Assembly and Stabilization of {E(*cyclo*-P_3)$_2$} (E = Sn, Pb) as a Bridging Ligand Spanning Two Triaryloxyniobium Units

*Alexandra Velian, Brandi M. Cossairt, Christopher C. Cummins**

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*Department of Chemistry, Massachusetts Institute of Technology, Cambridge MA 02139-4307 E-mail: ccummins@mit.edu

S.1 Experimental Section

S.1.1 General information

All manipulations were performed in a Vacuum Atmospheres model MO-40M glove box under an inert atmosphere of purified N_2. All solvents were obtained anhydrous and oxygen-free by bubble degassing (N_2) and purification through columns of alumina and Q5 using a Glass Contours Solvent Purification System built by SG Water.

$Na(THF)_3[P_3Nb(ODipp)_3]$[1] and KODipp were prepared according to the literature procedure.[2] Anhydrous $SnCl_2$ (purity, 98%), $PbCl_2$ (purity, 99%) and AgOTf (Tf = SO_2CF_3; purity, 99%) were purchased from Strem Chemicals and used without further purification. Pyridine-*N*-oxide (purity, 95%) was purchased from Aldrich and purified by sublimation before use. Deuterated solvents were purchased from Cambridge Isotope Labs. Benzene-d_6 was degassed and stored over molecular sieves (4 Å beads, 8-12 mesh) for at least 2 days prior to use. Celite 435 (EM Science) was dried by heating above 200 °C under dynamic vacuum for at least 24 h prior to use. All glassware was oven-dried for at least 3 h prior to use, at temperatures greater than 150 °C. NMR spectra were obtained on Bruker Avance 400 instruments equipped with Magnex Scientific superconducting magnets or on Varian Inova 300 and 500 instruments equipped with Oxford Instruments superconducting magnets. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual solvent proton resonances in benzene-d_6 (^{1}H = 7.16 ppm, ^{13}C = 128.06 ppm, respectively). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 (0 ppm). Elemental combustion and Inductively Coupled Plasma analyses were performed by Midwest Microlab LLC, Indianapolis, IN; by Robertson Microlit Laboratories or by ALS Environmental (formerly Columbia Analytical Services, Inc.).

S.1.2 $Sn[P_3Nb(ODipp)_3]_2$ ($Sn[\mathbf{1}\text{-}P_3]_2$)

A 100 mL Schlenk flask equipped with a Teflon-coated stir bar was charged with $[Na(THF)_3][\mathbf{1}\text{-}P_3]$ (1.000 g, 1.04 mmol, 2 equiv), $SnCl_2$ (100 mg, 0.53 mmol. 2.02 equiv) and benzene (50 mL). The flask was placed in an oil bath, pre-heated at 70°C, and after 2 h the initially bright orange mixture changed color to dark orange-red. The volatile materials were removed under reduced pressure and the brown residue suspended in 40 mL *n*-pentane and subjected to suction filtration through a pad of Celite. The volatile materials were removed under reduced pressure from the resulting filtrate, and the brown-red solids (770 mg, 0.50 mmol, 94%) were collected and identified as spectroscopically pure $Sn[\mathbf{1}\text{-}P_3]_2$. The material can be crystallized from a saturated *n*-pentane solution, at −35 °C. Elemental analysis (%) found (calculated) for $C_{72}H_{102}Nb_2O_6P_6Sn$: C 55.20(55.65), H 6.37(6.62). ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) δ: 7.11 (12H, d, $^3J_{H-H}$ = 7.53 Hz), 7.00 (6H, t, $^3J_{H-H}$ = 7.5 Hz), 3.75 (12H, sept, $^3J_{H-H}$ = 6.8 Hz), 1.28 (72H, d, ^3J = 6.8 Hz) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C, 75.4 MHz) δ: 159.98, 138.55, 123.95, 27.51, 24.69 ppm. ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C, 161.9 MHz) δ: –226 (s, $\Delta\nu_{1/2}$ = 9 Hz) ppm. No ^{119}Sn NMR signal was detected during an 15 h acquisition over the

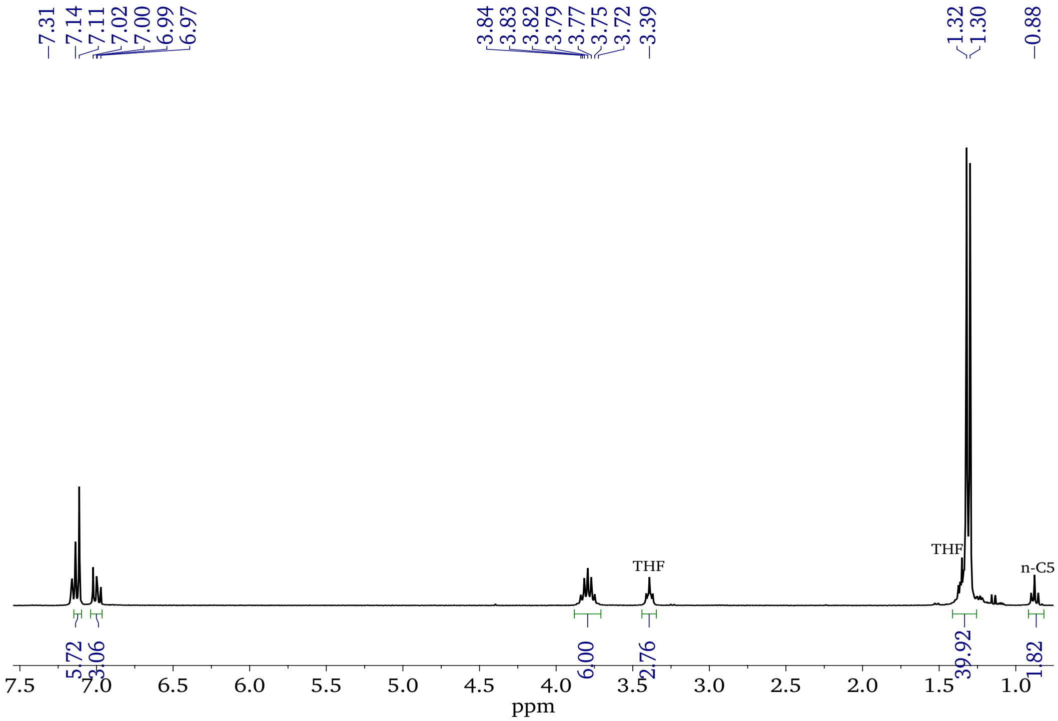

Figure S.1: ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) spectrum of (THF)Sn[**1**-P_3]$_2$.

spectral range of +300 to −1500 ppm.

S.1.3 (THF)Sn[P_3Nb(ODipp)$_3$]$_2$ ((THF)Sn[1-P_3]$_2$)

To a solution of [Na(THF)$_3$][**1**-P_3] (450 mg, 0.470 mmol, 2 equiv) in THF (2 mL) was added a solution of $SnCl_2$ (44.5 mg, 0.235 mmol, 1 equiv) in THF (15 mL) causing the reaction mixture to turn dark red. After 1 h of stirring the volatile materials were removed under reduced pressure, and the solid residue was triturated with *n*-hexane (2×5 mL), slurried in *n*-pentane (15 mL) and the resulting mixture subjected to filtration through a Celite pad. The resulting filtrate was brought to constant mass (360 mg, 0.221 mmol, 94%) yielding a dark red solid identified as spectroscopically clean (THF)Sn[**1**-P_3]$_2$. Elemental analysis for crystals of (THF)Sn[**1**-P_3]$_2$ (%) found (calculated) for $C_{76}H_{110}Nb_2O_7P_6Sn$: C 55.53(56.14), H 6.41(6.82). ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) δ: 7.13 (12H, d, $^{3}J_{H-H} = 7.5$ Hz), 7.00 (6H, dd, $^{3}J = 6.8, 8.3$ Hz), 3.79 (12H, sept, $^{3}J_{H-H} = 6.8$ Hz), 3.39 (4-6H, m, THF), 1.35 (4-6H, m, THF), 1.31 (72H, d, $^{3}J_{H-H} = 6.8$ Hz) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C, 100.6 MHz) δ: 160.70, 138.54, 123.80, 123.45, 68.05, 27.46, 25.66, 24.45 ppm. ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C, 202.4 MHz) δ: –219 (bs, $\Delta\nu_{1/2} = 185$ Hz) ppm. No ^{119}Sn NMR signal was detected during an 3 h acquisition over the spectral range of +300 to −1500 ppm.

