Conversion of $E_4$ ($E_4 = P_4$, $As_4$, $AsP_3$) by Ni(0) and Ni(I) Synthons – A Comparative Study

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Table of Contents

1. Synthetic procedures and experimental details.......................................................... 1
   1.1. Synthesis of \([\text{L}^1\text{Ni}]_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{As}_4)\) (2b).......................... 2
   1.2. Synthesis of \([\text{L}^1\text{Ni}]_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{AsP}_3)\) (2c).......................... 2
   1.3. Synthesis of \([\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{P}_3)\) (3a)............................................ 3
   1.4. Synthesis of \([\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{As}_3)\) (3b)............................................ 3
   1.5. Synthesis of \([\text{K}_2][\text{L}^1\text{Ni}]_2(\mu,\eta^{2,2}-\text{P}_4)\) (4)........................................ 4
   1.6. Synthesis of \([\text{K}@18\text{-crown}-6(\text{thf})_3][\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{P}_3)\) (5a).................. 4
   1.7. Synthesis of \([\text{K}@18\text{-crown}-6(\text{thf})_3][\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{As}_3)\) (5b).............. 5
   1.8. Synthesis of \([\text{K}_2][\text{L}^1\text{Ni}]_2(\mu,\eta^{1,1}-\text{N}_2)\) (6)............................................. 6
   1.9. Synthesis of \([\text{K}@18\text{-crown}-6(\text{thf})_3][\text{L}^1\text{Ni}(\eta^{1,1}-\text{P}_4)]\) (7a)..................... 6
   1.10. Synthesis of \([\text{K}@X(\text{thf})_2][\text{L}^1\text{Ni}(\eta^{1,1}-\text{As}_4)]\) (7b) \((X = 18\text{-crown-6, cryptand})\) 7

2. NMR studies .................................................................................................................... 8
   2.1. \([\text{L}^1\text{Ni}]_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{As}_4)\) (2b)...................................................... 8
   2.2. \([\text{L}^1\text{Ni}]_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{AsP}_3)\) (2c)...................................................... 8
   2.3. \([\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{P}_3)\) (3a)........................................................................ 9
   2.4. \([\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{As}_3)\) (3b)....................................................................... 10
   2.5. \([\text{K}_2][\text{L}^1\text{Ni}]_2(\mu,\eta^{2,2}-\text{P}_4)\) (4)................................................................. 10
   2.6. \([\text{K}@18\text{-crown}-6(\text{thf})_3][\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{P}_3)\) (5a)............................... 11
   2.7. \([\text{K}@18\text{-crown}-6(\text{thf})_3][\text{L}^1\text{Ni}]_2(\mu,\eta^{3,3}-\text{As}_3)\) (5b)............................... 12
   2.8. \([\text{K}_2][\text{L}^1\text{Ni}]_2(\mu,\eta^{1,1}-\text{N}_2)\) (6)................................................................. 13
   2.9. \([\text{K}@18\text{-crown}-6(\text{thf})_3][\text{L}^1\text{Ni}(\eta^{1,1}-\text{P}_4)]\) (7a)................................. 13
   2.11. \([\text{K}@18\text{-crown}-6(\text{thf})_2][\text{L}^1\text{Ni}(\eta^{1,1}-\text{As}_4)]\) (7b)............................. 15

3. Magnetic Measurements in Solution .............................................................................. 16
   3.1. Evans Methode........................................................................................................... 16
   3.2. EPR (Electrone Paramagnetic Resonance) measurements........................................ 17

4. Cyclic voltammetry (CV)............................................................................................... 18
5. Details on single crystal X-ray structure analysis .................................................. 19

5.1. [(L'Ni)₂(μ-η²,κ¹:η²,κ¹-As₄)] (2b) .................................................................. 20

5.2. [(L'Ni)₂(μ-η²,κ¹:η²,κ¹-AsP₃)] (2c) ................................................................. 21

5.3. [(L'Ni)₂(μ,η³:3-P₃)] (3a) ............................................................................. 23

5.4. [(L'Ni)₂(μ,η³:3-As₃)] (3b) ............................................................................. 24

5.5. [K₂][(L'Ni)₂(μ,η²²-2-P₄)] (4) ........................................................................ 25

5.6. [K@18-crown-6(thf)₂][(L'Ni)₂(μ,η³:3-P₃)] (5a) .............................................. 26

5.7. [K@18-crown-6(thf)₂][(L'Ni)₂(μ,η³:3-As₃)] (5b) ............................................. 27

5.8. [K₂][(L'Ni)₂(μ,η¹:1-N₂)] (6) .......................................................................... 28

5.9. [(K@18-crown-6)(thf)₂][L'Ni(η¹:1-As)] (7a) ................................................. 29

5.10. [K@cryptand][thf][L'Ni(η¹:1-As₄)] (7b) ...................................................... 30

5.11. Crystallographic information ........................................................................... 31

6. DFT calculations ................................................................................................. 34
1. Synthetic procedures and experimental details

General Remarks:
All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N₂ inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O₂). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/MgSO₄ catalyst as well as, concentrated H₂SO₄ and orange gel, respectively. All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d₆-benzene, d₃-acetonitrile, toluene-d₈ and thf-d₈ that were dried (over Na/K or CaH₂), refluxed for three hours and then distilled under inert atmosphere.

Characterisation methods
Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer or an Agilent Q-TOF 6540 UHD ES mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N₂ atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N₂ atmosphere. The X-band EPR measurements were carried out with a MiniScope MS400 device equipped with a Magnettech GmbH rectangular TE102 resonator at a frequency of 9.5 GHz. The compounds were dissolved in a glovebox under N₂ inert gas atmosphere, placed in tip-sealed pasteur pipettes, and were rubber plugged. The measurements were conducted at room temperature and 77 K, respectively (see chapter 3.2).

¹H and ³¹P NMR spectra were recorded on a Bruker Avance III HD 400 (¹H: 400.130 MHz, ¹³C: 100.613 MHz, ³¹P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (¹H) or 85 % H₃PO₄ (³¹P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Starting materials
The compounds [(L¹Ni)₂tol] (1),¹¹ potassiam graphite², P₄, AsP₃³ and As₄⁴ were prepared according to literature procedures (L¹ = [(N(C₆H₃Pr₂−2,6)C(Me)]₂CH⁻) or bought from chemical supplies and used as delivered or purified by sublimation (18-crown-6, cryptand).
1.1. Synthesis of [(L\(^1\)Ni)\(_2\)(μ-η\(^2\),κ\(^1\):η\(^2\),κ\(^1\)-As\(_4\))] (2b)

All preparations were performed under exclusion of light. 520 mg [(L\(^1\)Ni)\(_2\)tol] (0.5 mmol) were dissolved in 50 mL of toluene and added to a freshly prepared toluene solution saturated with As\(_4\). The mixture was stirred at room temperature for 2 hours and the color changed from red to greenish-brown. The solvent was removed in vacuum and the brown solid was extracted with Et\(_2\)O and filtered over diatomaceous earth to remove the insoluble As\(_{\text{grey}}\). By storing the greenish-brown solution at -30 °C, compound [(L\(^1\)Ni)\(_2\)(μ-η\(^2\),κ\(^1\):η\(^2\),κ\(^1\)-As\(_4\))] (2b) crystallized as dark greenish-brown blocks, suitable for X-ray analysis.

**Crystalline yield:** 240 mg (0.19 mmol, 38 %)

\(^1\)H NMR (C\(_5\)D\(_6\), 300 K): δ [ppm] = 7.49 (d, 8H, \(3J_{HH} = 8\) Hz, \(m\text{-C}_6\text{H}_5\)), 6.10 (t, 4H, \(3J_{HH} = 8\) Hz, \(\rho\text{-C}_6\text{H}_5\)), 3.94 (s, 2H, C(\(CH_3\))C\(\text{H}_3\)(CH\(_3\))), 3.45 (sept, 8H, \(3J_{HH} = 7\) Hz, CH(\(CH_3\))\(_2\)), 1.30 (d, 24H, \(3J_{HH} = 6\) Hz, CH(\(CH_3\))\(_2\)), 1.16 (d, 24H, \(3J_{HH} = 6\) Hz, CH(\(CH_3\))\(_2\)), 0.92 (s, 12H, C(\(CH_3\))CH\(\text{H}_3\)).

LIFDI MS (toluene): m/z (%) = 1252.30 (68.33, [M]+), 1177.38 (100, [(L\(^1\)Ni)\(_2\)As\(_3\)]\(^+\)).

EA: calculated for: C\(_{58}\)H\(_{62}\)N\(_8\)Ni\(_2\)As\(_4\): C: 55.63, H: 6.6, N: 4.47, found [%]: C: 56.01, H: 6.10, N: 4.49.

1.2. Synthesis of [(L\(^1\)Ni)\(_2\)(μ-η\(^2\),κ\(^1\):η\(^2\),κ\(^1\)-AsP\(_3\))] (2c)

All preparations were performed under exclusion of light. 50 mg [(L\(^1\)Ni)\(_2\)tol] (0.05 mmol, 1eq) and 8 mg AsP\(_3\) (0.05 mmol, 1eq) were dissolved in 5 mL of toluene. The mixture was stirred at room temperature for 2 hours and the color changed from red to green. The solvent was removed in vacuum and the green solid was extracted with Et\(_2\)O and filtered over diatomaceous earth. By storing the green solution in a double Schlenk (with 1 mL of toluene at the other side) at -30 °C, compound [(L\(^1\)Ni)\(_2\)(μ-η\(^2\),κ\(^1\):η\(^2\),κ\(^1\)-AsP\(_3\))] (2c) crystallized as dark green needles, suitable for X-ray analysis.

