Supplementary material for:

Heavier Pnictinidene Gold(I) Complexes.

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Table S1. Relevant crystallographic data for the studied compounds.

	2	(**3**$^+$)[$Au_2(C{\equiv}CPh)_3]^-$	(**4**$^+$)[$Au(C{\equiv}CPh)_2]^-$
chemical formula	$C_{16}H_{23}AuClN_2Sb.CH_2Cl_2$	$C_{32}H_{46}As_2AuN_4.C_{24}H_{15}Au_2$ .0.5(C_7H_8)	$2(C_{32}H_{46}AuN_4Sb_2).2(C_{16}H_{10}Au).C_4H_8O$
Cryst syst	monoclinic	triclinic	monoclinic
Space group	*P2$_1$/c*	*P-1*	*P2$_1$/c*
a[Å]	13.2510(8)	13.9980(12)	17.4908(13)
b[Å]	12.8921(11)	14.9401(11)	21.2341(13)
c[Å]	16.0880(7)	15.6470(12)	27.3532(19)
α[°]	90	89.143(6)	90
β[°]	126.448(6)	64.451(7)	100.939(2)
γ[°]	90	72.326(7)	90
Z	4	2	4
μ[mm^{-1}]	8.215	9.095	6.974
D_x [Mg m^{-3}]	2.050	1.879	1.815
Cryst size [mm]	0.27×0.25×0.18	0.48x0.22x0.09	0.19×0.09×0.02
θ range, [deg]	1-27.5	1-27.5	2.372-25.9877
T_{min}, T_{max}	0.228, 0.351	0.4178, 0.7456	0.355, 0.867
no. of reflns measd	21 379	33 182	146 576
no. of unique reflns, R_{int}	5061, 0.045	8885, 0.065	19587, 0.028
no. of obsd reflns	4360	5685	16058
no. of params	217	606	1109
S all data	1.120	0.989	1.054
final R indices [*I>2σ(I)*]	0.036	0.045	0.024
wR2 indices (all data)	0.090	0.075	0.048
Δρ, max., min. [e $Å^{-3}$]	3.203, -1.884	1.059, -0.917	0.867, -1.244

	(**5**$^+$)[$BF_4]^-$	(**6**$^+$)[$BF_4]^-$	(**7**$^+$)[$BF_4]^-$
chemical formula	$2(C_{43}H_{59}AsAuN_4).2(BF_4).C_6H_6$	$C_{42.75}H_{58.75}AuN_{3.75}Sb.BF_4$	$C_{43.25}H_{59.25}AuBiN_4.BF_4$
Cryst syst	Triclinic	monoclinic	monoclinic
Space group	*P-1*	*P21/c*	*P21/c*
a[Å]	13.3370(8)	10.9280(17)	10.9912(3)
b[Å]	17.4601(15)	24.306(5)	24.1964(6)
c[Å]	19.7050(17)	19.2240(17)	19.3350(2)
α[°]	86.893(7)	90	90
β[°]	83.441(6)	119.412(8)	119.362(4)
γ[°]	85.496(8)	90	90
Z	2	4	4
μ[mm^{-1}]	4.016	3.951	7.241
D_x [Mg m^{-3}]	1.507	1.539	1.672
Crys tsize [mm]	0.59×0.36×0.22	0.45×0.24×0.20	0.59×0.26×0.26
Θ range, [deg]	1-27.5	1-27.5	1-27.5
T_{min}, T_{max}	0.323, 0.551	0.382, 0.608	0.192, 0.314
no. of reflns measd	94 388	35 980	37 310
no. ofunique reflns, R_{int}	20373, 0.054	10175, 0.079	10147, 0.086
no. of obsd reflns	15639	6683	6558
no. of params	1020	512	597
S all data	1.014	1.120	1.122
final R indices [*I>2σ(I)*]	0.043	0.066	0.072
wR2 indices (all data)	0.100	0.149	0.170
Δρ, max., min. [e $Å^{-3}$]	3.518, -2.592	1.821, -4.419	3.518, -2.592

Definitions: $R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | |F_o| - |F_c| | / \sum |F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