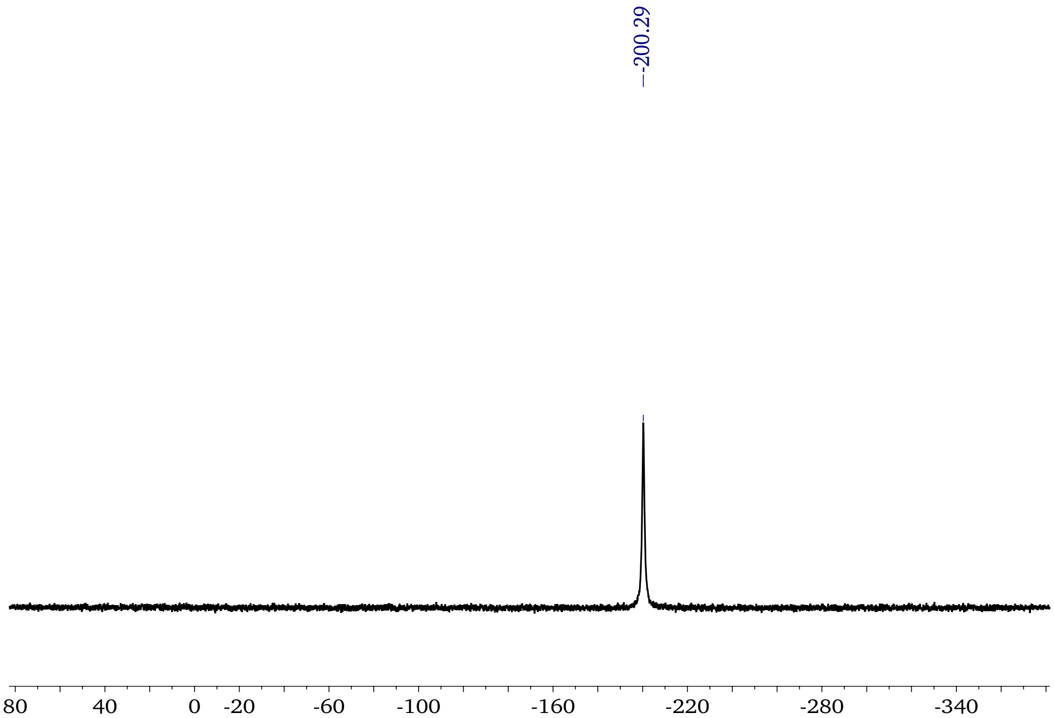

Figure S.2: $^{31}P\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 202.4 MHz) spectrum of (THF)Sn[**1**-P_3]$_2$.

S.1.4 (THF)$_2$Pb[P_3Nb(ODipp)$_3$]$_2$ ((THF)$_2$Pb[1-P_3]$_2$)

To a solution of [Na(THF)$_3$][**1**-P_3] (450 mg, 0.470 mmol, 2 equiv) in THF (2 mL) was added a solution of $PbCl_2$ (65 mg, 0.235 mmol, 1 equiv) in THF (15 mL) causing the reaction mixture to turn maroon. After 1 h of stirring the volatile materials were removed under reduced pressure, slurried in *n*-pentane (15 mL) and the resulting mixture subjected to filtration trough a Celite pad, under reduced pressure. The filtrate was brought to constant mass (405 mg, 0.227 mmol, 96% yield) yielding a maroon solid identified as spectroscopically clean (THF)$_2$Pb[**1**-P_3]$_2$. Elemental analysis (%) found (calculated) for crystals of (THF)$_2$Pb[**1**-P_3]$_2$ $C_{80}H_{118}Nb_2O_8P_6P$: C 54.09(53.78), H 6.57(6.66), P 10.40(11.62); powdered (THF)$_2$Pb[**1**-P_3]$_2$ did not pass elemental analysis. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) δ: 7.14 (12H, d, $^{3}J_{H-H} = 7.6$ Hz), 7.00 (6H, dd, $^{3}J = 6.9$, 8.2 Hz), 3.81 (12H, sept, $^{3}J_{H-H} = 6.8$ Hz), 3.43 (7-8H, m, THF), 1.36 (m, THF), 1.33 (72H, d, $^{3}J_{H-H} = 6.8$ Hz) ppm. $^{13}C\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 100.6 MHz) δ: 160.79, 138.53, 123.79, 123.32, 68.03, 27.51, 25.70, 24.48 ppm. $^{31}P\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 202.4 MHz) δ: –212 (bs, $\Delta\nu_{1/2} = 180$ Hz) ppm.

S.1.5 [AgP_3Nb(ODipp)$_3$]$_4$ ({[Ag][1-P_3]}$_4$)

A solution of [Na(THF)$_3$][**1**-P_3] (0.500 g, 0.523 mmol, 1 equiv) in THF (15 mL) and AgOTf (0.134 g, 0.523 mmol, 1 equiv) in THF (15 mL) were prepared separately and cooled to −35 °C. Then, the AgOTf solution was added dropwise to the stirring solution of [Na(THF)$_3$][**1**-P_3]. The resulting mixture was stirred at room temperature for 1.5 h. The volatile

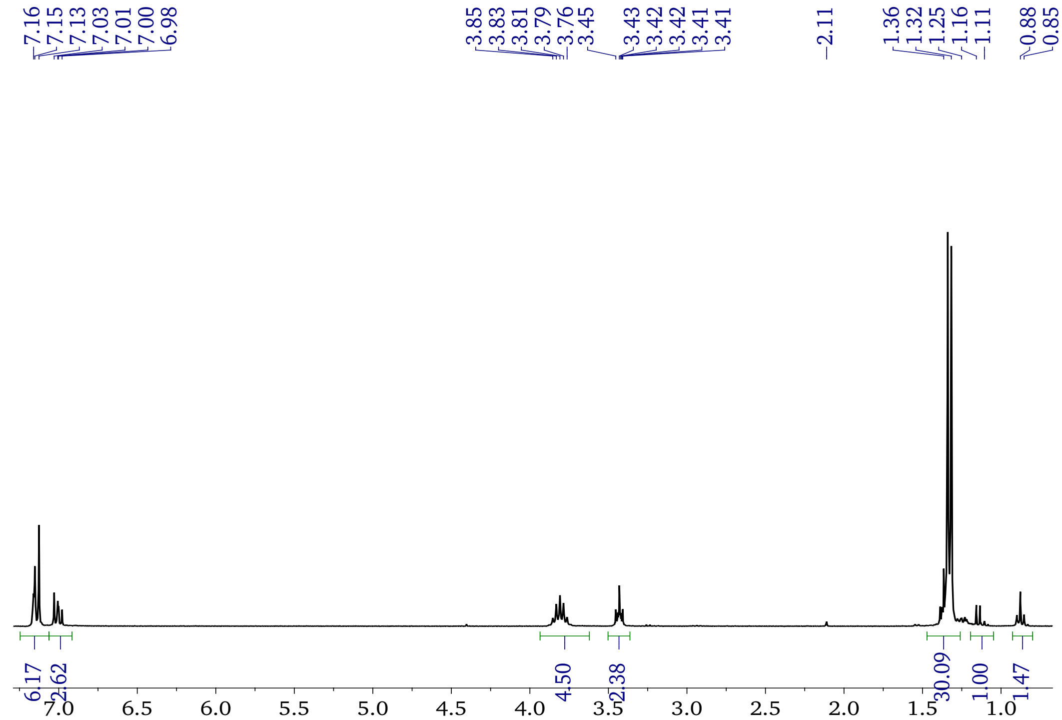

Figure S.3: ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) spectrum of $(THF)_2Pb[\mathbf{1}\text{-}P_3]_2$.