**Yield:** 30 mg (0.03 mmol, 23 %)

\(^1\)H NMR (C\(_5\)D\(_6\), 300 K): δ [ppm] = 7.21 (d, 8H, \(3J_{HH} = 8\) Hz, \(m\text{-C}_6\text{H}_5\)), 6.72 (t, 4H, \(3J_{HH} = 8\) Hz, \(\rho\text{-C}_6\text{H}_5\)), 4.52 (s, 2H, C(\(CH_3\))C\(\text{H}_3\)(CH\(_3\))), 3.24 (sept, 8H, \(3J_{HH} = 7\) Hz, CH(\(CH_3\))\(_2\)), 1.36 (s, 12H, C(\(CH_3\))CH\(\text{H}_3\)), 1.26 (d, 24H, \(3J_{HH} = 7\) Hz, CH(\(CH_3\))\(_2\)), 1.12 (d, 24H, \(3J_{HH} = 7\) Hz, CH(\(CH_3\))\(_2\)), contaminated with NacnacH.

\(^31\)P\(^{1}\)H NMR (tol-d\(_6\), 300 K): δ [ppm] = 226.2 (br, 1P), 125.0 (br, 2P).

LIFDI MS (toluene): m/z (%) = 1120.3 ([M]+, 16.28).
1.3. Synthesis of [(L\textsuperscript{1}Ni)\textsubscript{2}(\mu,\eta\textsuperscript{3:3}-P\textsubscript{3})] (3a)

**Route 1:** 0.34 g (0.3 mmol) [(L\textsuperscript{1}Ni)\textsubscript{2}tol] (1) were dissolved in 100 mL hexane. To this boiling solution a solution of 50 mL hexane with P\textsubscript{4} (40 mg, 0.3 mmol) were added. The mixture was refluxed for three hours and the color changed from red to green. The solvent was removed in vacuum and the compound was purified by column chromatography (SiO\textsubscript{2}, 18 cm, Ø 4 cm, T = 25 °C). Using a mixture of hexane/toluene (4:1) as an eluent 3a can be obtained as a green fraction. After removing the solvent in vacuum, the residue was dissolved in hexane and concentrated. After storage at +8 °C, 3a can be obtained as green chopsticks.

**Route 2:** 15 mg [(L\textsuperscript{1}Ni)\textsubscript{2}(\mu,\eta\textsuperscript{3:3}-P\textsubscript{4})] (2a) were refluxed in toluene for 2 hours. The conversion of 2a to 3a was tracked by NMR spectroscopy. (Stirring the solution at 60 °C for a hour do not lead to a conversion of 2a to 3a.)

**Crystalline Yield:** 150 mg (0.14 mmol, 44 %)

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 300 K): \(\delta [ppm] = 12.67 \text{ (b, 8H, m-C\textsubscript{6}H\textsubscript{3})}, 7.97 \text{ (b, 4H, p-C\textsubscript{6}H\textsubscript{3})}, 2.31 \text{ (b, 24H, CH(C\textsubscript{6}H\textsubscript{3})\textsubscript{2})}, 1.79 \text{ (b, 24H, CH(C\textsubscript{6}H\textsubscript{3})\textsubscript{2})}, -3.17 \text{ (b, 4H, \textit{CH}(CH\textsubscript{3})\textsubscript{2})}, -13.32 \text{ (b, 12H, C(C\textsubscript{6}H\textsubscript{3})CHC(C\textsubscript{6}H\textsubscript{3}))}, -25.13 \text{ (b, C(CH\textsubscript{3})C\textsubscript{6}HCH(CH\textsubscript{3}))}.\)

\textsuperscript{1}H NMR (Evans-method, C\textsubscript{6}D\textsubscript{6}, 300 K): \(\Delta \nu = 18.9 \text{ Hz, } \mu_{\text{eff}} = 2.12 \mu_{\text{B}}, n = 1.35\).

\textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}, 300 K): no signal detected in the range of: 600 ppm to -600 ppm.

LIFDI-MS (toluene): m/z (%) = 1043.4 (100, [M\textsuperscript{+}]).

1.4. Synthesis of [(L\textsuperscript{1}Ni)\textsubscript{2}(\mu,\eta\textsuperscript{3:3}-As\textsubscript{3})] (3b)

**Route 1:** All preparations were performed under exclusion of light. 490 mg [(L\textsuperscript{1}Ni)\textsubscript{2}tol] (0.47 mmol) were dissolved in 50 mL toluene and added to a freshly prepared toluene solution saturated with As\textsubscript{4} at +60 °C. The mixture was cooled to room temperature and the color changed from red to brown. The solvent was removed in vacuum and the brown compound was purified by column chromatography (SiO\textsubscript{2}, hexane, 17 cm, Ø 4 cm). Using a mixture of hexane/toluene (4:1) as an eluent 3b can be obtained as brown fraction. By storing the concentrated brown solution at +8 °C, compound [(L\textsuperscript{1}Ni)\textsubscript{2}(\mu,\eta\textsuperscript{3:3}-As\textsubscript{3})] (3b) crystallized as brown blocks, suitable for X-ray analysis.

**Route 2:** 10 mg [(L\textsuperscript{1}Ni)\textsubscript{2}(\mu,\eta\textsuperscript{3:3}-As\textsubscript{4})] (2b) were refluxed in toluene for 2 hours. The conversion of 2b to 3b was tracked by NMR spectroscopy. (Stirring the solution at 60 °C for a hour do not lead to a conversion of 2b to 3b.)

**Crystalline Yield:** 0.45 g (0.38 mmol, 81 %)
1H NMR (C6D6, 300 K): δ [ppm] = 12.01 (b, 8H, m-C6H3), 8.6 (b, 4H, p-C6H3), 2.19 (b, 24H, CH(CH3)2), 1.77 (b, 24H, CH(CH3)2), -2.18 (b, 4H, CH(CH3)2), -12.46 (b, 12H, C(CH3)CHC(CH3)), -23.31 (b, 2H, C(CH3)CHC(CH3)).

1H NMR (Evans-method, C6D6, 300 K): Δν = 18.8 Hz, μeff = 2.13 μB, n = 1.35.

LIFDI-MS (toluene): m/z (%) = 1175.2 (100, [M]+).

EA: calculated for: C58H62N4Ni2As3 (+ 7 % L'H see NMR): C: 59.72, H: 7.09, N: 4.80, found [%]: C: 59.92, H: 7.08, N: 4.49.

1.5. Synthesis of [K2][(L1Ni)2(μ,η2:2-P4)] (4)

100 mg of 1 (0.1 mmol) and 12.4 mg P4 (0.1 mmol) were dissolved in 10 mL toluene. To this green solution was added 28.4 mg (0.21 mmol) potassium graphite. The color changed within minutes to red and the solution was stirred for three hours. The solution was filtrated over diatomaceous earth and concentrated to 5 mL volume. By storing the solution at -30 °C, compound [K2][(L1Ni)2(μ,η2:2-P4)] (4) crystallized as brown blocks, suitable for X-ray analysis.

Crystalline Yield: 20 mg (17 %)

1H NMR (C6D6, 300 K): δ [ppm] = 6.9 (d, 4H, 3JHH = 7 Hz, m-C6H3), 6.67 (d, 4H, 3JHH = 7 Hz, m-C6H3), 6.43 (t, 4H, 3JHH = 7.5 Hz, p-C6H3), 5.31 (sept, 4H, 3JHH = 7 Hz, CH(CH3)2), 5.07 (s, 2H, C(CH3)CHC(CH3)), 3.84 (sept, 4H, 3JHH = 7 Hz, CH(CH3)2), 1.97 (d, 12H, 3JHH = 7 Hz, CH(CH3)2), 1.46 (s, 12H, C(CH3)CHC(CH3)), 1.43 (d, 12H, 3JHH = 7 Hz, CH(CH3)2), 1.05 (d, 12H, 3JHH = 7 Hz, CH(CH3)2), 1.01 (d, 12H, 3JHH = 7 Hz, CH(CH3)2).

31P(1H) NMR (C6D6, 300 K): δ [ppm] = 80.3 (s).

EA calculated for: C58H62N4Ni2K2P4 · C7H8: C: 62.61, H: 7.28; N: 4.49, found [%]: C: 62.34, H: 7.27, N: 4.22.

