Electronic Supplementary Material (ESI) for Chemical Communications.

Terminal Tungsten Pnictide Complex Formation through Pnictaethynolate Decarbonylation

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Supporting Information

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S.1 Synthetic Details and Characterization of Products

S.1.1 General Information

All manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N_2. Where mentioned, room temperature indicates 22–24 °C. All solvents were obtained anhydrous and oxygen-free by bubble degassing (Ar), purification through columns of alumina and/or Q5,[1] and storage over molecular sieves.[2] Deuterated solvents were purchased from Cambridge Isotope Labs, degassed and stored over molecular sieves for at least 2 days prior to use. Celite 435 (EM Science) and activated charcoal were dried by heating above 250 °C under dynamic vacuum for at least 48 h prior to use. Glassware was oven-dried for at least three hours at temperatures greater than 150 °C. Tungsten tetrakis(2,6-diisopropylphenolate), [W(ODipp)$_4$] (**1**), was prepared as previously described by Schrock and coworkers.[3,4] [Na(dioxane)$_{2.5}$][OCP] was prepared as previously described by the Grützmacher group.[5] [Na(dioxane)$_{2.5}$][OCAs] was provided as a gift from the Driess and Grützmacher groups;[6] [TBA][N_3] (TBA = tetra-*n*-butylammonium) and [TBA][NCO] were recrystallized from THF prior to use; 1,4,7,10-tetraoxacyclododecane (or 12-crown-4, 12c4) was deaerated by sparging with dinitrogen for 1 h and stored over molecular sieves for several days prior to use.

NMR spectra were obtained on Varian Inova 300 and 500 instruments equipped with Oxford Instruments superconducting magnets, on a Jeol ECZ-500 instrument equipped with an Oxford Instruments superconducting magnet, or on a Bruker Avance 400 instrument equipped with a Magnex Scientific or with a SpectroSpin superconducting magnet. ^{1}H NMR and ^{13}C NMR spectra were referenced internally to residual solvent signals.[7] ^{15}N NMR spectra were referenced internally to the residual azide resonance (δ 104 ppm measured independently against nitromethane at δ 381 ppm by ^{14}N NMR spectroscopy). ^{31}P NMR spectra were referenced externally to 85% aqueous H_3PO_4.

Attenuated total reflection infrared (ATR-IR) spectra were recorded on a Bruker Tensor 37 Fourier transform IR (FTIR) spectrometer.

Electrospray ionization mass spectra (ESI-MS) were acquired on a Micromass Q-TOF ESI spectrometer. Samples (acetonitrile solutions) were prepared in a glovebox and placed into 1.5 mL GC vials sealed with a septa. Prior to sample injection, the capillary tubing was flushed with 3 mL of dry acetonitrile. A source temperature of 100 °C, desolvation gas temperature of 150 °C, and voltage of 3200 V were used.

Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ, USA).

S.1.2 Synthesis of [TBA][1≡N]

S.1.2.1 Using Tetrabutylammonium Azide

A solution of tetra-*n*-butylammonium azide (32.0 mg, 0.110 mmol, 1.0 equiv) in THF (2 mL) was added at 25 °C to a solution of **1** (100.0 mg, 0.110 mmol, 1.0 equiv) in THF (2 mL). The reaction mixture was vigorously stirred at 25 °C for 14 h. During this time, the color of the reaction mixture turned bright yellow. All volatile materials were removed *in vacuo* to give a yellow residue which was washed with pentane (2 × 1 mL) and solubilized in THF (ca. 1 mL). This solution was filtered through a glassfiber filter, pentane (ca. 3 mL) was slowly added, and stored at –35 °C for 48 h. Bright yellow crystalline blocks formed which were separated from the supernatant and dried under vacuum to give the title compound. Yield: 85.1 mg (0.074 mmol, 67%).

S.1.2.2 Using Tetrabutylammonium Cyanate

A solution of tetra-*n*-butylammonium cyanate (3.2 mg, 0.011 mmol, 1.0 equiv) in benzene-d_6 (0.4 mL) was added to a solution of **1** (10.0 mg, 0.011 mmol, 1.0 equiv) in benzene-d_6 (0.4 mL). Upon addition the color of the mixture changed to dark-brown. The mixture was transferred to an NMR tube and analyzed after 14 h at 25 °C. During this time, the color of the reaction mixture turned to yellow. ^{1}H NMR analysis indicated quantitative formation of the title compound.

Elem. Anal. Found(Calc'd) for $C_{64}H_{104}N_2O_4W$: C 66.64 (66.88), H 9.40 (9.12), N 2.43 (2.44); ESI-MS(–): 906.5269 m/z (calcd for $C_{48}H_{68}O_4NW$: 906.4666 m/z); ^{1}H NMR (benzene-d_6, 400 MHz, 20 °C) δ 7.25 (d, $^3J_{HH}$ = 7.4 Hz, 8H, $H_{ar\text{-}meta}$ ODipp), 6.93 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $H_{ar\text{-}para}$ ODipp), 4.48 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, C*H*$(CH_3)_2$), 1.99 (m, 8H, NCH_2 TBA), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 48H, CH(C*H*$_3)_2$, 0.85 (m, 8H, CH_2 TBA), 0.67 (m, 20H, CH_2, CH_3 TBA); ^{1}H NMR (acetonitrile-d_3, 500 MHz, 20 °C) δ 6.87 (d, $^3J_{HH}$ = 7.6 Hz, 8H, $H_{ar\text{-}meta}$ ODipp), 6.60 (t, $^3J_{HH}$ = 7.6 Hz, 4H, $H_{ar\text{-}para}$ ODipp), 3.91 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, C*H*$(CH_3)_2$), 3.07 (m, 8H, NCH_2 TBA), 1.59 (m, 8H, CH_2 TBA), 1.34 (m, 8H, CH_2 TBA), 0.96 (m, 12H, CH_3 TBA), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 48H, CH(C*H*$_3)_2$); ^{13}C{^{1}H} NMR (acetonitrile-d_3, 126 MHz, 20 °C): δ 160.4 (s, C_{ipso} ODipp), 139.1 (s, C_{ortho} ODipp), 123.4 (s, C_{meta} ODipp), 119.6 (s, C_{para} ODipp), 59.3 (s, NCH_2 TBA), 26.1 (s, *C*H$(CH_3)_2$), 24.4 (s, CH(*C*H$_3)_2$, 24.3 (s, CH_2 TBA), 20.3 (s, CH_2 TBA), 13.8 (s, CH_3 TBA). No nitride resonance was observed by ^{14}N NMR specroscopy (acetonitrile-d_3, 29 MHz, 25 °C) after 110,000 transients (relaxation delay of 0.3 s, acquisition time of 0.1 s). The 50% ^{15}N-labeled nitride

complex was synthesized using terminally ^{15}N-labeled sodium azide in DME, enabling the acquisition of a ^{15}N NMR spectrum: ^{15}N NMR (acetonitrile-d_3, 51 MHz, 20 °C): δ 575 ($^1J_{WN}$ = 59 Hz).

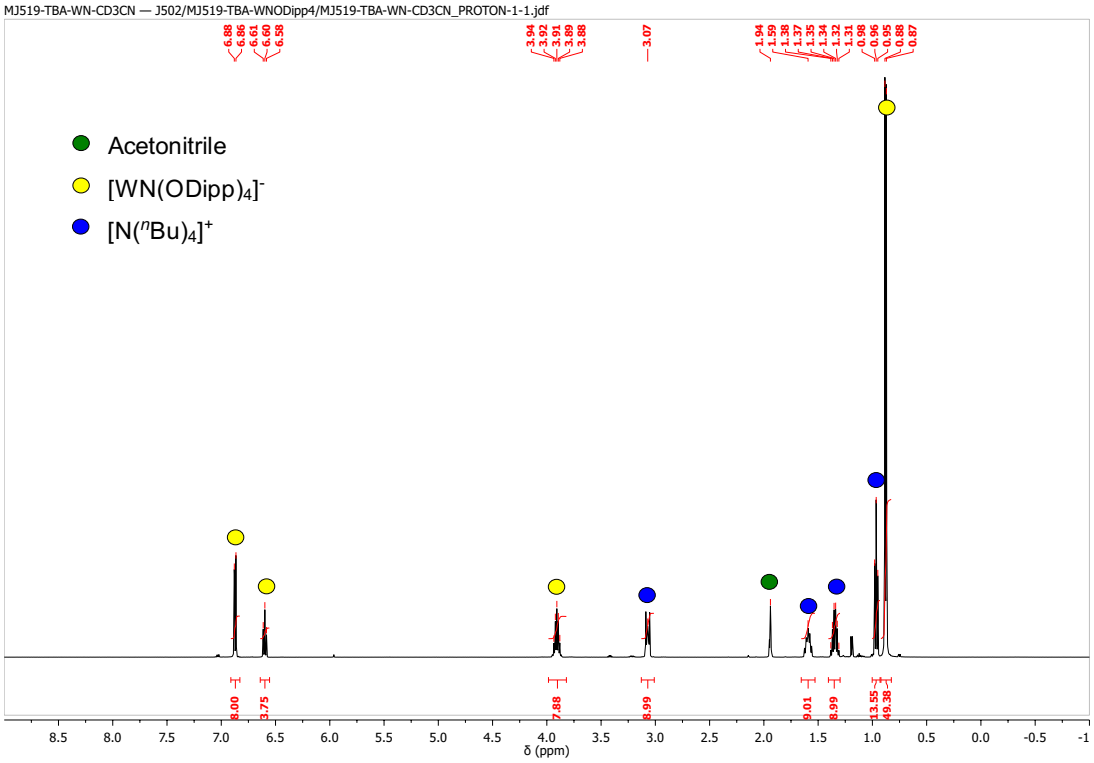

Figure S.1: ^{1}H NMR spectrum (acetonitrile-d_3, 500 MHz, 20 °C) of [TBA][**1**≡N].

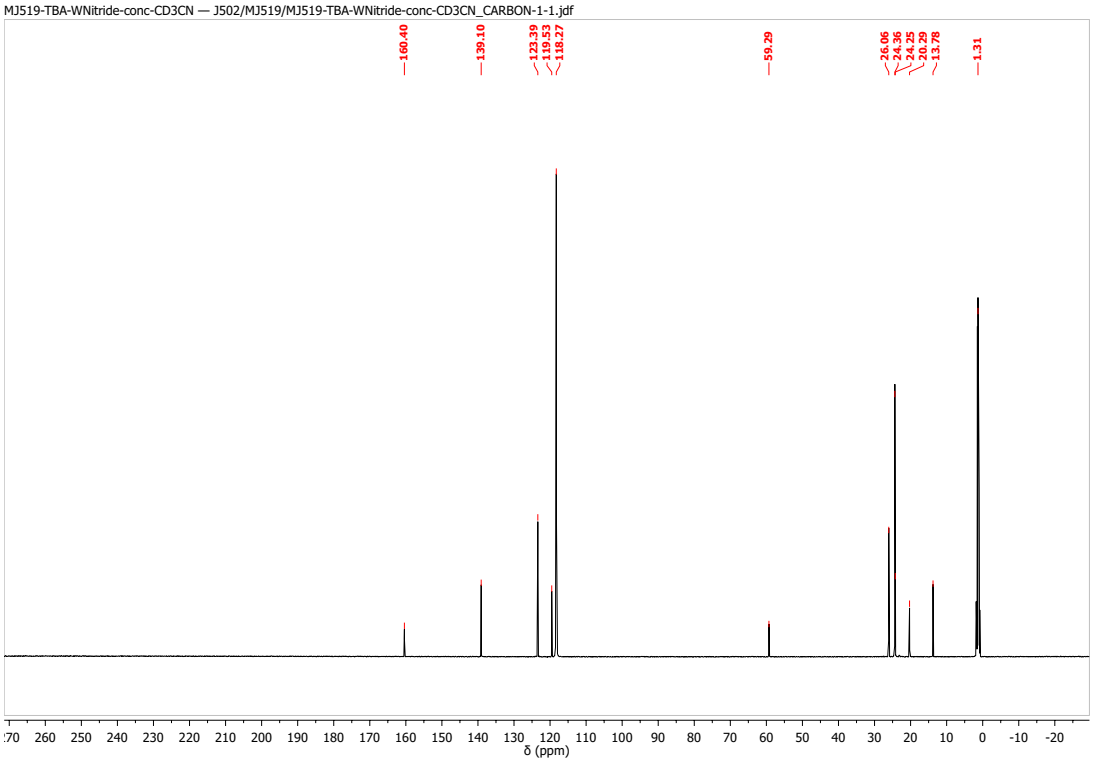

Figure S.2: ^{13}C{^{1}H} NMR spectrum (acetonitrile-d_3, 126 MHz, 20 °C) of [TBA][**1**≡N].