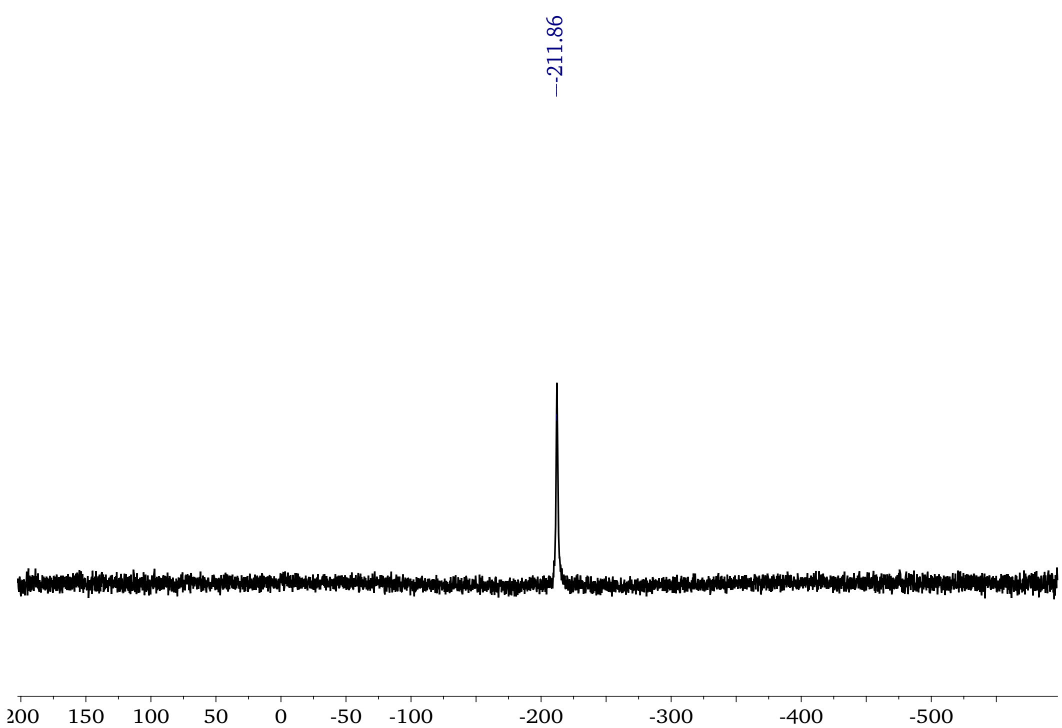

Figure S.4: ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C, 202.4 MHz) spectrum of $(THF)_2Pb[\mathbf{1}\text{-}P_3]_2$.

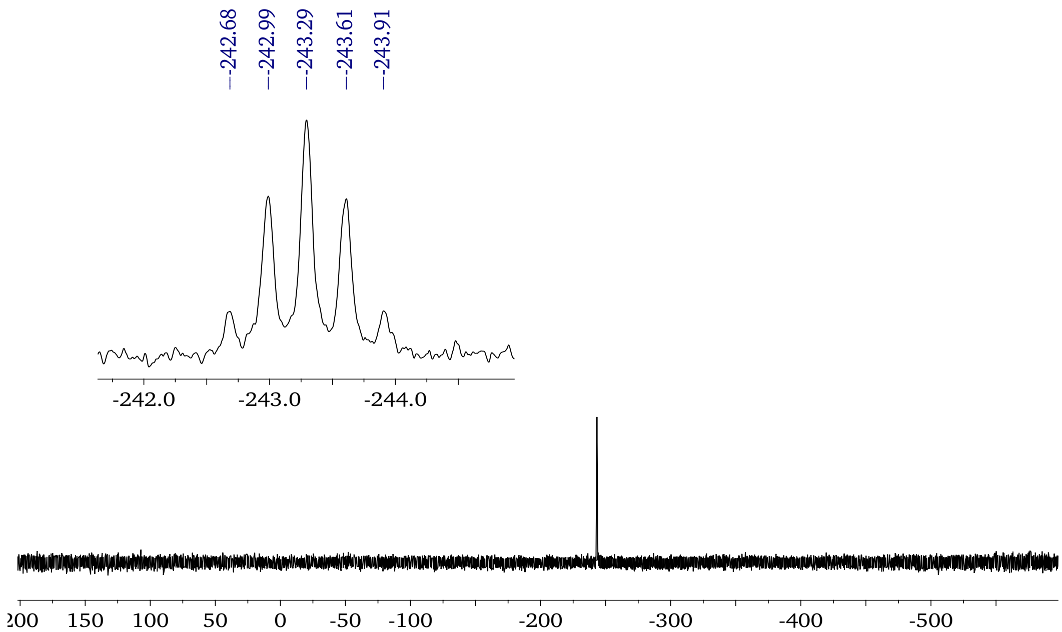

Figure S.5: $^{31}P\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 161.9 MHz) spectrum of $\{[Ag][\mathbf{1}\text{-}P_3]\}_4$.

materials were removed under reduced pressure, and and the residue was triturated twice with *n*-hexane (2 × 2 mL). The resulting solids were slurried in a mixture of *n*-pentane (ca. 75 mL) and diethyl ether (ca. 50 mL), and the slurry was subjected to filtration through a pad of Celite. The volatile materials were removed under reduced pressure from the collected brick-red filtrate. The resulting solids were dissolved in THF (ca. 5 mL) and *n*-pentane (10 mL) was added; the solution was set at −35 °C overnight. Spectroscopically clean $\{[Ag][\mathbf{1}\text{-}P_3]\}_4$ was collected upon suction filtration as a brick-red powder (358 mg, 0.434 mmol, 83%). Elemental analysis (%) found (calculated) for $C_{36}H_{51}AgNbO_3P_3$: C 52.34(52.38), H 6.05(6.23), P 11.52(11.26). ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) δ: 7.09 (6H, d, $^{3}J_{H-H} = 7.5$ Hz), 6.93 (3H, dd, $^{3}J = 7.4, 7.7$ Hz), 3.70 (6H, sept, $^{3}J_{H-H} = 6.8$ Hz), 1.28 (36H, d, $^{3}J_{H-H} = 6.8$ Hz) ppm. $^{13}C\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 75.4 MHz) δ: 159.98, 138.55, 123.95, 27.51, 24.69 ppm. $^{31}P\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 161.9 MHz) δ: –243 (quintet, $J_{^{107/109}Ag-P} = 37$ Hz) ppm. The diffusion coefficient of $\{[Ag][\mathbf{1}\text{-}P_3]\}_4$ in benzene-d_6 was determined to be 3.5×10^{-10} m^{-2} s^{-1}. Diffusion Ordered NMR is based on the ratio of the diffusion coefficients of two molecules in the same solvent being proportional to the cube root of the inverse ratio of their molecular weights.[3] Using this relationship and the molecular weight of **2**-P_3 of 698.55 g/mol, the calculated value of the molecular weight of the silver complex in solution is 3519.3 g/mol. This number is close to the expected value of 3301.9 g/mol for the tetramer $\{[Ag][\mathbf{1}\text{-}P_3]\}_4$.

S.1.6 $P_3Nb(ODipp)_2(py)_2$ (2-P_3)

A 30 mL Schlenk flask equipped with a Teflon stopper and a magnetic stir bar was charged with solid $[Na(THF)_3]$[**1**-P_3] (120 mg, 0.126 mmol, 1 equiv), $MgCl_2$ (6 mg, 0.064 mmol, 0.51 equiv), THF (5 mL) and pyridine (0.5 mL). The sealed reaction flask was placed in a pre-heated oil bath at 70 °C for 3 h, during which time the reaction mixture turned from the initial orange color to bright green. Next, the volatile materials were removed under reduced pressure and the residue was triturated twice with *n*-hexane (2 × 2 mL). The resulting green solids were slurried in additional *n*-hexane (ca. 7 mL) for ca. 30 min, before the slurry was subjected to suction filtration under reduced pressure. The green solids collected on the sintered frit were then washed with *n*-hexane (ca. 3 mL). The green filter cake was then dissolved in benzene, the obtained slurry was subjected to filtration, and the green filtrate was brought to constant mass and identified as spectroscopically clean **2**-P_3 (84 mg, 0.120 mmol, 95% yield). Elemental analysis (%) found (calculated) for $C_{34}H_{44}N_2NbO_2P_3$: C 58.31(58.46), H 6.29(6.35). ^1H NMR (benzene-d_6, 20 °C, 300 MHz) δ: 8.94 (4H, d, $J = 5.0$ Hz), 7.24 (4H, d, $^3J_{H-H} = 7.5$ Hz), 7.08 (2H, t, $^3J_{H-H} = 7.5$ Hz), 6.56 (2H, t, $J = 7.5$ Hz), 6.21 (t, 4H, $J = 6.4$ Hz), 3.78 (4H, sept, $^3J_{H-H} = 6.8$ Hz), 1.21 (24H, d, $^3J_{H-H} = 6.8$ Hz) ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6, 20 °C, 125.8 MHz) δ: 158.85, 151.36, 137.99, 137.67, 124.12, 124.03, 121.81, 26.92, 24.79 ppm. $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C, 161.9 MHz) δ: –78 (s) ppm. The diffusion coefficient of **2**-P_3 in benzene-d_6 was determined to be 6.0×10^{-10} m^{-2} s^{-1}.