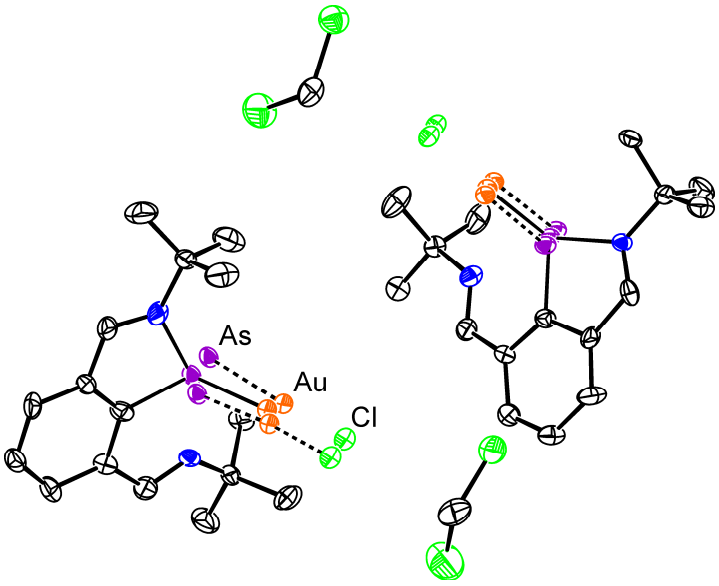
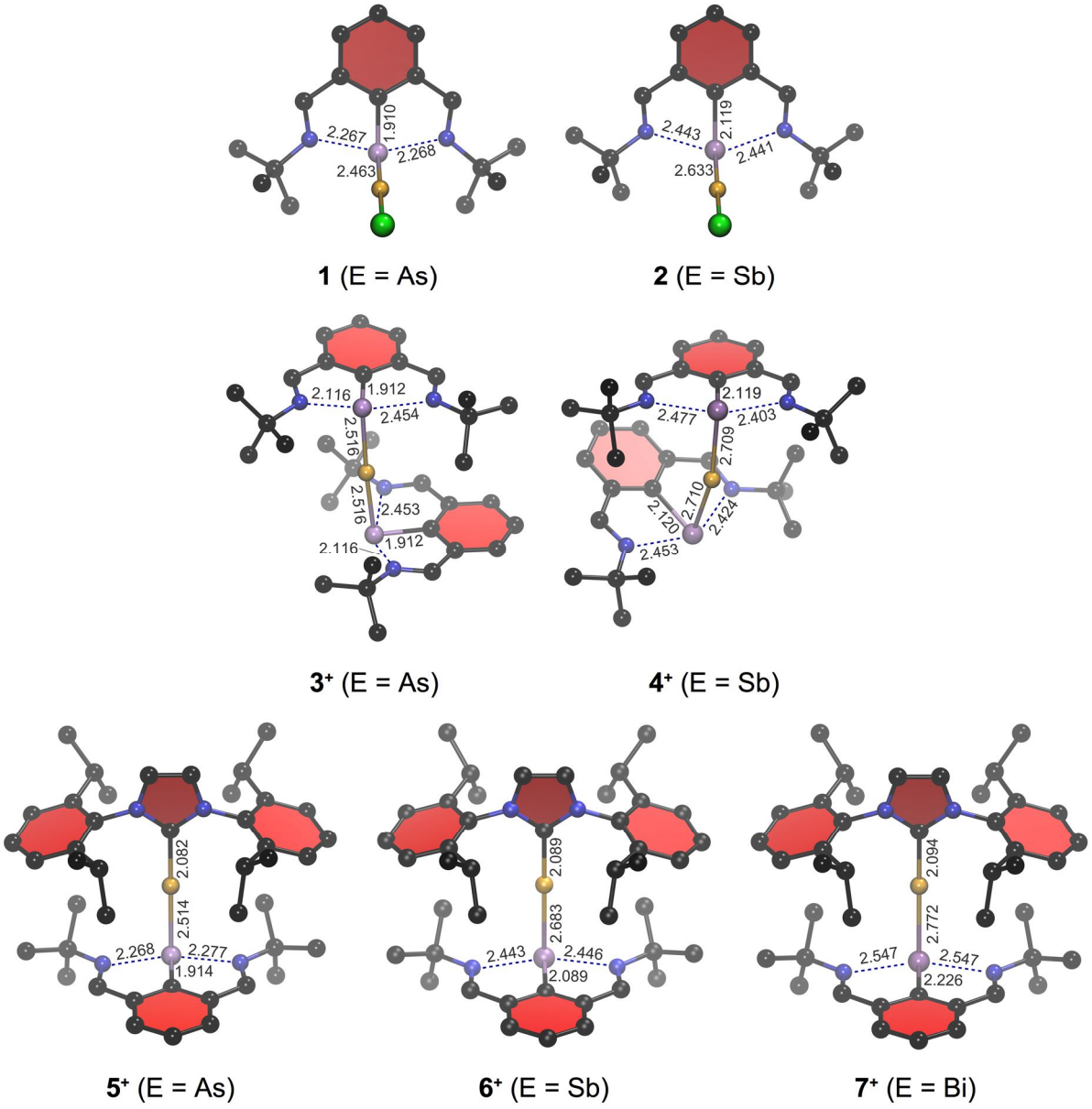