1.6. Synthesis of [K@18-crown-6](thf)3][(L1Ni)2(μ,η3:3-P3)] (5a)

50 mg of [(L1Ni)2(μ,η3:3-P3)] (3a, 0.05 mmol, 1eq) and 7 mg (0.05 mmol, 1.1eq) potassium graphite were dissolved in 5 mL of toluene, the solution turned greenish-brown. The solution was stirred for 3 hours and then filtered over diatomaceous earth and 13 mg (0.05 mmol, 1eq) 18-crown-6 were added. The solvent was removed in vacuum and the brown residue was taken up in 3 mL THF. The solution was layered under 10 mL hexane and stored at -30 °C. Compound [K@18-crown-6](thf)3][(L1Ni)2(μ,η3:3-P3)] (5a) crystallized as brown plates, suitable for X-ray analysis.
**Crystalline Yield**: 20 mg (0.01 mmol, 27 %)

\[ ^1H \text{NMR} \ (\text{thf-d}_8, 300 \text{ K}): \delta \ [\text{ppm}] = 7.12 \ (\text{br}, 7\text{H}), 6.24 \ (\text{br}, 3\text{H}), 3.60 \ (\text{br, thf-coordinated (8H) + 18-c-6 (24H)}), 1.77 \ (\text{thf-coordinated, 8H}), 1.22 \ (\text{br, 24H, CHMeMe}), 0.98 \ (\text{br, 24H, CHMeMe}), 0.59 \ (\text{br, 8H, CHMeMe}). \]

Compound 5a show broad signals in the \(^1H\) NMR spectrum at room temperature and also at 193 K, this is due to dynamic behaviour of 5a, a paramagnetic nature was excluded by Evans-NMR and EPR spectroscopy.

\[ ^1H \text{NMR} \ (\text{Evans-method, thf-d}_8, 300 \text{ K}): \text{no signal shift detected.} \]

\[ \text{EPR}: \text{silent at room temperature and 77 K.} \]

\[ ^{31}\text{P}^{(1)}\text{H} \text{NMR} \ (\text{thf-d}_8, 300 \text{ K}): \text{no signal detected in the range of: 500 ppm to -600 ppm.} \]

\[ ^{31}\text{P}^{(1)}\text{H} \text{NMR} \ (\text{thf-d}_8, 193 \text{ K}): -268.4 \text{ ppm (s).} \]

\[ \text{ESI-MS (CH}_3\text{CN): m/z = 1045.6} \ (88, [\text{M}]), 555.2 \ (100, [\text{C}_{33}\text{H}_{47}\text{N}_{4}\text{Ni}]), 535.2 \ (46, [\text{C}_{29}\text{H}_{41}\text{N}_{2}\text{NiP}_{2}])), 507.2 \ (16, [\text{C}_{29}\text{H}_{41}\text{N}_{2}\text{NiP}]), 303.0 \ (100, [\text{K@18-crown-6}]). \]

1.7. **Synthesis of** \([\text{K@18-crown-6}(\text{thf})_3][\text{(L}^1\text{Ni)}_2(\mu,\eta^{3,3}\text{-As})] \ (5b)\]

All manipulations were performed under exclusion of light.

**Route 1**: 50 mg \([\text{(L}^1\text{Ni)}_2(\mu,\eta^{3,3}\text{-As})] \ (3b), 0.04 \text{ mmol, 1eq}) \text{ and 6 mg (0.04 mmol, 1eq) potassium graphite were dissolved in 5 mL of toluene. The brown solution was stirred for 3 hours and then filtered over diatomaceous earth and 11.3 mg (0.04 mmol, 1eq) 18-crown-6 were added. The solvent was removed in vacuum and the brown residue was taken up in THF. The solution was layered under 10 mL hexane and stored at -30 °C. Compound [K@18-crown-6](thf)_3][(L}^1\text{Ni)}_2(\mu,\eta^{3,3}\text{-As})] \ (5b) crystallized as brown needles, suitable for X-ray analysis.**

**Crystalline Yields**: 53 mg (0.02 mmol, 53 %)

**Route 2**: 350 mg \([\text{K}_2][\text{(L}^1\text{Ni)}_2\text{N}_2] \ (6), 0.3 \text{ mmol}) \text{ was dissolved in 25 mL of toluene and added to a freshly prepared solution of yellow arsenic in toluene. The reaction mixture was stirred at room temperature for 1 hour. The solvent was removed in vacuum and the brown residue was taken up in THF. The solution was filtered over diatomaceous earth to remove the insoluble As_grey. 180 mg (0.6 mmol) 18-crown-6 were added. By storing the brown solution at -30 °C, compound [K@18-crown-6](thf)_3][(L}^1\text{Ni)}_2(\mu,\eta^{3,3}\text{-As})] \ (5b) crystallized as brown blocks, suitable for X-ray analysis.**

**Crystalline Yields**: 150 mg (0.09 mmol, 30 %)
1 H NMR (thf-d8, 300 K): δ [ppm] = 6.84 (d, 8H, 3 JHH = 8 Hz, m-C6H5), 6.73 (t, 4H, 3 JHH = 8 Hz, p-C6H5), 4.31 (s, 2H, C(CH3)CH(CH3)), 3.63 (s, 18-crown-6), 3.47 (sept, 8H, CH(CH3)2), 1.77 (thf), 1.28 (s, 12H, C(CH3)CH(CH3)), 1.25 (d, 24H, CH(CH3)2), 0.94 (d, 24H, CH(CH3)2).

EA calculated for: \([C_{58}H_{82}N_{5}Ni_{2}As_{3}]K[\text{C}_{12}H_{24}O_{6}]\text{(C}_{4}H_{8}O)_{3}3\wedge]\): C: 58.21, H: 7.79; N: 3.23, found [%]: C: 58.24, H: 7.68, N: 3.38.

1.8. Synthesis of \([K_{2}][(L^{1}Ni)_{2}(\mu,\eta^{1:1}-N_{2})]\) (6)

All preparations were performed under N2 gas atmosphere. In a 250 mL round flask were performed under N2 gas atmosphere. In a 250 mL round flask 3.0 g L1H (7.2 mmol, 1eq) in toluene (30 mL) were cooled to 0 °C and 4.5 mL tBuLi (7.17 mmol, 1eq, 1.6 M in t-hexane) were added. The solution was stirred at r.t. over night. The solution was added to a suspension of NiBr2 . DME (2.21 g, 7.17 mmol, 1 eq.) in toluene (20 mL) under stirring and heated to reflux for 24 h. This solution was added to a suspension of K2 (4.36 g, 32.3 mmol, 4.5 eq.) in toluene. At room temperature gaseous N2 was bubbled through the reaction mixture for 20 minutes. The color changed to deep purple and the reaction mixture was stirred over night. After filtration over celite the solvent was removed in vacuum and redissolved in hexane for crystallization. By storing the solution at -30 °C, compound \([K_{2}][(L^{1}Ni)_{2}(\mu,\eta^{1:1}-N_{2})]\) (6) crystallized as dark purple needles, suitable for X-ray analysis.

Crystalline Yield: 1.8 g (3.6 mmol, 47 %)

1 H NMR (CD6, 300 K): δ = 6.83 (m, 12H, C6H5), 4.69 (s, 2H, C(CH3)CH(CH3)), 3.67 (sept, 8H, 3 JHH = 7 Hz, C(CH3)2), 1.51 (s, 12H, C(CH3)CH(CH3)), 1.33 (d, 24H, 3 JHH = 7 Hz, CH(CH3)2), 1.15 (d, 24H, 3 JHH = 7 Hz, CH(CH3)2).

EA calculated for: \([C_{58}H_{82}N_{5}Ni_{2}K_{2}]\): C: 65.79, H: 7.81, N: 7.94, found [%]: C: 65.48, H: 8.19, N: 7.53.

Raman: ν(NN) = 1572 cm⁻¹.

1.9. Synthesis of \([(K@18-crown-6)(thf)_{2}]L^{1}Ni(\eta^{1:1}-P_{4})\) (7a)

A solution of 25 mg (0.09 mmol) 18-crown-6 in THF was added to a stirred solution of 6 (50 mg, 0.05 mmol). To the red solution was added 12 mg (0.09 mmol) white phosphorus and the color changed from red to yellow-red. The solution was filtrated over diatomaceous earth and was reduced in vacuum. The concentrated solution was layered under hexane. Compound \([(K@18-crown-6)(thf)_{2}]L^{1}Ni(\eta^{1:1}-P_{4})\) (7a) crystallized as orange blocks, suitable for X-ray analysis at -30 °C.

Crystalline Yield: 42 mg (0.04 mmol, 42 %)
$^1$H NMR (thf-d$_8$, 300 K): $\delta$ [ppm] = 6.93 (d, 4H, $^3J_{HH} = 8$ Hz, $p$-C$_6$H$_3$), 6.70 (t, 2H, $^3J_{HH} = 8$ Hz, m-C$_6$H$_3$), 4.44 (s, 1H, C(CH$_3$)$_2$CHC(CH$_3$)), 3.82 (sept, 4H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$), 3.62 (thf), 3.56 (s, 24H, 18-crown-6), 1.78 (thf), 1.55 (d, 12H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$), 1.39 (s, 6H, C(CH$_3$)$_2$CHC(CH$_3$)), 1.12 (d, 12H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$).

$^{31}$P{$^1$H} NMR (thf-d$_8$, 300 K): $\delta$ [ppm] = -212.9 (t, 2P, $^1J_{PP} = 132$ Hz), -378.3 (t, 2P, $^1J_{PP} = 132$ Hz).