S.1.7 Generation of $[KP_3Nb(ODipp)_3]_2$ from 2-P_3 and KODipp

To a solution of **2**-P_3 (0.200 g, 0.286 mmol, 1 equiv) in THF (ca. 5 mL) was added KODipp (0.062 g, 0.286 mmol, 1 equiv) as a solution in THF (ca. 10 mL). Upon mixing the two reagents the reaction mixture turned dark orange. After ca. 30 min stirring at room temperature the volatile materials were removed under reduced pressure. The oily residue was triturated with *n*-hexane (2×5 mL), and then all volatile materials were removed under reduced pressure. The resulting brown-red solids were dissolved in THF (5 mL) and the resulting mixture was subjected to filtration. All volatile materials were removed from the orange filtrate, and the residue was slurried in HMDSO (hexamethyldisiloxane, 5 mL), and placed in a refrigerator at a temperature of −35 °C. A bright orange precipitate was collected on a sintered frit by suction filtration (130 mg, 0.172 mmol, ca 60%) containing ca 5% free HODipp, as measured by ^1H NMR spectroscopy. Further purification efforts, including crystallization attempts and reprecipitation from HMDSO were unsuccessful. Satisfactory combustion elemental analysis was not obtained for this compound. ^1H NMR (benzene-d_6, 20 °C, 300 MHz) δ: 7.13 (6H, d, $^3J_{H-H} = 7.5$ Hz), 6.92 (3H, dd, $^3J = 7.4, 7.7$ Hz), 3.92 (6H, sept, $^3J_{H-H} = 6.7$ Hz), 1.37 (36H, d, $^3J_{H-H} = 6.7$ Hz) ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6, 20 °C, 75.4 MHz) δ: 161.45, 139.09, 123.43, 121.90, 27.32, 24.38 ppm. $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C, 121.5 MHz) δ: –195 (s) ppm. The diffusion coefficient of {[K][**1**-P_3]}$_2$ in benzene-d_6 was determined to be 4.3×10^{-10} m^{-2} s^{-1}.[4]

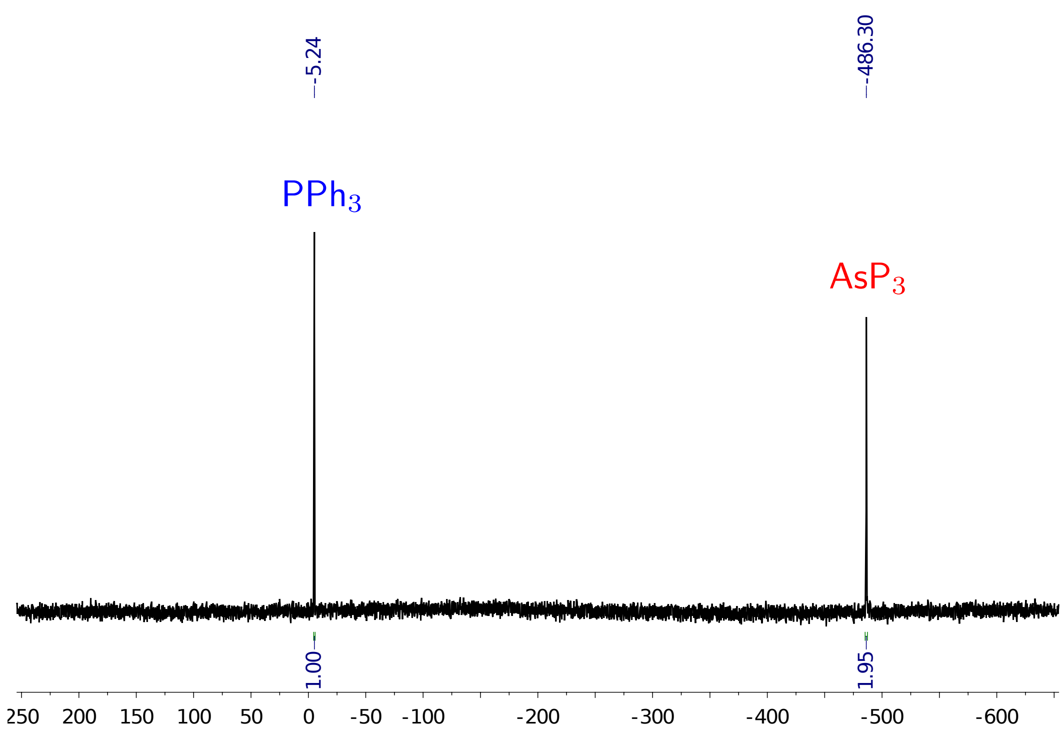

Figure S.6: $^{31}P\{^{1}H\}$ NMR (benzene-d_6, 20 °C, 161.9 MHz) spectrum of the reaction mixture resulted in the reaction of **2**-P_3 with $AsCl_3$, after addition of PPh_3 as an internal standard.

S.1.8 Synthesis of AsP_3 from 2-P_3 and $AsCl_3$

To a thawing solution of **2**-P_3 (0.050 g, 0.072 mmol, 1 equiv) in toluene (5 mL) was added dropwise a thawing solution of $AsCl_3$ (0.013 g, .072 mmol, 1 equiv) in toluene (1 mL). Upon warming to room temperature the reaction mixture turned changed color from dark green to bright orange. After approx. 20 min of stirring at room temperature, the reaction mixture was subjected to filtration to remove dark red solids that formed during the reaction. To the bright orange filtrate was added PPh_3 (13 mg, 0.049 mmol) as an internal standard, and an aliquot of the resulting solution was analyzed by ^{31}P NMR to reveal that AsP_3 was produced in 45% spectroscopic yield (^{31}P NMR δ: –486 ppm).[1]

S.1.9 Solid state structure of [1-P_3(py)]$_2$

X-ray quality crystals of **2**-P_3 as well as of the $[P_3Nb(ODipp)_3(py)]_2$ dimer (Fig.S.7) were obtained serendipitously from a mixture of the previously reported *cyclo*-P_4 dimer $[P_2Nb(ODipp)_3]_2$[5] and pyridine which was exposed to air. The solid state structure of [**1**-P_3(Py)]$_2$ reveals a long P–P interaction connecting the two NbP_3 units of 2.238(1) Å. Each niobium center has a molecule of pyridine coordinated to it and interacts with only two P atoms of the *cyclo*-P_3 unit.

