Molecular 1,1'-bifunctional mixed-valence P-P compounds, enabled through metal complexation

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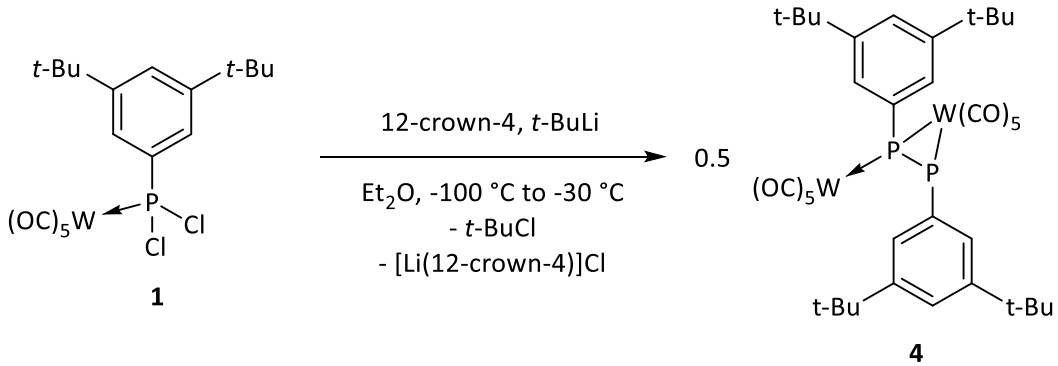
1. Experimental details and devices

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Diethyl ether, tetrahydrofuran, *n*-pentane and petrol ether were dried over sodium wire and benzophenone. Dichloromethane was dried over CaH_2. The solvents were freshly distilled before usage. The NMR spectra were recorded on a Bruker Avance I 300 (300.1 MHz for ^{1}H NMR, 75.5 MHz for ^{13}C NMR, 121.5 MHz for ^{31}P NMR), Bruker Avance I 400 (400.1 MHz for ^{1}H NMR, 100.6 MHz for ^{13}C NMR, 162.0 MHz for ^{31}P NMR) and Bruker Avance III HD Ascend 500 (500.2 MHz for ^{1}H NMR, 125.8 MHz for ^{13}C NMR, 202.5 MHz for ^{31}P NMR) spectrometers at 25 °C. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents; the ^{31}P NMR spectra were referenced to 85 % H_3PO_4 as external standards, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type Sor a Carl Roth Type MPM-2 apparatus and are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Thermo Finnigan MAT 90 and MAT 95 XL device using 70 eV voltage. For collecting MALDI spectra a Bruker Daltonik ultrafleXtreme TOF/TOF spectrometer was utilized while using DCTB as matrix material. LIFDI and ESI measurements were carried out on a Thermo Finnigan MAT 90 and on a Thermo Fisher Scientific Orbitrap XL spectrometer equipped with a HPLC auto sampler. The IR spectra were recorded on a Thermo Nicolet 380 FT-IR spectrometer with an attenuated total reflection (ATR) attachment or a Bruker Alpha Diamond ATR FTIR spectrometer. X-ray data were collected with a Bruker X8-KappaApexII or a STOE IPDS-2T diffractometer. CCDC 2021629-2021632 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

2. Experimental procedures and NMR spectra for 4-9

Complex 4



Scheme S 1*. Reaction of complex* ***1*** *with t-BuLi in presence of 12-crown-4 to yield complex* ***4****.*

In a 250 mL Schlenk tube complex **1** (1.23 g, 2.00 mmol, 1.00 eq.) was dissolved in 80 mL Et_2O and 12-crown-4 (0.32 mL, 2.00 mmol, 1.00 eq.) was added. At -100 °C *t*-BuLi (1.7 M in *n*-hexane) (1.24 mL, 2.10 mmol, 1.05

eq.) was added dropwise to the reaction solution which turned red after complete addition of *t*-BuLi. The solution was allowed to warm up until -30 °C whereby a color change from red to orange was observed. The reaction was stopped by removing the solvent and all volatiles under reduced pressure ($5 \cdot 10^{-2}$ mbar). The residue was purified via column chromatography (Al_2O_3, -20 °C, petrol ether and CH_2Cl_2, h=4 cm, Ø=5 cm). The product was obtained as an orange fraction (petrol ether and CH_2Cl_2 1:3). After removal of the solvent under reduced pressure ($5 \cdot 10^{-2}$ mbar) crude product was washed with *n*-pentane (4 * 3 mL). After drying the orange solid for 2 h the final product **4** was obtained in 57 % yield (620 mg, 0.57 mmol).

^{1}H NMR (300.1 MHz, 213 K, $CDCl_3$): δ / ppm = 1.28 (br s, 18H, tBu), 1.30 (br s, 18H, tBu), 7.42 (m, 4H, *ortho*-H), 7.56 (m, 2H, *para*-H).

^{13}C{^{1}H} NMR (75.5 MHz, 213 K, $CDCl_3$): δ / ppm = 31.1 (s, tBu), 35.1 (d, $^{4}J_{PC}$ = 2.3 Hz, tBu), 124.8 (br m, *para*-C), 130.4 (br m, *ortho*-C), 150.6 (d, $^{1}J_{PC}$ = 7.6 Hz, *ipso*-C), 151.4 (s, *meta*-C), 196.1 (d, $^{2}J_{PC}$ = 6.6 Hz, *cis*-CO), 199.5 (d, $^{2}J_{PC}$ = 28.2 Hz, *trans*-CO).

^{31}P{^{1}H} NMR (121.5 MHz, 213 K, $CDCl_3$): δ / ppm = -2.25 (d, $^{1}J_{PP}$ = 476.4 Hz), 8.85 (d_{sat}, $^{1}J_{PP}$ = 476.4 Hz, $^{1}J_{WP}$ = 226.9 Hz, $^{1+2}J_{WP}$ = 28.7 Hz, PW).

MS (EI, 70 eV): m/z (%) = 1089.2 (10) $[M+H]^{+\cdot}$, 1005.9 (10) $[M+H-3CO]^{+}$, 976.1 (10) $[M-4CO]^{+}$, 948.0 (10) $[M-5CO]^{+}$, 892.0 (10) $[M-7CO]^{+}$, 864.0 (10) $[M-8CO]^{+}$, 807.9 (10) $[M-10CO]^{+}$.

IR (ATR): ν /cm^{-1} = 2090 (s, CO), 2066 (s, CO), 1990 (s, CO), 1914 (vs, CO), 560 (vs, P=P).

Melting point: 173 °C.

Elemental analysis: cal. C 42.88, H 4.62; found C 42.48, H 4.79.