EA calculated for: C$_{49}$H$_{85}$N$_2$NiK$_2$P$_4$: C: 56.16, H: 7.79, N: 2.67; found [%]: C: 55.75, H: 7.65, N: 2.47.

1.10. Synthesis of [(K@X)(thf)$_2$][L$^1$Ni(η$^{1:1}$-As$_4$)] (7b) (X = 18-crown-6, cryptand)

All manipulations were performed under exclusion of light. A solution of 200 mg (0.2 mmol) 1 and 71.1 mg cryptand/ 100 mg 18-crown-6 in toluene were added to a freshly prepared solution of As$_4$ in toluene. The solution was stirred for 2 hours at room temperature and the color changed to reddish-brown. The solvent was evaporated by vacuum and the crude product was taken up in THF, filtrated over diatomaceous earth and concentrated to 7 mL. The concentrated solution was layered under hexane. Compound [(K@X)(thf)$_2$][L$^1$Ni(η$^{1:1}$-As$_4$)] (7b) crystallized as red-brownish plates/ needles, suitable for X-ray analysis at -30 °C.

**Crystallin yield:** 185 mg (X = cryptand), 0.16 mmol, 39 %

$^1$H NMR (thf-d$_8$, 300 K): $\delta$ [ppm] = 6.95 (d, 4H, $^3J_{HH} = 8$ Hz, $p$-C$_6$H$_3$), 6.67 (t, 2H, $^3J_{HH} = 8$ Hz, m-C$_6$H$_3$), 4.43 (s, 1H, C(CH$_3$)$_2$CHC(CH$_3$)), 3.94 (sept, 4H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$), 3.61 (thf, 3H), 3.55 (s, 12H, cryptand), 3.50 (m, 12H, cryptand), 2.51 (m, 12H, cryptand), 1.77 (thf, 3H), 1.58 (d, 12H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$), 1.35 (s, 6H, C(CH$_3$)$_2$CHC(CH$_3$)), 1.11 (d, 12H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$).

EA calculated for: C$_{51}$H$_{85}$N$_4$NiKO$_2$As$_4$ (X = cryptand): C: 48.47, H: 6.78, N: 4.43; found [%]: C: 48.57, H: 6.72, N: 4.30.

**Crystallin yield:** 90 mg (X = 18-crown-6, 0.08 mmol, 19 %)

$^1$H NMR (thf-d$_8$, 300 K): $\delta$ [ppm] = 6.96 (d, 4H, $^3J_{HH} = 8$ Hz, $p$-C$_6$H$_3$), 6.66 (t, 2H, $^3J_{HH} = 8$ Hz, m-C$_6$H$_3$), 4.43 (s, 1H, C(CH$_3$)$_2$CHC(CH$_3$)), 3.94 (sept, 4H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$), 3.62 (thf), 3.58 (s, 24H, 18-crown-6 + thf), 1.78 (thf), 1.55 (d, 12H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$), 1.39 (s, 6H, C(CH$_3$)$_2$CHC(CH$_3$)), 1.12 (d, 12H, $^3J_{HH} = 7$ Hz, CH(CH$_3$)$_2$).
2. NMR studies

2.1. \([(L^1\text{Ni})_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{As}_4)] \) (2b)

Figure 1S. $^1\text{H}$ NMR spectrum of 2b in C$_6$D$_6$ at room temperature.

2.2. \([(L^1\text{Ni})_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{AsP}_3)] \) (2c)

Figure 2S. $^{31}\text{P}[^1\text{H}]$ NMR of the reaction solution of 2c in toluene-d$_8$ at room temperature.
2.3. \[ \{(\text{L}^1\text{Ni})_2(\mu,\eta^{3:3}\text{-P}_3)\} \ (3a) \]

Figure 3S. $^1$H NMR of the reaction solution of 2c in toluene-d$_8$ at room temperature (* = L$^1$H).

Figure 4S. $^1$H NMR spectrum of 3a in C$_6$D$_6$ at room temperature.
2.4. \([((\text{L}^1\text{Ni})_2(\mu,\eta^{3:3}-\text{As}_3))\text{]}\text{ (3b)}\)

Figure 5S. \(^1\text{H} \text{NMR spectrum of 3b in C}_6\text{D}_6 \text{ at room temperature } (* = \text{L}^1\text{H}).

2.5. \([\text{K}_2][(\text{L}^1\text{Ni})_2(\mu,\eta^{2:2}-\text{P}_4)]\text{ (4)}\)

Figure 6S. \(^{31}\text{P}[^1\text{H}] \text{NMR spectrum of 4 in C}_6\text{D}_6 \text{ at room temperature.}\)
2.6. \([\text{K@18-crown-6(thf)}_3][\text{([L}^1\text{Ni})_2(\mu,\eta^{3-3}P_3)]\) (5a)

Figure 7S. VT $^{31}$P($^1$H) NMR spectra of crystals of 5a at different temperatures in thf-d$_8$. Crystals were dissolved at -80 °C and the NMR spectra are measured from 193 K to room temperature. Afterwards also another spectrum at 193 K was recorded. * decomposition of 5a during warming.

Figure 8S. $^{31}$P($^1$H) NMR spectra of 5a in thf-d$_8$ at 193 K before and after the VT NMR measurement. * irreversible decomposition of 5a during warming.
Figure 9S. $^1$H NMR spectrum of 5a in thf-$d_8$ at room temperature.

2.7. $[\text{K@18-crown-6(thf)}_3][(L^1\text{Ni})_2(\mu,n^{3.3}\cdot\text{As}_3)]$ (5b)

Figure 10S. $^1$H NMR spectrum of 5b in thf-$d_8$ at room temperature.
2.8. \([K_2[(L^1Ni)_2(\mu,\eta^{1:1}-N_2)]] (6)\)

Figure 11S. \(^1\)H NMR spectrum of 6 in C\(_6\)D\(_6\) at room temperature.

2.9. \([(K@18\text{-crown-6}(\text{thf}_2)][L^1Ni(\eta^{1:1}\cdot P_4)] (7a)\)

Figure 12S. \(^1\)H NMR spectrum of 7a in thf-ds at room temperature.
Figure 13S. $^{31}$P(1H) NMR spectrum of 7a in thf-d$_8$ at room temperature.

2.10. \[\{(\text{K@cryptand})(\text{thf})\}[\text{L}^1\text{Ni}(\eta^{1:1}\text{As}_4)]\] (7b)

Figure 14S. $^1$H NMR spectrum of 7b (cryptand) in thf-d$_8$ at room temperature.
2.11. \([\texttt{([K@18-crown-6](thf)}_{2})][\texttt{L}^{1}\texttt{Ni(}\eta^{1:1}-\texttt{As}_{4})]\) (7b)

![Figure 15S. \(^1\text{H NMR spectrum of 7b (18-crown-6) in thf-d}_8 \text{ at room temperature.}
]
3. Magnetic Measurements in Solution

3.1. Evans Method

The effective magnetic moment \( \mu_{\text{eff}} \) of paramagnetic compounds were determined by the Evans method.\(^5\) The Evans method is based on the chemical shift difference of the residual solvent peak between the inner tube containing a solution of the paramagnetic species and the outer tube, which contains the pure deuterated solvent. The \(^1\)H NMR spectra are recorded at room temperature\(^6\) on a Bruker Avance III HD 400 (\(^1\)H: 400.13 MHz) spectrometer.

The molar paramagnetic susceptibility \( \chi_P \) was obtained from the measured molar magnetic susceptibility \( \chi_M \) after the correction for diamagnetic contribution \( \chi_D \) according to equation (1).\(^7\)

The magnetic susceptibility \( \chi_M \) and the effective magnetic moment \( \mu_{\text{eff}} \) of the paramagnetic compounds was determined according to equation (2)\(^6\) and (3)\(^7\).

\[
\chi_P = \chi_M - \chi_D \quad (1)
\]

\[
\chi_M = \frac{3000 \cdot \Delta \nu}{4\pi \cdot \nu_0 \cdot c} \quad (2)
\]

\[
\mu_{\text{eff}} = \sqrt{8 \cdot T \cdot \chi_P} \quad (3)
\]

Finally, the number of unpaired electrons is calculated by the ‘spin-only’ formula\(^8\) (equation 4):

\[
n = -1 + \sqrt{\mu_{\text{eff}}^2 + 1} \quad (4)
\]

Where

- \( \chi_M \) is the measured susceptibility of the sample in emu \cdot mol\(^{-1}\),
- \( \chi_P \) is the molar paramagnetic susceptibility of the sample in emu \cdot mol\(^{-1}\),
- \( \chi_D \) is the molar diamagnetic susceptibility of the sample in emu \cdot mol\(^{-1}\),
- \( \Delta \nu \) is the chemical shift difference between the solvent in presence of paramagnetic solute and pure solvent in [Hz],
- \( \nu_0 \) is the measuring frequency of the NMR spectrometer [Hz],
- \( c \) is the concentration of paramagnetic sample in mol \cdot L\(^{-1}\),
- \( T \) is the absolute temperature in K,
- \( \mu_{\text{eff}} \) is the effective magnetic moment in \( \mu_B \), and
- \( n \) is the number of unpaired electrons.
3.2. EPR (Electrone Paramagnetic Resonance) measurements

The X-band EPR measurements were carried out with a MiniScope MS400 device equipped with a Magnettech GmbH rectangular TE102 resonator at a frequency of 9.5 GHz. The compounds were dissolved in a glovebox under N₂ inert gas atmosphere, placed in tip-sealed pasteur pipettes, and were rubber plugged. The measurements were conducted at room temperature and 77 K, respectively. With EPR, a magnetic field is applied to the sample, which interacts with the unpaired electrons. The simulation has been performed using the EasySpin[9] program.