We have unsuccessfully explored several routes to independently and reproducibly synthesize [**1**-P_3(Py)]$_2$ including chemical oxidation of $[Na(THF)_3]$[**1**-P_3], direct synthesis from $Cl_2Nb(ODipp)_3$ and P_4 under reducing conditions (analogous to preparation of $[Na(THF)_3]$[**1**-P_3]), and photolysis of$(THF)_2Pb$[**1**-P_3]$_2$ or {[Ag][**1**-P_3]}$_4$. The only other reported complex with a bridging $[P_6]^{4-}$ ligand is $[P_3Nb(OSi^tBu)_3]_2$.[6]

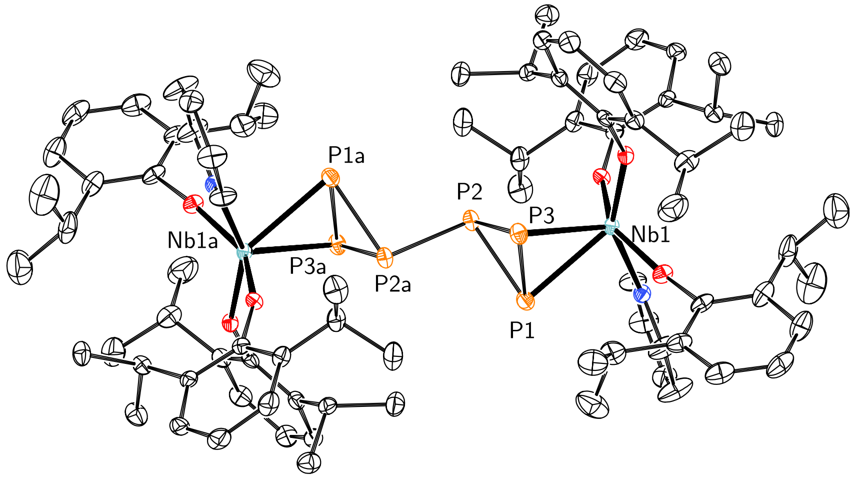

Figure S.7: Solid-state molecular structure of [**1**-P_3(Py)]$_2$ with ellipsoids at the 50% probability level and rendered using PLATON.[7] Hydrogen atoms and the co-crystallized solvent (benzene) were omitted for clarity. Selected interatomic distances (Å) and angles (°): P(2)a–P(2) 2.2380(10), P(2) –P(1) 2.2089(10), P(1)–P(3) 2.1727(11), P(3)–P(2) 2.2036(10), Nb(1)–P(1) 2.5653(9), Nb(1)–P(3) 2.5252(8), P(3)a–P(1)a 2.1727(11), P(1)a–P(2)a 2.2089(10), P(2)a–P(3)a 2.2036(10), Nb(1)a–P(3)a 2.5252(8), Nb(1)a–P(1)a 2.5653(9), P(1)–P(2)–P(2)a 97.21(4), P(3)–P(2)–P(2)a 95.50(4), P(1)–P(2)–P(3) 59.00(3), P(2)–P(1)–P(3)–Nb(1) 98.33(3).

S.1.10 Treatment of (THF)Sn[1-P_3]$_2$ with pyridine-*N*-oxide

To a solution of (THF)Sn[**1**-P_3]$_2$ (400 mg, 0.245 mmol, 1 equiv) in THF (20 mL) at room temperature was added a solution of pyridine-*N*-oxide (46.8 mg, 0.490 mmol, 2 equiv) in THF (20 mL). The reaction mixture was then stirred ca. 6 h, at which point Et_2O (ca. 20 mL) was added to aid the precipitation of the fine black solids produced during the reaction. The reaction mixture was then subjected to filtration, and a solid metallic-black material was collected on a sintered frit (127 mg), while the yellow filtrate was brought to constant mass (294 mg). Pale yellow crystals of O[**1**(Py)] were obtained by cooling a THF/pentane solution of the yellow residue to −35 °C, over 2 crops (243 mg, 0.338 mmol, 69%). Elemental analysis (%) found (calculated) for $C_{41}H_{56}NNbO_4$: C 68.52(68.41), H 7.72(7.84). Elemental analysis of the black material (combustion and ICP; %) found for batch 1: C 26.77, H 3.19, N 0.73, P 35.69; batch 2: C 15.97, H 1.39, N 1.30, Sn 29.21; batch 3: C 17.38, H 2.06, N 1.27, P 40.13. Further characterization of this material is described below, in the section S.2.

S.2 Characterization of the black material formed in the reaction of (THF)Sn[1-P_3]$_2$ with Py-O

Powder Diffraction experiments were conducted at the MIT Center for Materials Science and Engineering (CMSE) X-ray facility using a Panalytical X'Pert Pro diffractometer with a Bragg-Brentano geometry and High Speed X'Celerator

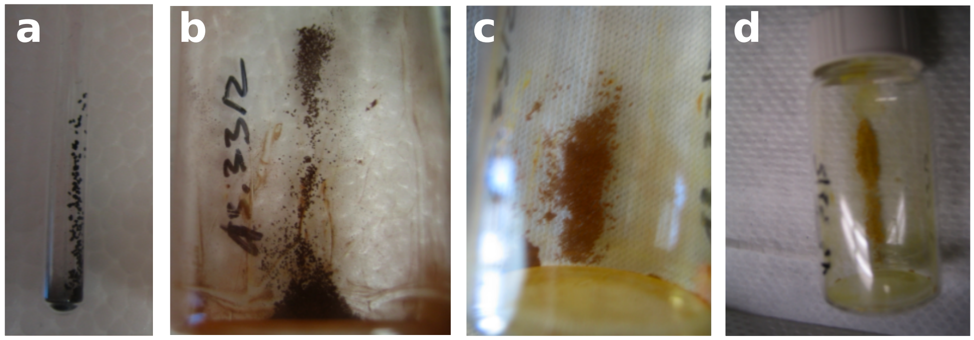

Figure S.8: The black precipitate obtained in the reaction of (THF)Sn[**1**-P_3]$_2$ with Py-O right after isolation (a) and after 2 h (b), 3 days (c) and 5 days (d) of exposure to air.

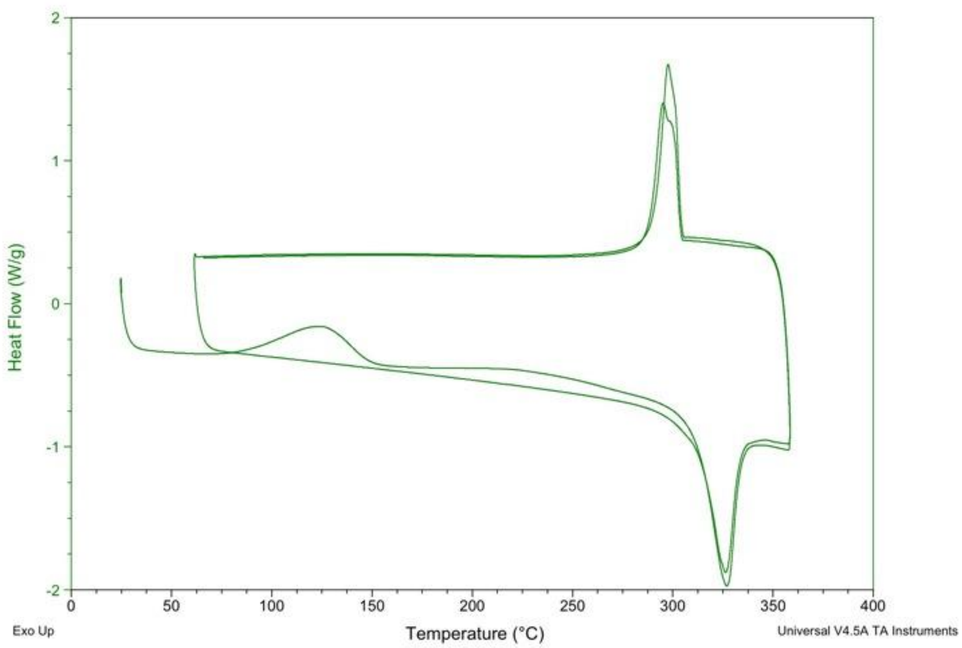

Figure S.9: Plot of heat flow (W/s) against temperature (°C) for the black precipitate (9.4100 mg) obtained in the reaction of (THF)Sn[**1**-P_3]$_2$ with Py-O using an Universal V4.5A TA instrument.

Detector. All PXRD data was analyzed using X'pert HighScore Plus Program (Fig. S.10).[8] Energy-dispersive X-ray (EDX) spectroscopy was performed at the MIT Center for Materials Science and Engineering (CMSE), by using a JEOL JSM-5910 scanning electron microscope (Fig. S.11). Differential scanning calorimetry analysis was performed in the Materials Research Science and Engineering Center at Harvard University using a TA Q200 Instrument. The sample was heated in an aluminum pan (DSC) under a nitrogen flow with a heating ramp of 10 °C/ min up to 360 °C (Fig. S.9). ^{31}P CP-MAS NMR spectra were referenced externally to 85% H_3PO_4 (0 ppm) (Fig. S.13).