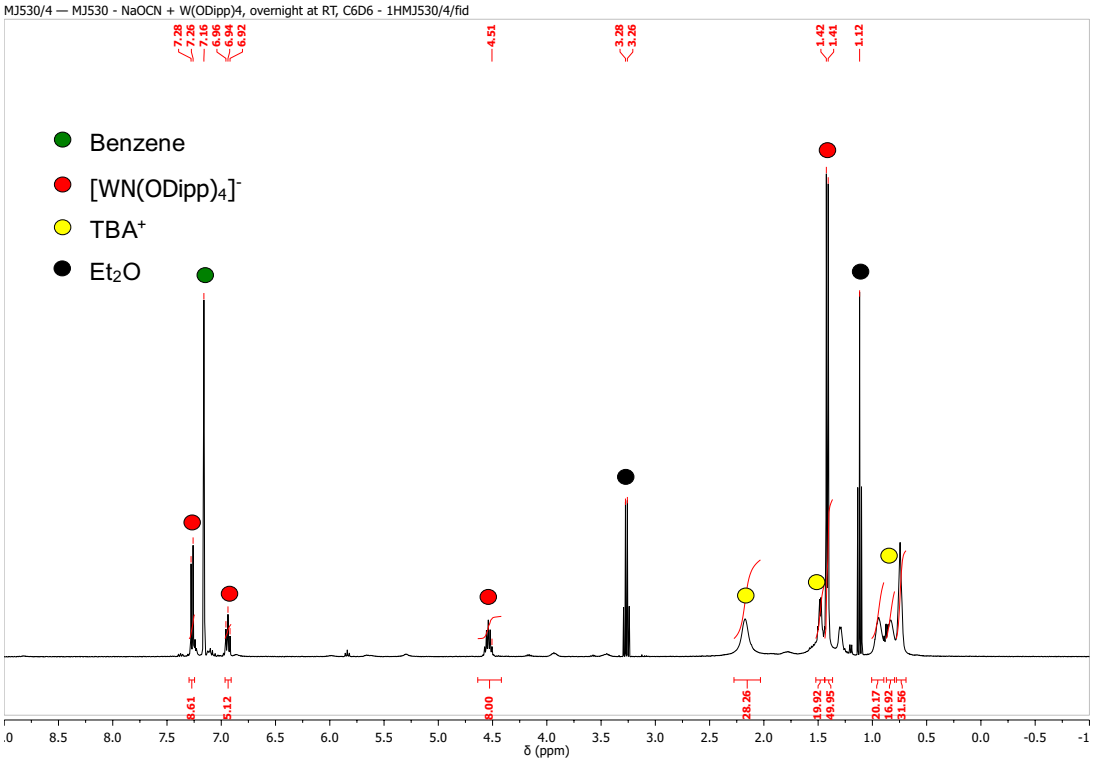

Figure S.3: ^{1}H NMR spectrum (acetonitrile-d_3, 400 MHz, 20 °C) of crude [TBA][**1**≡N] prepared from [TBA][NCO].

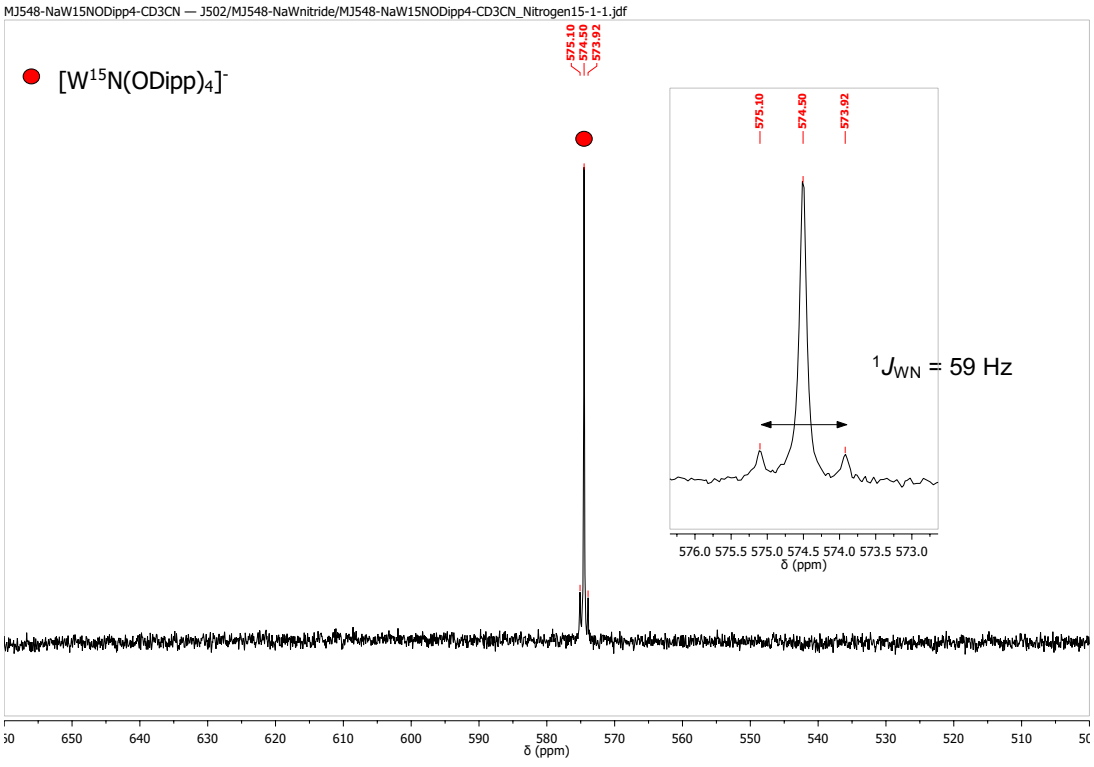

Figure S.4: ^{15}N{^{1}H} NMR spectrum (acetonitrile-d_3, 51 MHz, 20 °C) of [Na(DME)$_3$][**1**≡^{15}N].

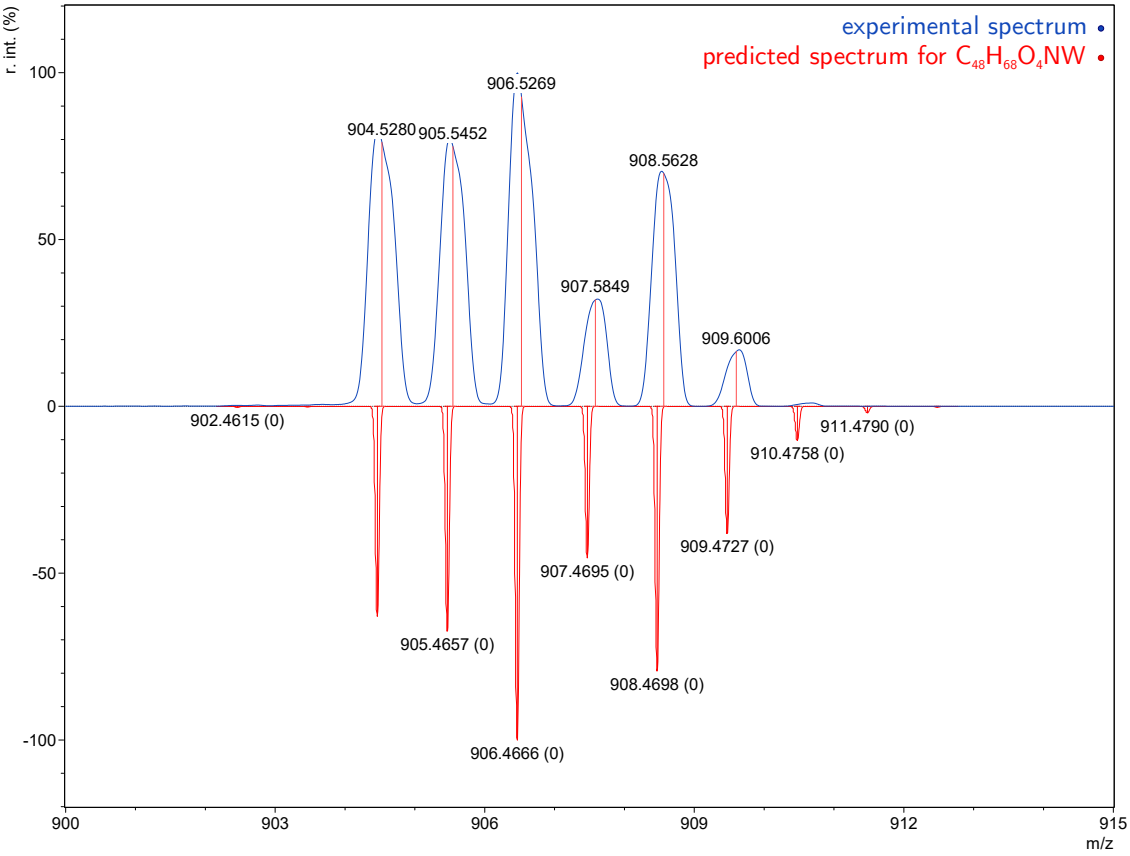

Figure S.5: Experimental (blue) and predicted (red) ESI-MS(–) spectra of [TBA][**1**≡N].