Table S1. Experimental and fitted parameters used for the simulation of the X-band EPR spectrum of 3a, see Figure 1 (Paper).

| SysP, g         | Exp.Range          |
|-----------------|--------------------|
| [2.254 2.108 2.063] | [284.2615 354.3425] |

| SysP, lw       | Exp.nPoints |
|----------------|-------------|
| [0.5]          | 4096        |

| SysP, A        | Exp.mwFreq |
|----------------|-------------|
| [27 88 80; 59.8 55 80] | 9.440920   |

| SysP.HStrain  | Exp.Temperature |
|---------------|-----------------|
| [70 80 55]    | 77              |

| SysP.Astrain  | Exp.ModAmp |
|---------------|------------|
| [150 250 78]  | 0.05       |

Table S2. Experimental and fitted parameters used for the simulation of the X-band EPR spectrum of 3b.

| Sys.g          | Exp.Range          |
|----------------|--------------------|
| [2.2705 2.135 2.055] | [281.3095 351.3905] |

| Sys.lw        | Exp.nPoints |
|---------------|-------------|
| [2.5]         | 4096        |

| Sys.HStrain   | Exp.mwFreq |
|---------------|-------------|
| [150 180 300] | 9.440920    |

| Exp.Temperature |
|-----------------|
| 77              |

| Exp.ModAmp |
|------------|
| 0.05       |
4. Cyclic voltammetry (CV)

All cyclic voltammetry measurements were performed in THF at 300 K in a three electrode setup, with a glassy carbon electrode (working electrode), an Ag-wire (pseudo-reference electrode) an a Pt (auxiliary electrode), in combination with a Methrom Autolab PGSTAT101 potentiostat. Bu₄NPF₆ was used as supporting electrolyte and all cyclic voltammograms are referenced against Cp₂Fe/Cp₂Fe⁺ redox couple.

![Cyclic voltammogram of 3b in THF at 100 mV/s scan rate.](image)

Figure 17S. Cyclic voltammogram of 3b in THF at 100 mV/s scan rate.
5. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) equipped with a Ruby CCD detector (4), on a SuperNova diffractometer (Agilent Technologies) equipped with an Atlas CCD detector (3a, 3b, 6), on a SuperNova Dualflex diffractometer (Rigaku) equipped with a TitanS2 CCD detector (2b, 7a), or a XtaLAB Synergy R, DW system (Rigaku) equipped with a HyPix Arc 150° detector (2c, 5a, 5b, 7b). All measurements were performed at 123 K or 100 K, respectively. Data collection and reduction were performed with CrysAlisPro\textsuperscript{[10]} (Version 171.37.33, 2014 (3a, 3b, 4, 6), 171.41.88a, 2020 (2b, 5a, 5b, 7a, 7b), 171.41.90a, 2020 (2c)). For all compounds a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. Using Olex2,\textsuperscript{[11]} were the structures solved by direct methods with ShelXT\textsuperscript{[12]} and refined by full-matrix least-squares method against $F^2$ in anisotropic approximation using ShelXL\textsuperscript{[13]}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

Figures were created with Olex2.\textsuperscript{[11]}

CCDC-2109927 (2b), CCDC-2109928 (2c), CCDC-2109929 (3a), CCDC-2109930 (3b), CCDC-2109931 (4), CCDC-2109932 (5a), CCDC-2109933 (5b), CCDC-2109934(6), CCDC-2109935 (7a), CCDC-2109936 (7b) 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).
5.1. [(L¹Ni)₂(μ-η², κ¹:η², κ¹-As₄)] (2b)

Compound 2b crystallized from a concentrated solution in Et₂O at -30 °C in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of 2b and 0.5 molecules of Et₂O. The structure in the solid state is given in Figure S18.

![Figure 18S. Molecular structure of 2b in solid state. Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-As1 2.3111(7), Ni1-As2 2.4606(6), Ni1-As3 2.3244(6), Ni2-As2 2.3308(6), Ni2-As3 2.4565(6), Ni2-As4 2.3169(6), As1-As2 2.4115(5), As1-As4 2.3917(5), As3-As4 2.4141(5), As2···As3 2.7192(5), Ni1···Ni2 3.93952(3), Ni1-As2-Ni2 110.58(2), Ni1-As3-Ni2 110.95(2), As2-Ni2-As3 69.166(18), As2-Ni1-As3 69.193(18), Ni1-As1-As4 101.90(2), As1-As4-As376.930(17), As4-As3-Ni1 100.83(2), As3-Ni1-As1 80.32(2), As1-As2-Ni2 56.622(17), As2-Ni2-As4 81.73(2), Ni2-As4-As1 100.33(2), As4-As1-As2 78.554(16).]
5.2. \([\text{([L}^1\text{Ni})_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{AsP}_3)] \ (2c)\)]

Compound 2c crystallized from a concentrated solution in Et\(_2\)O at -30 °C in the monoclinic space group \(C2/c\). The asymmetric unit contains three times 0.5 molecule of 2c and two molecules of Et\(_2\)O. All three independent half molecules of 2c show a disorder of the AsP\(_3\) unit were the As atom is distributed over all positions (molecule 1: 35:5; molecule 2: 34:6; molecule 3: 33:0). Further, co-crystalizes 2c with the compound \([\text{([L}^1\text{Ni})_2(\mu-\eta^2,\kappa^1:\eta^2,\kappa^1-\text{P}_4)] \) (molecule 1+2: 80:20; molecule 3: 66:34). Additionally, is one Et\(_2\)O solvent molecule disordered over two positions (68:32). The second Et\(_2\)O molecule was heavily disorded. Therefore, was a solvent mask calculated. 352 electrons were detected in a volume of 2104 Å\(^3\) in 4 voids per unit cell. This is consistent with the presence of one Et\(_2\)O molecule per asymmetric unit, which accounts for 336 electrons per unit cell. The structure in the solid state is given in Figure S19-S21.

![Figure 19S. Asymmetric unit of 2c in solid state.](image)
Figure 20S. Molecular structure of 2c in solid state. Molecule 1: 2c (ratio of the arsenic atom: As1 0.35, As2 0.05). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-N1 1.965(2), Ni1-N2 1.938(2), Ni1-Ni1’ 3.8407(9), Ni1-P1 2.238(4), Ni1-P2 2.385(6), Ni1-P2’ 2.330(8), Ni1-As1 2.16(3), Ni1-As2 2.445(6), Ni1-As2’ 2.251(7), P1-P1’ 2.157(7), P1-P2 2.316(9), P1-As2 2.215(7), P1-As1’ 2.37(3), As1-As1’ 2.198(15), P1-Ni1-As2 56.25(17), P1-Ni1-As2’ 77.02(17), P1-Ni1-P2 79.7(2), P2'-Ni1-P2 70.7(3), As1-Ni1-P2 57.6(5), Ni1'-As2-Ni1 109.7(3), P1-As2-Ni1 106.3(3), P1-As2-Ni1’ 51.16(13), P1'-As2-Ni2 79.5(2), Ni1'-P2-Ni1 109.1(3), As1-P2-Ni1 56.1(8), Ni1-As1-P2 66.3(6), Ni1-P2-As1’ 51.70(12), As1-P2-Ni1 66.6(2), P2'-P2-Ni1 102.81(12).

Figure 21S. Molecule structure of 2c in solid state. Molecule 2 (left, ratio of the arsenic atom: As3 0.34, As4 0.06) and molecule 3 (right, ratio of the arsenic atom: As6 0.33) of 2c. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Molecule 2: N3-Ni2 1.942(2), N4-Ni2 1.966(2), Ni2-Ni2’ 3.7918(9), Ni2-P3 2.252(5), Ni2-P4 2.393(5), Ni2-As3 2.21(3), Ni2-As4 2.378(3), Ni2-As4’ 2.275(4), Ni2-P4’ 2.29646(3), As3-P4 2.32(3), P3-As4 2.245(6), P3-As3’ 2.41963(3), P3-P4 2.24190(2), P3-P3’ 2.153(8), As4'-Ni2-As4 70.82(16), P3-Ni2-As4 57.93(15), P3-Ni1-As4’ 77.58(14), As3-Ni1-P4 60.5(8), Ni2'-As4-Ni2 109.14(16), P3-As4-Ni2 99.23(17), P3-As4-Ni3 58.22(15), As4-P3-Ni2 63.85(18), P3'-P3-Ni2 102.8(2), P3'-P3-As4 80.28(16), Ni2'-P4-Ni2 107.89(19), Ni2'-P4-As3 105.0(7), As3-P4-Ni1 55.8(8); Molecule 3: N5-Ni3 1.940(2), N6-Ni3 1.965(2), Ni3-Ni3’ 3.8345(9), Ni3-P5A 2.2383(10), Ni3-P5B 2.248(16), Ni3-P6 2.374(7), Ni3-P6’ 2.421(7), Ni3-As6 2.437(7), Ni3-As6’ 2.220(6), P5A-P5A’ 2.1968(15), P5A-P6 2.322(7), P5B-P5B’ 2.172(17), P5B-P6 2.155(13), P5B-As6 2.220(6).
2.208(17), As6'-Ni3-P5A 79.70(17), P5A-Ni3-As6 59.39(16), P5A-Ni3-P6 75.8(2), P5B-Ni3-P6 75.9(3), Ni3'-As1-P5A 99.3(2), P5A-As6-Ni3 56.05(15), Ni3-P5A-As6 64.56(16), P5A'-P5A-Ni3 102.63(3), P5A'-P5A-As6 78.37(15), Ni3-P6-Ni3' 106.2(3), P5B'-P6-Ni3 99.1(4), P6'-P5B-Ni3 66.7(5), P5B'-P5B-Ni3 102.6(5).

