 21.1 (s, CH_3, C47).

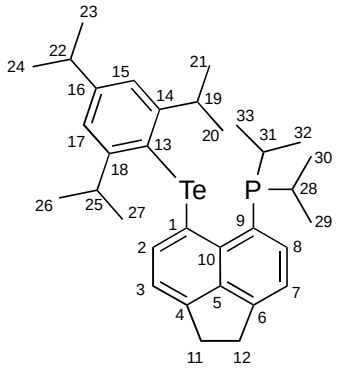
^{31}P NMR (145.78 MHz, $CDCl_3$): δ [ppm] = −29.5 (s, J(P,^{125}Te) = 1212.8 Hz, J(P,^{123}Te) = 1006.0 Hz, J(P,C) = 74.4 Hz).

^{125}Te NMR (113.68 MHz, $CDCl_3$): δ [ppm] = 410.8 (d, J(Te,P) = 1213.6 Hz).

HR-EIMS: Calcd for $C_{33}H_{29}PTe$: 586.10636, found: 586.10673.

EA calcd (%) for $C_{33}H_{29}PTe$: C 67.85; H 5.00, found: C 67.97; H 4.93.

B.6 SYNTHESIS OF TipTe–Acenap–P(^{i}Pr)$_2$ (5)



Synthesis according to the general procedure: Bis(2,4,6-triisopropylphenyl)ditelluride (TipTeTeTip) (474 mg, 0.72 mmol, 0.5 eq) was used as starting material. (Yield: 53 %)

M.p. 152 °C (dec.).

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 7.73 (dd, 1H, ^3J(H,P) = 3.8 Hz, ^3J(H,H) = 7.1 Hz, H8, Acenap*H*), 7.35 (d, 1H, ^3J(H,H) = 7.1 Hz, H7, Acenap*H*), 7.26 (d, 1H, ^3J(H,H) = 7.3 Hz, H2, Acenap*H*), 7.17 (s, 2H, H15+17, Tip*H*), 6.96 (d, 1H, ^3J(H,H) = 7.4 Hz, H3, Acenap*H*), 3.82 (sep, 2H, H19+H25, (Tip)^{i}Pr-*H*), 3.39 (m, 2H, H12, AcenapCH_2), 3.32 (m, 2H, H11, AcenapCH_2), 3.00 (sep, 1H, H22, (Tip)^{i}Pr-*H*), 2.28 (m, 2H, H28+H31, C*H*), 1.37 (s, 12H, H20+21+26+27, 2xTipCH_3), 1.36 (s, 6H, H23+24, TipCH_3), 1.30 (dd, 6H, ^3J(H,P) = 15.2 Hz, ^3J(H,H) = 7.0 Hz, H29 or 30 + 32 or 33, CH_3), 1.04 (dd, 6H, ^3J(H,P) = 12.5 Hz, ^3J(H,H) = 7.0 Hz, H29 or 30 + 32 or 33, CH_3).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ [ppm] = 154.6 (s, qC, C14+C18), 149.7 (s, qC, C16), 149.0 (s, qC, C6), 144.64 (d, qC, ^3J(C,P) = 1.7 Hz, C4), 140.3 (d, qC, ^3J(C,P) = 7.8 Hz, C5), 139.4 (d, qC, ^2J(C,P) = 27.1 Hz, C10), 135.4 (s, CH, C2), 134.7 (d, qC, J(C,P) = 91.7 Hz, C13), 133.8 (d, CH, ^3J(C,P) = 2.7 Hz, C8), 129.2 (d, qC, ^2J(C,P) = 15.4 Hz, C9), 121.2 (d, CH, ^7J(C,P) = 4.7 Hz, C15+C17), 120.8 (s, CH, C3), 118.9 (s, CH, C7), 115.0 (d, qC, ^3J(C,P) = 5.7 Hz, C1), 39.0 (s, CH, C25+19), 34.2 (s, CH, C22), 30.4 (s, CH_2, C12), 29.4 (s, CH_2, C11), 25.7 (d, CH, ^1J(C,P) = 13.5 Hz, C28+C31), 24.1 (s, CH_3, C20+21+26+27), 24.0 (s, CH3, C23+C24), 20.3 (s, CH_3, C29/30/32/33), 20.1 (s, CH_3, C29/30/32/33), 19.7 (s, CH_3, C29/30/32/33), 19.6 (s, CH_3, C29/30/32/33).

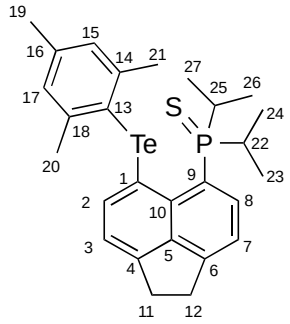
^{31}P NMR (202.46 MHz, [D_8]toluene): δ [ppm] = −21.6 (s, J(P,^{125}Te) = 1366.8 Hz, J(P,^{123}Te) = 1133.5 Hz), J(P,C) = 91.2 Hz).

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 320.9 (J(^{125}Te,P) = 1359.6 Hz).

HR-MS (ASAP, *m/z*), 603.2390 [M^++H] (calculated for $C_{33}H_{46}PTe$: 603.2397 [M^++H], 100%).

EA calcd (%) for $C_{33}H_{45}PTe$: C 66.03, H 7.56, found: C 66.02, H 7.51.

B.7 SYNTHESIS OF MesTe–Acenap–P(S)(^{i}Pr)$_2$ (6a)



Sulfur flowers (14 mg, 0.43 mmol, 1.1 eq.) are added to a solution of (^{i}Pr)$_2$P–Acenap–TeMes (**4a**) (200 mg, 0.39 mmol) dissolved in toluene (15 mL). The suspension is stirred at 80 °C for 12 h and then filtered to remove the excess sulfur. The solvent is removed under vacuum and the solid material recrystallized from *n*-hexane at −40 °C to afford colorless crystals in an overall yield of 91 %.

M.p. 178 °C (dec.).