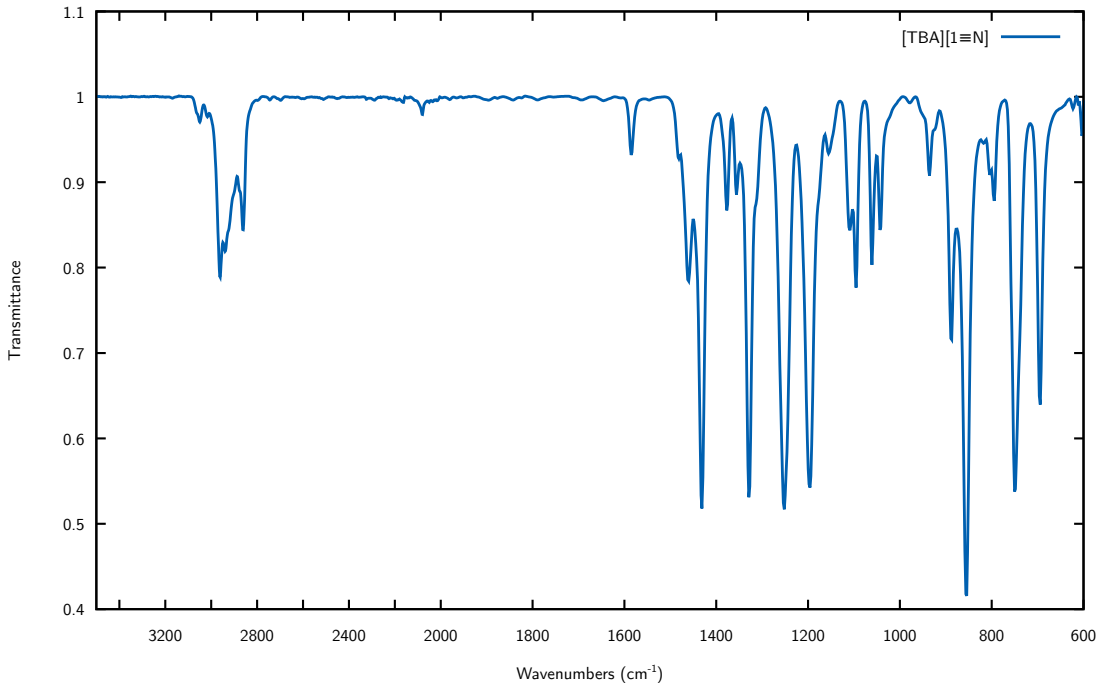

Figure S.6: IR spectrum (ATR) of [TBA][**1**≡N].

S.1.3 Synthesis of [Na(12-crown-4)$_2$][1≡P]

A thawing solution of [Na(dioxane)$_{2.5}$][OCP] (16.9 mg, 0.056 mmol, 1.0 equiv) in THF (2 mL) was added slowly to a thawing solution of **1** (50.0 mg, 0.056 mmol, 1.0 equiv) in THF (2 mL). The reaction mixture was allowed to warm to 25 °C and was stirred for further 20 min. Upon warming to 25 °C a color change to purple was observed. 3 drops from a Pasteur pipette of 12-crown-4 were added. All volatile materials were removed *in vacuo*. The dark residue was washed with pentane (2 mL, solubilized in THF (ca. 1 mL) and the resulting dark purple solution was filtered through a glassfiber filter. Vapour diffusion of hexanes (ca. 4 mL) into this solution at 25 °C resulted in formation of dark green crystalline plates over the course of 3 days, during which time the mother liquor almost completely decolorized. The crystalline residue was separated from the supernatant, washed with benzene (2 mL) and dried under vacuum to give the title compound 67.2 mg (0.052 mmol, 92%).

Elem. Anal. Found(Calc'd) for $C_{64}H_{100}NaO_{12}PW$: C 59.05 (59.16), H 8.00 (7.76); ESI-MS(–): 923.5642 m/z (calcd for $C_{48}H_{68}O_4PW$: 923.4373 m/z); ^{1}H NMR (THF-d_8, 400 MHz, 20 °C) δ 6.82 (d, $^3J_{HH}$ = 7.6 Hz, 8H, $H_{ar\text{-}meta}$ ODipp), 6.51 (t, $^3J_{HH}$ = 7.6 Hz, 4H, $H_{ar\text{-}para}$ ODipp), 4.14 (sept, $^3J_{HH}$ = 6.9 Hz, 8H, CH(CH$_3$)$_2$), 3.65 (s, 32H, H crown ether), 0.93 (d, $^3J_{HH}$ = 6.9 Hz, 48H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz, 20 °C): δ 162.0 (s, C_{ipso} ODipp), 138.5 (s, C_{ortho} ODipp), 122.9 (s, C_{meta} ODipp), 118.6 (s, C_{para} ODipp), 66.5 (s, CH_2 crown ether), 26.4 (s, CH(CH$_3$)$_2$), 24.7 (s, CH(CH$_3$)$_2$); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, 20 °C): δ 886.1 (s, $^1J_{WP}$ = 189.0 Hz, WP).

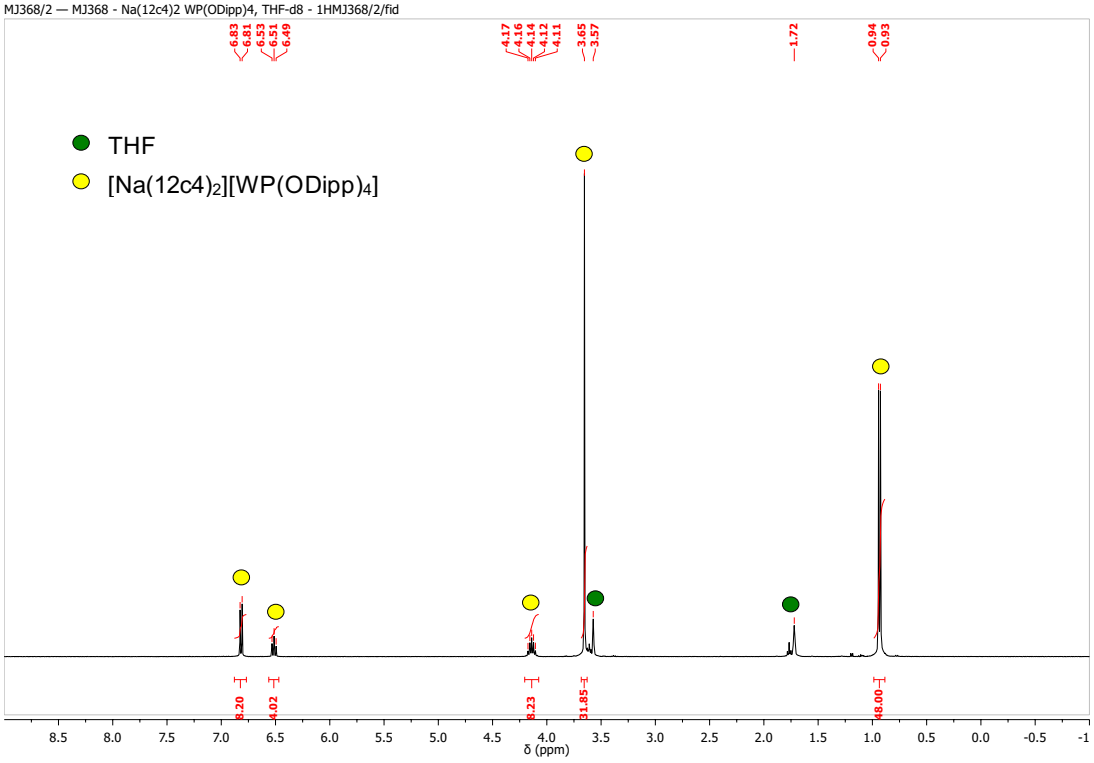

Figure S.7: ^{1}H NMR spectrum (THF-d_8, 400 MHz, 20 °C) of [Na(12-crown-4)$_2$][**1**≡P].

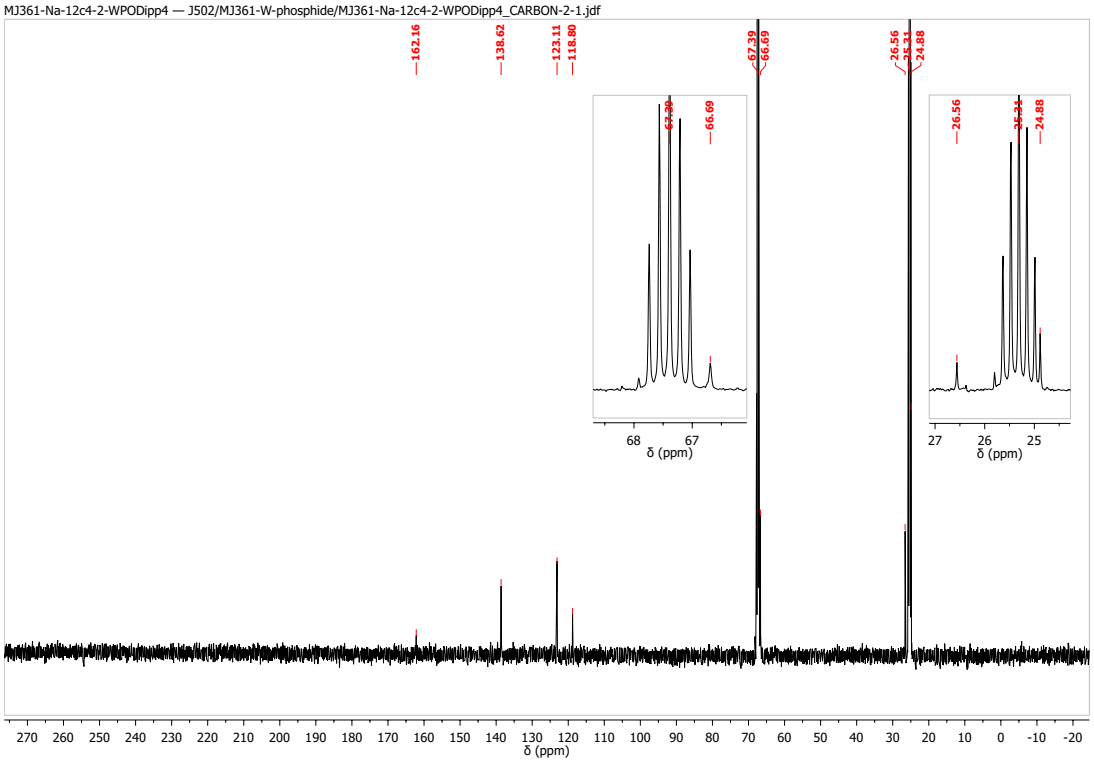

Figure S.8: $^{13}C\{^{1}H\}$ NMR spectrum (THF-d_8, 126 MHz, 20 °C) of [Na(12-crown-4)$_2$][**1**≡P].

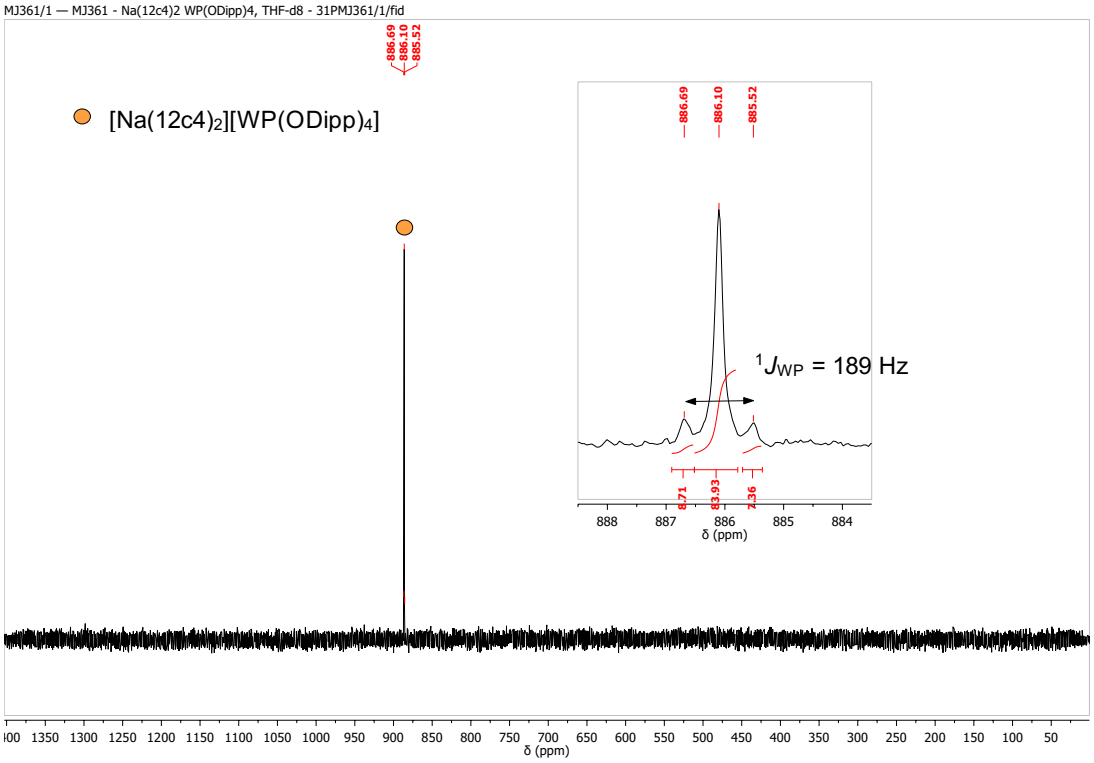

Figure S.9: $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8, 162 MHz, 20 °C) of [Na(12-crown-4)$_2$][**1**≡P].

