Ring Expansion vs. Addition – Reactivity of a *cyclo*-P₄ Complex Towards Pnictogenium Cations

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Supporting Information

Author Contributions

Christoph Riesinger – performing experimental work, writing of original draft, X-ray data acquisition and finalization, performing DFT calculations.

Alexander Erhard – performing experimental work (synthesis of 1 and 4).

Manfred Scheer – project administration, funding acquisition, co-writing final manuscript.

All authors contributed to prepare the manuscript.

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1. Synthesis and Analytical Data

1.1. General Considerations

All manipulations were carried out using standard Schlenk techniques at a Stock apparatus under N_2 as an inert gas or in a glove box with Ar atmosphere. All glassware was dried with a heat gun (600 °C) for at least 30 min prior to use. o-DFB (1,2-difluorobenzene) was distilled from P₂O₅, CD₂Cl₂ was distilled from CaH₂ and other solvents were directly taken from an MBraun SPS-800 solvent purification system and degassed at room temperature. Solution ¹H (400.130 MHz), ¹⁹F (376.498 MHz)a and ³¹P (161.976 MHz) NMR spectra were recorded at an Avance400 (Bruker) spectrometer using (H₃C)₄Si (¹H, ¹³C), CFCl₃ (¹⁹F) or 85% phosphoric acid (^{31}P) , respectively, as external standards. Chemical shifts (δ) are provided in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets br = broad and m = multiplet. Mass spectra were recorded at the internal mass spectrometry department using a ThermoQuest Finnigan TSQ 7000 (ESI) or Finnigan MAT 95 (LIFDI) mass spectrometer or by the first author on a Waters Micromass LCT ESI-TOF mass-spectrometer and peak assignment was performed using the Molecular weight calculator 6.50.¹ Elemental analysis of the products was conducted by the elemental analysis department at the University of Regensburg using an Elementar Vario EL. The starting materials $[Cp''Ta(CO)_2(\eta^4-P_4)]$ (**A**), $[Cp''Ta(CO)_2(\eta^4-P_4)]$ (**B**),² TI[TEF],³ Cy₂AsBr⁴ and [Cp'''Sbl][TEF]⁵ were synthesized according to literature procedures. All other chemicals were purchased from commercial vendors and used without further purification.

1.2. Synthesis of [Cp‴Ta(CO)₂(η⁴-P₅Ph₂)][TEF] (1)

A solution of TI[TEF] (117 mg, 0.1 mmol, 1 eq.) in 4 mL *o*-DFB was added to a solution of **A** (59 mg, 0.1 mmol, 1 eq.) and Ph₂PCI (0.5 mL stock solution in toluene (c = 0.2 M), 0.1 mmol, 1 eq.) resulting in the rapid precipitation of colourless solid and a slow colour change to orange. After stirring the mixture for 2 h, 50 mL of *n*-hexane were added to precipitate a yellow solid. The supernatant was decanted, the solid dried and then resuspended in 4 mL of CH₂Cl₂. The yellow solution was filtered, constrained to 2 mL and again 50 mL of *n*-hexane were added to precipitate the product [Cp''Ta(CO)₂(η^4 -P₅Ph_2)][TEF] (1) as a yellow solid. After drying, 1 could be isolated as a yellow powder. Single crystals suitable for X-ray diffraction studies can be obtained by layering a concentrated solution of 1 in 3 mL of *o*-DFB with 15 mL of *n*-hexane and storing the mixture at -30 °C for 10 days.

Yield:	130 mg (0.075 mmol, 75%).		
Elemental analysis:	calc. (%) for C ₄₇ H ₃₉ O ₆ F ₃₆ AlP ₅ Ta•(C ₆ H ₁₄) _{0.3} : C: 33.07, H: 2.46.		
	found (%): C: 33.12, H: 2.28.		
	Notably, <i>n</i> -hexane is not found in the crystal structure of 1.		
	However, the ¹ H NMR spectrum of crystalline 1 reveals signals		
	in agreement with the presence of <i>n</i> -hexane, even after		
	extensive drying under reduced pressure.		
ESI(+) MS (o-DFB):	m/z (%) = 779.1 (90, [1] ⁺), 751.1 (100, [1-CO] ⁺), 723.2 (20, [2-		
	2CO] ⁺).		

NMR (CD ₂ Cl ₂ , r.t.):	¹ H : δ/ppm = 1.27 (s, 9 H, C ₅ H ₂ <u>^tBu₃</u>), 1.37 (s, 9 H, C ₅ H ₂ <u>^tBu₃</u>), 1.54
	(s, 9 H, C₅H₂ <u>′Bu₃</u>), 5.65 (s, 1 H, C₅ <u>H₂</u> ′Bu₃), 6.02 (m, 1 H,
	C5 <u>H2</u> ′Bu3), 7.21 (m, 2 H, Ph), 7.44 (m, 2 H, Ph), 7.54 (m, 1 H, Ph),
	7.66 (m, 2 H, Ph), 7.78 (m, 1 H, Ph), 8.16 (m, 2 H, Ph).
	³¹ P{¹H} : δ/ppm = 119.6 (m, 1 P, P ^A), -7.0 (m, 1 P, P ^M), -25.9 (m,
	1 P, P ^N), -104.9 (m, 1 P, P ^X), -108.3 (m, 1 P, P ^Y), coupling
	constants given with the spectral simulation (vide infra).
	³¹ P : δ/ppm = 119.6 (m (broadened), 1 P, P ^A), -7.0 (m, 1 P, P ^M), -
	25.9 (m, 1 P, P ^N), -104.9 (m, 1 P, P ^X), -108.3 (m, 1 P, P ^Y),
	coupling constants given with the spectral simulation (vide infra).
	¹⁹ F{ ¹ H} : δ/ppm = -75.6 (s, [TEF] ⁻).
IR (ATR, r. t.):	$\tilde{\nu}/\text{cm}^{-1}$ = 2975 (w), 2045 (m), 2008 (m), 1352 (m), 1297 (m), 1274
	(s), 1238 (vs), 1209 (vs), 1163 (s), 1096 (m), 969 (vs), 831 (w),
	742 (w), 726 (s), 701 (m), 689 (m)

1.3. Synthesis of [Cp''Ta(CO){Cp''Ta(CO)₂(μ , $\eta^{4:1}$ -P₄)}(η^{4} -P₅Cy₂)][TEF] (2)

Cy₂PBr (29 μ L stock solution in toluene (c = 1.07 M), 0.05 mmol, 0.5 eq.) was added to a solution of **B** (54 mg, 0.1mmol, 1 eq.) and TI[TEF] (58 mg, 0.05 mmol, 0.5 eq.) in 3 mL *o*-DFB resulting in the rapid precipitation of colourless solid and a slow colour change to orange-red. After stirring the mixture for one day, 50 mL of *n*-hexane were added to precipitate an orange solid. The supernatant was decanted, the solid dried and then resuspended in 3 mL of *o*-DFB. The solution was filtered, and again 60 mL of *n*-hexane were added to precipitate the product [Cp'Ta(CO){Cp'Ta(CO)₂(μ , $\eta^{4:1}$ -P₄}(η^4 -P₅Cy₂)][TEF] (**2**) as an orange-red solid. Single crystals suitable for X-ray diffraction studies could be obtained by layering a concentrated solution of **2** in 4 mL of *o*-DFB with 30 mL of *n*-hexane and storing the mixture at r. t. for 8 days.