Figure S1. View on the heavily disordered structure of **1.**

Computational details

All calculations were carried out using Density Functional Theory (DFT) as implemented in the Gaussian09 quantum chemistry program.[S1] Geometry optimizations were carried out at the M06/cc-pVDZ[S2] level of theory (for heavier atoms - As, Sb, Bi, and Au - the cc-pVDZ-PP[S3] basis set including small-core relativistic pseudopotentials that account also for relativistic effects was used). The electronic energies were re-evaluated by additional single point calculations on each of all optimized geometries using the triple-ζ-quality cc-pVTZ(-PP) basis set. Analytical vibrational frequencies within the harmonic approximation were computed with the cc-pVDZ basis set to confirm a proper convergence to well-defined minima or saddle points on the potential energy surface. The subsequent NBO analysis[S4] and calculation of Wiberg bond indices[S5] were performed at the M06/cc-pVTZ(-PP) level.

Computational results



1 (E = As) **2** (E = Sb)

3$^+$ (E = As) **4**$^+$ (E = Sb)

5$^+$ (E = As) **6**$^+$ (E = Sb) **7**$^+$ (E = Bi)

Figure S2. M06/cc-pVDZ(-PP) optimized geometries of compounds **1**-**7**$^+$ (Hydrogen atoms are omitted for clarity) along with selected distances (in Å).

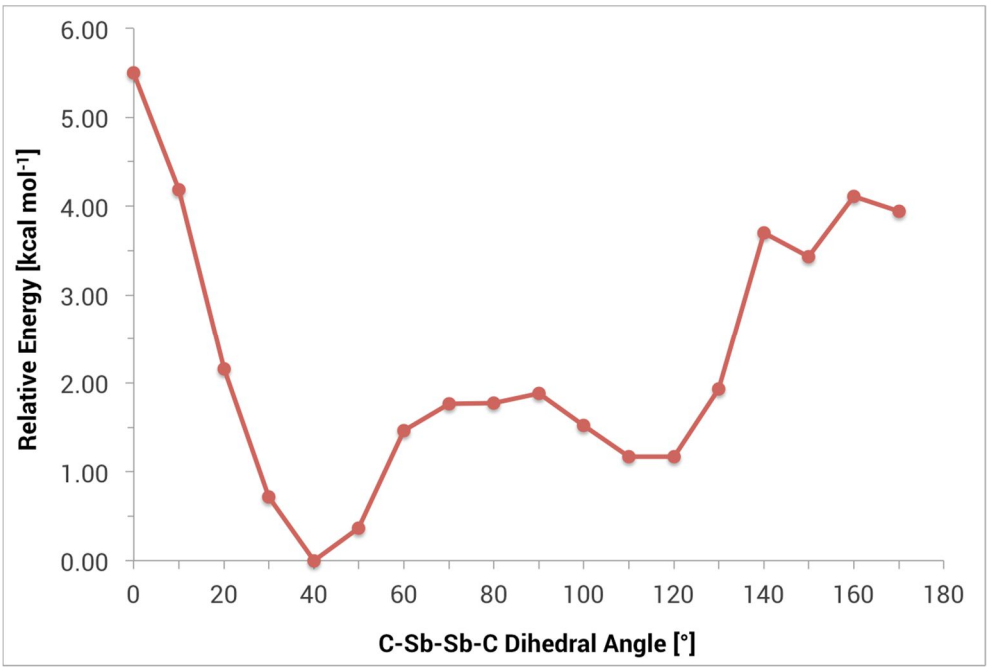


Figure S3. Relaxed potential energy scan along the C-Sb-Sb-C dihedral angle in $\mathbf{4}^{+}$.