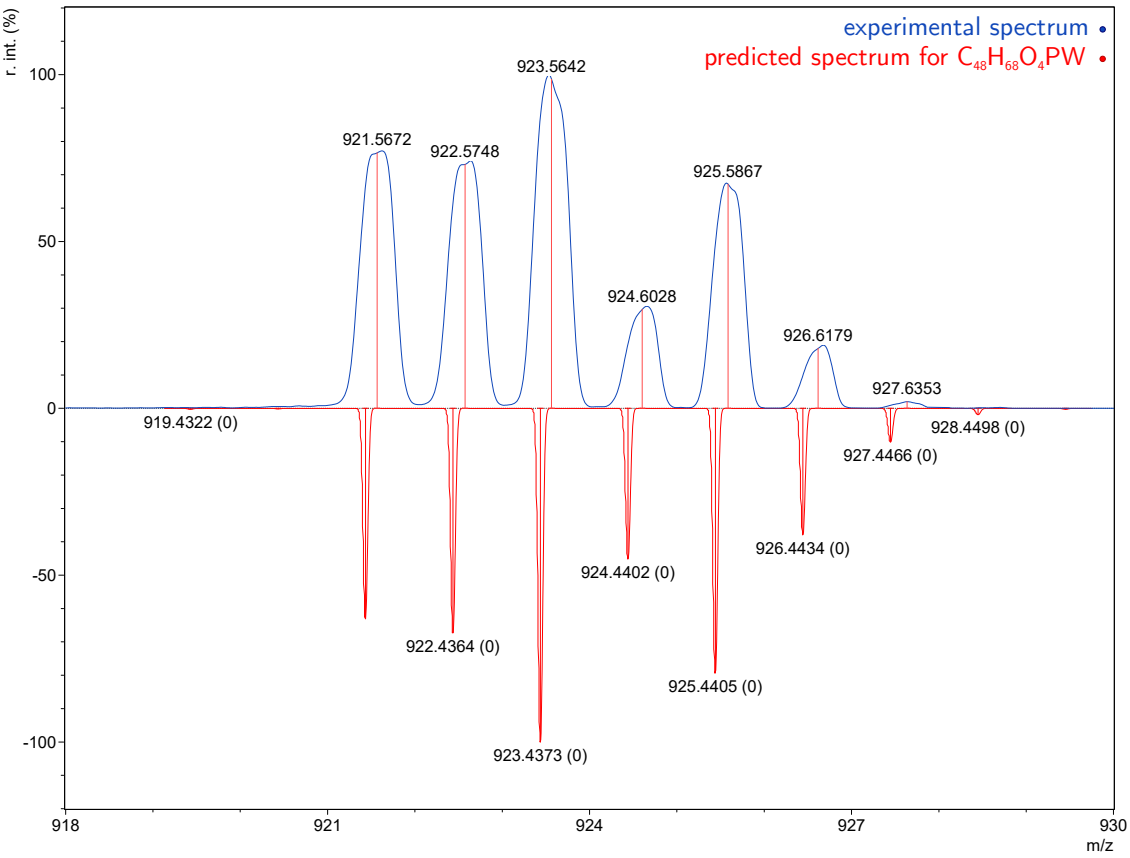

Figure S.10: Experimental (blue) and predicted (red) ESI-MS(–) spectra of [Na(12-crown-4)$_2$][**1**≡P].

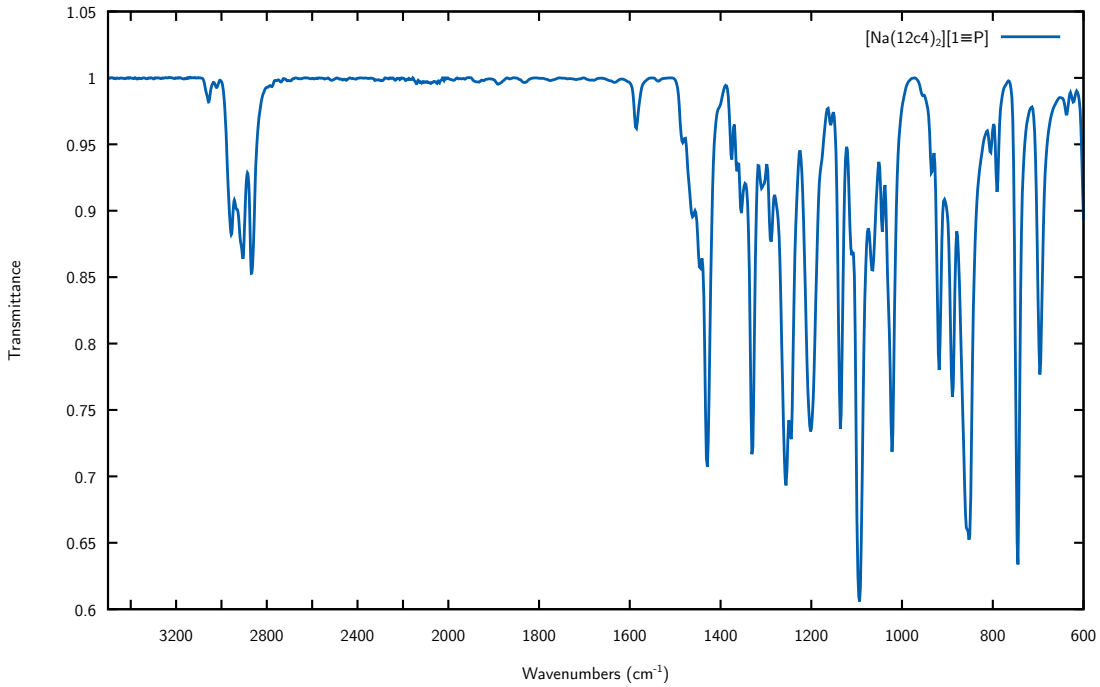

Figure S.11: IR spectrum (ATR) of [Na(12-crown-4)$_2$][**1**≡P].

S.1.4 Synthesis of [Na(DME)$_3$][**1**≡P]

All attempts to obtain crystals of [Na(12-crown-4)$_2$][**1**≡P] suitable for an X-ray diffraction analysis failed due to severe twinning. Modification of the counter-cation allowed to obtain crystals suitable for X-ray diffraction analysis: A solution of [Na(dioxane)$_{2.5}$][OCP] (16.9 mg, 0.056 mmol, 1.0 equiv) in THF (1.5 mL) was added dropwise at 25 °C to a solution of **1** (50.0 mg, 0.056 mmol, 1.0 equiv) in THF (1.5 mL). The mixture was stirred for 30 min at 25 °C, concentrated under vacuum to a volume of ca. 1 mL. DME (2 mL) was added. All volatile materials were removed *in vacuo* and washed with a small amount (ca. 1 mL) of pentane. Yield: 64.8 mg (0.053 mmol, 95%). Crystals suitable for an X-ray diffraction analysis were grown at –35 °C by layering a solution of the title compound (20.0 mg) in DME (0.5 mL) with toluene (ca. 0.3 mL) and then pentane (ca. 1.5 mL) in an NMR tube. Red, crystalline blocks formed after 3 days at –35 °C.

^{1}H NMR (benzene-d_6, 400 MHz, 20 °C) δ 7.13 (d, $^3J_{HH}$ = 7.7 Hz, 8H, $H_{ar\text{-}meta}$ ODipp), 6.91 (t, $^3J_{HH}$ = 7.7 Hz, 4H, $H_{ar\text{-}para}$ ODipp), 4.10 (sept, $^3J_{HH}$ = 6.6 Hz, 8H, C*H*(CH$_3$)$_2$), 2.98 (s, 12H, CH$_2$ DME), 2.78 (s, 18H, CH$_3$ DME), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 48H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (benzene-d_6, 126 MHz, 20 °C): δ 160.5 (s, C_{ipso} ODipp), 138.3 (s, C_{ortho} ODipp), 124.3 (s, C_{meta} ODipp), 121.4 (s, C_{para} ODipp), 71.2 (s, CH$_2$ DME), 58.9 (s, CH$_3$ DME), 26.8 (s, *C*H(CH$_3$)$_2$), 24.9 (s, CH(*C*H$_3$)$_2$); ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz, 20 °C): δ 906.5 (s, $^1J_{WP}$ = 185.0 Hz, WP).

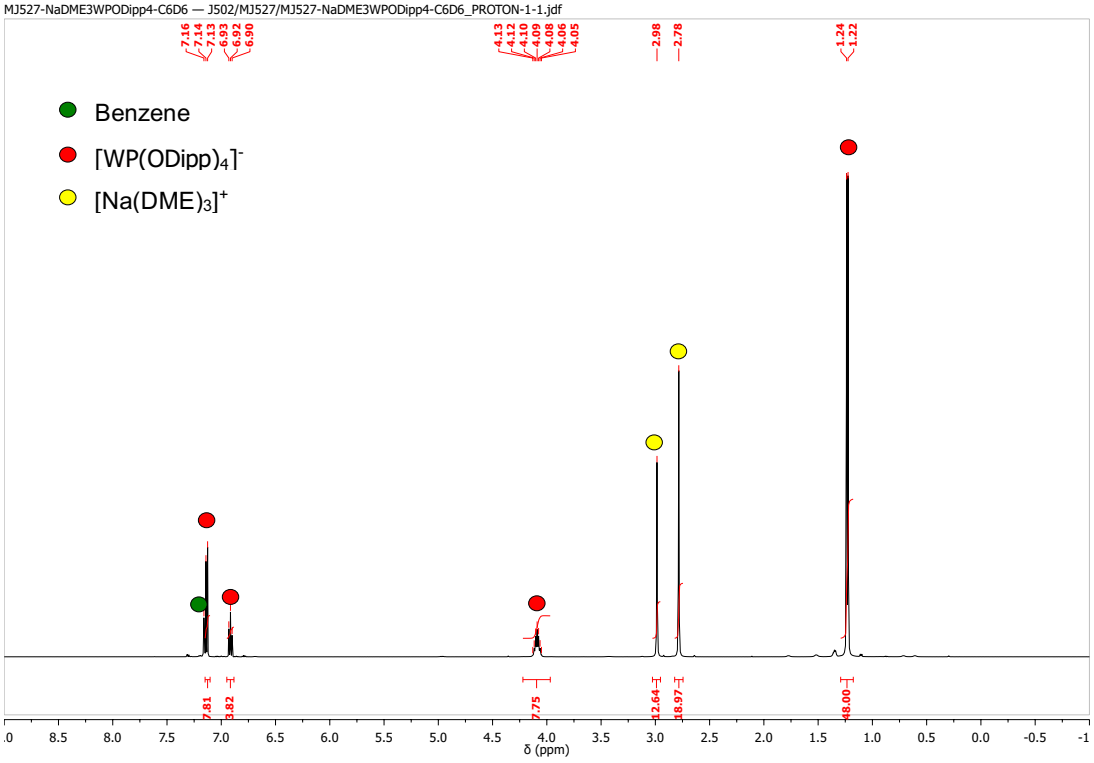

Figure S.12: ^{1}H NMR spectrum (benzene-d_6, 400 MHz, 20 °C) of [Na(DME)$_3$][**1**≡P].