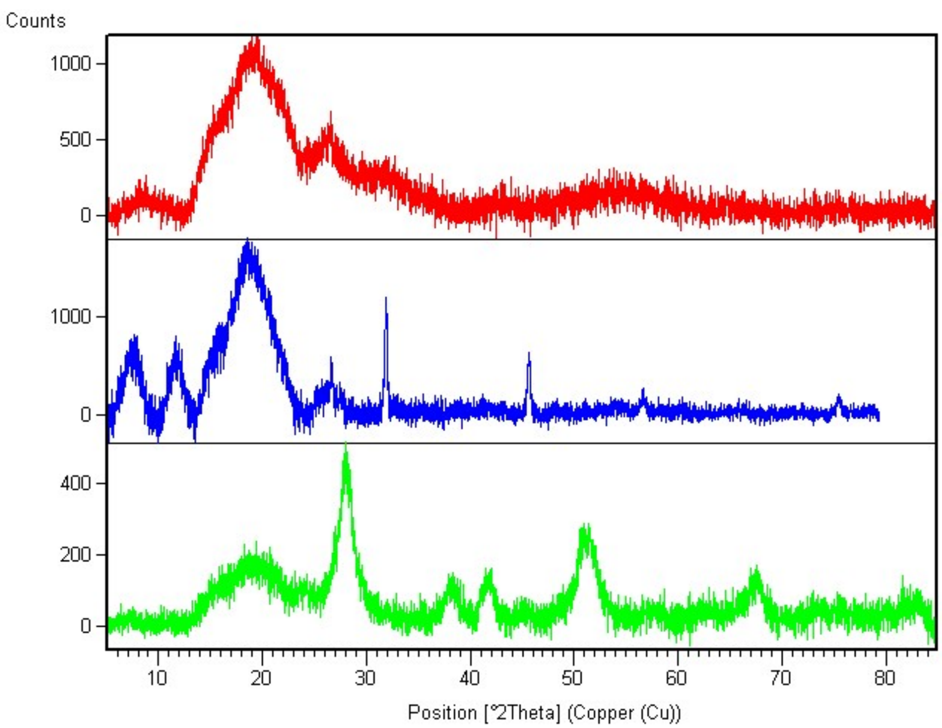

Figure S.10: Powder Diffraction spectrum of the black precipitate as produced from the reaction of (THF)Sn[**1**-P_3]$_2$ with Py-O (top), after 3 days of heating inside a sublimator under static vacuum at 290 °C with formation of Sn_4P_3 (middle), after 3 days of heating inside a sublimator under static vacuum at 250 °C with formation of SnP (bottom).

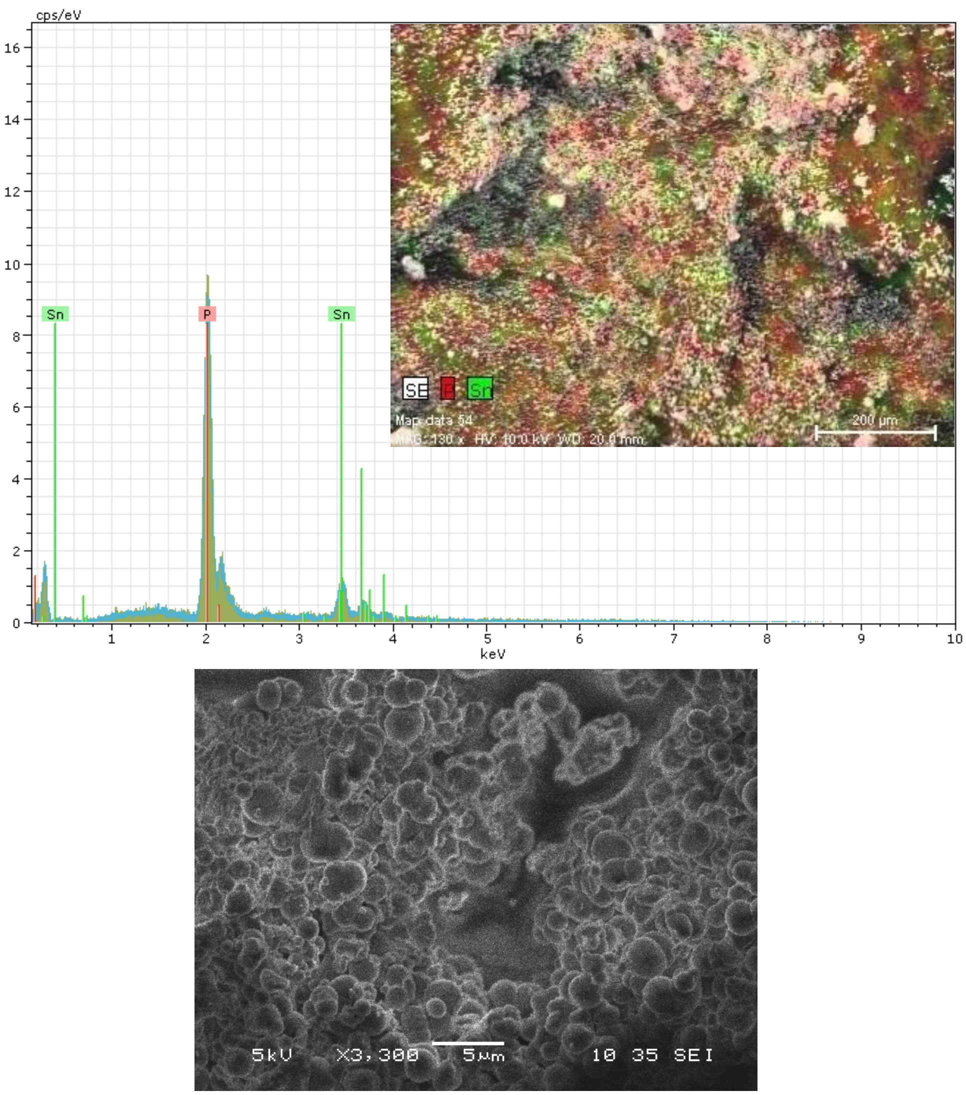

Figure S.11: Elemental mapping of the black precipitate produced in the reaction of (THF)Sn[**1**-P_3]$_2$ with Py-O by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX) showing a ratio of Sn:P of 1:5.4 and a homogeneous distribution of the two elements throughout the sample.

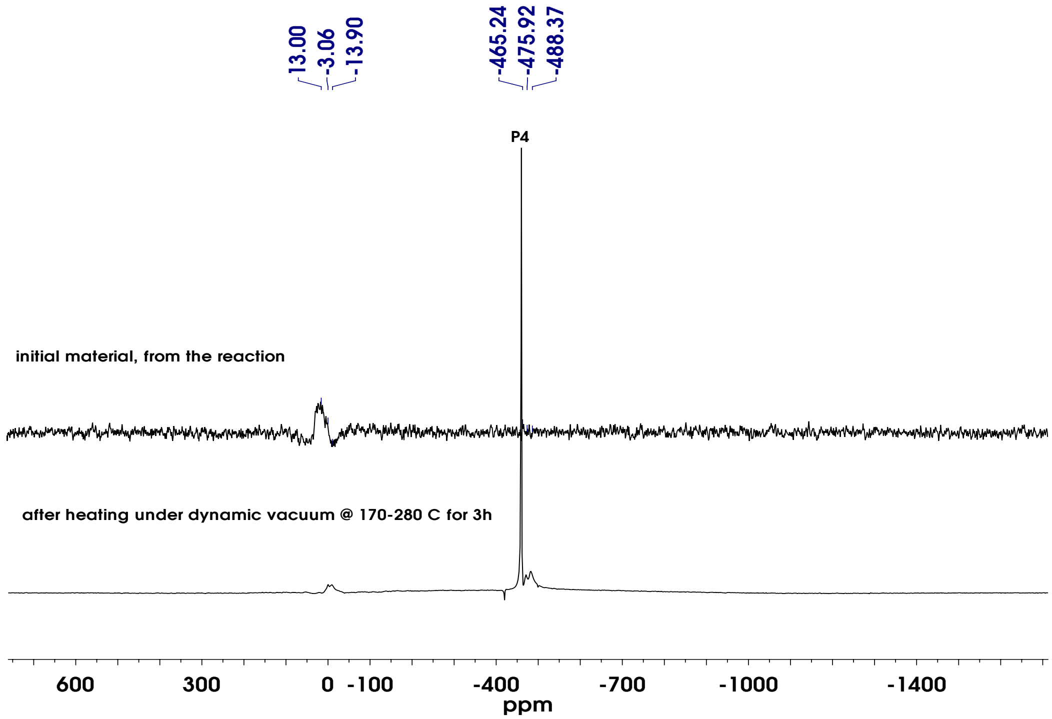

Figure S.12: ^{31}P CP-MAS NMR spectra of the black precipitate as produced in the reaction of (THF)Sn[**1**-P_3]$_2$ with Py-O (top), and after heating under dynamic vacuum from 170 to 280°C for 3h, obtained using a 202.4 MHz magnet and recorded at a spinning frequency of 8 kHz at 22 °C.