5.3. [(L¹Ni)₂(μ,η⁴-P₃)] (3a)

Compound 3a crystallized from a concentrated solution of hexane at +8 °C in the orthorhombic space group Pbca. The asymmetric unit contains one molecule of 3a. The cyclo-P₃ ring is disordered over two positions in a ratio of 59:41. The structure in solid state is shown in Figure S22.

Figure 22S. Molecular structure of 3a in solid state (Left: best view; right: disorder of the P₃ ring). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-P1A 2.312(9), Ni1-P2A 2.356(6), Ni1-P3A 2.300(11), Ni2-P1A 2.220(8), Ni2-P2A 2.279(6), Ni2-P3A 2.344(11), Ni1-P1B 2.190(13), Ni1-P2B 2.347(8), Ni1-P3B 2.252(15), Ni2-P1B 2.317(13), Ni2-P2B 2.330(9), Ni2-P3B 2.326(15), P1A-P2A 2.202(11), P2A-P3A 2.158(10), P3A-P1A 2.206(14), P1B-P2B 2.164(17), P2B-P3B 2.168(16), P3B-P1B 2.16(2), Ni1-N1 1.9173(16), Ni1-N2 1.9175(16), Ni2-N3 1.9131(15), Ni2-N4 1.9157(15), P1A-P2A-P3A 60.8(4), P2A-P3A-P1A 60.6(4), P3A-P1A-P2A 58.7(4), P1B-P2B-P3B 59.7(6), P2B-P3B-P1B 60.0(6), P3B-P1B-P2B 60.2(5).
5.4. \([\{L^1\text{Ni}\}_2(\mu,\eta^{3:3}\text{-As}_3)\}] (3b)

Compound 3b crystallized from a concentrated solution of hexane at +8 °C in the orthorhombic space group \textit{Pbca}. The asymmetric unit contains one molecule of 3b. The \textit{cyclo-As}_3 ring is disordered over three positions in a ratio of 50:25:25. The structure in solid state is shown in Figure S23.

![Molecular structure of 3b in solid state](image)

Figure 23S. Molecular structure of 3b in solid state (left: best view, right: disorder of the As3 ring). Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50% probability level. Selected bond lengths [Å] and angles [°]: Ni1-As1A 2.353(5), Ni1-As2A 2.381(4), Ni1-As3A 2.460(4), Ni2-As1A 2.385(6), Ni2-As2A 2.418(4), Ni2-As3A 2.421(4), As1A-As2A 2.390(7), As2A-As3A 2.376(6), As3A-As1A 2.375(7), Ni1-As1B 2.469(8), Ni1-As2B 2.327(6), Ni1-As3B 2.476(9), Ni2-As1B 2.277(9), Ni2-As2B 2.508(8), Ni2-As3B 2.443(9), As1B-As2B 2.389(13), As2B-As3B 2.429(12), As3B-As1B 2.458(14), Ni1-As1C 2.387(11), Ni1-As2C 2.440(10), Ni1-As3C 2.519(9), Ni2-As1C 2.478(11), Ni2-As2C 2.453(11), Ni2-As3C 2.397(6), As1C-As2C 2.574(14), As2C-As3C 2.480(13), As3C-As1C 2.474(12), As1A-As2A-As3A 59.8(2), As2A-As3A-As1A 60.4(2), As3A-As1A-As2A 59.8(2), As1B-As2B-As3B 61.3(4), As2B-As3B-As1B 58.5(4), As3B-As1B-As2B 60.1(4), As1C-As2C-As3C 58.6(4), As2C-As3C-As1C 62.6(4), As3C-As1C-As2C 58.8(4).
5.5. \([\text{K}_2[(\text{L}^1\text{Ni})_2(\mu,\eta^{2,2-}\text{P}_4)]] (4)\)

Compound 4 crystallized from a concentrated solution of toluene at -30 °C in the monoclinic space group \(P2_1/n\). The asymmetric unit contains half a molecule of 4 and two toluene molecules. The \(P_4\) unit is disordered over two positions (93:7). Further, one of the toluene molecules is disordered over two positions (75:25). The structure in solid state is shown in Figure S24.

![Molecular structure of 4 in solid state](image)

Figure 24S. Molecular structure of 4 in solid state. Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50% probability level. Selected bond lengths [Å] and angles [°]: Ni-P1 2.2467(7), Ni-P2 2.2471(8), Ni-P1A 2.232(12), Ni-P2A 2.405(11), P1-P2 2.2611(10), P1-P2' 2.1360(10), P1A-P2A 2.053(17), P1A-P2A' 2.213(15). P1-P2-P1' 89.80(3), P2'-P1-P2 90.21(3), P1A-P2A-P1A' 82.2(6).
5.6. [K@18-crown-6(thf)]2[(L\textsuperscript{1}Ni)\textsubscript{2}(\mu,\eta\textsuperscript{3-3}:P\textsubscript{3})] (5a)

Compound 5a crystallized from a concentrated solution in thf layered with hexane at -30 °C in the triclinic space group \(P\overline{1}\) as brown plates. The asymmetric unit contains one molecule of 5a, two times half the unit [K(18-c-6)(thf)\textsubscript{2}] and a further thf molecule. The \(P\textsubscript{3}\) ring is disordered over two positions (ratio: 90:10). Additionally, are the thf molecules disordered over two positions (65:35; 54:46). The structure in solid state is shown in Figure S25.

Figure 25S. Molecular structure of 5a in solid state (left: best view, right: disorder of the \(P\textsubscript{3}\) ring). Counterion and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-P1A 2.2490(7), Ni1-P2A 2.2694(7), Ni1-P3A 2.3574(6), Ni2-P1A 2.2872(6), Ni2-P2A 2.3051(7), Ni2-P3A 2.2683(6), Ni1-P1B 2.207(5), Ni1-P2B 2.237(7), Ni1-P3B 2.335(6), Ni2-P1B 2.328(5), Ni2-P2B 2.275(7), Ni2-P3B 2.267(6), P1A-P2A 2.2065(10), P2A-P3A 2.1848(10), P3A-P1A 2.1760(10), P1B-P2B 2.130(9), P2B-P3B 2.133(9), P3B-P1B 2.171(8), P1A-P2A-P3A 59.41(4), P2A-P3A-P1A 60.79(4), P3A-P1A-P2A 59.80(3), P1B-P2B-P3B 61.2(3), P2B-P3B-P1B 59.3(3), P3B-P1B-P2B 59.4(3).
5.7. \([\text{K@18-crown-6(thf)}_2][\text{(L}^1\text{Ni)}_2(\mu,\eta^{3,3}\text{-As}_3)]\) (5b)

Compound 5b crystallized from a concentrated solution in thf layered with hexane at - 30 °C in the monoclinic space group \(\text{P2}_1/\text{a}\) as brown needle. The asymmetric unit contains one molecule of 5b, one potassium ion chelated by one molecule of 18-crown-6 with 2 molecules of thf and a further 1.5 thf molecules. The As₃ ring is disordered over two positions (ratio: 61:39). Additionally, is one of the thf molecules disordered over two positions (58:42). The other half occupied thf molecule was heavily disordered and therefore, a solvent mask was calculated. In its volume of 1060 Å³ were 168 electrons found in two voids per unit cell. This is consistent with the presence of half a thf molecule per asymmetric unit, which accounts for 160 electrons per unit cell. The structure in solid state is shown in Figure S26.

![Molecular structure of 5b in solid state](image)

Figure 26S. Molecular structure of 5b in solid state (left: best view, right: disorder of the As₃ ring). Counterion and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-As1A 2.516(3), Ni1-As2A 2.357(4), Ni1-As3A 2.362(2), Ni2-As1A 2.404(3), Ni2-As2A 2.472(4), Ni2-As3A 2.353(3), Ni1-As1B 2.437(4), Ni1-As2B 2.408(7), Ni1-As3B 2.370(4), Ni2-As1B 2.354(4), Ni2-As2B 2.470(7), Ni2-As3B 2.351(4), As1A-As2A-As3A 60.44(13), As2A-As3A-As1A 59.37(12), As3A-As1A-As2A 60.19(11), As1B-As2B-As3B 60.5(2), As2B-As3B-As1B 59.5(2), As3B-As1B-As2B 60.05(17)
5.8.  $[\text{K}_2\{\text{(L}^1\text{Ni)}_2(\mu,\eta^{1-1}\text{-N}_2)\}]$ (6)

Compound 6 crystallized from a concentrated solution of hexane at $+8 \, ^\circ\text{C}$ in the orthorhombic space group $Pbcn$. The asymmetric unit contains half a molecule of 6. The structure in solid state is shown in Figure S27.