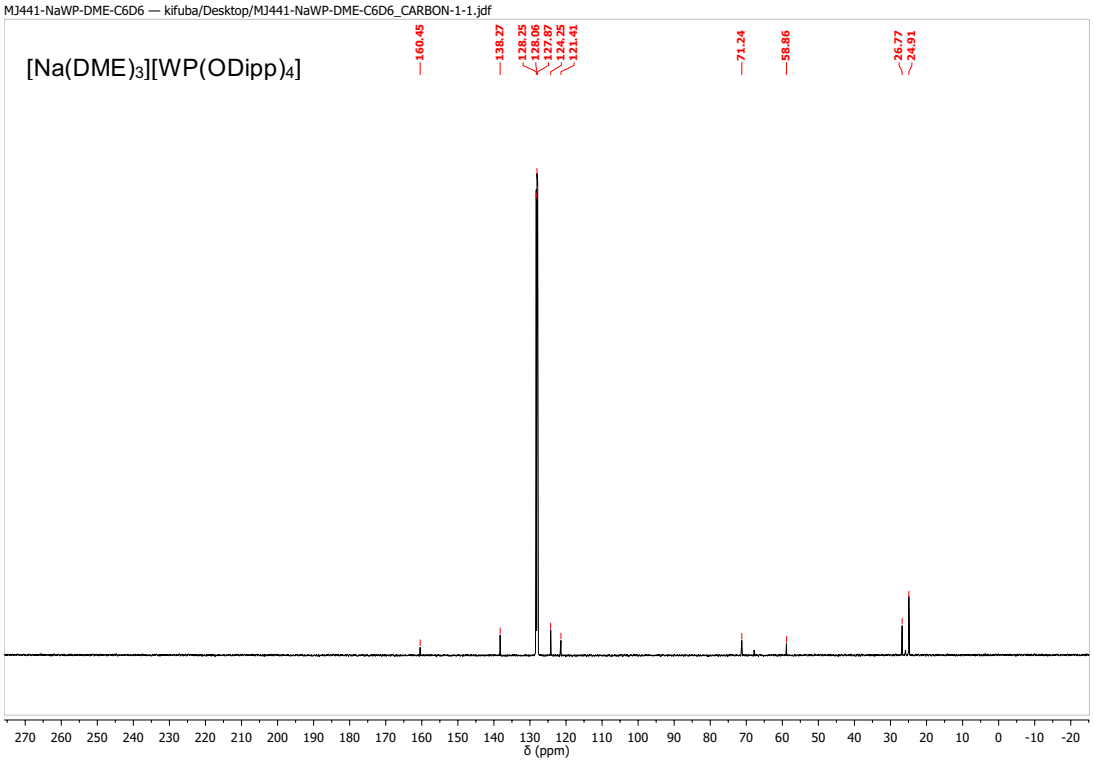

Figure S.13: $^{13}C\{^{1}H\}$ NMR spectrum (benzene-d_6, 126 MHz, 20 °C) of [Na(DME)$_3$][**1**≡P].

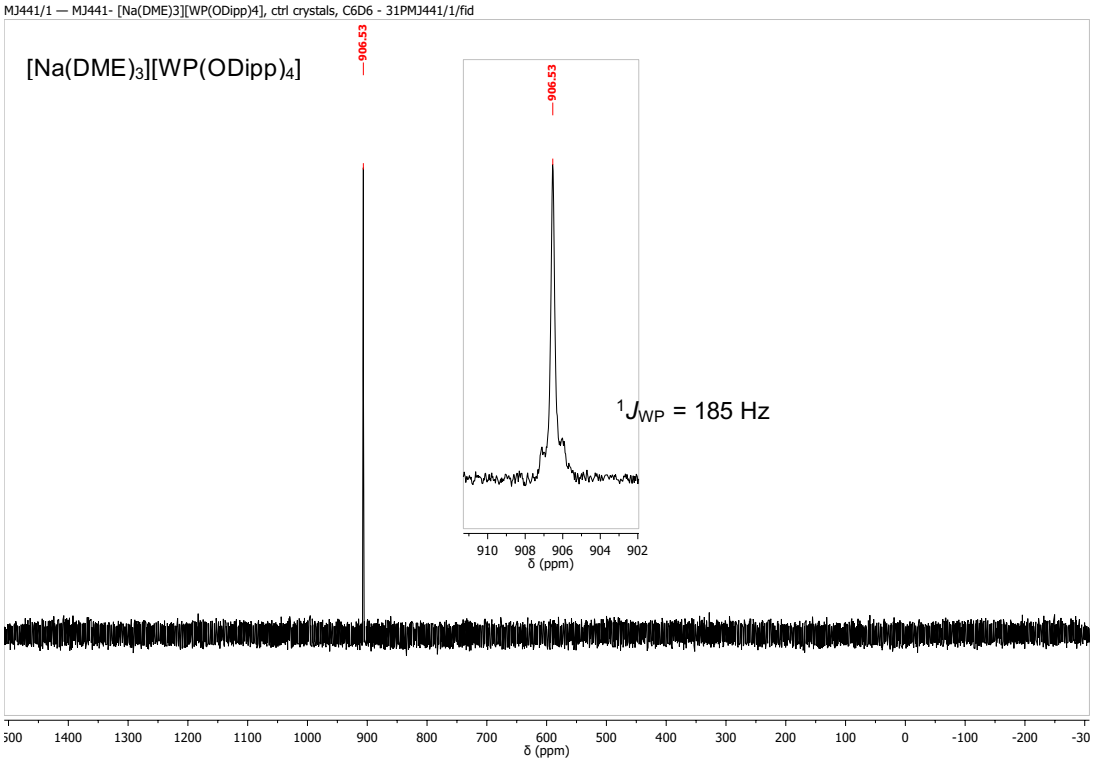

Figure S.14: $^{31}P\{^{1}H\}$ NMR spectrum (benzene-d_6, 162 MHz, 20 °C) of [Na(DME)$_3$][**1**≡P].

S.1.5 Synthesis of [Na(12-crown-4)$_2$][**1**≡As]

A thawing solution of [Na(dioxane)$_{2.5}$][OCAs] (19.4 mg, 0.056 mmol, 1.0 equiv) in THF (2 mL) was added slowly to a thawing solution of **1** (50.0 mg, 0.056 mmol, 1.0 equiv) in THF (2 mL). After warming to 25 °C, the dark green mixture was stirred for 30 min at 25 °C. 3 drops from a Pasteur pipette of 12-crown-4 were added and all volatile materials were removed *in vacuo*. The remaining sticky, green residue was washed with pentane (2 × 2 mL). The remaining solid was dried under vacuum, dissolved in THF (2 mL) and filtered through a glassfiber filter. Pentane (ca. 3 mL) was allowed to vapor-diffuse into this solution for 2 days, inducing crystallization. This mixture was then stored for 7 days at –35 °C. The brownish supernatant was removed, and the remaining green crystalline precipitate was washed with cold pentane (1 mL) and dried under vacuum to give the title compound. Yield: 28.5 mg (0.021 mmol, 38%).

This compound is highly sensitive to oxygen and moisture. Even under an inert atmosphere, it seemed to decompose over several days in THF solution. Several attempts to obtain satisfactory elemental analysis data for [Na(12-crown-4)$_2$][**1**≡As] were unsuccessful. Elem. Anal. Found(Calc'd) for $C_{64}H_{100}NaO_{12}AsW$: C 55.68 (57.23), H 7.69 (7.50); ESI-MS(–): 967.5060 m/z (calcd for $C_{48}H_{68}O_4AsW$: 967.3851 m/z); ^{1}H NMR (acetonitrile-d_3, 400 MHz, 20 °C) δ 6.92 (d, $^3J_{HH}$ = 7.5 Hz, 8H, $H_{ar\text{-}meta}$ ODipp), 6.65 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $H_{ar\text{-}para}$ ODipp), 4.03 (sept, $^3J_{HH}$ = 6.9 Hz, 8H, C*H*(CH$_3$)$_2$), 3.62 (s, 32H, H crown ether), 0.95 (d, $^3J_{HH}$ = 6.9 Hz, 48H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (acetonitrile-d_3, 126 MHz, 20 °C): δ 162.0 (s, C_{ipso} ODipp), 134.5 (s, C_{ortho} ODipp), 123.7 (s, C_{meta} ODipp), 119.6 (s, C_{para} ODipp), 67.1 (s, CH_2 crown ether), 27.1 (s, *C*H(CH$_3$)$_2$), 24.8 (s, CH(*C*H$_3$)$_2$).

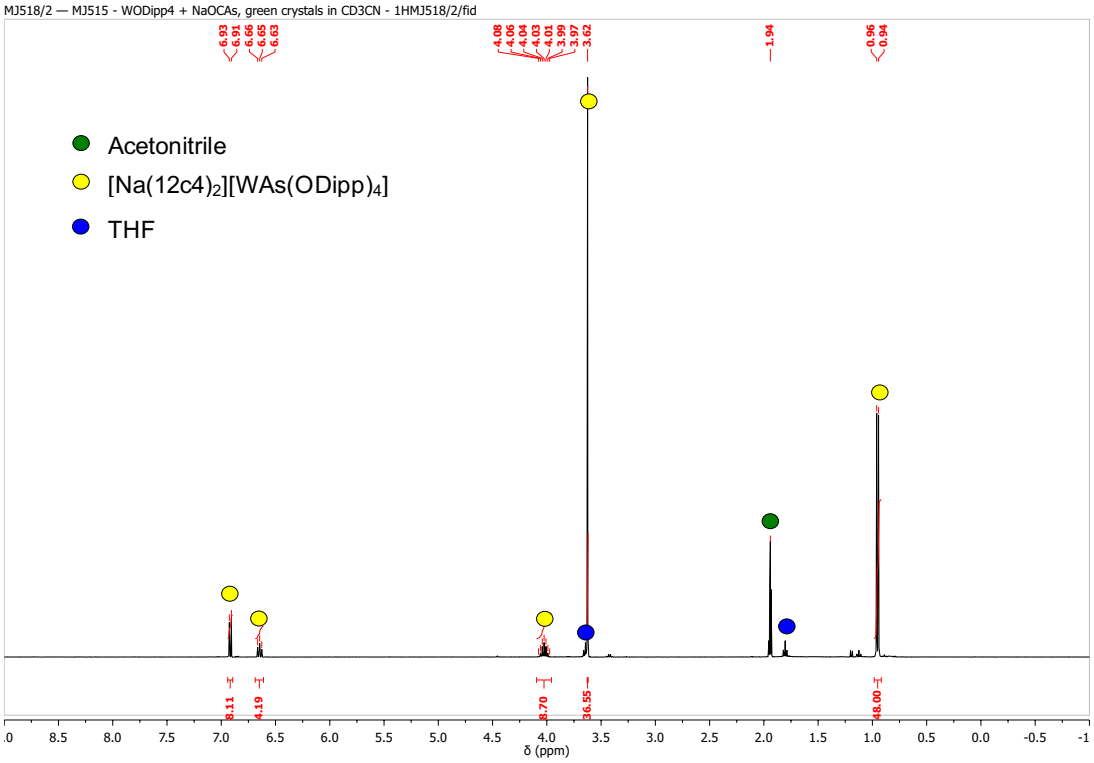

Figure S.15: ^{1}H NMR spectrum (acetonitrile-d_3, 500 MHz, 20 °C) of [Na(12-crown-4)$_2$][**1**≡As].