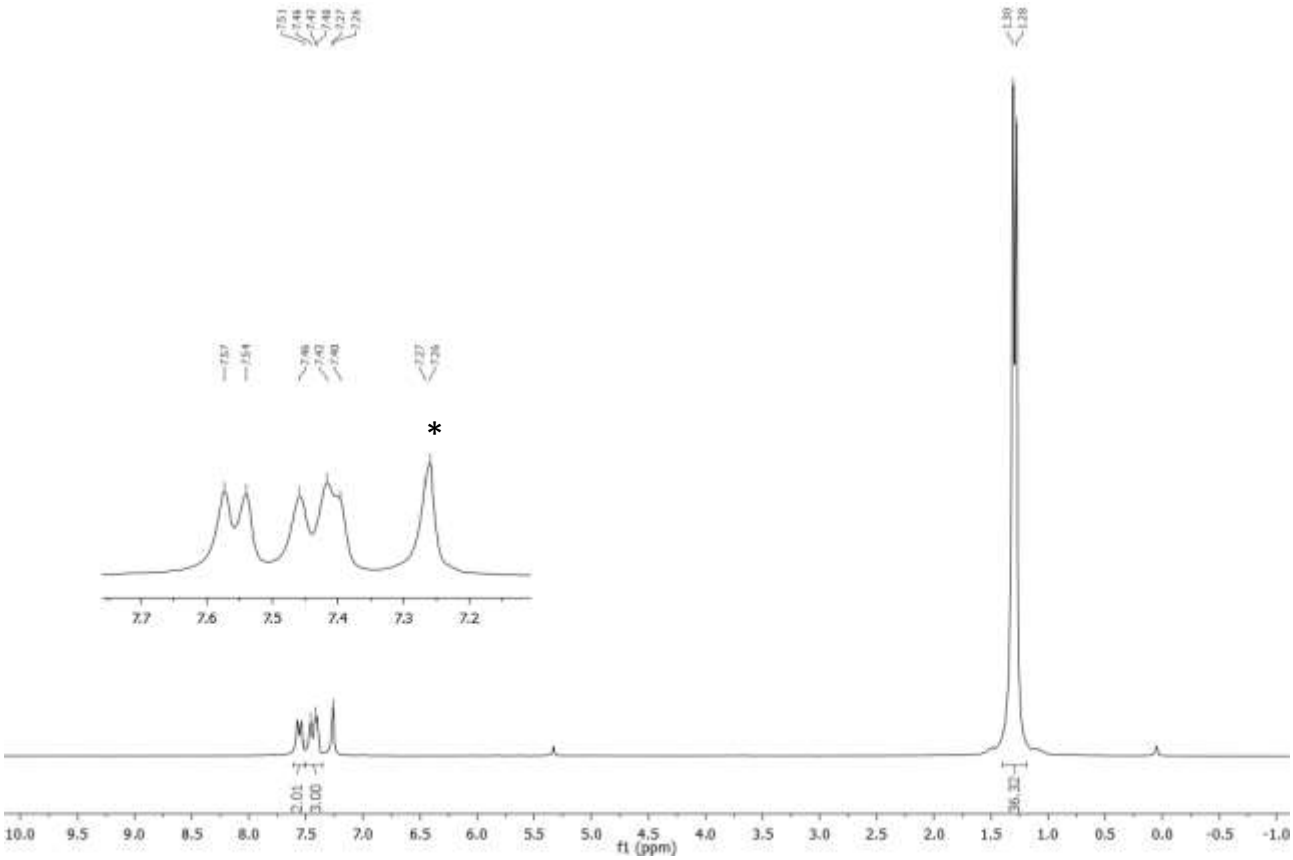


***Figure S 1**. ^{1}H NMR spectrum of **4** at -60 °C (*$CDCl_3$).*

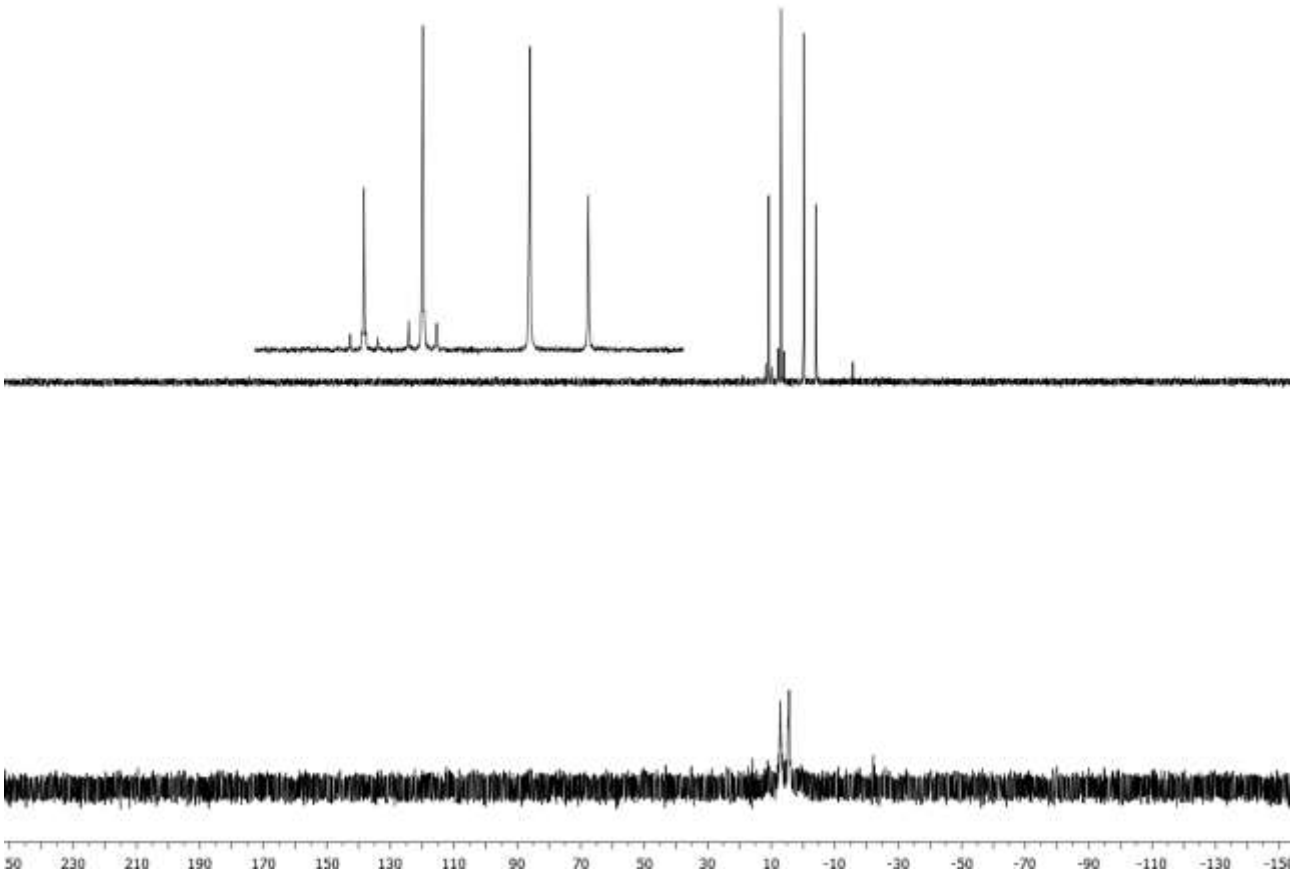


***Figure S 2**. $^{31}P\{^{1}H\}$ NMR spectrum of **4** at -60 °C (top) and 25 °C (bottom) in $CDCl_3$.*

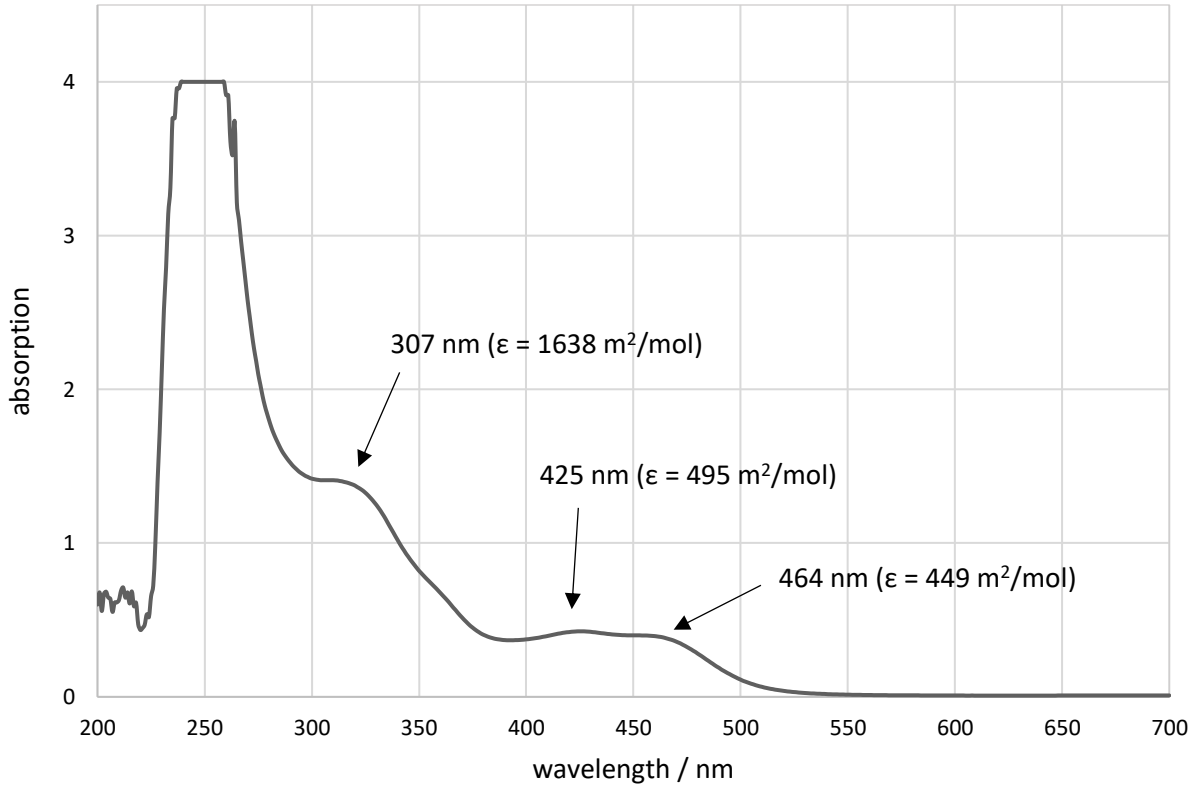


***Figure S 3**. UV/VIS spectrum of **4** in CH_2Cl_2 (c = 8.6*10^{-5} mol/L).*

VT-$^{31}P\{^{1}H\}$ NMR experiment from 1 to 4

In a 10 mL Schlenk tube complex **1** (50.7 mg, 82.4 µmol, 1.00 eq.) was dissolved in 3 mL THF and 12-crown-4 (13.0 µL, 81.3 µmol, 0.99 eq.) was added. At -100 °C *t*-BuLi (1.7 M in *n*-hexane) (0.05 mL, 85.0 µmol, 1.03 eq.) was added dropwise to the reaction solution which turned red after complete addition of *t*-BuLi. Then 0.5 mL of the reaction solution was transferred via an oven-dried steel canula into a precooled (-100 °C) Young-NMR tube. After transfer the sample was submitted immediately while keeping it at -100 °C (Figure S 4).