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 7.98 (d, 1H, ^3J(H,H) = 7.2 Hz, H2, Acenap*H*), 7.74 (dd, 1H, ^3J(H,H) = 7.3 Hz, ^3J(H,P) = 13.6 Hz, H8, Acenap*H*), 7.31 (dd, 1H, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.4 Hz, H7, Acenap*H*), 6.94 (d, 1H, ^3J(H,H) = 7.2 Hz, H3 Acenap*H*), 6.79 (s, 2H, H15+17, Mes*H*), 3.59 (m, 2H, H22+H25, C*H*), 3.37 (m, 2H, H12, AcenapCH_2), 3.33 (m, 2H, H11, AcenapCH_2), 2.21 (s, 3H, H19, MesCH_3), 2.12 (s, 6H, H20+21, 2xMesCH_3), 1.45 (d, 3H, ^3J(H,H) = 7.0 Hz, H23 or 24+26 or 27, CH_3), 1.43 (d, 3H, ^3J(H,H) = 7.0 Hz, H23 or 24+26 or 27, CH_3), 1.29 (d, 3H, ^3J(H,H) = 7.1 Hz, H23 or 24+26 or 27, CH_3), 1.25 (d, 3H, ^3J(H,H) = 7.1 Hz, H23 or 24+26 or 27, CH_3).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ [ppm] = 152.7 (s, qC, C6), 146.7(s, qC, C4), 143.3 (s, qC, C13), 143.3 (s, CH, C2), 140.5 (d, qC, ^2J(C,P) = 9.2 Hz, C5), 139.0 (s, qC, C10), 137.3 (s, qC, C16), 134.7 (s, qC, C14+C18, 134.01 (d, CH, ^2J(C,P) = 8.3 Hz, C8), 127.4 (s, CH, C15+C17), 122.2 (d, qC, ^1J(C,P) = 71.2 Hz, C9), 121.7 (s, CH, C3), 117.4 (d, CH, ^4J(C,P) = 12.3 Hz, C7), 113.3 (s, qC, C1), 30.6 (s, CH, C22 or C25), 30.2 (s, CH, C22 or C25), 30.1 (s, CH_2, C12), 29.6 (s, CH_2, C11), 28.1 (s, CH_3, C20+21), 20.9 (s, CH_3, C19), 17.4 (s, CH_3, C23/24/26/27; correlates to 1.29 ppm and 1.25 ppm in the ^{1}H), 16.5 (s, CH_3, C23/24/26/27;correlates to 1.45 ppm and 1.43 ppm in the ^{1}H).

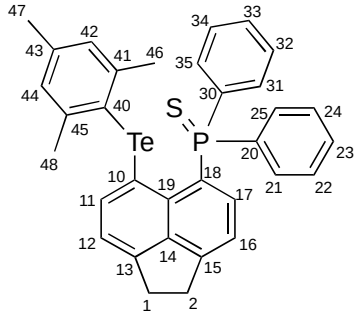
^{31}P NMR (202.46 MHz, $CDCl_3$): δ [ppm] = 62.8 (s)

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 447.0 (s).

HR-MS (ASAP, *m/z*), 551.1177 [M^++H] (calculated for $C_{27}H_{34}PTeS$: 551.1175 [M^++H], 100%).

EA calcd (%) for $C_{27}H_{33}PTeS$: C 59.16, H 6.07, found: C 58.98, H 6.15.

B.8 SYNTHESIS OF MesTe–Acenap–P(S)Ph$_2$ (6b)



Sulfur (3.30 mg, 0.10 mmol) was added to a solution of Ph_2P-Acenap-TeMes (**4b**) (50.0 mg, 0.09 mmol) and toluene (2 ml) and the reaction mixture was stirred 12 h under reflux. The solvent was removed under reduced pressure and the residue was recrystallized by dichloromethane and *n*-hexane to yield **6b** as red-brown crystals (34.8 mg, 0.06 mmol, 66 %).

M.p. 142 °C (dec.).

^{1}H NMR (360.32 MHz, $CDCl_3$): δ [ppm] = 7.90 (d, 1H, ^3J(H,H) = 7.3 Hz, H2, Acenap*H*), 7.83-7.78 (m, 3H), 7.55-7.44 (m, 7H), 7.29 (dd, 1H, ^3J(H,P) = 17.8, ^3J(H,H) = 7.3, H8, Acenap*H*), 7.13 (dd, 1H, ^3J(H,H) = 7.3 Hz, ^4J(H,P) = 0.6 Hz, H3 or H7, Acenap*H*), 6.97 (d, 1H, ^3J(H,H) = 7.3 Hz, H7 or H3, Acenap*H*), 6.76 (s, 2H, H15+H17, Mes*H*), 3.36 (m, 4H, H11+H12, AcenapCH_2), 2.21 (s, 3H, H19, MesCH_3), 2.05 (s, 6H, H20+H21, 2xMesCH_3).

^{13}C{^{1}H}-NMR (90.60 MHz, $CDCl_3$): δ [ppm] = 153.8 (d, qC, ^4J(C,P) = 3.1 Hz, C15), 146.8 (d, qC, ^4J(C,P) = 2.1 Hz, C13), 143.8 (s, CH, C11), 142.8 (s, qC, C40), 140.6 (d, qC, ^3J(C,P) = 10.3 Hz, C14), 138.6 (d, CH, ^2J(C,P) = 12.1 Hz, C17), 137.7 (d, qC, ^2J(C,P) = 8.8 Hz, C19), 137.5 (s, qC, C43), 132.9 (s, qC, C41+C45), 132.5 (d, CH, ^2J(C,P) = 10.2 Hz, C21+C25+C31+C35), 131.2 (d, CH, ^4J(C,P) = 2.9 Hz, C23+C33), 128.4 (d, CH, ^3J(C,P) = 12.7 Hz, C22+C24+C32+C34), 127.6 (d, qC, ^1J(C,P) = 96.3 Hz, C20+C30), 127.1 (s, CH, C42+C44), 123.6 (d, qC, ^1J(C,P) = 85.3 Hz, C18), 122.0 (s, CH, C12), 117.5 (d, CH, ^3J(C,P) = 14.4 Hz, C16), 113.6 (d, qC, ^3J(C,P) = 2.6 Hz, C10), 30.1 (s, CH_2, C1 or C2), 29.7 (s, CH_2, C2 or C1), 28.3 (s, CH_3, C46+C48), 20.9 (s, CH_3, C47).

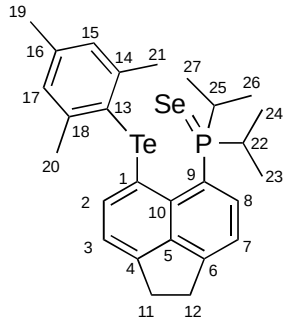
^{31}P NMR (145.78 MHz, $CDCl_3$): δ [ppm] = 46.5 (s).

^{125}Te NMR (113.68 MHz, $CDCl_3$): δ [ppm] = 488.1 (s).

HR-EIMS: Calcd for $C_{33}H_{29}PSTe$: 618.07843, found: 618.08033.

EA calcd (%) for $C_{33}H_{29}PTe$: C 64.32, H 4.74, found: C 62.21, H 4.88.

B.9 SYNTHESIS OF MesTe–Acenap–P(Se)(^{i}Pr)$_2$ (7a)



Selenium powder (34 mg, 0.43 mmol, 1.1 eq.) is added to a solution of (^{i}Pr)$_2$P–Acenap–TeMes (**4a**) (200 mg, 0.39 mmol) dissolved in toluene (15 mL). The suspension is stirred at 80 °C for 12 h and then filtered to remove the excess selenium. The solvent is removed under vacuum and the solid material recrystallized from *n*-hexane at −40 °C to afford colorless crystals in an overall yield of 86 %.
M.p. 204 °C (dec.).