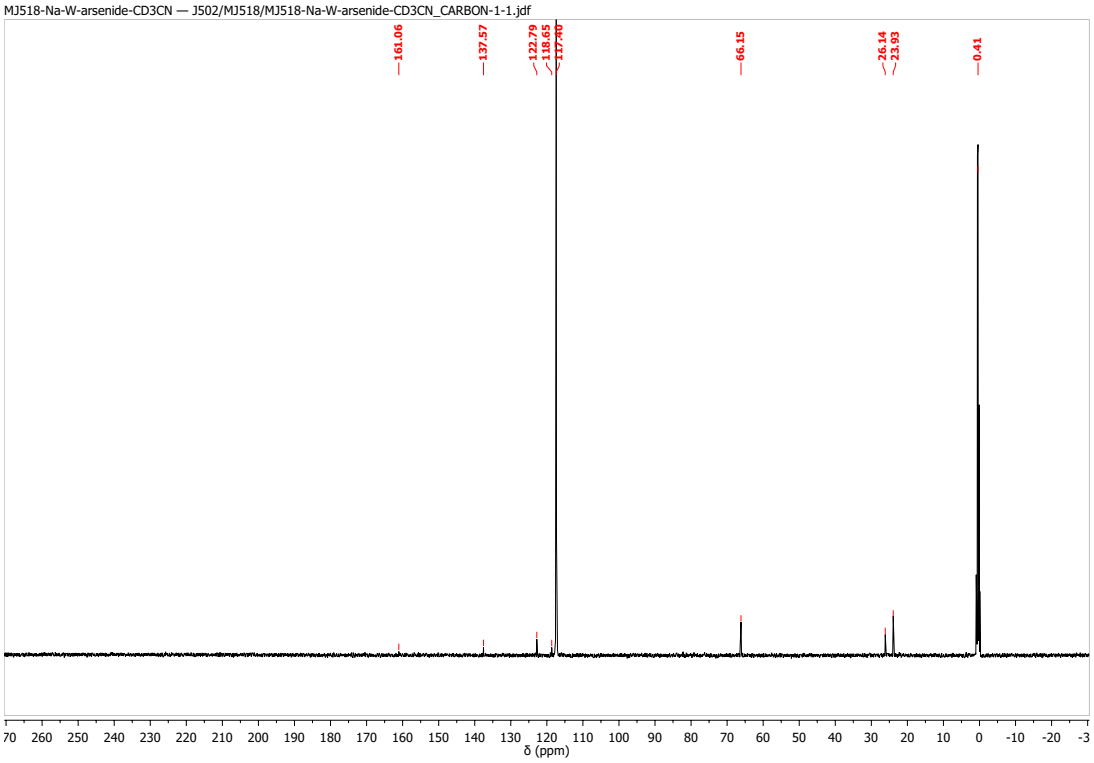

Figure S.16: ^{13}C{^{1}H} NMR spectrum (acetonitrile-d_3, 126 MHz, 20 °C) of [Na(12-crown-4)$_2$][**1**≡As].

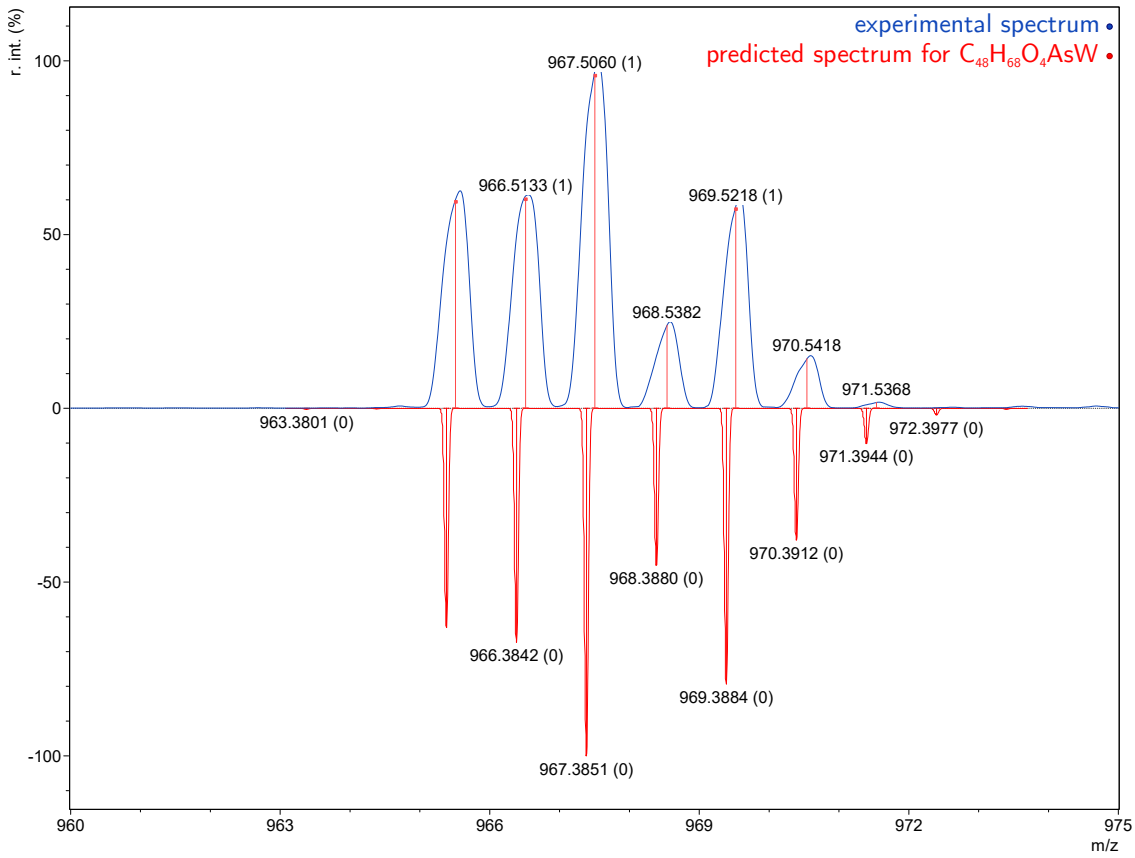

Figure S.17: Experimental (blue) and predicted (red) ESI-MS(–) spectra of [Na(12-crown-4)$_2$][**1**≡As].

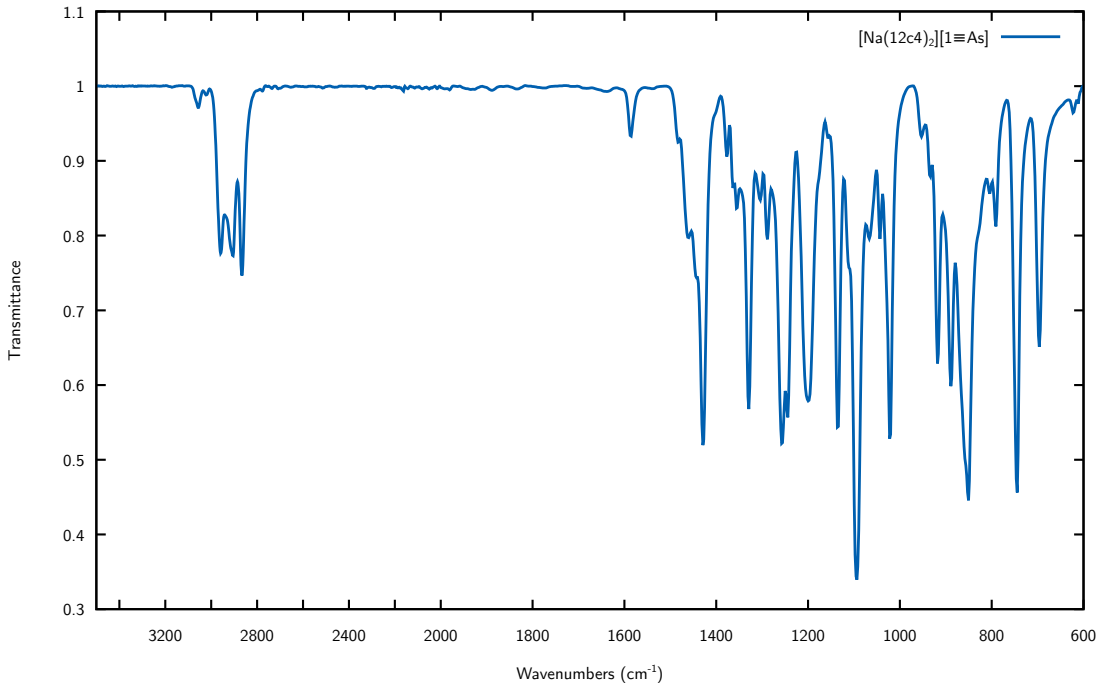

Figure S.18: IR spectrum (ATR) of [Na(12-crown-4)$_2$][**1**≡As].

S.1.6 Synthesis of [Na(DME)$_3$][1≡As]

A solution of [Na(dioxane)$_{2.5}$][OCAs] (8.8 mg, 0.028 mmol, 1.0 equiv) in DME (1.5 mL) was added dropwise at 25 °C to a solution of **1** (25.0 mg, 0.028 mmol, 1.0 equiv) in DME (1.5 mL). The mixture was stirred for 60 min at 25 °C. All volatile materials were removed *in vacuo* and the residue was washed with pentane (3 ×1 mL). Yield: 32.2 mg (0.026 mmol, 91%). Crystals suitable for an X-ray diffraction analysis were grown at 25 °C by dissolving this material in DME (1 mL) and 1,4-dioxane (2 mL), and layering this solution with pentane (2 mL). Grey-greenish plates formed in the course of ca. 14 h.

^{1}H NMR (acetonitrile-d_3, 500 MHz, 20 °C) δ 6.91 (d, $^3J_{HH}$ = 7.6 Hz, 8H, H$_{ar\text{-}meta}$ ODipp), 6.65 (t, $^3J_{HH}$ = 7.6 Hz, 4H, H$_{ar\text{-}para}$ ODipp), 4.02 (sept, $^3J_{HH}$ = 6.9 Hz, 8H, C*H*(CH$_3$)$_2$), 3.46 (s, 12H, CH$_2$ DME), 3.29 (s, 18H, CH$_3$ DME), 0.95 (d, $^3J_{HH}$ = 6.9 Hz, 48H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (acetonitrile-d_3, 126 MHz, 20 °C): δ 162.0 (s, C$_{ipso}$ ODipp), 138.5 (s, C$_{ortho}$ ODipp), 123.7 (s, C$_{meta}$ ODipp), 119.6 (s, C$_{para}$ ODipp), 72.4 (s, CH$_2$ DME), 58.9 (s, CH$_3$ DME), 27.1 (s, *C*H(CH$_3$)$_2$), 24.9 (s, CH(*C*H$_3$)$_2$).