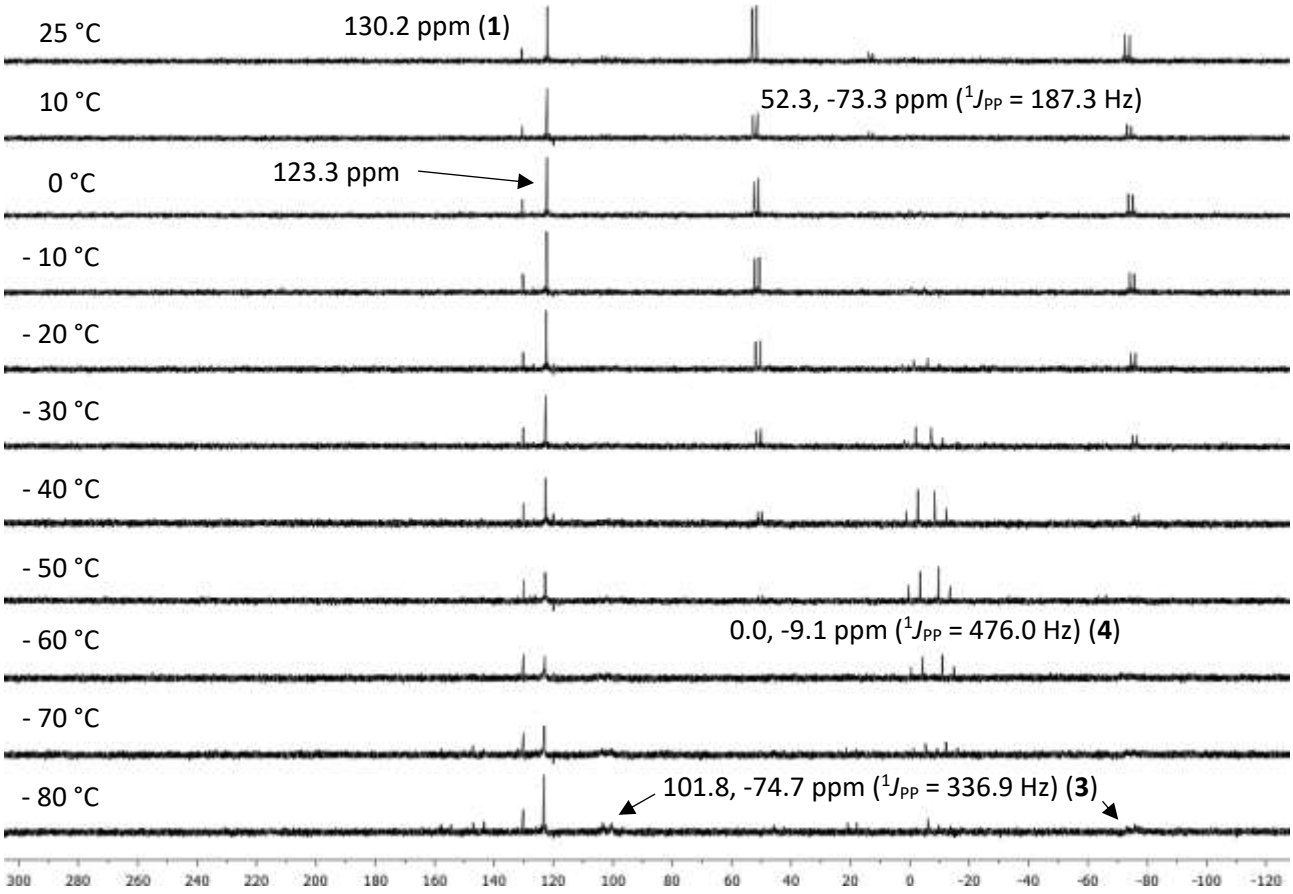
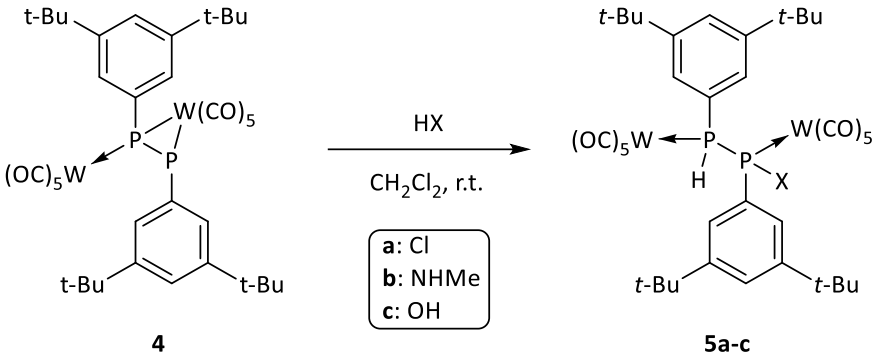


***Figure S 4**. VT-$^{31}P\{^{1}H\}$ NMR experiment from -80 °C (bottom) to 25 °C (top) in THF.*

Complexes 5a-c



***Scheme S 2**. Reaction of complex **4** with HCl, $MeNH_2$ and H_2O in CH_2Cl_2 to yield complexes **5a-c**.*

In a 10 mL Schlenk tube complex **4** (163 mg, 0.15 mmol, 1.00 eq.) was dissolved in 4 mL CH_2Cl_2 and the corresponding reagent was added as an excess. In case of H_2O the reaction was completed after two days. For the other reactions the solution was stirred for 1 h. The solvent and all volatiles were removed under reduced pressure ($5\cdot10^{-2}$ mbar) and the residue washed with *n*-pentane with some drops of Et_2O. The final products were obtained as colorless solids after drying for 2 h under reduced pressure ($5\cdot10^{-2}$ mbar). Yields: **5a** 45 % (75.9 mg, 0.08 mmol), **5b** 66 % (111 mg, 0.10 mmol), **5c** 43 % (72.0 mg, 0.06 mmol). This observation speaks for a (partially) reaction of **4** and not his *E*-isomer ***E*-4**, which can be formed by a preliminary equilibrium!

5a: ^{1}H-NMR (500.1 MHz, 298 K, C_6D_6): δ / ppm = 1.27 (s, 18H, tBu), 1.28 (s, 18H, tBu), 6.92 (dd, $^{1}J_{PH}$ = 320.7 Hz, $^{2}J_{PH}$ = 19.4 Hz, 1H, PH), 7.60 (m, 1H, *para*-H), 7.63 (m, 1H, *para*-H), 7.70 (br d, $^{3}J_{PH}$ = 12.8 Hz, 2H, *ortho*-H (PH)), 7.76 (dd, $^{3}J_{PH}$ = 13.7 Hz, $^{4}J_{HH}$ = 1.65 Hz, 2H, *ortho*-H (PCl)).

^{13}C{^{1}H}-NMR (125.8 MHz, 298 K, C_6D_6): δ / ppm = 31.2 (s, tBu), 31.2 (s, tBu), 35.3 (s, tBu), 35.4 (s, tBu), 123.6 (dd, $^{2}J_{PC}$ = 1.3 Hz, $^{3}J_{PC}$ = 15.0 Hz, *ortho*-C), 127.2 (m, *para*-C), 127.3 (m, *para*-C), 127.9 (dd, $^{2}J_{PC}$ = 2.7 Hz, $^{3}J_{PC}$ = 11.0 Hz, *ortho*-C), 152.8 (dd, $^{3}J_{PC}$ = 10.0 Hz, $^{4}J_{PC}$ = 0.7 Hz, *meta*-C), 153.0 (dd, $^{3}J_{PC}$ = 9.3 Hz, $^{4}J_{PC}$ = 1.3 Hz, *meta*-C), 195.2 (d_{sat}, $^{2}J_{PC}$ = 6.8 Hz, $^{1}J_{WC}$ = 126.4 Hz, *cis*-CO), 195.6 (d_{sat}, $^{2}J_{PC}$ = 6.1 Hz, $^{1}J_{WC}$ = 126.4 Hz, *cis*-CO), 197.9 (m, *trans*-CO).

^{31}P-NMR (202.5 MHz, 298 K, C_6D_6): δ / ppm = 15.6 (d_{sat}, $^{1}J_{WP}$ = 235.5 Hz, $^{1}J_{WP}$ = 166.2 Hz, PH), 102.0 (d_{sat}, $^{1}J_{WP}$ = 277.8 Hz, $^{1}J_{WP}$ = 166.2 Hz, PCl).

MS (LIFDI): m/z (%) = 1123.9 (100) $[M]^{+\cdot}$.