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 8.03 (d, 1H, ^3J(H,H) = 7.2 Hz, H2, Acenap*H*), 7.73 (dd, 1H, ^3J(H,P) = 13.2 Hz, ^3J(H,H) = 7.4 Hz, H8, Acenap*H*), 7.28 (dd, 1H, ^3J(H,H) = 7.3 Hz, ^4J(H,P) = 1.4 Hz, H7, Acenap*H*), 6.92 (d, 1H, ^3J(H,H) = 7.2 Hz, H3, Acenap*H*), 6.75 (s, 2H, C15+C17, Mes*H*), 3.70 (m, 2H, H22+25, C*H*), 3.33 (m, 2H, H12, AcenapCH_2), 3.29 (m, 2H, H11, AcenapCH_2), 2.18 (s, 3H, H19, MesCH_3), 2.07 (s, 6H, H20+21, 2xMesCH_3), 1.44 (d, 3H, ^3J(H,H) = 7.0 Hz, H23 or 24+26 or 27, CH_3), 1.41 (d, 3H, ^3J(H,H) = 7.0 Hz, H23 or 24+26 or 27, CH_3), 1.28 (d, 3H, ^3J(H,H) = 7.1 Hz, H23 or 24+26 or 27, CH_3), 1.24 (d, 3H, ^3J(H,H) = 7.0 Hz, H23 or 24+26 or 27, CH_3).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ [ppm] = 152.9 (s, qC, C4), 146.9 (s, qC, C6), 143.1 (s, qC, C13), 140.6 (d, qC, ^3J(C,P) = 9.2 Hz, C5), 139.5 (d, qC, ^2J(C,P) = 6.6 Hz, C10), 137.3 (s, qC, C16), 143.6 (s, CH, C2), 135.8 (s, qC, C14+C18), 134.01 (d, CH, ^2J(C,P) = 6.3 Hz, C8), 127.5 (s, CH, C15+C17), 121.8 (s, CH, C3), 120.6 (d, qC, ^1J(C,P) = 63.8 Hz, C9), 117.4 (d, CH, ^4J(C,P) = 11.8 Hz, C7), 113.1 (s, qC, C1), 30.0 (s, CH_2, C11/12), 29.7 (s, CH_2, C11/12), 28.0 (s, CH, C22+C25), 28.0 (s, CH_3, C19), 20.9 (s, CH_3, C20+21), 18.3 (s, CH_3, C23/24/26/27), 16.6 (s, CH_3, C23/24/26/27).

^{31}P NMR (109.37 MHz, [D_8]toluene): δ [ppm] = 55.6 (s, ^1J(P,^{77}Se) = 694.9 Hz, , J(P,^{125}Te) = 12.5 Hz).

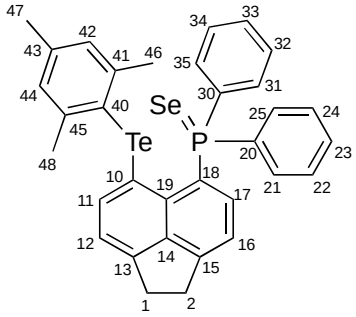
^{77}Se NMR (51.52 MHz, [D_8]toluene): δ [ppm] = −353.7 (d, ^1J(^{77}Se,P) = 696.6 Hz).

^{125}Te NMR (85.24 MHz, [D_8]toluene): δ [ppm] = 448.5 (dd, J(^{125}Te,P) = 13.3 Hz, J(^{125}Te,P) = 2.6 Hz, J(^{125}Te,^{77}Se) = 684.4 Hz).

HR-MS (ASAP, *m/z*), 597.0605 [M^++H] (calculated for $C_{27}H_{34}PTeSe$: 597.0614 [M^++H]).

EA calcd (%) for $C_{27}H_{33}PTeSe$: C 54.50, H 5.59, found: C 54.57, H 5.53.

B.10 SYNTHESIS OF MesTe–Acenap–P(Se)Ph$_2$ (7b)



Selenium (8.10 mg, 0.10 mmol) was added to a solution of Ph_2P-Acenap-TeMes (**4b**) (50.0 mg, 0.09 mmol) and THF (2 ml) and the reaction mixture was stirred 12 h under reflux. The solvent was removed under reduced pressure and the residue was recrystallized by dichloromethane and *n*-hexane to yield **7b** as yellow crystals (29.7 mg, 0.05 mmol, 52 %).

M.p. 170 °C (dec.).

^{1}H NMR (360.32 MHz, $CDCl_3$): δ [ppm] = 7.96 (d, 1H, ^3J(H,H) = 7.3 Hz, H2, Acenap*H*), 7.92-7.72 (m, 3H), 7.53-7.44 (m, 7H), 7.30 (dd, 1H, ^3J(H,P) = 17.7, ^3J(H,H) = 7.4, H8, Acenap*H*), 7.13 (d, 1H, ^3J(H,H) = 7.3 Hz, H3 or H7, Acenap*H*), 6.98 (d, 1H, ^3J(H,H) = 7.2 Hz, H7 or H3, Acenap*H*), 6.75 (s, 2H, H15+H17, Mes*H*), 3.35 (m, 4H, H11+H12, AcenapCH_2), 2.20 (s, 3H, H19, MesCH_3), 2.03 (s, 6H, H20+H21, 2xMesCH_3).

^{13}C{^{1}H}-NMR (90.60 MHz, $CDCl_3$): δ [ppm] = 153.9 (d, qC, ^4J(C,P) = 3.1 Hz, C15), 146.9 (d, qC, ^4J(C,P) = 2.2 Hz, C13), 143.6 (s, CH, C11), 143.0 (s, qC, C40), 140.7 (d, qC, ^3J(C,P) = 10.3 Hz, C14), 138.4 (d, CH, ^2J(C,P) = 10.9 Hz, C17), 138.0 (d, qC, ^2J(C,P) = 9.5 Hz, C19), 137.4 (s, qC, C43), 134.4 (s, qC, C41+C45), 132.8 (d, CH, ^2J(C,P) = 10.2 Hz, C21+C25+C31+C35), 131.2 (d, CH, ^4J(C,P) = 3.0 Hz, C23+C33), 128.4 (d, CH, ^3J(C,P) = 12.7 Hz, C22+C24+C32+C34), 127.6 (d, qC, ^1J(C,P) = 96.4 Hz, C20+C30), 127.2 (s, CH, C42+C44), 122.3 (d, qC, ^1J(C,P) = 76.7 Hz, C18), 121.9 (s, CH, C12), 117.6 (d, CH, ^3J(C,P) = 14.0 Hz, C16), 113.5 (d, qC, ^3J(C,P) = 2.6 Hz, C10), 30.1 (s, CH_2, C1 or C2), 29.7 (s, CH_2, C2 or C1), 28.3 (s, CH_3, C46+C48), 20.8 (s, CH_3, C47).