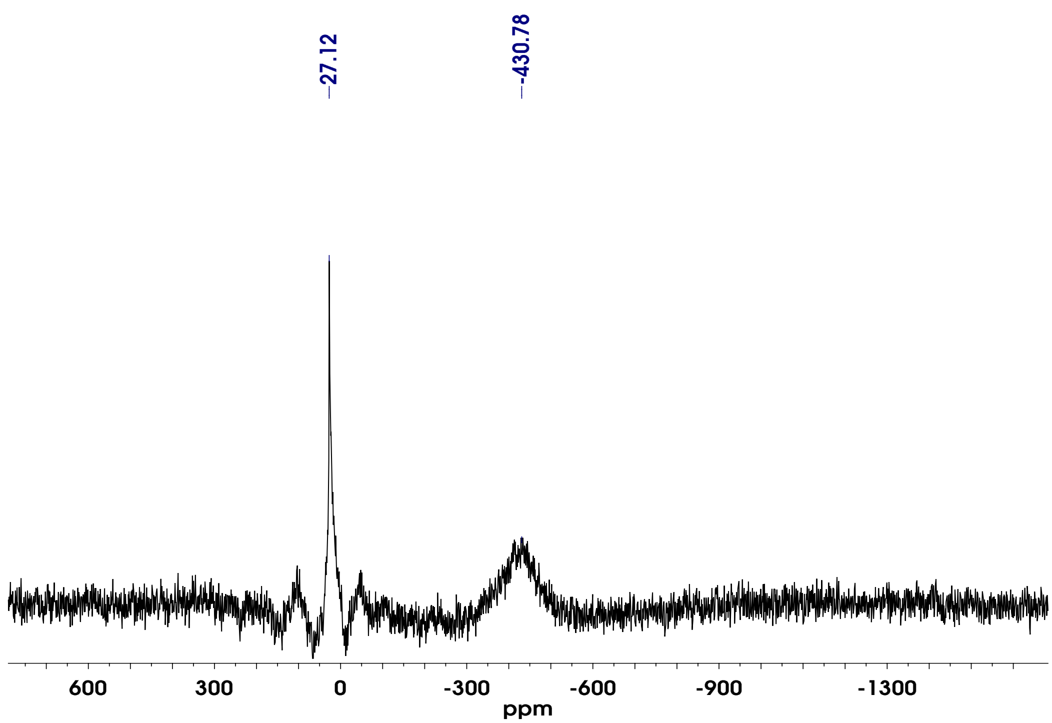

Figure S.13: ^{31}P CP-MAS NMR spectrum of red phosphorus purchased from Aldrich, using a 202.4 MHz magnet and recorded at a spinning frequency of 8 kHz at 22 °C.

S.3 X-ray Diffraction Studies

Diffraction-quality, dark red crystals of (THF)Sn[**1**-P_3]$_2$, Sn[**1**-P_3]$_2$, (THF)$_2$Pb[**1**-P_3]$_2$ and O[**1**(Py)] were grown at -35 °C by vapour diffusion of Et_2O in a saturated solution of (THF)Sn[**1**-P_3]$_2$ in toluene, from a saturated *n*-pentane solution of Sn[**1**-P_3]$_2$, from a saturated *n*-pentane solution of (THF)$_2$Pb[**1**-P_3]$_2$ and from a saturated solution of O[**1**(Py)] in a THF/*n*-pentane mixture, respectively. Diffraction-quality green crystals of **2**-P_3 and [**1**-P_3(Py)]$_2$ were serendipitously grown from benzene, at room temperature. The crystals were mounted in hydrocarbon oil on a nylon loop or a glass fiber. Low-temperature (100 K) data were collected on a a Bruker D8 three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) or on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo Kα radiation (λ = 0.71073 Å) with ϕ- and ω-scans. A semi-empirical absorption correction was applied to the diffraction data using SADABS.[9] All structures were solved by direct or Patterson methods using SHELXS[10,11] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[11,12] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups).[13] Descriptions of the individual refinements follow below and details of the data quality and a summary of the residual values of the refinements for all structures are given in the following tables. Further details are provided in the form of *.cif* files available from the CCDC.[14]

The tin phosphide (THF)Sn[**1**-P_3]$_2$ crystallized in the orthorhombic space group $Pca2(1)$ with two molecules per asymmetric unit and two Et_2O molecules. One of twenty four isopropyl groups of the Dipp unit is disordered over two positions. The tin phosphide Sn[**1**-P_3]$_2$ crystallized in the monoclinic space group $P2(1)/c$ with one molecule per asymmetric unit and a molecule of benzene, which is disordered with a toluene molecule. Two of twelve isopropyl groups of the Dipp unit are disordered over two positions. The lead phosphide complex (THF)$_2$Pb[**1**-P_3]$_2$ crystallized in the monoclinic space group $C2/c$ with one molecule per asymmetric unit, containing the Pb atom in a plane of symmetry relating the two Nb centers as well as two molecules of benzene, one of which is disordered with a molecule of *n*-pentane. The other benzene molecule is disordered over two positions. The two THF molecules coordinated to the lead atom are disordered over two positions. **2**-P_3 crystallized in in the monoclinic space group $P21/n$ with one molecule per asymmetric unit and 1.5 benzene molecules, the benzene with half occupancy being disordered over the inversion center. O[**1**(Py)] crystallized in the orthorhombic space group $Pna2(1)$ with one molecule per asymmetric unit and one THF molecule. This molecule has no disorders. Dimer [P_3Nb(ODipp)$_3$(py)]$_2$ crystallized in the triclinic space group $P\bar{1}$ with one molecule per asymmetric unit and a benzene molecule disordered over two positions. Further details are provided in Tables 1 and 2.

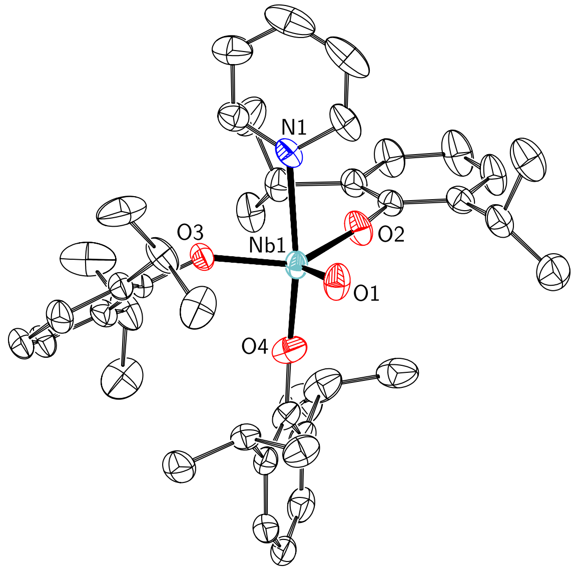

Figure S.14: Solid-state molecular structure of O[**1**(Py)] with ellipsoids at the 50% probability level and rendered using PLATON.[7] Hydrogen atoms and the co-crystallized solvent (THF) were omitted for clarity. Selected interatomic distances (Å) and angles (°): O1–Nb1 1.707(2), Nb1–N1 2.336(3), O3–Nb1–O1 112.1(1), O3–Nb1–O4 93.53(9).