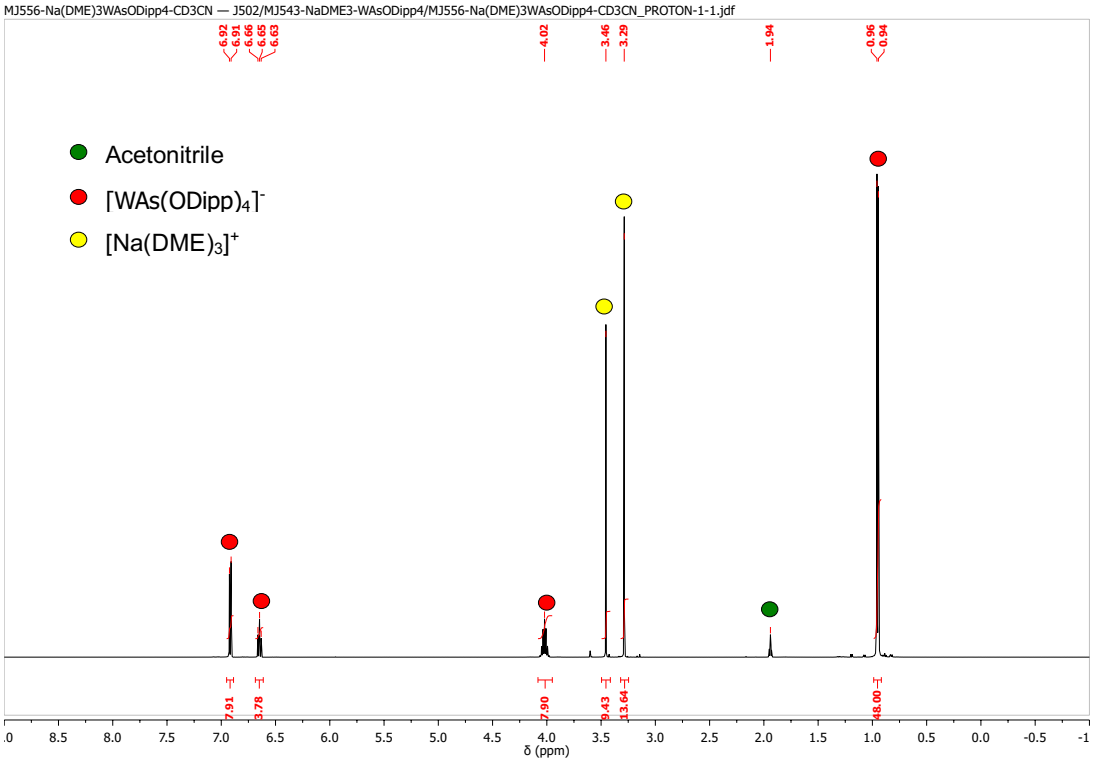

Figure S.19: ^{1}H NMR spectrum (acetonitrile-d_3, 500 MHz, 20 °C) of [Na(DME)$_3$][**1**≡As].

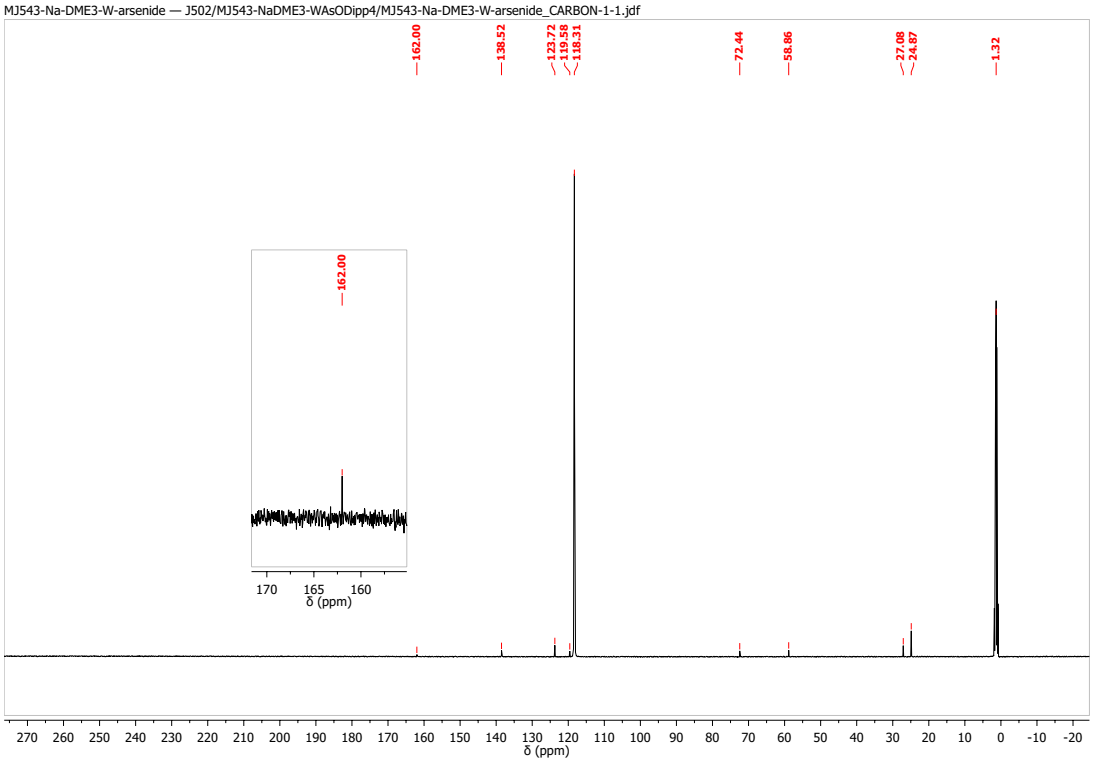

Figure S.20: ^{13}C{^{1}H} NMR spectrum (acetonitrile-d_3, 126 MHz, 20 °C) of [Na(DME)$_3$][**1**≡P].

S.1.7 Protonation of [Na(12-crown-4)$_2$][1≡P] with Lutidinium Triflate

A solution of lutidinium triflate (4.4 mg, 0.015 mmol, 1.0 equiv) in acetonitrile-d_3 (0.4 mL) was added at 25 °C to a solution of [Na(12c4)$_2$][**1**≡P] (20.0 mg, 0.015 mmol, 1.0 equiv) in acetonitrile-d_3(0.4 mL). Upon addition, the purple color of the solution of the phosphide complex quickly changed to orange-brown. A small amount of a brown material deposited at the bottom of the tube. The mixture was transferred to an NMR tube and analyzed by ^{1}H NMR, ^{31}P{^{1}H} NMR, and ^{13}C{^{1}H} NMR spectroscopy, indicating complete conversion of the starting material. The formed products correspond to HODipp, lutidine (by comparison with authentic samples) and likely the neutral tungsten phosphide complex [WP(ODipp)$_3$]. Attempts to isolate this species resulted in its decomposition upon removal of volatile materials. Characteristic NMR data are listed below.

^{1}H NMR (acetonitrile-d_3, 500 MHz, 20 °C) δ 7.17 (d, $^3J_{HH}$ = 7.7 Hz, 6H, $H_{ar\text{-}meta}$ ODipp), 6.96 (t, $^3J_{HH}$ = 7.7 Hz, 3H, $H_{ar\text{-}para}$ ODipp), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 6H, C*H*(CH$_3$)$_2$), 1.21 (d, $^3J_{HH}$ = 6.7 Hz, 36H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (acetonitrile-d_3, 126 MHz, 20 °C): δ 139.2 (s, C_{ortho} ODipp), 124.4 (s, C_{meta} ODipp), 123.4 (s, C_{para} ODipp), 27.6 (s, *C*H(CH$_3$)$_2$), 23.2 (s, CH(*C*H$_3$)$_2$), C_{ipso} not detected; ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz, 20 °C): δ 1033.8 (s, $^1J_{WP}$ = 176.0 Hz, WP).

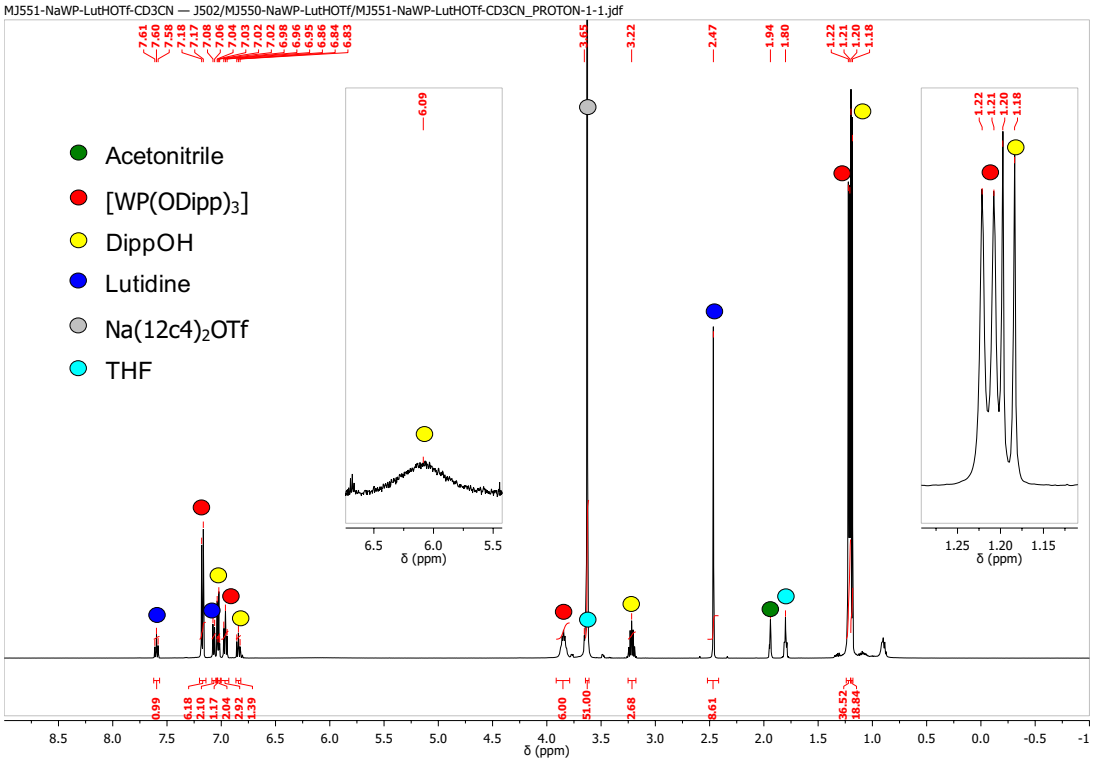

Figure S.21: ^{1}H NMR spectrum (benzene-d_6, 400 MHz, 20 °C) of reaction mixture containing [W≡P(ODipp)$_3$].