^{31}P NMR (145.78 MHz, $CDCl_3$): δ [ppm] = 35.0 (s, ^1J(P,Se) = 696.7 Hz, J(P,Te) = 23.5 Hz).

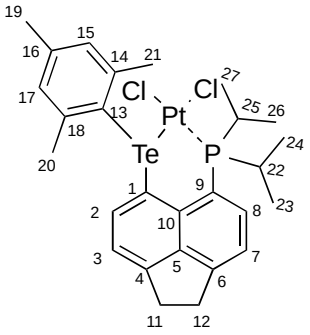
^{77}Se NMR (68.72 MHz, $CDCl_3$): δ [ppm] = −177.8 (d, ^1J(Se,P) = 695.5 Hz).

^{125}Te NMR (113.68 MHz, $CDCl_3$): δ [ppm] = 492.8 (d, J(Te,P) = 20.9 Hz, J(Te,Se) = 566.3 Hz).

HR-EIMS: Calcd for $C_{24}H_{18}PSeTe$: 546.93681, found: 546.93503 $[M\text{-}Mes]^+$.

EA calcd (%) for $C_{33}H_{29}PTe$: C 59.77, H 4.41, found: C 59.66, H 4.32.

B.11 SYNTHESIS OF [MesTe–Acenap–P(^{i}Pr)$_2$][μ-PtCl$_2$] (8)



A solution of (COD)PtCl$_2$ (145 mg, 0.39 mmol, 1.0 eq.) was added to a stirred solution of (^{i}Pr)$_2$P–Acenap–TeMes (**4a**) (200 mg, 0.39 mmol) dissolved in DCM by cannula. The mixture was stirred for 2 h at RT, filtered and the solvent removed under vacuum. Recrystallization from dichloromethane (DCM) afforded colorless crystals in a yield of 93 %.

M.p. 136 °C (dec.).

^{1}H NMR (500.13 MHz, $CDCl_3$): δ [ppm] = 8.07 (dd, 1H, ^3J(H,H) = 7.6 Hz, ^3J(H,P) = 10.8 Hz H8, Acenap*H*), 7.45 (m, 1H, H7, Acenap*H*), 7.42 (m, 1H, H2, Acenap*H*), 7.16 (d, 1H, ^3J(H,H) = 7.2 Hz, H3, Acenap*H*), 6.96 (s, 2H, H15+17, Mes*H*), 4.39 (m, 1H, H25, C*H*), 3.45 (m, 4H, H11+12, AcenapCH_2), 2.74 (s, 6H, H20+21, 2xMesCH_3), 2.61 (m, 1H, H22, C*H*), 2.32 (s, 3H, H19, MesCH_3), 1.61 (dd, 3H, ^3J(H,P) = 17.6 Hz, ^3J(H,H) = 4.8 Hz, H23,24, CH_3), 1.39 (m, 3H, ^3J(H,P) = 4.0 Hz, ^3J(H,H) = 7.0 Hz, H26,27, CH_3), 1.23 (dd, 3H, ^3J(H,P) = 18.4 Hz, ^3J(H,H) = 6.7 Hz, H23,24, CH_3), 1.05 (m, 3H, ^3J(H,P) = 18.9 Hz, ^3J(H,H) = 6.9 Hz, H26,27, CH_3).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ [ppm] = 153.0 (s, qC, C6), 150.8 (s, qC, C4), 142.6 (s, qC, C16), 141.1 (s, qC, C13), 140.3 (d, qC, ^3J(C,P) = 7.4 Hz, C5), 137.4 (d, qC, ^2J(C,P) = 7.4 Hz, C10), 136.8 (s, CH, C2), 134.6 (d, CH, ^2J(C,P) = 3.5 Hz, C8), 129.2 (s, CH, C15,17), 123.8 (s, qC, C14+18), 121.0 (s, CH, C3), 119.1 (d, CH, ^4J(C,P) = 9.2 Hz, C7), 116.2 (d, qC, ^1J(C,P) = 47.6 Hz, C9), 101.3 (d, ^3J(C,P) = 6.5 Hz, C1), 30.4 (d, CH, ^1J(C,P) = 36.7 Hz, C22), 30.1 (s, CH_2, C11/12), 28.2 (s, CH_3, C20/21), 25.3 (d, CH, ^1J(C,P) = 33.9 Hz, C25), 21.11 (s, CH_3, C19), 20.5 (s, CH_3, C23,24), 19.2 (s, CH_3, C23,24), 18.7 (s, CH_3, C26,27), 18.1 (d, CH_3, ^2J(C,P) = 6.3 Hz, C26,27).

^{31}P NMR (109.37 MHz, $CDCl_3$): δ [ppm] = 14.5 (s, ^1J(P,^{195}Pt) = 3481.6 Hz).

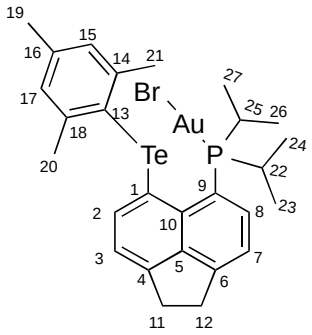
^{125}Te NMR (85.24 MHz, $CDCl_3$): δ [ppm] = 472.9 (d, J(^{125}Te,P) = 16.9 Hz; ^1J(^{125}Te,^{195}Pt) = 694.5 Hz).

^{195}Pt NMR (58.08 MHz, $CDCl_3$): δ [ppm] = −4412 (d, ^1J(^{195}Pt,P) = 3484.8 Hz).

HR-MS (ESI$^+$, *m/z*), 747.0691 [M^+−Cl] (calculated for $C_{27}H_{33}PPtTeCl$: 747.0693 [M^+−Cl]).

EA calcd (%) for $C_{27}H_{33}PCl_2TePt$: C 41.46, H 4.25, found: C 41.33, H 4.34.

B.12 SYNTHESIS OF [MesTe–Acenap–P(^{i}Pr)$_2$][AuBr] (9)



A solution of AuCl•THT (124 mg, 0.19 mmol, 1.0 eq.) was added to a stirred solution of (^{i}Pr)$_2$P–Acenap–TeMes (**4a**) (with LiBr impurities) (100 mg, 0.19 mmol) dissolved in DCM by cannula. The mixture was stirred for 2 h at RT, filtered and the solvent removed under vacuum. Recrystallization from dichloromethane (DCM) afforded colorless crystals in a yield of 16 %.