Yield:	98 mg (0.043 mmol, 86%).
Elemental analysis:	calc. (%) for C ₅₇ H ₆₄ O ₇ F ₃₆ AlP ₉ Ta ₂ : C: 30.94, H: 2.92.
	found (%): C: 30.55, H: 2.91.
ESI(+) MS (o-DFB):	m/z (%) = 1244.9 (70, [2] ⁺), 1217.1 (10, [2 -CO] ⁺), 707.0 (100, [2 -
	B] ⁺), 679.1 (15, [2-B- CO] ⁺).
NMR (CD ₂ Cl ₂ , r.t.):	¹ H : δ/ppm = 1.09 (s, 9 H, C ₅ H ₃ ^{<i>i</i>} Bu ₂), 1.12 (s, 9 H, C ₅ H ₃ ^{<i>i</i>} Bu ₂), 1.14
	(s, 9 H, C ₅ H ₃ ^{<i>i</i>} <u>Bu</u> ₂), 1.52 (s, 9 H, C ₅ H ₃ ^{<i>i</i>} <u>Bu</u> ₂), 0.8 - 2.3 (several
	overlapping multiplets, Cy), 4.33 (m, 1 H, C ₅ <u>H</u> ₃ ^t Bu ₂), 5.37 ((m, 1
	H, $C_5 \underline{H_3}^t Bu_2$), 5.82 (m, 1 H, $C_5 \underline{H_3}^t Bu_2$), 6.10 (m, 1 H, $C_5 \underline{H_3}^t Bu_2$),
	6.16 (m, 1 H, C₅ <u>H</u> ₃′Bu₂), 6.33 (m, 1 H, C₅ <u>H</u> ₃′Bu₂).
	³¹ P{¹H} : δ/ppm = 129.7 (m, 1 P, P ^A), 3.3 (m, 1 P, P ^M), -12.1 (m, 1
	P, P ^N), -22.0 (m, 1 P, P ^O), -43.9 (m, 1 P, P ^P), -70.9 (m, 1 P,
	P ^Q), -74.7 (m, 1 P, P ^R), -127.4 (m, 1 P, P ^X), -129.3 (m, 1 P, P ^Y),
	coupling information is discussed below (vide infra).

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1.4. Synthesis of [Cp''Ta(CO)₂(η^4 -P₄AsCy₂)][TEF] (3)

Cy₂AsBr (15 μ L, 0.1 mmol, 1 eq.) was added to a solution of **B** (54 mg, 0.1 mmol, 1 eq.) and TI[TEF] (117 mg, 0.1 mmol, 1 eq.) in 4 mL *o*-DFB resulting in the rapid precipitation of colourless solid and a slow colour change to orange. After stirring the mixture for 3 h, the solution was constrained to 1 mL and 50 mL of *n*-hexane were added to precipitate an orange solid. The supernatant was decanted, the solid dried and then resuspended in 4 mL of *o*-DFB. The solution was filtered, and again 30 mL of *n*-hexane were added to precipitate the product [Cp''Ta(CO)₂(η^4 -P₄AsCy₂)][TEF] (**3**) as a red oil. This oil was washed with 5 mL of toluene and two times with 10 mL of *n*-hexane, each, affording **3** as a red solid, which could be isolated after drying under reduced pressure (10⁻³ mbar). Single crystals suitable for X-ray diffraction studies could be obtained by layering a concentrated solution of **3** in 2 mL of *o*-DFB with 20 mL of *n*-hexane and storing the mixture at -30 °C for one month.

Yield:	125 mg (0.072 mmol, 72%).
Elemental analysis:	calc. (%) for C ₄₃ H ₄₃ O ₆ F ₃₆ AlP ₄ AsTa•(C ₆ H ₄ F ₂) _{0.4} : C: 30.43, H: 2.51.
	found (%): C: 30.33, H: 2.54.
ESI(+) MS (o-DFB):	m/z (%) = 779.1 (40, [3] ⁺), 751.1 (100, [3 -CO] ⁺), 723.2 (40, [2 -
	2CO] ⁺), 483.2 (90, [B -2CO+H] ⁺).
NMR (<i>o</i> -DFB/C ₆ D ₆ , r.t.):	¹ H : δ/ppm = 1.28 (s, 9 H, C ₅ H ₃ ^{<i>i</i>} <u>Bu</u> ₂), 1.39 (s, 9 H, C ₅ H ₃ ^{<i>i</i>} <u>Bu</u> ₂), 1.0
	- 2.5 (several overlapping multiplets, Cy), 5.12 (m, 1 H,
	C₅ <u>H</u> ₃ [′] Bu₂), 5.74 (m, 1 H, C₅ <u>H</u> ₃ [′] Bu₂), 5.89 (m, 1 H, C₅ <u>H</u> ₃ [′] Bu₂).
	³¹ P { ¹ H }: δ /ppm = -11.7 (td, ¹ J_{PA-PM} = 361 Hz, ¹ J_{PA-PX} = 359 Hz,
	${}^{2}J_{PA-PY} = 46$ Hz, 1 P, P ^A), -33.7 (ddd, ${}^{1}J_{PM-PY} = 388$ Hz, ${}^{1}J_{PM-PA} =$
	361 Hz, ${}^{2}J_{PM-PX}$ = 48 Hz, 1 P, P ^M), -108.2 (dd, ${}^{1}J_{PX-PA}$ = 359 Hz,
	${}^{2}J_{PX-PM} = 48$ Hz, 1 P, P ^X), -111.0 (dd, ${}^{1}J_{PY-PM} = 388$ Hz, ${}^{2}J_{PY-PA} =$
	46 Hz, 1 P, P ^Y).
	³¹ P : δ/ppm = -11.7 (td, ${}^{1}J_{PA-PM}$ = 361 Hz, ${}^{1}J_{PA-PX}$ = 359 Hz, ${}^{2}J_{PA-PY}$
	= 46 Hz, 1 P, P ^A), -33.7 (ddd, ${}^{1}J_{PM-PY}$ = 388 Hz, ${}^{1}J_{PM-PA}$ = 361 Hz,
	${}^{2}J_{\text{PM-PX}}$ = 48 Hz, 1 P, P ^M), -108.2 (dd, ${}^{1}J_{\text{PX-PA}}$ = 359 Hz, ${}^{2}J_{\text{PX-PM}}$ =
	48 Hz, 1 P, P ^X), -111.0 (dd, ${}^{1}J_{PY-PM} = 388$ Hz, ${}^{2}J_{PY-PA} = 46$ Hz, 1
	P, P ^Y).