IR (ATR): ν /cm^{-1} = 2381 (w, PH), 2070 (s, CO), 2007 (w, CO), 1996 (w, CO), 1930 (vs, CO), 1906 (vs, CO).

Melting point: over 200 °C.

Elemental analysis: cal. C 40.58, H 3.85; found C 40.58, H 3.87.

5b: Isomer 1: ^{1}H-NMR (500.1 MHz, 298 K, $CDCl_3$): δ / ppm = 1.35 (s, 36H, tBu), 2.49 (qd, $^{2}J_{PH}$ = 1.7 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1H, NH), 3.10 (ddd, $^{3}J_{PH}$ = 12.9 Hz, $^{3}J_{HH}$ = 5.4 Hz, $^{4}J_{PH}$ = 2.7 Hz, 3H, NMe), 6.32 (dd, $^{1}J_{PH}$ = 320.1 Hz, $^{2}J_{PH}$ =

14.6 Hz, 1H, PH), 7.31 (dd, $^3J_{PH}$ = 12.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, *ortho*-H), 7.46 (ddd, $^3J_{PH}$ = 12.5 Hz, $^4J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 2H, *ortho*-H), 7.49 (m, 1H, *para*-H), 7.53 (m, *para*-H).

Isomer 2: ^{1}H-NMR (500.1 MHz, 298 K, $CDCl_3$): δ / ppm = 1.15 (s, 36H, tBu), 2.49 (m, 1H, NH), 3.06 (m, 3H, NMe), 6.62 (dd, $^1J_{PH}$ = 330.2 Hz, $^2J_{PH}$ = 19.3 Hz, 1H, PH), 6.98 (dd, $^3J_{PH}$ = 12.4 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, *ortho*-H), 7.08 (dm, $^3J_{PH}$ = 12.4 Hz, *ortho*-H), 7.46 (dm, $^3J_{PH}$ = 12.4 Hz, 2H, *ortho*-H), 7.30 (m, 1H, *para*-H), 7.30 (m, *para*-H).

Isomer 1: ^{13}C{^{1}H}-NMR (125.8 MHz, 298 K, $CDCl_3$): δ / ppm = 31.3 (s, tBu), 31.4 (s, tBu), 33.3 (s, NMe), 35.3 (s, tBu), 122.2 (dd, $^3J_{PC}$ = 12.6 Hz, $^2J_{PC}$ = 2.0 Hz, *ortho*-C), 125.7 (m, *para*-C), 125.9 (m, *para*-C), 127.5 (dd, $^3J_{PC}$ = 10.7 Hz, $^2J_{PC}$ = 2.4 Hz, *ortho*-C), 152.2-152.4 (m, *ipso*-C u. *meta*-C), 195.8 (d_{sat}, $^2J_{PC}$ = 7.1 Hz, $^1J_{WC}$ = 124.4 Hz, *cis*-CO), 195.9 (d_{sat}, $^2J_{PC}$ = 6.2 Hz, $^1J_{WC}$ = 125.6 Hz, *cis*-CO), 198.1 (d_{sat}, $^2J_{PC}$ = 25.0 Hz, *trans*-CO), 198.6 (d_{sat}, $^2J_{PC}$ = 6.2 Hz, *trans*-CO).

Isomer 2: ^{13}C{^{1}H}-NMR (125.8 MHz, 298 K, $CDCl_3$): δ / ppm = 31.3 (s, tBu), 31.3 (s, tBu), 35.1 (s, tBu), 124.0 (d, $^3J_{PC}$ = 13.0 Hz, *ortho*-C), 124.6 (m, *para*-C), 125.7 (m, *ortho*-C), 130.3 (dd, $^1J_{PC}$ = 34.8 Hz, $^2J_{PC}$ = 3.8 Hz, *ipso*-C), 138.0 (dd, $^1J_{PC}$ = 41.7 Hz, $^2J_{PC}$ = 14.3 Hz, *ipso*-C).

Isomer 1: ^{31}P-NMR (202.5 MHz, 298 K, $CDCl_3$): δ / ppm = -14.0 (d_{sat}, $^1J_{PP}$ = 153.5 Hz, $^1J_{WP}$ = 216.4 Hz, $^1J_{PH}$ = 320.1 Hz, PH), 67.1 (d_{sat}, $^1J_{PP}$ = 153.5 Hz, $^1J_{WP}$ = 266.0 Hz, P-N).

Isomer 2: ^{31}P-NMR (202.5 MHz, 298 K, $CDCl_3$): δ / ppm = -10.0 (d_{sat}, $^1J_{PP}$ = 201.2 Hz, $^1J_{WP}$ = 212.8 Hz, $^1J_{PH}$ = 330.2 Hz, PH), 66.3 (d_{sat}, $^1J_{PP}$ = 201.3 Hz, $^1J_{WP}$ = 260.4 Hz, P-N).

MS (+ESI): m/z (%) = 1119.172 (2) $[M]^{+\cdot}$, (-ESI) m/z = 1118.163 (100) $[M-H]^{-\cdot}$.

IR (ATR): ν /cm^{-1} = 3432 (w, NH), 2306 (w, PH), 2066 (s, CO), 1981 (w, CO), 1907 (vs, CO).

Melting point: 184-186 °C.

Elemental analysis: cal. C 41.85, H 4.23, N 1.25; found C 41.73, H 4.37, N 1.26.

5c: ^{1}H-NMR (500.1 MHz, 298 K, $CDCl_3$): δ /ppm = 1.33 (s, 18H, tBu), 1.35 (s, 18H, tBu), 3.65 (br s, 1H, OH), 6.23 (dd, $^1J_{PH}$ = 327.0 Hz, $^2J_{PH}$ = 16.0 Hz, 1H, PH), 7.36 (d, $^3J_{PH}$ = 12.9 Hz, 2H, *ortho*-H), 7.38 (d, $^3J_{PH}$ = 12.9 Hz, 2H, *ortho*-H), 7.55 (br s, 1H, *para*-H), 7.56 (br s, 1H, *para*-H).

^{13}C{^{1}H}-NMR (125.8 MHz, 298 K, $CDCl_3$): δ / ppm = 31.3 (s, tBu), 31.4 (s, tBu), 122.1 (dd, $^2J_{PC}$ = 14.6 Hz, $^3J_{PC}$ = 2.1 Hz, *ortho*-C), 122.1 (dd, $^2J_{PC}$ = 14.6 Hz, $^3J_{PC}$ = 2.1 Hz, *ortho*-C), 126.6 (s, *para*-C), 127.3 (dd, $^2J_{PC}$ = 11.1 Hz, $^3J_{PC}$ = 2.6 Hz, *ortho*-C), 129.0 (dd, $^1J_{PC}$ = 33.4 Hz, $^2J_{PC}$ = 3.3 Hz, *ipso*-C), 138.3 (dd, $^1J_{PC}$ = 33.3 Hz, $^2J_{PC}$ = 9.3 Hz, *ipso*-C), 152.1 (dd, $^3J_{PC}$ = 10.1 Hz, $^4J_{PC}$ = 1.5 Hz, *meta*-C), 152.6 (d, $^3J_{PC}$ = 9.3 Hz, *meta*-C), 195.2 (d_{sat}, $^1J_{WC}$ = 126.1 Hz, $^2J_{PC}$ = 7.6 Hz, *cis*-CO), 195.2 (d_{sat}, $^1J_{WC}$ = 125.6 Hz, $^2J_{PC}$ = 6.6 Hz, *cis*-CO), 198.0 (d, $^2J_{PC}$ = 25.6 Hz, *trans*-CO), 198.1 (d, $^2J_{PC}$ = 30.2 Hz, *trans*-CO).

^{31}P-NMR (202.5 MHz, 298 K, $CDCl_3$): δ / ppm = 0.2 (ddt_{sat}, $^1J_{PH}$ = 327.0 Hz, $^1J_{PP}$ = 144.7 Hz, $^1J_{WP}$ = 222.8 Hz, $^3J_{PH}$ = 12.9 Hz, PH), 115.9 (dtd_{sat}, $^1J_{PP}$ = 144.7 Hz, $^2J_{PH}$ = 16.0 Hz, $^1J_{WP}$ = 279.2 Hz, $^3J_{PH}$ = 12.9 Hz, POH).

MS (-ESI): m/z (%) = 1105.132 (100) $[M-H]^{-\cdot}$.

IR (ATR): ν /cm^{-1} = 3495 (m, OH), 2372 (w, PH), 2068 (s, CO), 1917 (vs, CO).

Melting point: over 200 °C.

Elemental analysis: cal. C 41.25, H 4.01; found C 41.35, H 3.92.