The compound showed decomposition during the NMR measurements, which prevented the reliable assignment of ^{1}H NMR and ^{13}C NMR resonances (appearance of a mixture; depositing of a metal thin film on the glass tube) as well as elemental analysis.

^{31}P NMR (109.37 MHz, $CDCl_3$): δ [ppm] = 46.8 (s, J(P,^{125}Te) = 292.0 Hz).

^{125}Te NMR (85.24 MHz, $CDCl_3$): δ [ppm] = 470.1 (d, J(^{125}Te,P) = 297.2 Hz).

HR-MS (ESI$^+$, *m/z*), 715.1036 [M^+−Br] (calculated for $C_{27}H_{33}PAuTe$: 715.1044 [M^+−Br]); Lowest *m/z* isotopes in envelope: 707.1006 [M^+−Br] (calculated for $C_{27}H_{33}PAu^{122}Te$: 707.1010 [M^+−Br]).

II. Computations

Starting from the coordinates of X-ray crystallography, the molecular geometries were fully optimized in the gas phase at the B3PW91 level[15] using the Stuttgart-Dresden (SDD) effective core potentials along with the associated valence basis sets for Te[16] (double zeta augmented with a set d-polarization functions with exponents 0.237),[17] Pt and Au.[18] Curtis and Binning's 962+(d) basis[19] on Se and Br, and 6-311+G(d) basis elsewhere. All structures were confirmed as minima through computation of the harmonic vibrational frequencies and Wiberg bond indices[20] were obtained in a natural bond orbital analysis[21] at the same level. Similar levels have been useful for interpreting experimental findings for *peri*-naphthalene telluride derivatives.[22] For technical reasons 6-311G(d) instead of 6-311+G(d) basis had to be used to plot the NBOs (single point calculation on the optimized geometries) ; all NBOs have been plotted with the same isovalue of 0.04 a.u.. A fine integration grid (75 radial shells with 302 angular points per shell) was used throughout. These computations were performed using the Gaussian 09 program.[23]

NMR chemical shifts and indirect spin-spin coupling constants (SSCCs) were computed[24] at the BP86[25] level for the B3PW91 minima with the relativistic zeroth-order regular approximation including spin-orbit coupling (ZORA-SO),[26, 27] together with a TZ2P basis of Slater-type orbitals and a fine integration grid (Integration 6). These calculations were performed with the ADF program.[28, 29] ^{125}Te, ^{31}P, ^{77}Se and ^{191}Pt chemical shifts are reported relative to Me_2Te (s = 3187.0 ppm), PPh_3 (s = 309.6 ppm), Me_2Se (s = 1783.9 ppm) and cis-$PtCl_2(NH_3)_2$ (s = 3474.7 ppm), respectively (in parentheses: absolute shielding constants computed at the same level).

For the Atoms In Molecules (AIM) analyses, wavefunction files were analyzed using AIM2000.[30] DGrid was used to analyze the ELI-D related bond descriptors using a grid step size of 0.05 a.u. [31]

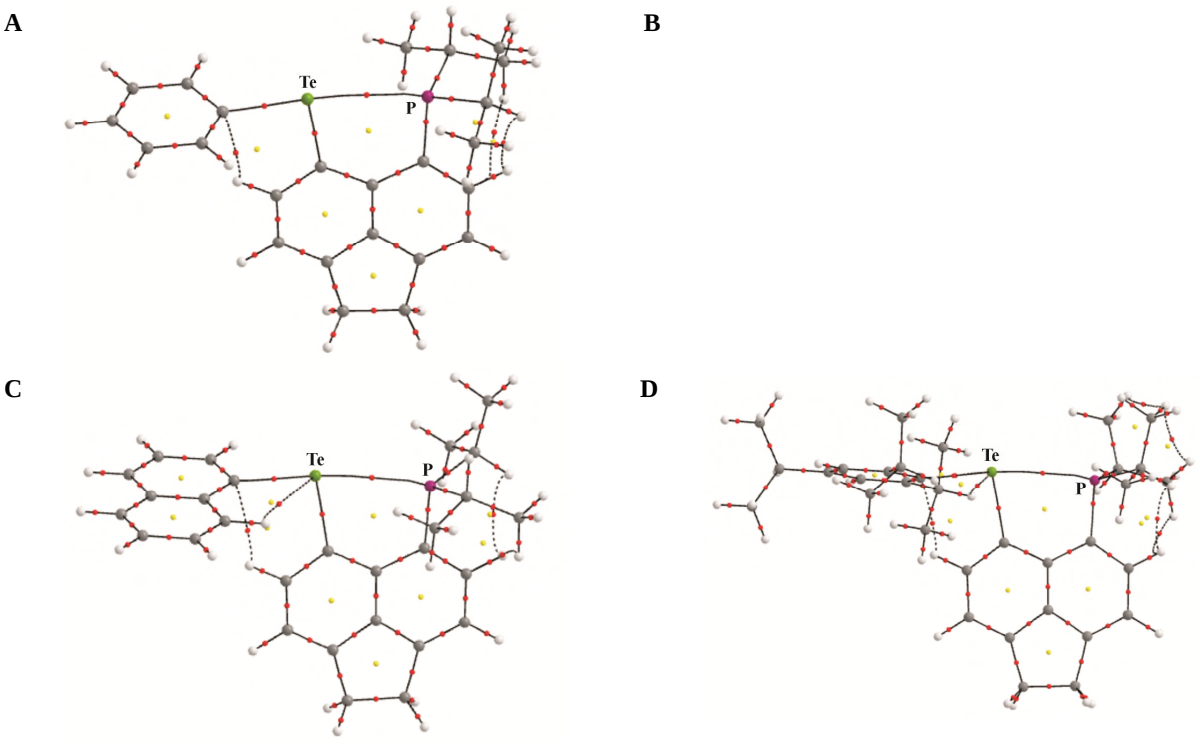


Figure S1. AIM bond paths of **1** (A), **2** (B), **3** (C) and **5** (D). Bond critical points are given as red dots and ring critical points are shown as yellow dots. All structures are AIM2000 representations.