	¹⁹ F{ ¹ H}: δ/ppm = -75.5 (s, [TEF] ⁻).
IR (ATR, r. t.):	$\tilde{\nu}$ /cm ⁻¹ = 2933 (w), 2039 (w), 2001 (w), 1351 (m), 1297 (m), 1274
	(s), 1210 (vs), 1164 (s), 969 (vs), 8857 (m), 831 (w), 756 (w), 726
	(s)

1.5. Synthesis of [{Cp''Ta(CO)₂(η^{4} -P₄)}₂SbPh₂][TEF] (4)

A solution of Ph₂SbCl (31 mg, 0.01 mmol, 1 eq.) in 2 mL *o*-DFB was added to a solution of **B** (108 mg, 0.2 mmol, 2 eq.) and TI[TEF] (117 mg, 0.1 mmol, 1 eq.) in 4 mL of *o*-DFB resulting in the rapid precipitation of colourless solid and a slow colour change to brownish yellow. After stirring the mixture for 2 h, 50 mL of *n*-hexane were added to precipitate a yellow solid. The supernatant was decanted, the solid dried and then resuspended in 4 mL of CH₂Cl₂. The yellowish solution was filtered, constrained to 2 mL and again 50 mL of *n*-hexane were added to precipitate the product [{Cp'Ta(CO)₂(η^4 -P₄)}₂SbPh₂][TEF] (**4**) as a brownish yellow solid. After drying, **4** could be isolated as a brownish yellow powder. Single crystals suitable for X-ray diffraction studies could be obtained by slow addition of 20 mL of *n*-hexane to a concentrated solution of **4** in 2 mL of *o*-DFB.

Yield:	170 mg (0.073 mmol, 73%).		
Elemental analysis:	calc. (%) for C ₅₈ H ₅₂ O ₈ F ₃₆ AlP ₈ SbTa ₂ : C: 30.03, H: 2.26.		
	found (%): C: 30.15, H: 2.28.		
ESI(+) MS (o-DFB):	m/z (%) = 1323.1 (20, [4 -CO] ⁺), 813.0 (100, [4 - B] ⁺), 539.1 (70,		
	$[\mathbf{B}+\mathbf{H}]^{+})$, 483.1 (60, $[\mathbf{B}-2\mathbf{CO}+\mathbf{H}]^{+})$, several unidentified		
	fragmentation products.		
NMR (CD ₂ Cl ₂ , r.t.):	¹ H : δ /ppm = 1.11 (s, 36 H, C ₅ H ₃ ^{<i>i</i>} Bu ₂), 6.15 (m, 4 H, C ₅ H ₃ ^{<i>i</i>} Bu ₂),		
	6.45 (m, 2 H, C ₅ <u>H</u> 3 ^t Bu ₂), 7.62 (m (br), 6 H, Ph), 7.79 (m (br), 4 H,		
	Ph).		
	³¹ P{¹H} : δ/ppm = 40.1 (t (br), ${}^{1}J_{PA-PX}$ = 297 Hz, 1 P, P ^A), 16.7 (t		
	(br), ${}^{1}J_{PM-PX} = 247$ Hz, 1 P, P ^M), -4.7 (dd (br), ${}^{1}J_{PX-PA} = 297$ Hz,		
	${}^{1}J_{PX-PM} = 247 \text{ Hz}, 2 \text{ P}, \text{ P}^{X}$).		
	³¹ P : δ/ppm = 40.1 (t (br), ${}^{1}J_{PA-PX}$ = 297 Hz, 1 P, P ^A), 16.7 (t (br),		
	${}^{1}J_{PM-PX} = 247$ Hz, 1 P, P ^M), -4.7 (dd (br), ${}^{1}J_{PX-PA} = 297$ Hz, ${}^{1}J_{PX-PM}$		
	= 247 Hz, 2 P, P ^x).		
	¹⁹ F{ ¹ H}: δ/ppm = -75.6 (s, [TEF] ⁻).		
IR (ATR, r. t.):	\tilde{v} /cm ⁻¹ = 2963 (w), 2030 (m), 2020 (s), 1986 (s), 1367 (m), 1351		
	(m), 1296 (s), 1274 (s), 1239 (s), 1211 (vs), 1164 (s), 1061 (m),		
	971 (vs), 919 (m), 880 (m), 859 (m), 830 (m), 726 (vs), 693 (m)		

1.6. Synthesis of [Cp‴Ta(CO)₂(η⁴-P₄Sb(I)Cp‴)][TEF] (5)

A solution of Cp^{'''}Sbl₂ (61 mg, 0.1 mmol, 1 eq.) in 2 mL *o*-DFB was added to a solution of **A** (59 mg, 0.1 mmol, 1 eq.) and TI[TEF] (117 mg, 0.1 mmol, 1 eq.) in 4 mL of *o*-DFB resulting in the rapid precipitation of pale yellow solid and a slow colour change to clear red. After stirring the mixture for 2 h, 50 mL of *n*-hexane were added to precipitate a red solid. The supernatant was decanted, the solid dried and then resuspended in 4 mL of CH₂Cl₂. The red solution was filtered, constrained to 2 mL and again 50 mL of *n*-hexane were added to precipitate the product [Cp^{'''}Ta(CO)₂(η^4 -P₄Sb(I)Cp^{'''})][TEF] (**5**) as a clear red solid. After drying, **5** could be isolated as a red powder. Single crystals suitable for X-ray diffraction studies could be obtained by layering a concentrated solution of **5** in 3 mL of CH₂Cl₂ with 30 mL of *n*-hexane and storing the mixture at -30 °C for two weeks.