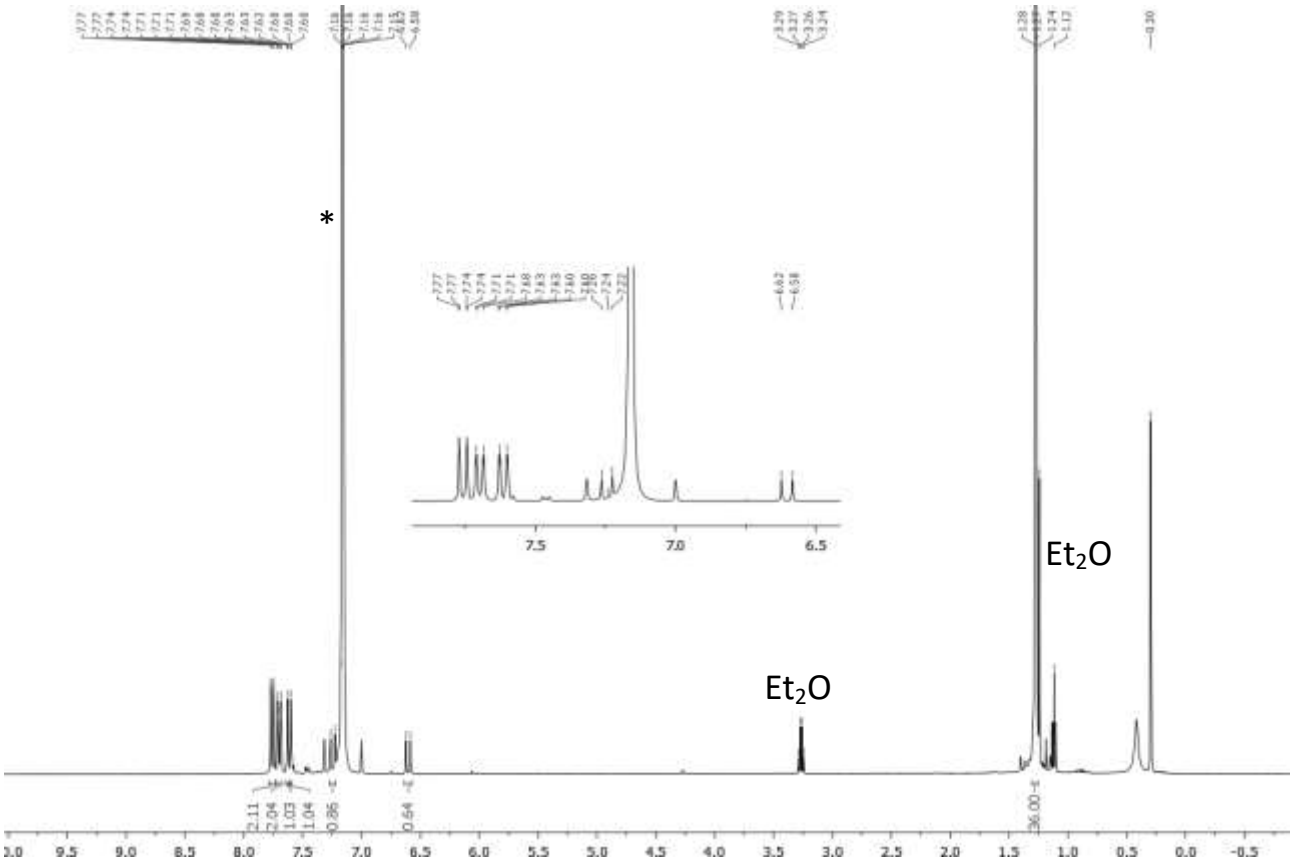


***Figure S 5**. [1]H NMR spectrum of **5a** (*C_6D_6).*

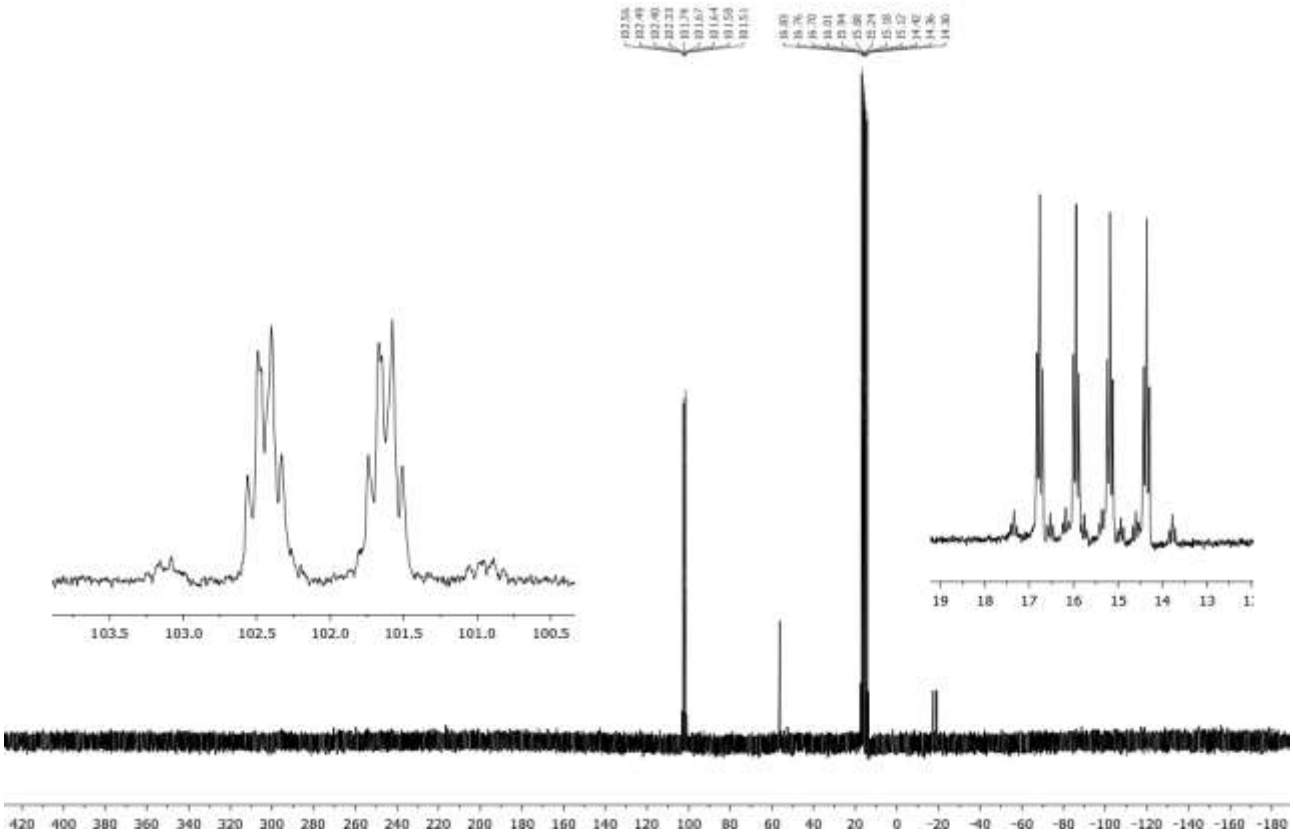


***Figure S 6**. [31]P NMR spectrum of **5a** in C_6D_6.*

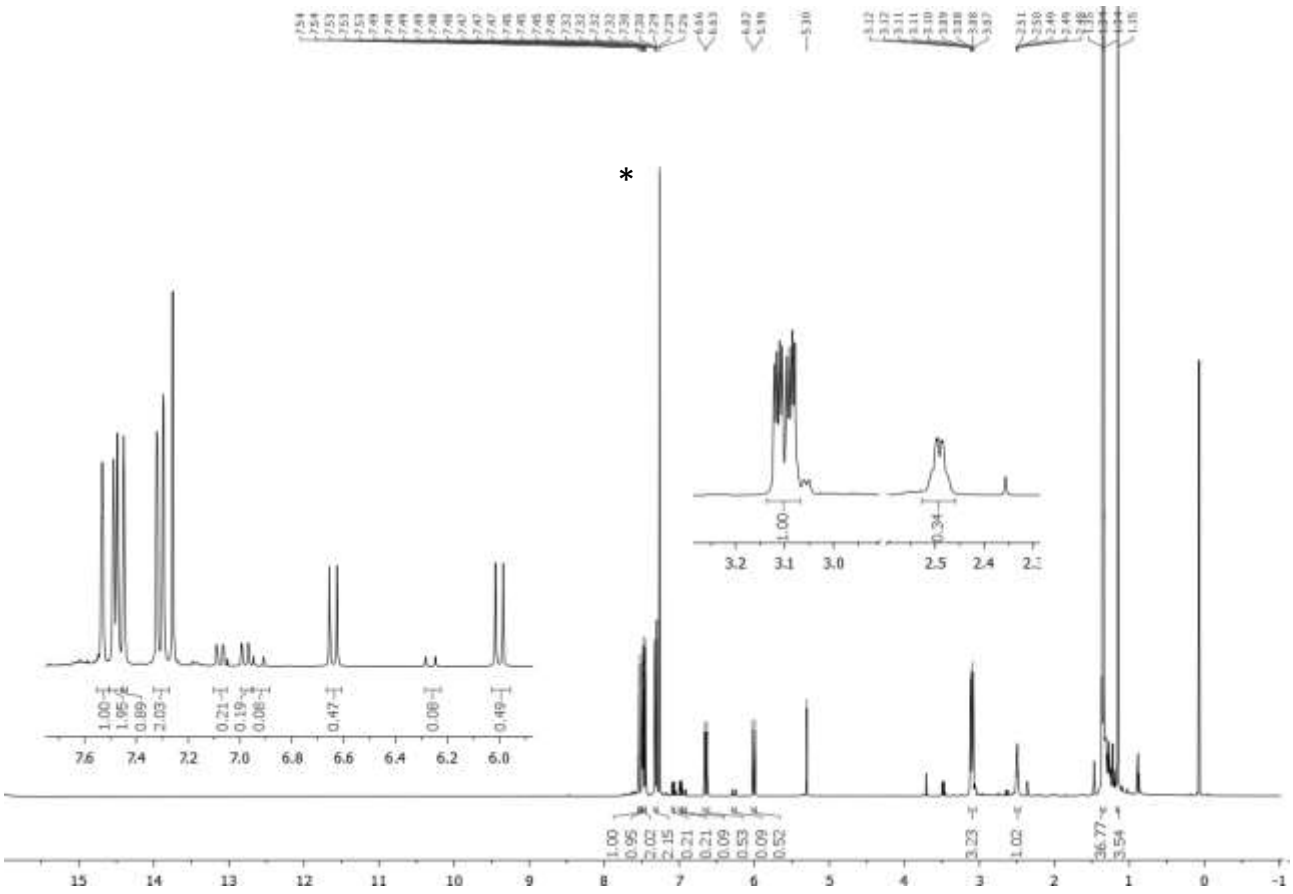


***Figure S 7**. ^{1}H NMR spectrum of **5b** (*$CDCl_3$).*

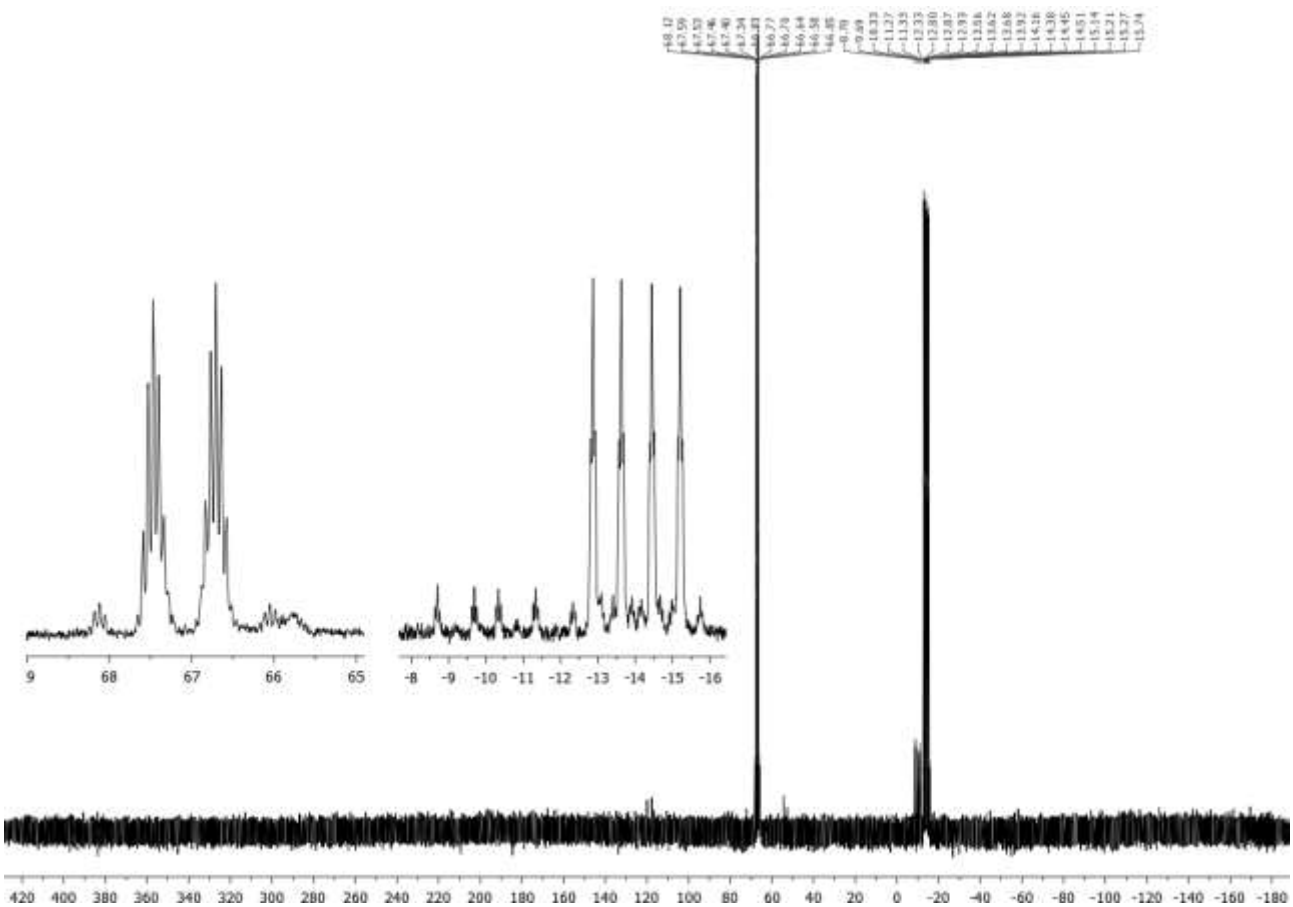


***Figure S 8**. ^{31}P NMR spectrum of **5b** in $CDCl_3$.*

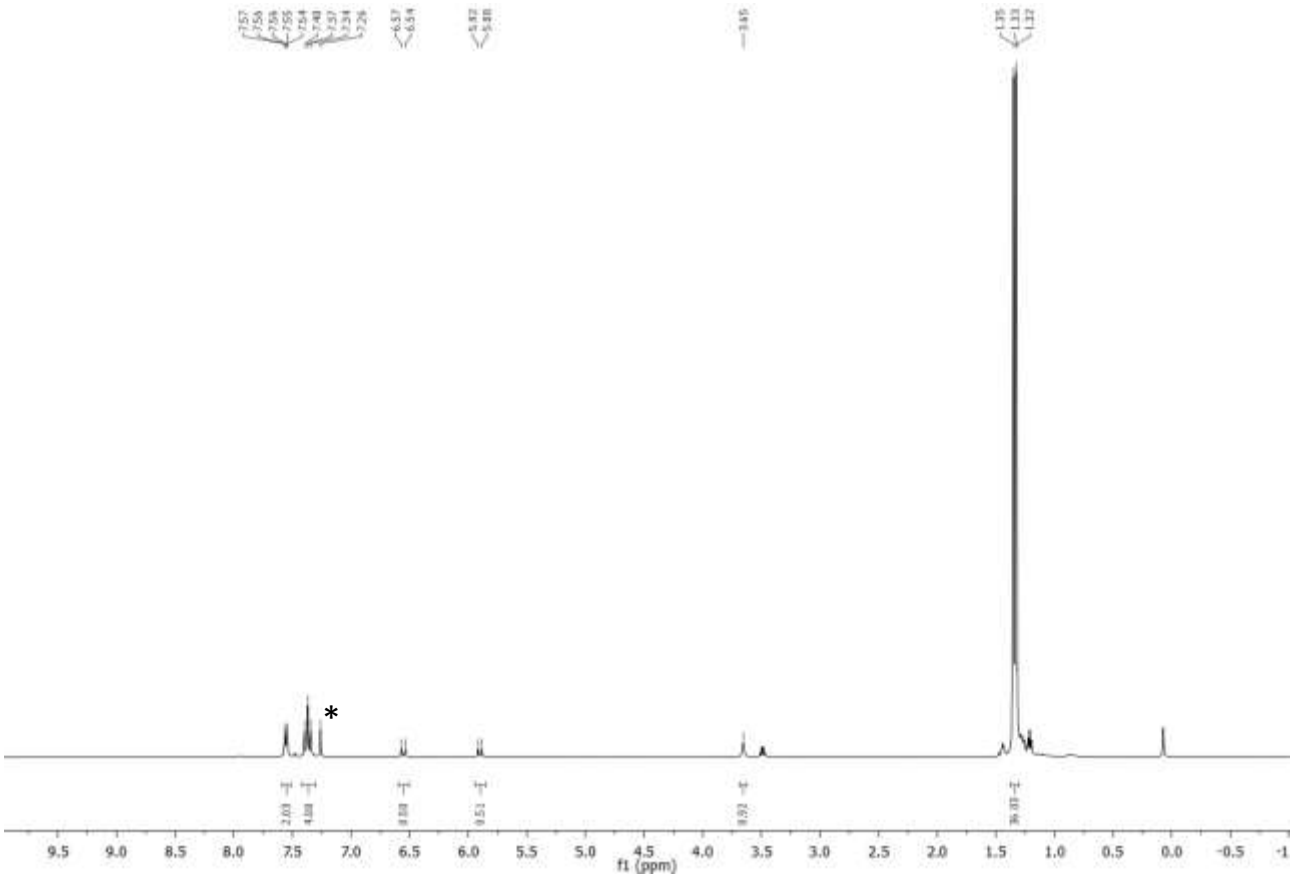


Figure S 9. *^{1}H NMR spectrum of **5c** (*$CDCl_3$).*

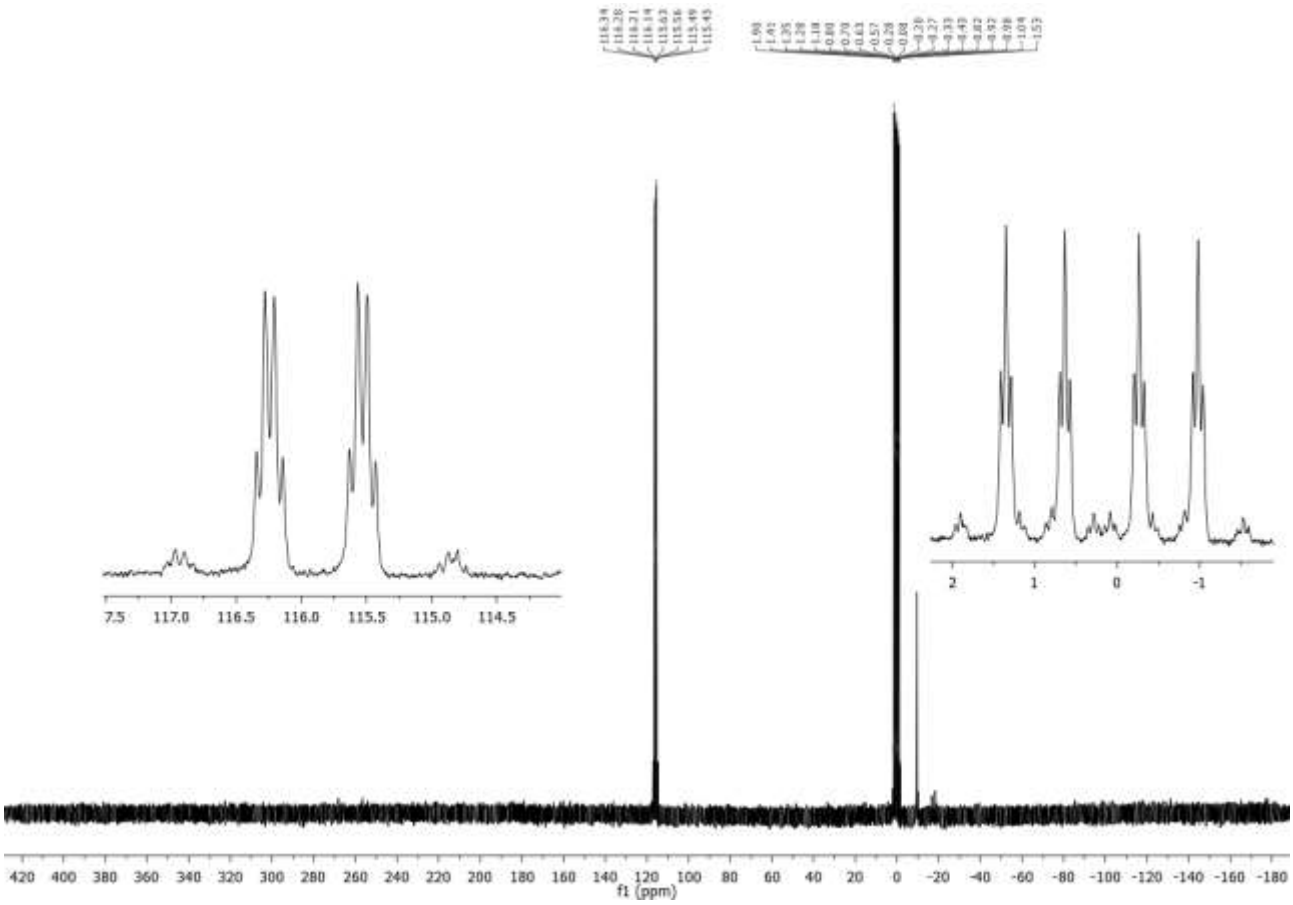
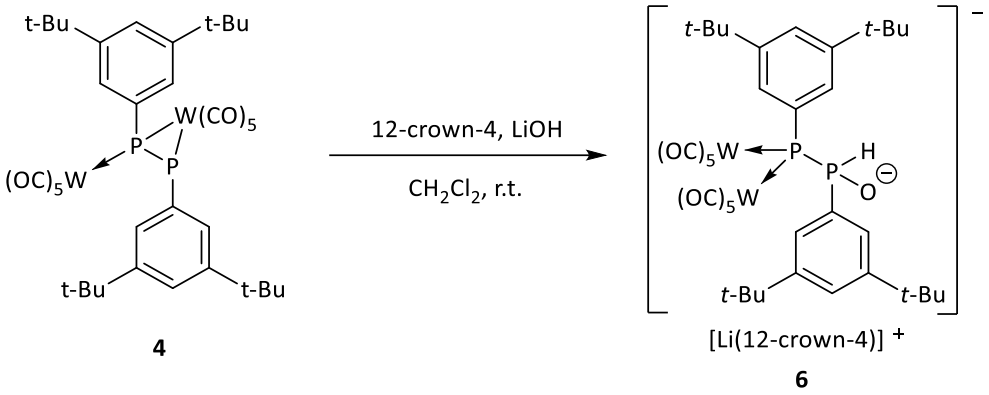


Figure S 10. *^{31}P NMR spectrum of **5c** in $CDCl_3$.*

Complex 6