Table 1: Crystallographic Data for Sn[**1**-$P_3]_2 \cdot C_6H_6$, (THF)Sn[**1**-$P_3]_2 \cdot Et_2O$ and $(THF)_2$Pb[**1**-$P_3]_2 \cdot 2.6\ C_6H_6$

	Sn[**1**-$P_3]_2 \cdot C_6H_6$	(THF)Sn[**1**-$P_3]_2 \cdot Et_2O$	$(THF)_2$Pb[**1**-$P_3]_2 \cdot 2.6\ C_6H_6$
CCDC code	1421301	1421302	1421303
Empirical formula, FW (g/mol)	$C_{78.24}H_{108.49}Nb_2O_6P_6Sn$, 1635.35	$C_{80}H_{120}Nb_2O_8P_6Sn$, 1700.09	$C_{97.60}H_{138.40}Nb_2O_8P_6Sn$, 2018.52
Color / Morphology	Red / Block	Orange / Shard	Red / Hexagonal Plate
Crystal size (mm^3)	$0.02 \times 0.13 \times 0.14$	$0.10 \times 0.13 \times 0.25$	$0.05 \times 0.30 \times 0.40$
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, Space group	Monoclinic, $P2(1)/c$	Orthorhombic, $Pca2(1)$	Monoclinic, $C2/c$
Unit cell dimensions (Å, °)	$a = 19.234(2)$, $\alpha = 90$	$a = 27.951(3)$, $\alpha = 90$	$a = 23.997(1)$, $\alpha = 90$
	$b = 20.735(2)$, $\beta = 92.989(2)$	$b = 25.525(3)$, $\beta = 90$	$b = 12.5011(7)$, $\beta = 102.473(1)$
	$c = 20.601(2)$, $\gamma = 90$	$c = 24.007(3)$, $\gamma = 90$	$c = 33.949(2)$, $\gamma = 90$
Volume ($Å^3$)	8205(2)	17127(3)	9944(1)
Z	4	8	4
Density (calc., g/cm^3)	1.324	1.319	1.348
Absorption coefficient (mm^{-1})	0.741	0.714	2.063
$F(000)$	3392	7088	4168
Theta range for data collection (°)	1.39 to 30.61	0.80 to 28.28	1.74 to 29.57
Index ranges	$-27 \le h \le 27$, $-29 \le k \le 29$,	$-37 \le h \le 37$, $-34 \le k \le 34$,	$-33 \le h \le 33$, $-17 \le k \le 17$,
	$-28 \le l \le 29$	$-31 \le l \le 31$	$-47 \le l \le 47$
Reflections collected	193614	348710	109407
Independent reflections, R_{int}	18222 (0.0364)	32792 (0.0469)	12695 (0.0271)
Completeness to θ_{max} (%)	99.4	195/1.00	100.1
Absorption correction	Multi-scan (SADABS)	Multi-scan (SADABS)	Multi-scan (SADABS)
Max. and min. transmission	0.901 and 0.985	0.8417 and 0.9320	0.481 and 0.902
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	25131 / 162 / 888	42449 / 107 / 1829	13959 / 485 / 668
Goodness-of-fit[a]	1.028	1.023	1.111
Final R indices[b] $[I > 2\sigma(I)]$	$R_1 = 0.0364$, $wR_2 = 0.0692$	$R_1 = 0.0469$, $wR_2 = 0.0842$	$R_1 = 0.0271$, $wR_2 = 0.0569$
R indices[b] (all data)	$R_1 = 0.0656$, $wR_2 = 0.0796$	$R_1 = 0.0765$, $wR_2 = 0.0975$	$R_1 = 0.0321$, $wR_2 = 0.0585$
Largest diff. peak and hole ($e \cdot Å^{-3}$)	1.014 and −0.540	0.967 and −0.489	1.089 and −1.295

[a] GooF = $\left[\frac{\Sigma[w(F_o^2-F_c^2)^2]}{(n-p)}\right]^{\frac{1}{2}}$ [b] $R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$; $wR_2 = \left[\frac{\Sigma[w(F_o^2-F_c^2)^2}{\Sigma[w(F_o^2)^2]}\right]^{\frac{1}{2}}$; $w = \frac{1}{\sigma^2(F_o^2)+(aP)^2+bP}$; $P = \frac{2F_c^2+\max(F_o^2,0)}{3}$

Table 2: Crystallographic Data for **2**-P_3, O[**1**(Py)] and [**1**-P_3(Py)]$_2$

	2-P_3	O[**1**(Py)]·THF	[**1**-P_3(Py)]$_2$
CCDC code	1421300	1421299	1421298
Empirical formula, FW (g/mol)	$C_{43}H_{53}N_2NbO_2P_3$, 815.69	$C_{45}H_{64}NNbO_5$, 791.88	$C_{88}H_{124}N_2Nb_2O_6P_6$, 1677.53
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.10$	$0.55 \times 0.11 \times 0.10$	$0.14 \times 0.08 \times 0.04$
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	1.54178	0.71073	0.71073
Crystal system, Space group	Monoclinic, P21/n	Orthorhombic, Pna2(1)	Triclinic, P-1
Unit cell dimensions (Å, °)	$a = 14.010(1)$, $\alpha = 90$	$a = 18.403(2)$, $\alpha = 90$	$a = 10.4029(7)$, $\alpha = 94.929(1)$
	$b = 16.529(1)$, $\beta = 92.662(4)$	$b = 23.170(2)$, $\beta = 90$	$b = 13.729(1)$, $\beta = 93.683(1)$
	$c = 18.096(1)$, $\gamma = 90$	$c = 10.0258(9)$, $\gamma = 90$	$c = 16.343(1)$, $\gamma = 95.884(1)$
Volume (Å^3)	4186.0(5)	4275.0(7)	2307.1(3)
Z	4	4	1
Density (calc., g/cm^3)	1.294	1.230	1.207
Absorption coefficient (mm^{-1})	3.707	0.325	0.401
$F(000)$	1708	1688	886
Theta range for data collection (°)	3.623 to 70.215	1.41 to 27.10	1.86 to 28.28
Index ranges	$-17 \leq h \leq 16$, $-20 \leq k \leq 20$	$-23 \leq h \leq 23$, $-29 \leq k \leq 29$	$-13 \leq h \leq 13$, $-18 \leq k \leq 18$
	$-21 \leq l \leq 22$	$-12 \leq l \leq 12$	$-21 \leq l \leq 21$
Reflections collected	87281	67735	57444
Independent reflections	7782	9407	11436
Completeness to $\theta_{\max}$ (%)	97.6	189/1.0	99.9
Absorption correction	Multi-scan (SADABS)	Multi-scan (SADABS)	Multi-scan (SADABS)
Max. and min. transmission	0.5870 and 0.7533	0.958 and 0.968	0.9460 and 0.9842
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7782 / 276 / 495	940 / 1 / 481	11436 / 156 / 563
Goodness-of-fit[a]	1.022	1.014	1.014
Final R indices[b] [$I > 2\sigma(I)$]	$R_1 = 0.0388$, $wR_2 = 0.0923$	$R_1 = 0.0395$, $wR_2 = 0.0801$	$R_1 = 0.0459$, $wR_2 = 0.0832$
R indices[b] (all data)	$R_1 = 0.0554$, $wR_2 = 0.1013$	$R_1 = 0.0614$, $wR_2 = 0.0901$	$R_1 = 0.0835$, $wR_2 = 0.0985$
Largest diff. peak and hole ($e \cdot$ Å^{-3})	0.351 and −0.559	0.488 and −0.362	0.879 and −0.741

[a] GooF = $\left[\frac{\Sigma[w(F_o^2-F_c^2)^2]}{(n-p)}\right]^{\frac{1}{2}}$ [b] $R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$; $wR_2 = \left[\frac{\Sigma[w(F_o^2-F_c^2)^2]}{\Sigma[w(F_o^2)^2]}\right]^{\frac{1}{2}}$; $w = \frac{1}{\sigma^2(F_o^2)+(aP)^2+bP}$; $P = \frac{2F_c^2+\max(F_o^2,0)}{3}$

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[14] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, http://www.ccdc.cam.ac.uk/data_request/cif.