Yield:	115 mg (0.056 mmol, 56%).			
Elemental analysis:	calc. (%) for C ₅₂ H ₅₈ O ₆ F ₃₆ AlP ₄ SbITa: C: 30.56, H: 2.86.			
	found (%): C: 30.92, H: 2.95.			
ESI(+) MS (<i>o</i> -DFB):	m/z (%) = 404.3 (70), 279.2 (100), 5 undergoes complete			
	fragmentation leading to decomposition under mass			
	spectrometric conditions.			
NMR (CD ₂ Cl ₂ , r.t.):	¹ H : δ/ppm = 1.05 (s, 9 H, C ₅ H ₂ ^t Bu ₃), 1.45 (s, 9 H, C ₅ H ₂ ^t Bu ₃), 1.52			
	(s, 18 H, C_5H_2 ^{<i>t</i>} Bu ₃), 1.56 (s, 18 H, C_5H_2 ^{<i>t</i>} Bu ₃), 6.38 (s, 2 H,			
	C₅ <u>H</u> ₂′Bu₃), 6.71 (s, 2 H, C₅ <u>H</u> ₂′Bu₃).			
	³¹ P { ¹ H }: \overline{o} /ppm = 39.4 (t (br), ¹ J _{PA-PX} = 300 Hz, 1 P, P ^A), 10.8 (t			
	(br), ${}^{1}J_{PM-PX} = 253$ Hz, 1 P, P ^M), -1.1 (dd (br), ${}^{1}J_{PX-PA} = 300$ Hz,			
	${}^{1}J_{PX-PM} = 253 \text{ Hz}, 2 \text{ P}, \text{ P}^{X}$).			
	³¹ P : δ /ppm = 39.4 (t (br), ¹ J _{PA-PX} = 300 Hz, 1 P, P ^A), 10.8 (t (br))			
	${}^{1}J_{PM-PX}$ = 253 Hz, 1 P, P ^M), -1.1 (dd (br), ${}^{1}J_{PX-PA}$ = 300 Hz, ${}^{1}J_{PX-PM}$			
	= 253 Hz, 2 P, P ^x).			
	¹⁹ F{ ¹ H}: δ/ppm = -75.6 (s, [TEF] ⁻).			
IR (ATR, r. t.):	$\tilde{\nu}/\text{cm}^{-1}$ = 2975 (w), 2025 (m), 1988 (m), 1352 (m), 1297 (m), 1274			
	(s), 1239 (s), 1211 (vs), 1163 (s), 1061 (w), 970 (vs), 878 (w),			
	833 (w), 726 (vs), 693 (w), 680 (w)			

2. Crystallographic Data

2.1. General Consideration

The crystallographic data for all described compounds were collected on a SuperNova diffractometer (Rigaku) with a Titan^{S2} detector using Cu–K_{α} radiation (**3**, **5**), on an Xcalibur Gemini (Rigaku) with an Atlas^{S2} detector using Cu–K_{α} (**1**, **4**) radiation, or an XtaLAB Synergy R, DW System (Rigaku) with a HyPix-Arc 150 detector using Cu-K_{α} radiation from a rotating anode (**2**). Data reduction and absorption correction were performed with the CrysAlisPro software package.⁶ Structure solution and refinement was conducted in Olex2 (1.5-alpha)⁷ with ShelXT⁸ (solution) and ShelXL-2018/3⁹ (least squares refinement (F²)). All non-H atoms were refined with anisotropic displacement parameters and H atoms were treated as riding models with isotropic displacement parameters and fixed C–H bond lengths (sp³: 0.96 (CH₃), 0.97 (CH₂); sp²: 0.93 (CH)). Visualisation of the crystal structures was performed with Olex2 (1.5-alpha).⁷

CCDC-2280522 (1), CCDC-2280523 (2), CCDC-2280524 (3), CCDC-2280525 (4), and CCDC-2280526 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Table S 1: Crystallographic and refinement data for compounds 1 - 5.

Compound	1	2	3	4	5
Empirical formula	C47H39AlF36O6P5Ta	C57H64O7F36AlP9Ta2	C46H45AlAsF37O6P4Ta	C58H52O8F36AlP8SbTa2	C52H58O6F36AlP4SbITa
Formula weight	1746.71	2212.69	1803.55	2319.38	2043.44
Temperature/K	293(2)	123.01(10)	122.98(14)	123(2)	123.00(10)
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	14.9785(3)	15.59941(8)	10.4865(2)	11.8387(3)	10.6596(4)
b/Å	15.3177(3)	16.56789(7)	14.5949(3)	17.1357(3)	16.9425(5)
c/Å	15.6939(3)	16.90000(7)	21.4991(5)	20.9703(5)	21.4058(7)
$\alpha/^{\circ}$	95.299(2)	112.5307(4)	79.473(2)	111.931(2)	109.867(3)
β/°	108.400(2)	99.2052(4)	79.942(2)	96.332(2)	91.228(3)
γ/°	110.628(2)	91.6604(4)	85.7070(10)	90.449(2)	98.222(3)
Volume/Å3	3112.47(12)	3962.89(3)	3182.19(12)	3916.65(16)	3588.2(2)
Z	2	2	2	2	2
pcalcg/cm3	1.864	1.854	1.882	1.967	1.891
μ/mm-1	6.048	8.043	6.282	10.640	11.365
F(000)	1708.0	2160.0	1762.0	2236.0	1984.0
Crystal size/mm3	0.444 × 0.175 × 0.048	$0.34 \times 0.24 \times 0.13$	$0.31\times0.196\times0.124$	$0.322 \times 0.102 \times 0.034$	0.093 × 0.061 × 0.044
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
20 range for data collection/°	7.182 to 143.762	5.762 to 148.126	6.852 to 133.874	7.524 to 143.92	8.256 to 134.154
Index ranges	-17 ≤ h ≤ 18, -18 ≤	$-19 \leq h \leq 19, -20 \leq k \leq$	$-12 \leq h \leq 11, -14 \leq k \leq$	$-14 \leq h \leq 14, -16 \leq k \leq$	$-12 \leq h \leq 12, -20 \leq k \leq$
index ranges	k ≤ 18, -19 ≤ l ≤ 19	20, -21 ≤ l ≤ 20	17, -25 ≤ l ≤ 25	21, -25 ≤ l ≤ 25	20, -25 ≤ l ≤ 25
Reflections collected	34318	148006	55899	43183	38301
	11896 [Rint =	15538 [Rint =	11297 [Rint =	15015 [Rint =	12796 [Rint =
Independent reflections	0.0369, Rsigma =	0.0387, Rsigma =	0.0361, Rsigma =	0.0477, Rsigma =	0.0980, Rsigma =
	0.0368]	0.0141]	0.0227]	0.0512]	0.0931]
Data/restraints/parameters	11896/6336/1478	15538/660/1248	11297/404/1268	15015/78/1233	12796/146/1019
Goodness-of-fit on F2	1.038	1.149	1.064	1.024	1.012
Final R indexes [I>= 2σ (I)]	R1 = 0.0358, wR2 = 0.0929	R1 = 0.0249, wR2 = 0.0628	R1 = 0.0389, wR2 = 0.1024	R1 = 0.0381, wR2 = 0.0985	R1 = 0.0545, wR2 = 0.1290
Final R indexes [all data]	R1 = 0.0389, wR2 = 0.0953	R1 = 0.0250, wR2 = 0.0628	R1 = 0.0392, wR2 = 0.1026	R1 = 0.0441, wR2 = 0.1035	R1 = 0.0724, wR2 = 0.1427
Largest diff. peak/hole / e Å- 3	1.70/-0.63	0.89/-1.14	3.41/-0.98	1.77/-1.65	2.18/-1.94

2.2. [Cp'''Ta(CO)₂(η^4 -P₅Ph₂)][TEF] (1)

Compound **1** crystallizes in the triclinnic space group $P\overline{1}$ forming yellowish-orange plates from *o*-DFB/*n*-hexane mixtures at -30 °C (Figure S 1). The asymmetric unit contains the cation and one anion. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion and the cation was treated with appropriate restraints.