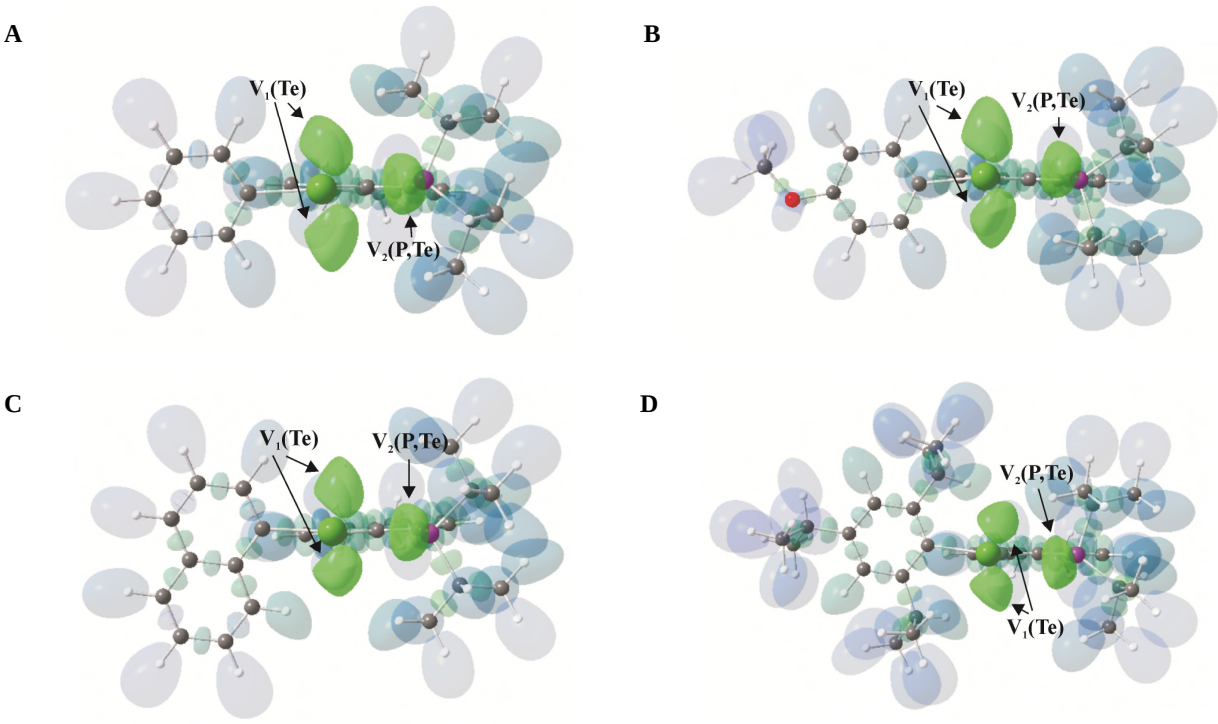


Figure S2. Isosurface representation of the localization domains of the ELI-D (Y = 1.40) of **1** (A), **2** (B), **3** (C) and **5** (D), the disynaptic basins V_2(Te,P) as well as the lone-pair basins (V_1) of Te are colored green. All remaining ELI-D basins are given in transparent mode for clarity reasons.

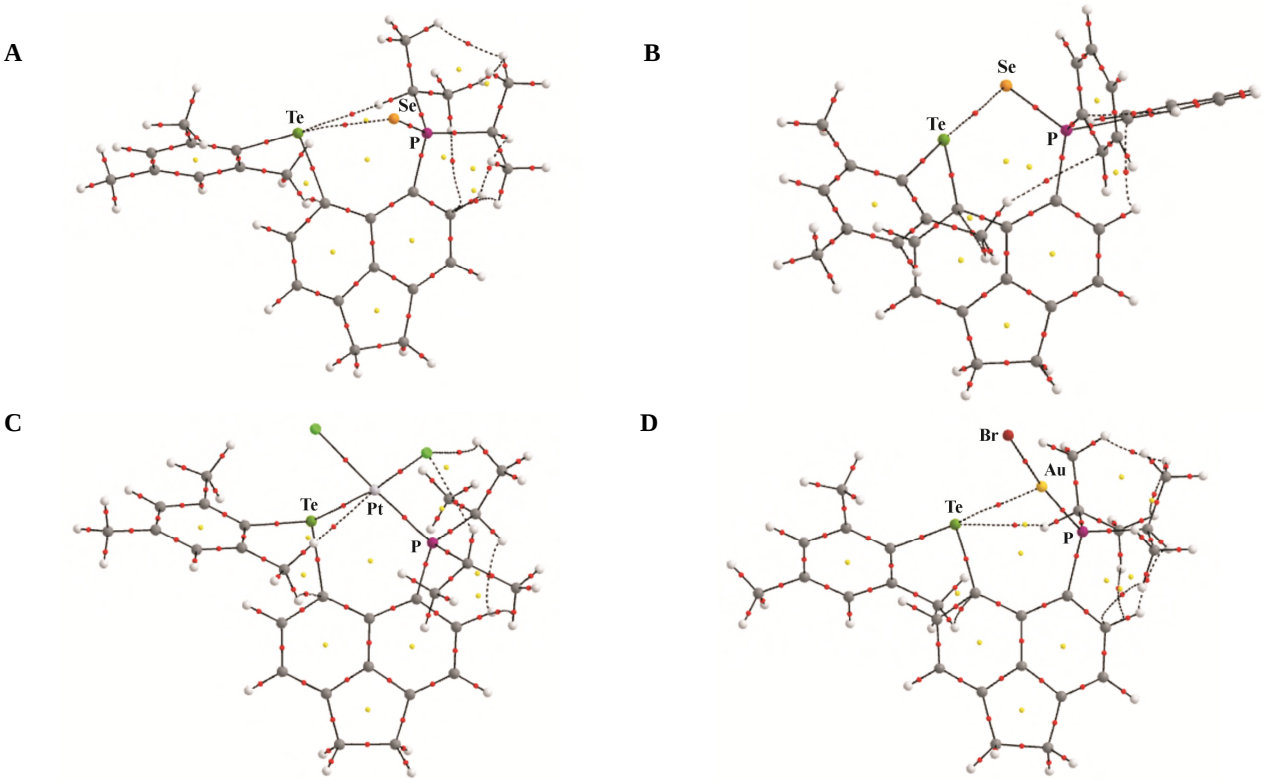
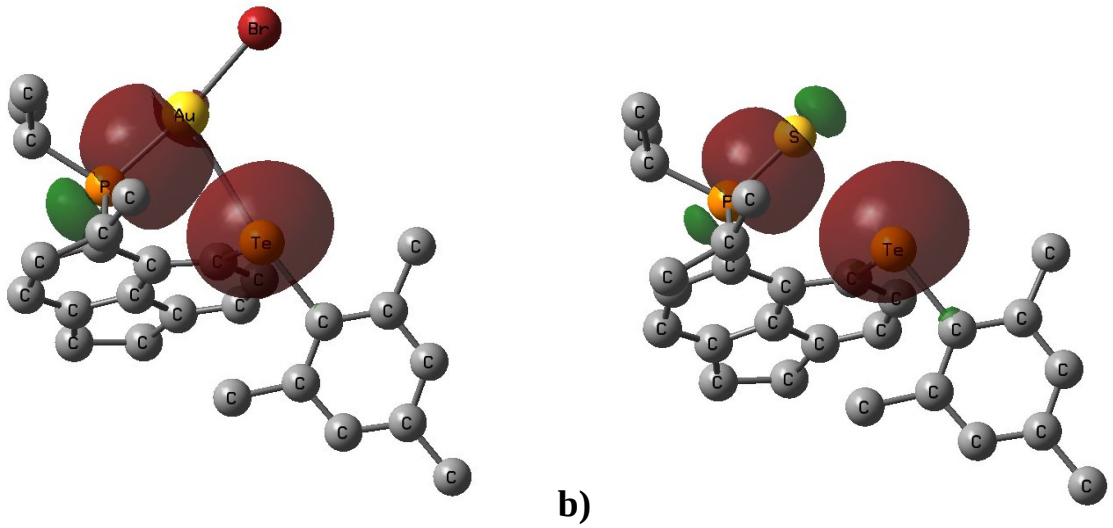