Figure 27S. Molecular structure of 6 in solid state. Thermal ellipsoids are drawn with 50 \% probability level. Selected bond lengths [Å] and angles [°]: Ni···K1 3.4757(9), Ni···K2 3.5923(9), Ni-N2 1.928(2), Ni-N3 1.919(2), Ni-N1 1.725(3), N1-N1’ 1.195(5), N1-K1 2.709(3), N1-K2 2.751(3), Ni-N1-N1’ 177.4(2)
5.9. \([(\text{K@18-crown-6})(\text{thf})_2][\text{L}^1\text{Ni(}\eta^{1:1}\cdot\text{P}_4)]\) (7a)

Compound 7a crystallized from a concentrated solution in thf layered with hexane at -30 °C in the non-centrosymmetric orthorhombic space group \(P2_12_12_1\) as orange needle. The asymmetric unit contains one molecule of 7a, one potassium ions chelated by one molecule of 18-crown-6 and 2 molecules of thf (both disordered over two positions: 84:16 and 58:42). The structure in solid state is shown in Figure S28.

![Molecular structure of 7a in solid state. Top: view of the asymmetric unit. Bottom: best view. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni-P1 2.1935(12), Ni-P2 2.1886(12), P1-P2 2.6759(15), P1-P3 2.2255(15), P1-P4 2.2209(16), P2-P3 2.2115(16), P2-P4 2.2282(17), P3-P4 2.1567(18), Ni-N1 1.972(3), Ni-N2 1.982(3), P1-Ni-P2 75.27(4), N1-Ni-N2 94.50(13), P3-P1-P2 52.67(5), P4-P1-P2 53.15(5), P4-P1-P3 58.03(6), P3-P2-P1 53.15(4), P3-P2-P4 58.13(6), P4-P2-P1 52.90(5), P2-P3-P1 74.18(5), P4-P3-P1 60.88(5), P4-P3-P2 61.32(6), P1-P4-P2 73.95(5), P3-P4-P1 61.09(5), P3-P4-P2 60.55(6).](image-url)
5.10. [K@cryptand][thf][L\(^{1}\)Ni(\(\eta^{1:1}\)-As\(_{4}\))] (7b)

Compound 7b crystallized from a concentrated solution in thf layered with hexane at - 30 °C in the triclinic space group \(P\overline{1}\) as brown needles. The asymmetric unit contains one molecule of 7b, one potassium ions chelated by one molecule of cryptand and one molecule of thf. The structure in solid state is shown in Figure S29.

![Molecular structure of 7b in solid state. Top: view of the asymmetric unit. Bottom: best view. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni-As1 2.3246(4), Ni-As2 2.3205(4), As1-As2 2.8963(3), As1-As3 2.4687(3), As1-As4 2.4506(4), As2-As3 2.4596(3), As2-As3 2.4666(4), N1-Ni 1.9669(17), N2-Ni 1.9705(18), As1-Ni-As2 77.144(13), As4-As2-As3 58.066(11), As4-As1-As3 58.155(11), As2-As3-As1 71.866(10), As4-As3-As2 60.819(11), As4-As3-As1 60.544(11), As1-As4-As2 72.292(11), As3-As4-As2 61.115(11), As3-As4-As1 61.302(11).](image-url)
## 5.11. Crystallographic information

Table S3. Crystallographic data and details of diffraction experiments for 2b, 2c, 3a and 3b.

| Compound | 2b | 2c | 3a | 3b |
|----------|----|----|----|----|
| CCD | 2109927 | 2109928 | 2109929 | 2109930 |
| Formula | C_{118}H_{169}As_8Ni_4O_{0.5}As_{2.26}Ca_{190}H_{286}N_{12}Ni_6O_{2.74} | C_{58}H_{118}N_4Ni_2P_3 | C_{58}H_{123}As_3N_4Ni_2 | |
| D_{calc} / g cm^{-3} | 1.433 | 1.254 | 1.231 | 1.377 |
| µ/mm^1 | 3.586 | 2.247 | 1.923 | 3.053 |
| Formula Weight | 2541.80 | 3625.52 | 1045.60 | 1177.45 |
| Color | dark green | green | green | brown |
| Shape | block-shaped | block-shaped | rod | rod |
| Size/mm³ | 0.34×0.29×0.14 | 0.09×0.08×0.06 | 0.30×0.07×0.02 | 0.36×0.06×0.06 |
| T/K | 123.00(10) | 100.01(10) | 123.01(10) | 123.00(10) |
| Crystal System | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Space Group | P2₁/c | C2/c | Pbca | Pbca |
| a/Å | 13.97930(10) | 24.0518(2) | 19.08692(18) | 18.9860(4) |
| b/Å | 15.8852(2) | 35.9443(4) | 23.0111(2) | 23.1897(3) |
| c/Å | 26.7832(2) | 23.2698(3) | 25.6877(3) | 25.7976(3) |
| α° | 90 | 90 | 90 | 90 |
| β° | 97.9450(10) | 107.3190(10) | 90 | 90 |
| γ° | 90 | 90 | 90 | 90 |
| V/Å³ | 5890.49(10) | 19205.2(4) | 11282.35(19) | 11358.2(2) |
| Z | 2 | 4 | 8 | 8 |
| Z' | 0.5 | 0.5 | 1 | 1 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | Cu Kα | Cu Kα | Cu Kα | Cu Kα |
| θ_{min}/° | 4.236 | 2.283 | 3.466 | 3.462 |
| θ_{max}/° | 67.023 | 73.341 | 70.654 | 76.541 |
| Measured Refl's. | 111628 | 80701 | 77497 | 31637 |
| Indep Refl's | 10449 | 18572 | 10687 | 11622 |
| Refl's I≥2σ(I) | 9997 | 14666 | 8685 | 9969 |
| R_{int} | 0.0572 | 0.0562 | 0.0473 | 0.0273 |
| Parameters | 677 | 1098 | 651 | 678 |
| Restraints | 26 | 139 | 0 | 12 |
| Largest Peak | 0.589 | 0.972 | 0.494 | 0.526 |
| Deepest Hole | -0.980 | -0.516 | -0.289 | -0.767 |
| Goof | 1.159 | 1.111 | 1.016 | 1.027 |
| wR₂ (all data) | 0.1041 | 0.1665 | 0.0931 | 0.0947 |
| wR₂ | 0.1028 | 0.1599 | 0.0852 | 0.0892 |
| R₁ (all data) | 0.0422 | 0.0657 | 0.0474 | 0.0428 |
| R₁ | 0.0407 | 0.0545 | 0.0347 | 0.0344 |
Table S4. Crystallographic data and details of diffraction experiments for 4, 5a, 5b.

| Compound | 4 | 5a | 5b |
|----------|---|----|----|
| CCDC     | 2109931 | 2109932 | 2109933 |
| Formula  | C₈₆H₁₁₄K₂Ni₂P₄ | C₈₂H₁₃₀KN₂Ni₂O₉P₃ | As₃C₈₆H₁₁₄K₂Ni₂O₉.5 |
| Dcalc    | 1.251 | 1.226 | 1.315 |
| µ/mm²    | 2.588 | 1.955 | 2.650 |
| Formula Weight | 1523.31 | 1565.32 | 1733.22 |
| Color    | brown | clear brown | clear brown |
| Shape    | block-shaped | plate-shaped | needle-shaped |
| Size/mm³ | 0.21×0.16×0.06 | 0.36×0.30×0.10 | 0.21×0.04×0.03 |
| T/K      | 123(1) | 123.00(10) | 123.01(10) |
| Crystal System | monoclinic | triclinic | monoclinic |
| Space Group | P2₁/n | P-1 | P2₁/a |
| a/Å      | 14.29612(14) | 12.98450(10) | 35.6437(4) |
| b/Å      | 14.53816(13) | 13.60660(10) | 13.2844(2) |
| c/Å      | 19.69075(16) | 24.7335(2) | 37.2813(5) |
| α/°      | 90 | 103.0540(10) | 90 |
| β/°      | 98.7928(8) | 94.0260(10) | 97.1640(10) |
| γ/°      | 90 | 92.2980(10) | 90 |
| V/Å³     | 4044.42(6) | 4239.31(6) | 17515.1(4) |
| Z        | 2 | 2 | 8 |
| Z'       | 1 | 1 | 1 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | CuKα | Cu Kα | Cu Kα |
| θmin/°   | 3.795 | 3.340 | 2.389 |
| θmax/°   | 66.611 | 73.254 | 73.180 |
| Measured Refl's. | 16391 | 65154 | 60090 |
| Indep't Refl's | 6974 | 16397 | 16692 |
| Refl's I≥2 σ(I) | 6519 | 15036 | 12366 |
| Rint     | 0.0238 | 0.0237 | 0.0581 |
| Parameters | 536 | 1052 | 1011 |
| Restraints | 210 | 138 | 219 |
| Deepest Hole | -0.415 | -0.437 | -0.574 |
| Goof     | 1.041 | 1.057 | 1.114 |
| wR² (all data) | 0.1378 | 0.1050 | 0.1490 |
| wR²     | 0.1353 | 0.1032 | 0.1406 |
| R₁ (all data) | 0.0517 | 0.0419 | 0.0691 |
| R₁      | 0.0495 | 0.0390 | 0.0511 |
Table S5. Crystallographic data and details of diffraction experiments for 6, 7a and 7b.