Figure S 1: Solid state structure of 1; Shown is the asymmetric unit containing one cation and one anion; ellipsoids are drawn at the 50% probability level.

2.3. [Cp''Ta(CO){Cp''Ta(CO)₂(μ , $\eta^{4:1}$ -P₄)}(η^{4} -P₅Cy₂)][TEF] (2)

Compound **2** crystallizes in the triclinnic space group $P\overline{1}$ forming clear orange blocks from *o*-DFB/*n*-hexane mixtures at room temperature (Figure S 2). The asymmetric unit contains the cation and one anion. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion was treated with appropriate restraints.



Figure S 2: Solid state structure of **2**; Shown is the asymmetric unit containing one cation and one anion; ellipsoids are drawn at the 50% probability level.

2.4. [Cp"Ta(CO)₂(η⁴-P₄AsCy₂)][TEF] (3)

Compound **3** crystallizes in the triclinnic space group $P\overline{1}$ forming clear orange blocks from o-DFB/*n*-hexane mixtures at -30 °C (Figure S 3). The asymmetric unit contains the cation, one anion and 0.4 o-DFB. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion was treated with appropriate restraints.



Figure S 3: Solid state structure of **3**; Shown is the asymmetric unit containing one cation, one anion and 0.4 o-DFB (treated with a solvent mask); ellipsoids are drawn at the 50% probability level.

2.5. [{Cp''Ta(CO)₂(η^4 -P₄)}₂SbPh₂][TEF] (4)

Compound **4** crystallizes in the triclinnic space group $P\overline{1}$ forming dark orange plates upon addition of *n*-hexane to a concentrated solution in *o*-DFB at room temperature (Figure S 4). The asymmetric unit contains the cation and one anion. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion was treated with appropriate restraints.



Figure S 4: Solid state structure of 4; Shown is the asymmetric unit containing one cation and one anion; ellipsoids are drawn at the 50% probability level.

2.6. [Cp'''Ta(CO)₂(η^4 -P₄Sb(I)Cp''')][TEF] (5)

Compound **5** crystallizes in the triclinnic space group $P\overline{1}$ forming intense yellow blocks from *o*-DFB/*n*-hexane mixtures at -30 °C (Figure S 5). The asymmetric unit contains the cation and one anion. All non-hydrogen atoms were refined anisotropically and the H atoms were treated as riding models. Disorder within the anion was treated with appropriate restraints.



Figure S 5: Solid state structure of **5**; Shown is the asymmetric unit containing one cation and one anion; ellipsoids are drawn at the 50% probability level.

3. Spectroscopic Data

3.1.[Cp‴Ta(CO)₂(η⁴-P₅Ph₂)][TEF] (1)



Figure S 6: ¹H NMR spectrum of **1** in CD₂Cl₂ recorded at room temperature; * marks the residual solvent signal of CH₂Cl₂.



Figure S 7: ³¹P and ³¹P{¹H} NMR spectra of **1** in CD_2Cl_2 recorded at room temperature and experimental (top) as well as simulated (bottom) spectra shown in the enlarged inserts.

Table S 2: Spectral parameters of the ${}^{31}P{}^{1}H$ NMR spectrum of **1** in CD₂Cl₂ recorded at room temperature.

	Ηz	δ	ppm
¹ <i>Ј</i> _{РА-РХ}	360.9	P ^A	119.6
¹ J _{PA-PY}	370.7	P ^M	-7.1
¹ J _{PM-PN}	366.8	P ^N	-25.9
¹ <i>J</i> _{PM-PY}	362.7	P ^x	-104.9
$^{1}J_{\text{PN-PX}}$	391.4	P ^Y	-108.3
² J _{PA-PM}	11.0		
${}^{2}J_{PA-PN}$	7.1		
² J _{PM-PN}	40.6		
$^{2}J_{\text{PN-PY}}$	41.4		
$^{2}J_{PX-PY}$	1.8		
R-factor (%)	6.8		



Figure S 8: ${}^{19}F{}^{1}H$ NMR spectrum of **1** in CD₂Cl₂ recorded at room temperature.

3.2. [Cp''Ta(CO){Cp''Ta(CO)₂(μ , $\eta^{4:1}$ -P₄)}(η^{4} -P₅Cy₂)][TEF] (2)

The formation of **2** via an intermediate, which is isostructural to **1**, is highly plausible and should then be followed by decarbonylation accompanied by addition of a second equivalent of **B**. However, already after one hour signals corresponding to **2** are clearly visible in the ³¹P NMR spectrum of the reaction mixture without any traces of an intermediate. This strongly points towards the rapid decarbonylation of the hypothetical intermediate under the reaction conditions (room temperature, *o*-DFB). Furthermore, this is supported by our observation of formation of **2** even in reactions of equimolar amounts of starting materials.



Figure S 9: ¹H NMR spectrum of **2** in CD₂Cl₂ recorded at room temperature; * marks the residual solvent signal of CH_2Cl_2 and * the signal from residual H-grease.



Figure S 10: ${}^{31}P{}^{1}H$ NMR spectrum of **2** in CD₂Cl₂ recorded at room temperature; * marks the signals of traces of unreacted **B**.



Figure S 11: ³¹P NMR spectrum of **2** in CD₂Cl₂ recorded at room temperature; * marks the signals of traces of unreacted **B**.



Figure S 12: ${}^{19}F{}^{1}H$ NMR spectrum of **2** in CD₂Cl₂ recorded at room temperature.

3.3. [Cp"Ta(CO)₂(η^4 -P₄AsCy₂)][TEF] (3)

While the solid state structure of **3** (Figure S 3) clearly shows a coordinated arsenium residue at the *cyclo*-P₄ ligand, the ³¹P NMR spectra in *o*-DFB point towards the insertion of the arsenium ion into the P₄ cycle and thus formation of a *cyclo*-P₄AsCy₂ ligand. The presence of four chemically inequivalent ³¹P nuclei of which two only show one ¹*J*_{P-P} coupling is clear indication for this insertion taking place in solution. The spectra are well reproduced even upon dissolving crystalline **3** in cold *o*-DFB. However, **3** rapidly degrades in CD₂Cl₂ solution limiting the temperature range to -30 °C.