Figure S3. AIM bond paths of **7a** (A), **7b** (B), **8** (C) and **9** (D). Bond critical points are given as red dots and ring critical points are shown as yellow dots. All structures are AIM2000 representations.



a) **b)**

Figure S4: Overlay of the s-type Te lone pair with a) the Au-P NBO in **9** (left) and b) the P-Se NBO in **6a** (right); note the visibly stronger overlap in the case of **9**, consistent with the sizeable (Te,P) coupling observed in this compound (although smaller than that in the parent compound **4a**, cf. Fig. 5B in the main paper).

III. X-ray crystallography

The geometrical structures of compounds **1** to **5** can be described by the conformation and arrangement of the acenaphthene ring and *iso*-propyl/phenyl moieties relative to the two C_{Acenap}-P9-C_R planes and the C_{Acenap}-Te1-$C_{R'}$ plane.

The ligands on the tellurium atom adopt a position that is mainly perpendicular to the acenaphthene backbone. Furthermore, the ligands on the tellurium as well as the phosphorus atom show slightly different C10-C1–Te1–C13 and C10–C9–P9–$C_{iPr/Ph}$ torsion angles (**Table S1**). These angles determine the conformation of the R-groups on the tellurium atom as well as on the phosphorus atom. The positioning of the ligands is a parameter to investigate the influences and presence of a "three-centre four-electron type interaction" with the C13, Te and P atoms involved.[32. 33, 34]

When the torsion angles (C10-C1–Te1–C13 and C10–C9–P9–C_{iPr}) approach 90° the arrangement is denoted axial, whereas an equatorial orientation is indicated by angles close to 180°.[32] Nakanishi *et al.* introduced a classification system,[34] where axial conformations are described as type A structures, equatorial as type B and the twist conformation as type C.[32, 34] All compounds **1** to **5** show very similar torsion angles with the predominant Nakanishi ligand arrangement[34] BCA and for the mesityl systems **4a** and **4b** an arrangement of CCA.

Furthermore, a linear alignment of the three centres (C13, Te, P) would support a weak "three-centre four-electron type interaction", which should lead to a more attractive interaction between the *peri*-substituted phosphorus and tellurium atoms (smaller *peri*-distance). As shown in **Table S1** the C13–Te1···P9 angles are in the range of 154.92 to 171.44°, whereas the angle of 180° supports a "three-centre four-electron interaction" best. If the R-group on the tellurium atom is in equatorial position the resulting C13–Te1···P9 angles are closer to this value supporting attractive interactions between the *peri*-substituted atoms. As the equatorial positions of the R-groups at the tellurium atom support a three-centre four-electron bond better the mesityl groups show comparably large P···Te *peri*-distances.

Table S1. (Torsion) angles [°] categorising the acenaphthene and ligand conformations in **1** to **5**.*

	C13–Te1···P9	**C10-C1–Te1–C13**	**C10–C9–P9–$C_{iPr1/Ph1}$**	**C10–C9–P9–$C_{iPr2/Ph2}$**
1	171.44	Ph: θ_1 171.77 equatorial-B	^{i}Pr: θ_2 149.86 twist-C	^{i}Pr: θ_3 103.04 axial-A
2	168.64	An: θ_1 169.90 equatorial-B	^{i}Pr: θ_2 149.63 twist-C	^{i}Pr: θ_3 100.16 axial-A
3	167.47	Nap: θ_1 179.52 equatorial-B	^{i}Pr: θ_2 150.10 twist-C	^{i}Pr: θ_3 101.48 axial-A
4a	158.78	Mes: θ_1 154.81 twist-C	^{i}Pr: θ_2 145.66 twist-C	^{i}Pr: θ_3 109.99 axial-A
4b	154.92	Mes: θ_1 152.74 twist-C	Ph: θ_2 157.18 twist-C	Ph: θ_3 94.80 axial-A
5	166.51	Tip: θ_1 163.75 equatorial-B	^{i}Pr: θ_2 142.92 twist-C	^{i}Pr: θ_3 106.90 axial-A

- 67.5-112.5°: axial-A; 157.5-202.5: equatorial-B; 112.5-157.5: twist-C.

Table S2. (Torsion) angles [°] categorising the acenaphthene and ligand conformations in compounds **6-9**.*

	C13–Te1⋯P9	**C10-C1–Te1–C13**	**C10–C9–P9–C$_{iPr1/Ph1}$**	**C10–C9–P9–C$_{iPr2/Ph2}$**	**C10–C9–P9–X**
6a	140.38	Mes: θ_1 120.59 twist-C	^{i}Pr: θ_2 142.37 twist-C	^{i}Pr: θ_3 102.51 axial-A	S: θ_4 24.21 twist-C
6b	148.73	Mes: θ_1 135.64 twist-C	Phr θ_2 156.36 twist-C	Ph: θ_3 90.47 axial-A	S: θ_4 38.72 twist-C
7a	139.25	Mes: θ_1 119.08 twist-C	^{i}Pr: θ_2 142.71 twist-C	^{i}Pr: θ_3 102.14 axial-A	Se: θ_4 25.30 twist-C
7b-1	144.97	Mes: θ_1 135.44 twist-C	Ph: θ_2 176.74 equat.-B	Ph: θ_3 76.96 axial-A	Se: θ_4 52.75 twist-C
7b-2	150.93	Mes: θ_1 137.39 twist-C	Ph: θ_2 160.36 equat.-B	Ph: θ_3 88.00 axial-A	Se: θ_4 42.31 twist-C
8	123.74	Mes: θ_1 119.59 twist-C	^{i}Pr:: θ_2 148.99 twist-C	^{i}Pr: θ_3 98.54 axial-A	Pt: θ_4 24.94 twist-C
9-1	141.79	Mes: θ_1 124.77 twist-C	^{i}Pr: θ_2 147.44 twist-C	^{i}Pr: θ_3 98.43 axial-A	Au: θ_4 29.42 twist-C
9-2	145.07	Mes: θ_1 123.32 twist-C	^{i}Pr: θ_2 138.85 twist-C	^{i}Pr: θ_3 106.30 axial-A	Au: θ_4 22.03 twist-C

* 67.5-112.5°: axial-A; 157.5-202.5: equatorial-B; 112.5-157.5: twist-C.