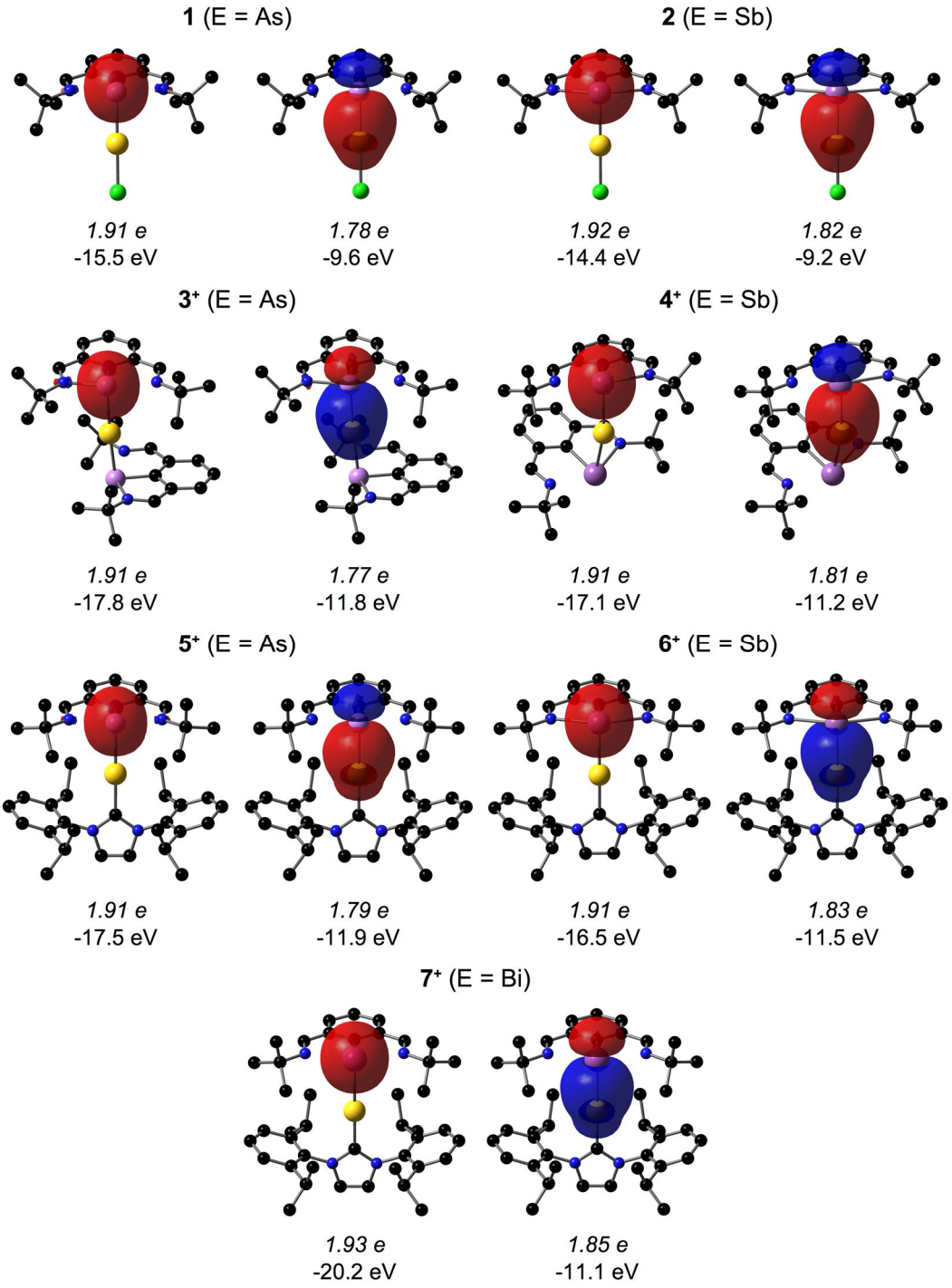


Figure S4. Relevant NBOs (isosurface 0.03 a.u.) showing the σ-type lone pair on the pnictogen center and E-Au σ-bond in **1**-**7**$^{+}$ (Hydrogen atoms are omitted for clarity). NBO populations and orbital energies are also displayed.