Figure S 13 ¹H NMR spectrum of **3** in o-DFB with C_6D_6 capillary recorded at room temperature; the signal of o-DFB is cut off for clarity.



Figure S 14: ${}^{31}P{}^{1}H{}$ NMR spectrum of **3** in o-DFB (with C_6D_6 capillary) recorded at room temperature; small additional signals indicate the rapid degradation of this compound in solution at room temperature.



Figure S 15: ³¹P NMR spectrum of **3** in o-DFB (with C_6D_6 capillary) recorded at room temperature; small additional signals indicate the rapid degradation of this compound in solution at room temperature.



Figure S 16: ${}^{19}F{}^{1}H$ NMR spectrum of **3** in CD₂Cl₂ recorded at room temperature; * marks the signal of o-DFB.

3.4. [{Cp''Ta(CO)₂(η^4 -P₄)}₂SbPh₂][TEF] (4)



Figure S 17: ¹H NMR spectrum of **4** in CD₂Cl₂ recorded at room temperature.

Figure S 18: ${}^{31}P{}^{1}H$ NMR spectrum of **4** in CD_2CI_2 recorded at room temperature.

Figure S 19: 31 P NMR spectrum of **4** in CD₂Cl₂ recorded at room temperature.

Figure S 20: ${}^{19}F{}^{1}H$ NMR spectrum of **4** in CD₂Cl₂ recorded at room temperature.

3.5. [Cp'''Ta(CO)₂(η^4 -P₄Sb(I)Cp''')][TEF] (5)

Figure S 21 ¹H NMR spectrum of **5** in CD₂Cl₂ recorded at room temperature.

Figure S 22: ${}^{31}P{}^{1}H$ NMR spectrum of **5** in CD₂Cl₂ recorded at room temperature.

Figure S 23: 31 P NMR spectrum of **5** in CD₂Cl₂ recorded at room temperature.

Figure S 24: ${}^{19}F{}^{1}H$ NMR spectrum of **5** in CD₂Cl₂ recorded at room temperature.

4. Computational Details

4.1. General Considerations

DFT calculations were performed using the Orca 5.0 software package.¹⁰ The sterically demanding Cp^R were replaced with unsubstituted Cp ligands and the dimethylpnictogenium cations [Me₂E]⁺ (E = P, As, Sb) were used to save computational resources. Geometry optimizations were performed at the ω B97X-D4¹¹/def2-TZVP¹² level of theory with PCM solvent correction for CH₂Cl₂.¹³ Stationary points were verified by analytical frequency calculations. Single point calculations were performed at the ω B97X-D4/def2-TZVP level of theory with solvent correction as described above. Imaginary modes with a value higher than -30 cm⁻¹ were not considered due to approximations implemented in Orca 5.0. The differences in energy between the ring expanded insertion products and the respective coordination products **1'** – **4''** are listed in Table S 3.

Table S 3: Computed (@ ω B97X-D4/def2-TZVP) energy differences between the ring expanded and the coordinated species in the model systems 1'-4''.

	1′	3′	4″
⊿G(Ins-Coord) [kJ/mol]	-86.0	-43.9	-1.5

4.2. NBO Analysis

NBO analyses were performed using the NBO7.0 software package.¹⁴ To gain further insight into the electronic structure of the coordinated species, NBO analysis was performed. Representative NBOs for **1'**coord, **3'**coord, **4"**coord and **4'** are provided in Figure S25. While the monocoordinated compounds all feature expressed P-E (E = P, As, Sb) bonding (WBI: 0.90 (**1'**coord), 0.83 (**3'**coord) and 0.71 (**4"**coord)), this bond becomes more polar going down the group. This is supported by NLMO analysis providing orbital contributions of 62% P: 38% P (**1'**coord), 68% P:32% As (**3'**coord) and 74% P: 26% Sb (**4"**coord). Accordingly, the WBIs decrease (0.90 (**1'**coord), 0.83 (**3'**coord), 0.71 (**4"**coord)) and the s-character of the lone-pair at the former pnictogenium cation increases (52% (**1'**coord), 63% (**3'**coord), 70% (**4"**coord)). This again is in line with the decreased "carbene-like" character of heavy pnictogenium cations and thus supports the formation of a ring expanded product for phosphenium ions, while their heavier congeners yield addition products. Furthermore, the bonding situation within **4'** is more complicated, as there are no directly bonding NBOs to be found for the P-Sb interactions. However, the linear combination of

NBOs 79 and 84 fits the symmetry of an empty p-orbital at Sb (NBO 157), supporting a more electrostatic attractive interaction within **4'**. This is in line with significantly decreased WBIs (P-Sb: 0.41/0.38) and earlier investigations on phosphine complexes of stibenium cations.¹⁵

Figure S 25: Selected NBOs for 1' - 4' from DFT calculations at the ω B97X-D4/def2-TZVP level of theory.

4.3. Optimized Geometries

1′_{Ins}

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -2264.25837190, Enthalpies/H = -2264.25742769, Free Energies/H = -2264.32298419, ZPVE/ kcal/mol = 130.86

Та	-10.77671291793124	6.29787527240214	-7.42909739228838
Ρ	-11.10429388134577	7.05392501628582	-4.12706015106119
Ρ	-9.45330932400105	6.11678109868220	-5.09528164783389
Ρ	-12.31295509064916	7.68006741957999	-5.77438840169302
Ρ	-8.91454344452395	7.75790104564301	-6.37034894919594
Ρ	-10.76295008544286	8.77057031367188	-6.73653142328607
0	-12.40649387566078	3.90747604733310	-5.93092995179368
0	-8.08575327051028	4.42379493023690	-7.65677429163008
С	-11.76658822186292	7.40750696193785	-9.30264803056991
Н	-12.02612168260922	8.45321813323559	-9.27688737809766
С	-12.61850388169845	6.32932866517455	-8.94251740691240
С	-11.82841714630421	4.74052372265521	-6.43549663015612
С	-11.95666607103136	5.85986074138507	-3.07940937472289
С	-10.52825136552373	6.86626837713934	-9.74203313229785
С	-11.91687898324245	5.11636806572546	-9.20392029826678
С	-10.64018991227360	5.45014958143115	-9.70139792685786
Н	-9.88376441976254	4.74590397773516	-10.01627474975063
С	-9.01709032090912	5.06216927483211	-7.58285584649716
С	-10.64187216191904	8.41002922025766	-3.04311666867286
Н	-9.67116551939285	7.42693148244136	-10.08458110261657
Н	-12.30106067424965	4.11583756579365	-9.06818626727832
Н	-13.63312672352465	6.41180957330057	-8.58200325934625
Н	-12.26016783036029	4.97775011952750	-3.63874996625421
Н	-11.27666039275378	5.56803332210560	-2.27636692966675
Н	-12.83692184943411	6.34509237644253	-2.65320924262597
Н	-10.09638125722726	9.16546004940720	-3.60732127216327
Н	-10.01242333244285	8.01572770220917	-2.24173186187671
н	-11.55115500541251	8.84404370442804	-2.62033134458743