Table S3. Crystallographic data for compounds **1-5.**

Compound	**1**	**2**	**3**	**4a**	**4b**	**5**
Empirical formula	$C_{24}H_{27}PTe$	$C_{28}H_{29}OPTe$	$C_{29}H_{31}Cl_2PTe$	$C_{29}H_{33}O_{0.5}PTe$	$C_{33}H_{29}PTe$	$C_{33}H_{45}PTe$
Formula weight	474.05	540.11	609.04	548.15	584.13	600.29
Temperature (°C)	173	173	93	125	173	173
Crystal color, habit	yellow prism	colorless prism	yellow prism	colorless plate	yellow block	colorless platelet
Crystal dimensions (mm^3)	0.360x0.250x 0.150	0.120 x0.090 x0.030	0.100x0.050x 0.030	0.150x0.120x0. 030	0.9x0.7x0.3	0.200x0.100x 0.010
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
a (Å)	8.6463(8)	25.365(3)	12.1171(13)	9.030(3)	12.048(3)	10.7116(14)
b (Å)	10.5753(11)	11.5214(13)	13.8840(15)	12.060(4)	8.8178(11)	26.482(3)
c (Å)	11.8312(10)	17.6915(19)	15.8702(18)	13.390(4)	24.867(5)	11.7583(15)
α (°)	87.512(5)	90.0000	90.0000	105.000(9)	90.0000	90.0000
β (°)	78.942(5)	93.517(8)	100.467(2)	97.000(10)	98.638(18)	116.705(3)
γ (°)	81.061(4)	90.0000	90.0000	92.000(11)	90.0000	90.0000
Volume ($Å^3$)	1048.73(17)	5160.4(10)	2625.5(5)	1394.6(8)	2611.8(9)	2979.6(6)
Space group	$P\bar{1}$	*C*2/*c*	*P*2/*c*	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Z value	2	8	4	2	4	4
D_{calc} (g/cm^3)	1.501	1.390	1.541	1.305	1.486	1.338
F_{000}	476.00	2176.00	1224.00	556.00	1176	1240.00
μ (Mo-K_α) (cm^{-1})	1.500	1.231	1.413	1.139	1.220	1.071
No. of reflections measured	12937	16293	18144	10569	6001	34273
R_{int}	0.0462	0.0445	0.0405	0.0309	0.0414	0.0417
Min. and max. transmissions	0.622, 0.799	0.475, 0.964	0.748, 0.958	0.764, 0.966	0.6273, 0.9031	0.882, 0.989
Unique reflections (number of parameters)	3818 (239)	4528 (295)	4732 (303)	4864 (302)	6001 (319)	5410 (316)
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0209	0.0382	0.0687	0.0360	0.0414	0.0275
Residuals: wR_2 (all reflections)	0.0454	0.0789	0.1971	0.1079	0.0923	0.0707
Goodness of fit indicator	0.971	1.093	1.206	1.154	1.129	1.043
Maximum peak in final diff. map ($e^-/Å^3$)	0.27	0.52	4.90	1.00	1.041	1.59
Minimum peak in final diff. map($e^-/Å^3$)	−0.70	−0.52	−0.98	−0.82	−0.818	−0.58

Table S4. Crystallographic data for compounds **6-9.**

Compound	**6a**	**6b**	**7a**	**7b**	**8**	**9**
Empirical formula	$C_{27}H_{33}PSTe$	$C_{33.50}H_{30}ClPSTe$	$C_{27}H_{33}PSeTe$	$C_{33.50}H_{30}ClPSeTe$	$C_{29}H_{37}C_{l6}PPtTe$	$C_{27}H_{33}AuBrPTe$
Formula weight	548.19	658.66	595.09	705.55	951.99	793.00
Temperature (°C)	173	173	173	173	173	173
Crystal color, habit	yellow prism	yellow plate	yellow prism	yellow block	yellow prism	colorless chip
Crystal dimensions (mm^3)	0.180x0.060 x0.060	0.9x0.7x0.2	0.140x0.050 x0.050	0.8x0.7x0.6	0.180x0.070 x0.060	0.020x0.020 x0.020
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
a (Å)	8.0020(6)	8.514(2)	7.9956(6)	12.718(4)	11.1070(8)	11.8160(10)
b (Å)	12.5836(10)	12.441(4)	12.6552(10)	16.843(6)	21.4081(16)	15.6910(17)
c (Å)	25.0953(19)	15.166(5)	25.1910(18)	16.874(6)	14.2556(10)	16.4486(16)
α (°)	90.0000	74.64(2)	90.0000	65.06(3)	90.0000	87.835(6)
β (°)	91.1510(19)	85.15(2)	91.600(2)	68.530(10)	92.1678(17)	73.923(6)
γ (°)	90.0000	71.93(2)	90.0000	68.94(2)	90.0000	82.403(6)
Volume ($Å^3$)	2526.4(3)	1472.6(8)	2548.0(3)	2958.7(18)	3387.3(4)	2904.7(5)
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z value	4	2	4	4	4	4
D_{calc} (g/cm^3)	1.441	1.485	1.551	1.584	1.867	1.813
F_{000}	1112.00	662	1184.00	1396	1832.00	1504.00
μ (Mo-K_α) (cm^{-1})	1.335	1.247	2.671	2.401	5.509	7.514
No. of reflections measured	30138	6688	30368	13321	41068	35781
R_{int}	0.0470	0.0394	0.0525	0.0494	0.0266	0.1227
Min. and max. transmissions	0.751, 0.923	0.7490, 1.0000	0.637, 0.875	0.4296, 1.0000	0.555, 0.719	0.680, 0.860
Unique reflections (number of parameters)	4644 (278)	6688 (355)	4680 (278)	13321 (682)	6228 (350)	10556 (573)
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0247	0.0394	0.0224	0.0494	0.0163	0.0699
Residuals: wR_2 (all reflections)	0.0682	0.1084	0.0584	0.1294	0.0401	0.1874
Goodness of fit indicator	1.062	1.031	1.015	1.017	1.020	0.987
Maximum peak in final diff. map ($e^-/Å^3$)	0.95	0.796	0.62	0.957	0.65	3.26
Minimum peak in final diff. map($e^-/Å^3$)	−0.24	−0.713	−0.33	−1.453	−0.59	−0.91

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