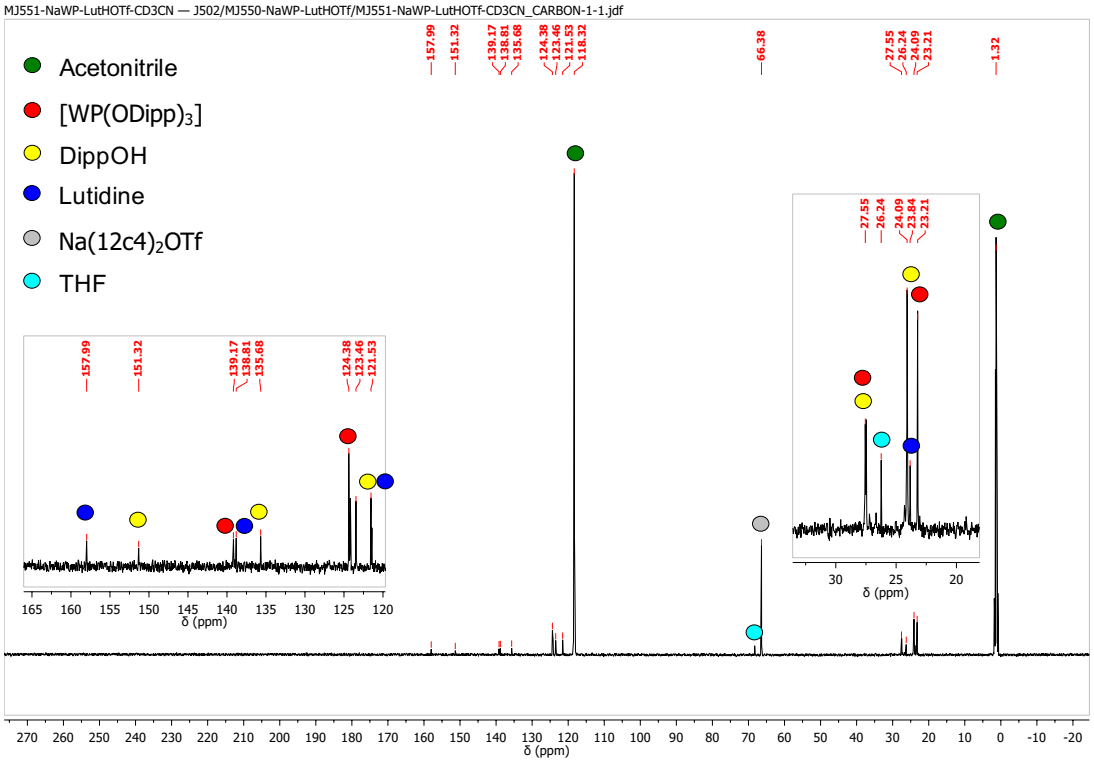

Figure S.22: $^{13}C\{^{1}H\}$ NMR spectrum (benzene-d_6, 126 MHz, 20 °C) of of reaction mixture containing [W≡P(ODipp)$_3$].

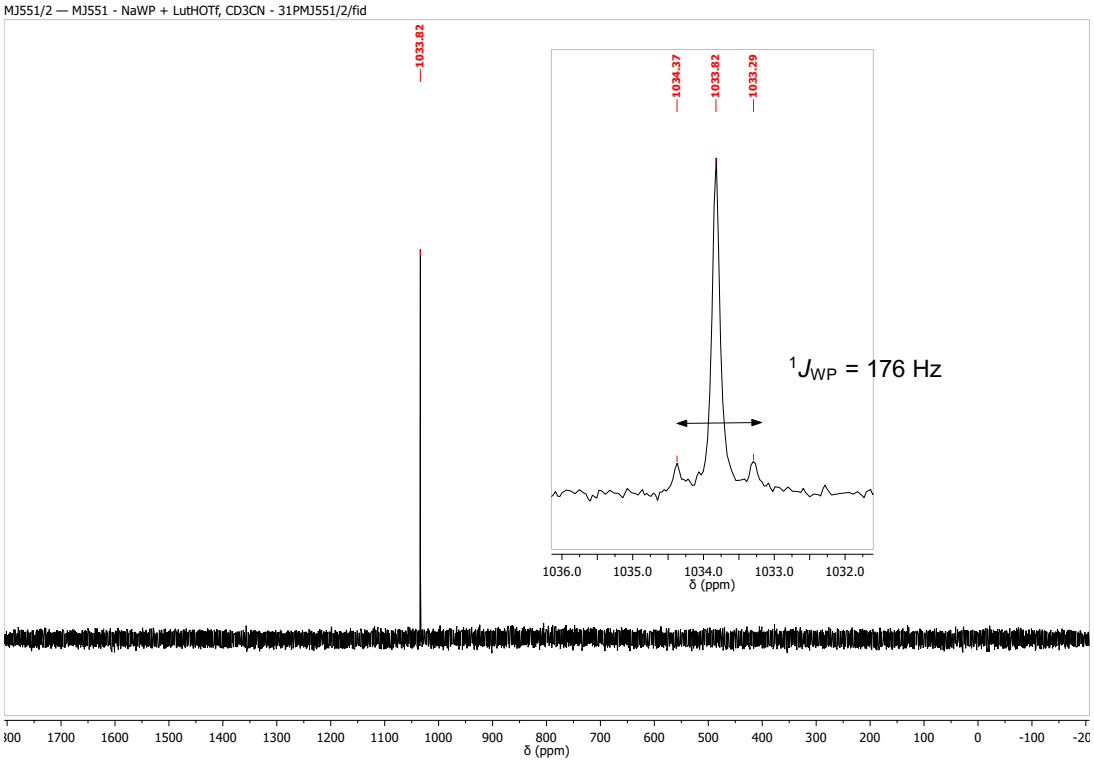

Figure S.23: $^{31}P\{^{1}H\}$ NMR spectrum (benzene-d_6, 162 MHz, 20 °C) of of reaction mixture containing [W≡P(ODipp)$_3$].

S.2 X-Ray Diffraction Studies

The crystals were mounted in hydrocarbon oil on a nylon loop or a glass fiber. Low-temperature (100 K) data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector or a Photon2 CPAD with Mo Kα radiation ($\lambda = 0.71073$ Å) with ϕ- and ω-scans. A semi-empirical absorption correction was applied to the diffraction data using SADABS.[8] All structures were solved by direct methods using SHELXT[9] and refined against F^2 on all data by full-matrix least squares with SHELXL-2015[10] using established methods. 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). 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 Table S.1. Further details can be found in the form of .cif files available from the CCDC.

Compound [TBA][**1**≡N] (TBA = tetra-*n*-butylammonium) crystallized in the monoclinic space group $P2_1/c$ with one molecule of [TBA][**1**≡N] and two molecules of tetrahydrofuran (THF) in the asymmetric unit. One arm of the tetra-*n*-butylammonium cation was disordered over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotopic displacement parameters. The disorder ratio freely refined to 0.7386(47).

Compound [Na(DME)$_3$][**1**≡P] (DME = 1,2-dimethoxyethane) crystallized in the monoclinic space group $P2_1/n$ with one molecule of [Na(DME)$_3$][**1**≡P] in the asymmetric unit. Every isopropyl group and two of the three DME units were disordered over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotopic displacement parameters. The disorder ratios for the isopropyl groups were refined freely and ranged from 0.540(94) to 0.840(24). The disorder ratios for the DME units freely refined to 0.623(10) and 0.534(23).

Compound [Na(DME)$_3$][**1**≡As] crystallized in the orthorhombic space group $Fdd2$ with 1.5 molecules of [Na(DME)$_3$][**1**≡As] and 1.5 molecules of 1,4-dioxane in the asymmetric unit. The half molecules were refined as whole molecules constrained to 50% occupancy over special positions, except dioxane which was further modeled as a two part disorder with ratio 0.593(17).

Table S.1: Crystallographic Data for [TBA][**1**≡N] and [Na(DME)$_3$][**1**≡P] and [Na(DME)$_3$][**1**≡As]

	[TBA][**1**≡N]·2THF	[Na(DME)$_3$][**1**≡P]	[Na(DME)$_3$][**1**≡As]·Dioxane
Reciprocal Net code / CCDC	X8_17131 / CCDC 1570077	X8_17069 / CCDC 1570078	P8_17003 / CCDC 1570079
Empirical formula, FW (g/mol)	$C_{72}H_{120}N_2O_6W$, 1293.54	$C_{60}H_{98}NaO_{10}PW$, 1217.19	$C_{48}H_{79.5}As_{0.75}Na_{0.75}O_9W_{0.75}$, 1011.93
Color / Morphology	Blue / Block	Red / Block	Blue / Block
Crystal size (mm^3)	$0.20 \times 0.12 \times 0.12$	$0.30 \times 0.18 \times 0.15$	$0.26 \times 0.20 \times 0.11$
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Orthorhombic, $Fdd2$
Unit cell dimensions (Å, °)	a = 18.4968(9), α = 90	a = 22.136(15), α = 90	a = 57.2329(15), α = 90
	b = 19.2772(10), β = 95.713(2)	b = 13.925(10), β = 106.996(10)	b = 18.4351(6), β = 90
	c = 19.4013(10), γ = 90	c = 22.594(15), γ = 90	c = 38.9112(11), γ = 90
Volume (Å^3)	6883.5(6)	6660(8)	41055(2)
Z	4	4	32
Density (calc., g/cm^3)	1.248	1.214	1.310
Absorption coefficient (mm^{-1})	1.728	1.814	2.229
$F(000)$	2752	2552	16896
Theta range for data collection (°)	1.106 to 36.472	1.133 to 30.508	2.321 to 30.518
Index ranges	$-30 \le h \le 30$, $-32 \le k \le 32$,	$-31 \le h \le 31$, $-19 \le k \le 19$,	$-81 \le h \le 81$, $-26 \le k \le 26$,
	$-32 \le l \le 32$	$-32 \le l \le 32$	$-55 \le l \le 55$
Reflections collected	434854	624949	420443
Independent reflections, R_{int}	33687, 0.0712	20299, 0.0802	31327, 0.0693
Completeness to θ_{max} (%)	100.0	100.0	99.9
Absorption correction	Semi-empirical from equiv.	Semi-empirical from equiv.	Semi-empirical from equiv.
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	33687 / 408 / 788	20299 / 3075 / 954	31327 / 4874 / 1442
Goodness-of-fit[a]	1.024	1.043	1.108
Final R indices[b] [$I > 2\sigma(I)$]	$R_1 = 0.0292$, $wR_2 = 0.0626$	$R_1 = 0.0274$, $wR_2 = 0.0601$	$R_1 = 0.0332$, $wR_2 = 0.0662$
R indices[b] (all data)	$R_1 = 0.0451$, $wR_2 = 0.0677$	$R_1 = 0.0440$, $wR_2 = 0.0681$	$R_1 = 0.0537$, $wR_2 = 0.0764$
Largest diff. peak and hole (e·Å^{-3})	3.249 and −2.354	0.638 and −1.319	1.760 and −1.471

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

S.3 Computational Studies

All calculations were performed with the ORCA 4.0.0 quantum chemistry package from the development team at the University of Bonn.[11,12] Initial anion geometries were taken from the atom positions in the X-ray diffraction study, and the isopropyl groups were replaced by hydrogen atoms. In the case of the arsenide, where two anions were modelled in the asymmetric unit, the anion lacking positional disorder was selected. X-ray diffraction is known to give incorrect hydrogen positions due to libration effects, so hydrogen atom positions were optimized at the RIJCOSX-ωB97X-D3/ma-Def2-TZVP level of theory with an effective core potential (ECP) on tungsten[13–19] using the following input file:

```
! PAL8 RIJCOSX wB97X-D3 ma-Def2-TZVP Def2/J
! TightSCF Grid5 FinalGrid6 GridX5 Opt
%geom
  OptimizeHydrogens true
  end
*xyzfile -1 1 init.xyz
```

The XYZ coordinates for each anion can be found in a supplemental .ALLXYZ file. The resulting .GBW file was imported into a second calculation at the RIJCOSX-ωB97X-D3/Def2-TZVP level of theory level of theory and fed into a natural bond orbital (NBO) calculation using NBO6.[20] The input file has been reproduced below. The NBO results are summarized in the main text.

```
! PAL8 RIJCOSX wB97X-D3 Def2-TZVP Def2/J
! TightSCF Grid5 FinalGrid6 GridX5 KDIIS SOSCF MORead NBO
%moinp "opt.gbw"
*xyzfile -1 1 opt.xyz
```

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