1'_{Coord}

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -2264.22439225, Enthalpies/H = -2264.22344804, Free Energies/H = -2264.29024895, ZPVE/ kcal/mol = 130.69

Та	0.93684224305866	11.62218082005737	14.75481474368288	
Ρ	-0.85870520576502	11.66300802145568	18.68350023998215	
Ρ	-0.54007190430828	12.41330091728528	16.67609433592016	
Ρ	-0.65346585926345	13.52245914650123	14.08611963796423	
Ρ	0.52491049408842	14.03209654763291	15.80895052825066	
Ρ	-1.69266436413892	11.87210941696067	14.98730354318340	
0	-0.15171438128351	8.84403005905352	16.05815679317590	
0	3.17629341911207	12.02372970175340	17.08203561739180	b /
С	0.23974920297009	9.80600730285957	15.60465497429614	
С	2.38318623533120	11.87060655154194	16.28654244322665	6
С	2.69069747247705	12.07478074612465	13.21172977979770	
С	2.00432637744132	9.89325676238276	13.43286953789614	
Н	1.96976999024223	8.85190063855423	13.71962993993326	
С	1.05300120229670	10.56777136319440	12.61908056413734	
С	3.00781412353697	10.81584296003625	13.79795922171451	
Н	3.87362883501240	10.59770297155577	14.40646918250802	
С	1.49485321627997	11.91053423927887	12.46024684375717	
Н	1.02108967293260	12.66397646384400	11.85252331098147	
Н	0.17492249687586	10.12678761959643	12.17055668621495	
Н	3.27848652346274	12.97762828142597	13.28834017184631	
С	-1.87963277581704	13.05210023403303	19.31426597972325	
Н	-2.82977972077705	13.07967714226700	18.77827226424055	
Н	-2.08388327733685	12.84567419899212	20.36820205182973	
Н	-1.37359247119919	14.01461130315964	19.22660713940468	
С	0.77700923757643	12.04761658734154	19.41706467987557	
н	0.64449215796510	11.98284143326108	20.50038123967777	
н	1.50788660571476	11.29752728460184	19.11688128056745	
Н	1.13285579551472	13.04899076624827	19.16694709681925	

3'Ins

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -4158.68068398, Enthalpies/H = -4158.67973977, Free Energies/H = -4158.74917894, ZPVE/ kcal/mol = 130.85

Та	-10.76545389970606	6.35203105425269	-7.48178231547535
As	-11.14025775518313	6.98220576484593	-4.06954223700013
Ρ	-9.32529414395121	6.32772679046288	-5.20987286718577
Ρ	-12.49251347421188	7.44862314547225	-5.79819020094191
Ρ	-9.13361705614616	8.06953434934127	-6.44353109705950
Ρ	-11.13133277481053	8.78260855892637	-6.73708789196408
0	-11.87685983086575	3.69613278905108	-5.95641857593015
0	-7.86503602425393	4.87270309443159	-7.89286493263317
С	-11.35979088548063	7.42292830542121	-9.56900531894278
Н	-11.22301734528950	8.48299150500114	-9.71286773018842
С	-12.53774719775664	6.79373723214070	-9.08453155454157
С	-11.48740562254246	4.62462378110092	-6.47533830354510
С	-11.81987689707721	5.58533360753680	-2.93908474757694
С	-10.40063218293233	6.41858620398381	-9.82703539891975
С	-12.32028460795525	5.39712333465616	-9.07144392274151
С	-10.99445555593595	5.15275385969627	-9.51194696124180
Н	-10.53815948736267	4.18294916627447	-9.64495716300122
С	-8.86167598395194	5.38714953202538	-7.74050801778153
С	-10.85515248507778	8.49654605862436	-2.92938966372164
Н	-9.41121178043398	6.57615863655791	-10.23078854684661
н	-13.04109893337638	4.64874368618566	-8.77422815253284
Н	-13.44565649005928	7.29662707459789	-8.78478484010052
Н	-11.99337822761166	4.67798285318604	-3.51285625290072
Н	-11.08495382944024	5.40120930112723	-2.15526737369578
Н	-12.75395339886139	5.94022632497070	-2.50251447053359
н	-10.42250378040889	9.30470441523515	-3.51675330026407
н	-10.17821802355299	8.20155408127397	-2.12685810635540
н	-11.82088096776333	8.79690925461964	-2.52000095437769

3'Coord

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -4158.66504282, Enthalpies/H = -4158.66409861, Free Energies/H = -4158.73246870, ZPVE/ kcal/mol = 130.11

As -0.82907175030898 11.55168316839394 18.79444899591147	
As -0.82907175030898 11.55168316839394 18.79444899591147	
P -0.53481746150933 12.37424666077960 16.67102643419237	
P -0.65919533075694 13.51240561496483 14.08399141053547	\bigwedge
P 0.52215729303163 14.00250884184918 15.81010387441973	
P -1.68556085638836 11.84871157963155 14.97286514098012	I
O -0.13965028043737 8.81739253326705 16.00485142151332	T
O 3.16192296691067 11.97818364917467 17.07973712827355	
C 0.25004792776328 9.78448554163872 15.55973630514270	<u> </u>
C 2.37733468534956 11.83715065175684 16.27318032488928	
C 2.70174313898708 12.08227790490528 13.20095168284461	
C 2.00430468565437 9.90041530542826 13.38243453412719	
H 1.96536719153665 8.85388795981807 13.64923964299645	
C 1.05939208566837 10.59279915358325 12.57685478062621	
C 3.01031776278942 10.81225740833193 13.76800740979682	
H 3.87406865557078 10.57881678671616 14.37380050825383	
C 1.50737011187729 11.93658825963530 12.44342300066112	
H 1.04044493455422 12.70199965825094 11.84536823504198	
H 0.18070665418899 10.16365120640163 12.11811145916517	
H 3.29411050340750 12.98063402237341 13.29346651087731	
C -1.99762285206619 13.00386191335119 19.38421977942871	
H -2.94620943992593 12.94581211431806 18.85038270722615	
H -2.17833387667529 12.84989204593992 20.45023248165501	
H -1.53344705290096 13.97746267027959 19.22832659125152	
C 0.85537571891327 12.22481600767523 19.51924674962334	
H 0.72681920490664 12.24723054890582 20.60342392705581	
H 1.66560391979620 11.54151660261389 19.27203029172533	
H 1.07835829214563 13.23158684147218 19.16419191697481	

4''Ins

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -2163.18677742, Enthalpies/H = -2163.18583321, Free Energies/H = -2163.25728000, ZPVE/ kcal/mol = 130.11