| Compound | 6   | 7a   | 7b   |
|----------|-----|------|------|
| CCDC     | 2109934 | 2109935 | 2109936 |
| Formula  | C₆₀H₈₂K₂Ni₂ | C₆₀H₈₁Ni₂NiO₄P₄ | C₅₁H₈₅AsNi₄NiO₇ |
| Dcalc    | 1.235 | 1.269 | 1.451 |
| μ/mm²    | 2.431 | 2.692 | 4.064 |
| Formula Weight | 1058.91 | 1047.84 | 1263.71 |
| Color    | dark violet | clear orange | clear dark brown |
| Shape    | needle | needle-shaped | needle-shaped |
| Size/mm³ | 0.35×0.03×0.02 | 0.17×0.14×0.05 | 0.66×0.08×0.06 |
| T/K      | 123(1) | 123.00(10) | 100.00(10) |
| Crystal System | orthorhombic | orthorhombic | triclinic |
| Flack Parameter | - | -0.012(8) | P-1 |
| Hooft Parameter | - | 0.003(5) | 13.2378(2) |
| Space Group | Pbcm | P2₁2₁2₁ | P2₁ |
| a/Å      | 10.6599(2) | 11.55370(10) | 15.9101(3) |
| b/Å      | 23.0876(5) | 19.6743(2) | 70.277(2) |
| c/Å      | 23.1458(4) | 24.1351(3) | 78.6870(10) |
| α/°      | 90 | 90 | 82.1540(10) |
| β/°      | 90 | 90 | 2893.00(10) |
| γ/°      | 90 | 90 | 2 |
| V/Å³     | 5696.4(2) | 5486.17(10) | 1 |
| Z        | 4 | 4 | 1.54184 |
| Z'       | 0.5 | 1 | Cu Kα |
| Wavelength/Å | 1.54184 | 1.54184 | 2.990 |
| Radiation type | Cu Kα | Cu Kα | Cu Kα |
| θ/min/°  | 3.820 | 4.242 | 117106 |
| θ/max/°  | 70.690 | 66.714 | 11379 |
| Measured Refl's. | 15295 | 40235 | 10524 |
| Indep't Refl's | 5287 | 9591 | 0.0496 |
| Refl's I≥2σ(I) | 4019 | 8495 | 641 |
| Rint     | 0.0504 | 0.0641 | 75 |
| Parameters | 318 | 687 | 1.121 |
| Restraints | 0 | 134 | -0.777 |
| Largest Peak | 0.624 | 0.368 | 1.079 |
| Deepest Hole | 0.434 | -0.272 | 0.0844 |
| Goof     | 1.029 | 0.975 | 0.0826 |
| wR₂(all data) | 0.1632 | 0.0999 | 0.0340 |
| wR₂     | 0.1421 | 0.0980 | 0.0312 |
| R₁(all data) | 0.0711 | 0.0443 | 0.071 |
| R₁      | 0.0529 | 0.0394 | 0.071 |
6. DFT calculations

Gaussian 09 program\cite{14} was used throughout. Density functional theory (DFT) in form of Becke’s three-parameter hybrid functional B3LYP\cite{15} or BP86\cite{16} (Becke’s exchange and Perdew 86 correlation functional) with def2-SVP all electron basis set was employed. The figures for the supporting information concerning the DFT calculations were created with Chemcraft.\cite{17} For solvents effects has been accounted by using continuous polarizable continuum model (CPM).\cite{18} The dielectric constant of thf (\(\varepsilon = 7.4257\)) has been used in the calculations of the anions (4, 5a, 5b). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.\cite{19} The long range dispersion correction GD3BJ was applied.\cite{20}

Table S6. Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).

|            | total energy [Ha]         |
|------------|--------------------------|
| 3a [(L\(^1\)Ni)\(_2\)(\(\mu\),\(\eta^{3:3}\)-P\(_3\))] | -6517.57987010 |
| 3b [(L\(^1\)Ni)\(_2\)(\(\mu\),\(\eta^{3:3}\)-As\(_3\))] | -12201.3925306 |

Table S7. Total energies for all optimized geometries (BP86/def2-SVP level of theory).

|            | total energy [Ha]         |
|------------|--------------------------|
| 2c-I [(L\(^1\)Ni)\(_2\)(AsP\(_3\))] | -8753.97439277 |
| 2c-II [(L\(^1\)Ni)\(_2\)(AsP\(_3\))] | -8753.96934262 |

Table S8. Total energies for optimized geometries of 4, 5a, 5b (BP86/def2-SVP level of theory).

|            | total energy [Ha]         |
|------------|--------------------------|
| 4 [(L\(^1\)Ni)\(_2\)(\(\mu\),\(\eta^{2:2}\)-P\(_3\))]\(^2\) singlet state | -6859.54186686 |
| 5a [(L\(^1\)Ni)\(_2\)(\(\mu\),\(\eta^{3:3}\)-P\(_3\))] singlet state | -6518.17456214 |
| 5b [(L\(^1\)Ni)\(_2\)(\(\mu\),\(\eta^{3:3}\)-As\(_3\))]\(^-\) singlet state | -12201.9939337 |
Figure 30S. Isosurfaces of the calculated spin density in 3a (left) and 3b (right) B3LYP/def2-SVP level of theory.
| H                  | 1.855077  | 3.704996  |
|--------------------|-----------|-----------|
| H                  | 3.967672  | 4.652145  | 2.096881 |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |
| P                  | 0.033501  | 1.116094  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.104382 | 0.754870  |
| C                  | 0.675083  | 3.658334  | 2.200221 |
| H                  | -0.183243 | 6.068035  |
| C                  | 1.861200  | 0.536768  | 6.000725 |
| H                  | 0.969952  | 2.316276  |
| C                  | 1.752278  | 2.884655  |

Table S9. Optimized geometries of 2c-I (left) and 2C-II (right). XYZ coordinated in angstroms. BP86/deff-SVP level of theory.
| H | 4.896779E000 | 5.006485E000 | 3.785387E000 | 2.678366E000 |
| H | 6.015914E000 | 7.860756E000 | 2.304306E000 | 4.699755E000 |
| H | 1.161399E000 | 1.251289E000 | 4.569402E000 | 2.419344E000 |
| H | 1.279754E000 | 6.083609E000 | 2.870851E000 | 3.305939E000 |
| H | 1.385800E000 | 2.715762E000 | 2.412643E000 | 4.699755E000 |
| H | 1.526223E000 | 0.429809E000 | 1.458694E000 | 0.913986E000 |
| H | 1.780407E000 | 6.083609E000 | 1.708764E000 | 0.716203E000 |
| H | 1.868375E000 | 2.741662E000 | 1.145450E000 | 4.699755E000 |

Table S10. Optimized geometries of 3a (left) and 3b (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.
Table S11. Optimized geometries of 4 singlet state. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.

| Element | X-Axis | Y-Axis | Z-Axis |
|---------|--------|--------|--------|
| H       | 1.456651 | 1.868799 | 3.280743 |
| C       | 0.691909  | 2.110042 | 0.457699 |
| H       | 0.677379  | 0.875734 | 0.377037 |
| P       | 0.832541  | 4.147042 | 0.598556 |

Optimized geometries of singlet state. XYZ coordinated in angstroms. B
|   | Ni  | 1.7037(1000) | 0.3731(1000) | 0.2611(1000) |
|---|-----|--------------|--------------|--------------|
|   | H   | 7.0931(1000) | 0.0537(1000) | 0.2762(1000) |
|   | As  | 0.6162(1000) | 0.0621(1000) | 0.0165(1000) |
|   | C   | 5.0805(1000) | -0.0947(1000) | 0.3750(1000) |
|   | C   | 3.7950(1000) | 1.0900(1000) | 0.7350(1000) |
|   | C   | 2.0923(1000) | 1.7000(1000) | 0.2900(1000) |
|   | C   | 3.2290(1000) | 1.6870(1000) | 0.7380(1000) |
|   | C   | 4.8350(1000) | 2.3050(1000) | 0.9450(1000) |
|   | C   | 0.3200(1000) | 0.0700(1000) | 0.0100(1000) |
|   | C   | 1.4300(1000) | 0.1800(1000) | 0.1200(1000) |
|   | C   | 1.3900(1000) | 0.4700(1000) | 0.2900(1000) |
|   | C   | 0.9500(1000) | 0.1300(1000) | 0.1400(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
| P  | 0.1300(1000) | -0.3700(1000) | -0.2100(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |
|   | H   | 6.4200(1000) | 0.2100(1000) | 0.7500(1000) |

Table S12. Optimized geometries of 5a singlet (left) and 5b singlet (right). XYZ coordinates in angstroms. BP86/def2-SVP level of theory.
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