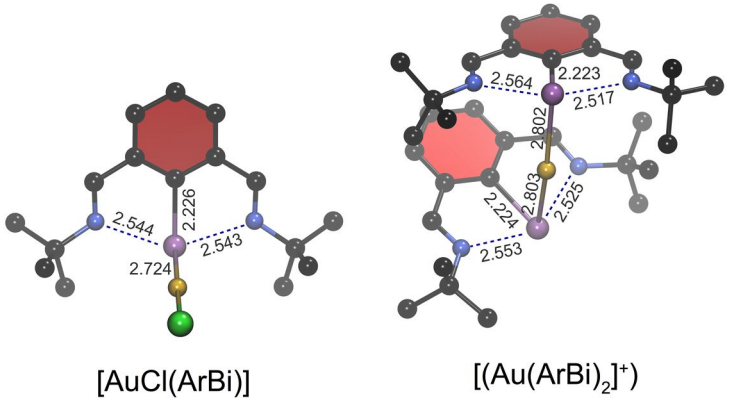


Figure S5. M06/cc-pVDZ(-PP) optimized geometries of compounds [AuCl(ArBi)] and $[Au(ArBi)_2]^+$ (Hydrogen atoms are omitted for clarity) along with selected distances (in Å).

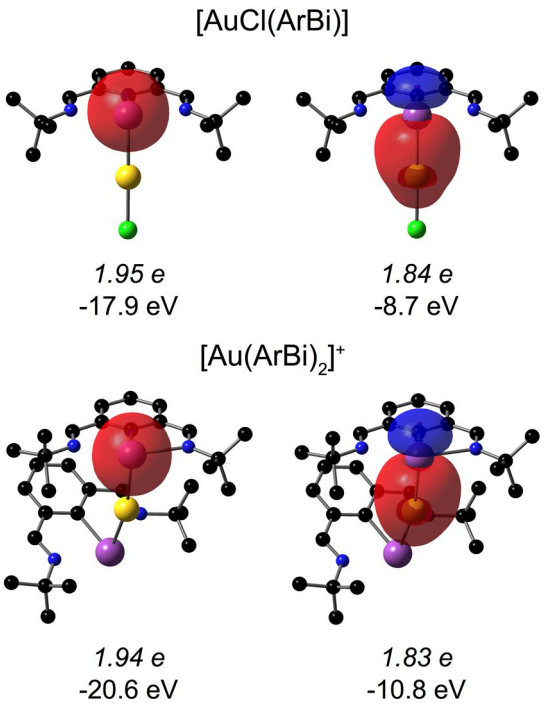


Figure S6. Relevant NBOs (isosurface 0.03 a.u.) showing the σ-type lone pair on the pnictogen center and E-Au σ-bond in [AuCl(ArBi)] and $[Au(ArBi)_2]^+$ (Hydrogen atoms are omitted for clarity). NBO populations and orbital energies are also displayed.

Table S2. Wiberg bond indices (WBI) and NPA atomic charges (q) for the compounds $[Au(IPr)(ACN)]^+$, $[Au(IPr)(DMAP)]^+$, $[Au(IPr)_2]^+$ and $[Au(IPr)(PPh_3)]^+$.

Compound	$WBI_{L\text{-}Au}$[a]	$WBI_{(IPr)\text{-}Au}$	q_{Au}	q_L[a]	$q_{C(IPr)}$
$[Au(IPr)(ACN)]^+$	0.33	0.65	0.43	-0.46	0.16
$[Au(IPr)(DMAP)]^+$	0.32	0.64	0.36	-0.59	0.17
$[Au(IPr)_2]^+$	0.51	0.51	0.19	0.14	0.14
$[Au(IPr)(PPh_3)]^+$	0.53	0.50	0.19	0.98	0.13

[a]L corresponds to the donor atom of the respective ligand.

References

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