Та	-10.75199789554422	6.34266287255867	-7.54419496315230
Sb	-11.15084606846920	6.96397293677675	-3.99955675150600
Ρ	-9.24501110432233	6.27317411469600	-5.30769184762453
Ρ	-12.52615027686681	7.45530439953257	-5.91821839114480
Ρ	-9.10790666697178	8.04440510707212	-6.50478677204104
Ρ	-11.10623659289750	8.77122023801611	-6.79535422523882
0	-11.86420033546302	3.71354379182049	-5.96915619615331
0	-7.86292753779993	4.85273917608671	-8.01801228783167
С	-11.35075885443675	7.41964612335973	-9.63036363560886
н	-11.21103855583630	8.47936146816003	-9.77345375529501
С	-12.52894046472884	6.79357233695036	-9.14515127802565
С	-11.47454804096616	4.62709790544788	-6.51425932326153
С	-11.91712276725933	5.45822446651066	-2.74562651712571
С	-10.39509634229458	6.41217766364058	-9.89076274336853
С	-12.31538166067885	5.39587902505314	-9.13166103454819
С	-10.99260602051471	5.14799376262371	-9.57701213824001
Н	-10.53943213967520	4.17691536697798	-9.71124278774766
С	-8.85332030998599	5.37032878646925	-7.83679982694997
С	-10.80905660987705	8.65559929324449	-2.80366512592336
Н	-9.40631775327047	6.56690407954586	-10.29710251559221
Н	-13.03704395957370	4.64972136619328	-8.83101582261298
Н	-13.43501096465162	7.29853420268936	-8.84433812669819
Н	-12.14159960427044	4.57016689946742	-3.33299970601442
Н	-11.16751101841051	5.23695596637749	-1.98620857825113
Н	-12.82368143109095	5.84713213077867	-2.28184214108322
Н	-10.35943536224129	9.42583989036909	-3.42868706143035
н	-10.13865462044486	8.37895106462428	-1.99010473529786
Н	-11.76858568345681	8.99237932595674	-2.41018261023219

4"_{Coord}

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -4006.37272524, Enthalpies/H = -4006.37178103, Free Energies/H = -4006.47815535, ZPVE/ kcal/mol = 209.74

Та	0.94578620509559	11.50546148787121	14.67930611904885
Sb	-0.52852953487125	11.36946841017280	19.03205153439098
Ρ	-0.57137314851128	12.17389335875307	16.64285785021037
Ρ	-0.87808331833939	13.18544044495526	13.99872217693818
Ρ	0.27982272045401	13.86487828394044	15.67450806719082
Ρ	-1.67784531700315	11.45140978785162	14.98007507540905
0	0.28071011428434	8.63354996971546	16.05517547308328
0	3.17370342521769	12.10590348379073	16.96787331315283
С	0.51820088984737	9.63289420863720	15.57445872653502
С	2.38408401692455	11.89357201838262	16.18160236812489
С	2.94332304201257	11.78975221699277	13.40523429421168
С	1.62972622333096	9.94380577429825	12.98507054764856
Н	1.25092783853908	8.93197827990246	12.96929934008751
С	1.06491650753365	11.04720186206009	12.31203754712793
С	2.78367230435182	10.39723890784028	13.68971920935553
Н	3.45530012669333	9.78464806843096	14.27284117125650
С	1.87964153433277	12.18701332566169	12.56737128703453
Н	1.70699588075956	13.18352002511461	12.18902798255870
Н	0.16584806037777	11.03483159179868	11.71321785424592
Н	3.74373883658557	12.42417734237296	13.75693747511141
С	-2.15466993419090	12.63866690934234	19.58464335914860
Н	-3.07506543317125	12.28253495074692	19.12187498281628
Н	-2.25364442009112	12.58284239778143	20.67079822163102
Н	-1.95319588315438	13.66714739508864	19.28648593101009
С	0.99349899673333	12.77470620653965	19.55568747270655
Н	0.87945600147076	12.95613151872408	20.62658809472874
Н	1.98181875289385	12.36191732810540	19.36401601809667
Н	0.85954085389406	13.71416392612728	19.01871833513806

4'

 ω B97XD/def2TZVP (CPCM (CH₂Cl₂)): Energies/H = -2163.18547273, Enthalpies/H = -2163.18452852, Free Energies/H = -2163.25672647, ZPVE/ kcal/mol = 129.88

Та	9.348003000	9.301170000	9.261573000
Та	2.388836000	12.873858000	3.580541000
Sb	5.743139000	11.634669000	6.840147000
Ρ	8.214897000	11.213538000	7.945028000
Ρ	0.647871000	13.655534000	5.314065000
Ρ	9.737447000	10.212249000	6.829228000
Ρ	11.102512000	10.934805000	8.311191000
Ρ	9.576849000	11.920868000	9.442327000
Ρ	3.272638000	12.571684000	5.995515000
Ρ	2.570674000	14.554699000	5.593106000
Ρ	1.357777000	11.667809000	5.672490000
0	3.649884000	9.881939000	3.588530000
0	5.389465000	14.106918000	3.428976000
0	7.104039000	7.831717000	7.434023000
0	7.070479000	10.291019000	11.355595000
С	7.891018000	8.342138000	8.076426000
С	4.339869000	13.673505000	3.479299000
С	9.289272000	7.272765000	10.476970000
Н	8.355669000	6.780568000	10.705802000
С	7.855248000	9.942082000	10.611616000
С	11.176277000	8.567536000	10.667973000
С	10.109834000	7.034461000	9.331903000
С	11.261520000	7.842007000	9.446214000
Н	12.066833000	7.905181000	8.729475000
С	1.017503000	14.159534000	2.059243000
С	3.210866000	10.930207000	3.579882000
С	1.432309000	11.951524000	1.586517000
С	9.973343000	8.207394000	11.309912000
Н	9.633000000	8.572887000	12.267866000
С	0.472952000	12.845005000	2.107259000
Н	-0.503438000	12.579803000	2.485355000
С	2.313627000	14.079178000	1.508488000
Н	2.975526000	14.912802000	1.324007000
С	2.592260000	12.706043000	1.232577000

Н	3.488433000	12.318064000	0.771580000
Н	0.523930000	15.059000000	2.396599000
Н	1.307119000	10.884706000	1.471473000
Н	9.892275000	6.351745000	8.523391000
Н	11.904396000	9.277252000	11.032172000
С	4.929168000	11.418544000	8.808078000
Н	5.095531000	10.393447000	9.139548000
Н	3.859558000	11.624539000	8.791776000
Н	5.425882000	12.112435000	9.485916000
С	6.279533000	13.706899000	6.941921000
Н	6.556425000	13.947836000	7.968005000
Н	7.127976000	13.880577000	6.279601000
Н	5.448729000	14.343068000	6.636866000

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