***Scheme S 3**. Reaction of complex **4** with LiOH in presence of 12-crown-4 in CH_2Cl_2 to yield complex **6**.*

In a 10 mL Schlenk tube complex **4** (163 mg, 0.15 mmol, 1.00 eq.) was dissolved in 4 mL CH_2Cl_2 and 12-crown-4 (24 µL, 0.15 mmol. 1.00 eq.) and LiOH (35.9 mg, 1.50 mmol, 10.0 eq.) was added as an excess. The reaction solution was stirred for 1 h. The solvent was removed under reduced pressure ($5\cdot10^{-2}$ mbar) and the residue was extracted with Et_2O. The product **6** was obtained in 36 % yield (69.6 mg, 0.05 mmol) as a yellow powder after drying for 2 h under reduced pressure ($5\cdot10^{-2}$ mbar).

^{1}H-NMR (500.1 MHz, 298 K, THF-d_8): δ / ppm = 1.14 (s, 18H, tBu), 1.34 (s, 18H, tBu), 3.63 (s, 16H, Krone), 7.24 (dd, $^{3}J_{PH}$ = 13.3 Hz, $^{4}J_{HH}$ = 1.8 Hz, 2H, *ortho*-H), 7.35 (m, 1H, *para*-H), 7.51 (m, 1H, *para*-H), 7.90 (d, $^{3}J_{PH}$ = 10.8 Hz, 2H, *ortho*-H), 8.04 (dd, $^{1}J_{PH}$ = 442.3 Hz, $^{2}J_{PH}$ = 32.7 Hz, 1H, PH).

^{13}C{^{1}H}-NMR (125.8 MHz, 298 K, THF-d_8): δ / ppm = 31.8 (s, tBu), 32.0 (s, tBu), 35.8 (s, tBu), 36.0 (s, tBu), 71.0 (s, Krone), 123.2 (s, *para*-C), 126.2 (d, $^{2}J_{PC}$ = 10.8 Hz, *ortho*-C), 127.4 (d, $^{4}J_{PC}$ = 2.6 Hz, *para*-C), 131.8 (dd, $^{2}J_{PC}$ = 6.7 Hz, $^{3}J_{PC}$ = 10.9 Hz, *ortho*-C), 134.6 (d, $^{1}J_{PC}$ = 75.3 Hz, *ipso*-C), 139.0 (s, $^{1}J_{PC}$ = 6.8 Hz, *ipso*-C), 150.9 (d, $^{3}J_{PC}$ = 7.6 Hz, *meta*-C), 151.8 (d, $^{3}J_{PC}$ =11.3 Hz, *meta*-C), 200.8 (m, *cis*-CO), 201.1 (m, *cis*-CO), 202.2 (m, *trans*-CO), 202.3 (m, *trans*-CO).

^{31}P-NMR (202.5 MHz, 298 K, THF-d_8): δ / ppm = -73.6 (ddt$_{sat}$, $^{1}J_{PP}$ = 188.2 Hz, $^{2}J_{PH}$ = 32.7 Hz, $^{3}J_{PH}$ = 10.8 Hz, $^{1}J_{WP}$ = 166.0 Hz, PW), 52.2 (ddt, $^{1}J_{PP}$ = 188.2 Hz, $^{1}J_{PH}$ = 442.3 Hz, $^{3}J_{PH}$ = 13.3 Hz, PH).

^{7}Li-NMR (194.4 MHz, 298 K, THF-d_8) δ / ppm = -0.29.

MS (-ESI): m/z (%) = 1105.120 (100) $[M\text{-}Li([12]Krone\text{-}4)]^{-\cdot}$, (+ESI) m/z (%) = 199.094 (100) $[Na([12]Krone\text{-}4)]^{+\cdot}$.

IR (ATR): ν /cm^{-1} = 2354 (w, PH), 2065 (m, CO), 2052 (m, CO), 1917 (vs, CO).

Melting point: over 200 °C.

Elemental analysis: cal. C 41.94, H 3.89; found C 41.35, H 3.95.

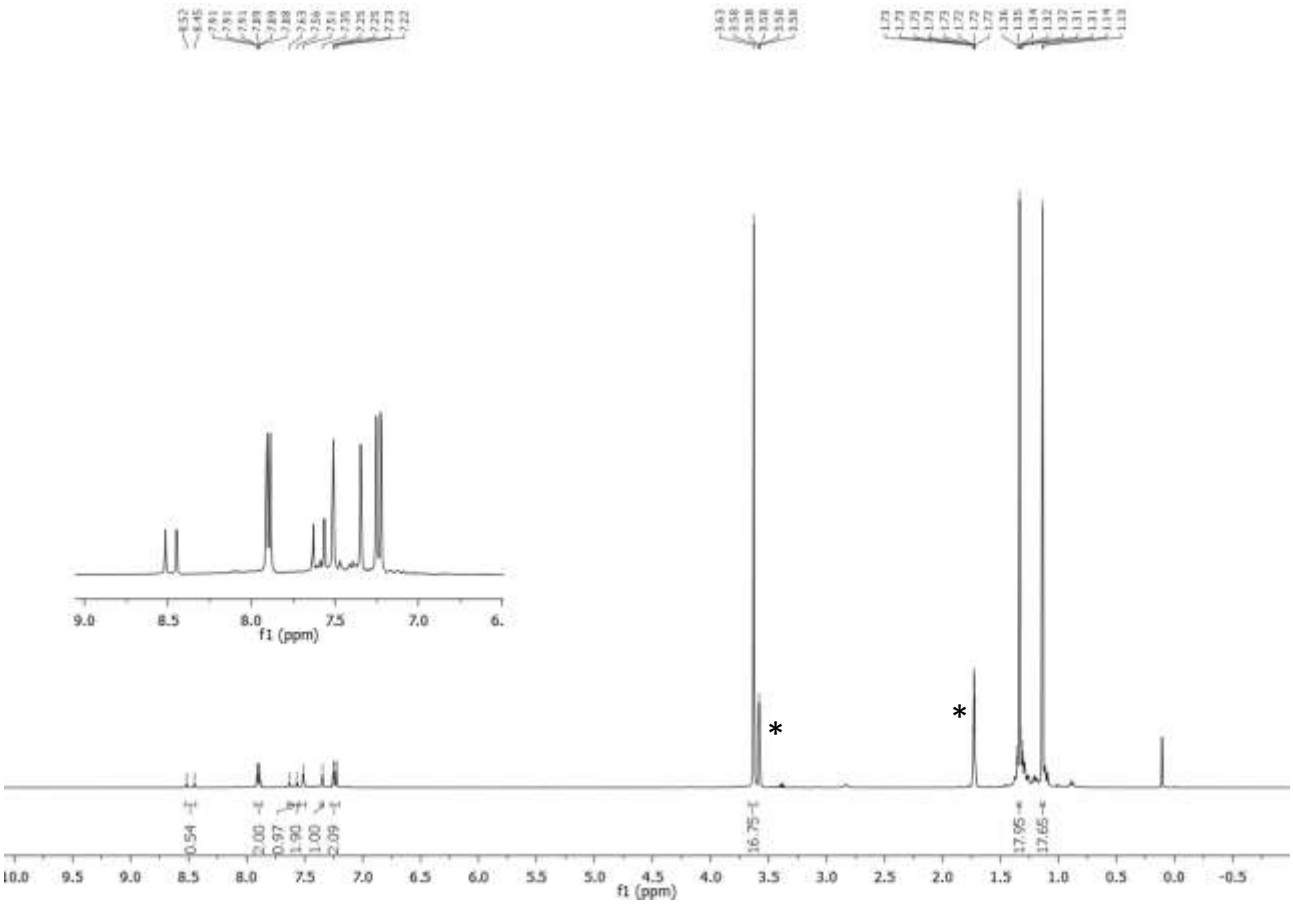


Figure S 11. *^{1}H NMR spectrum of **6** (*THF-d_8).*

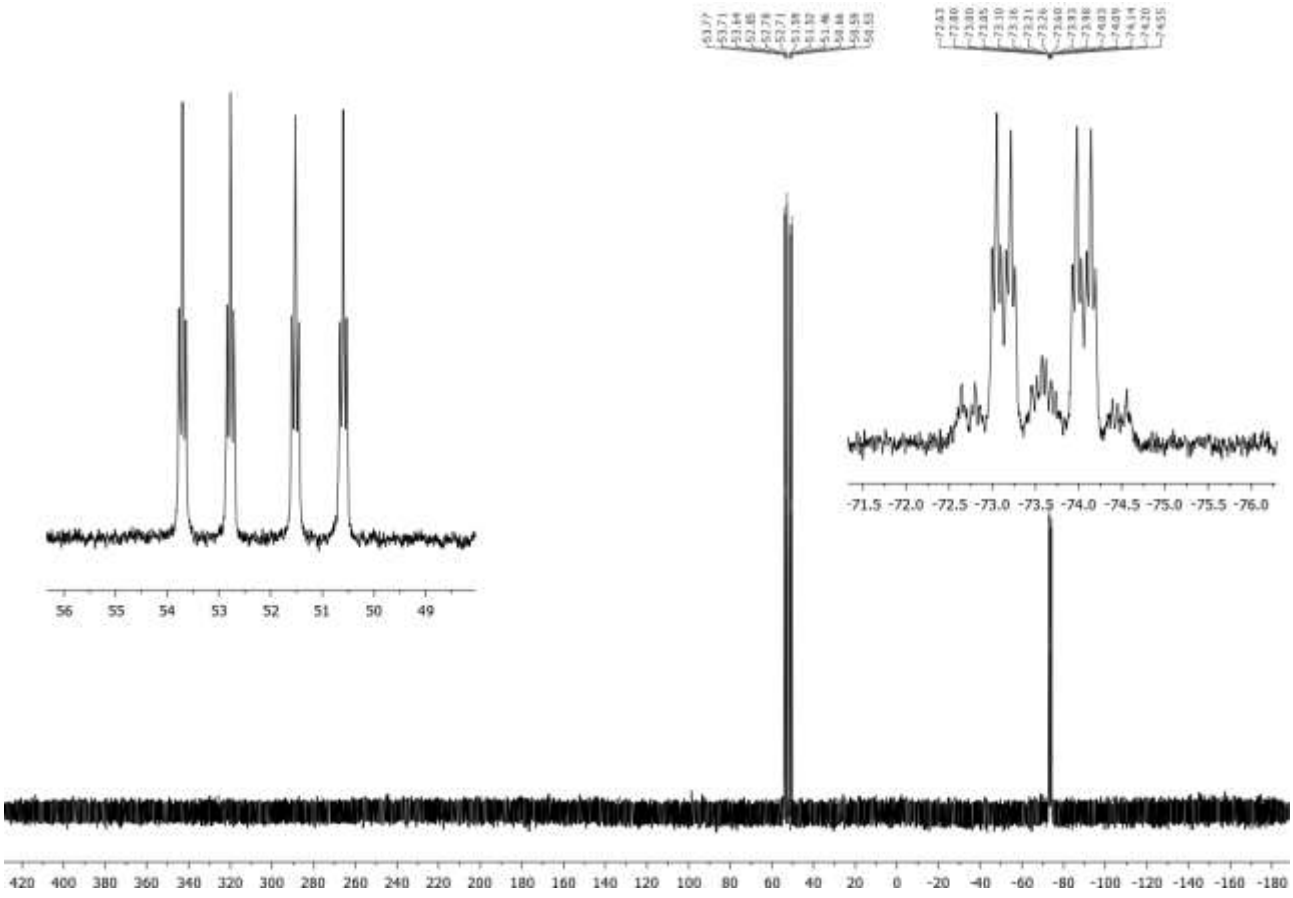
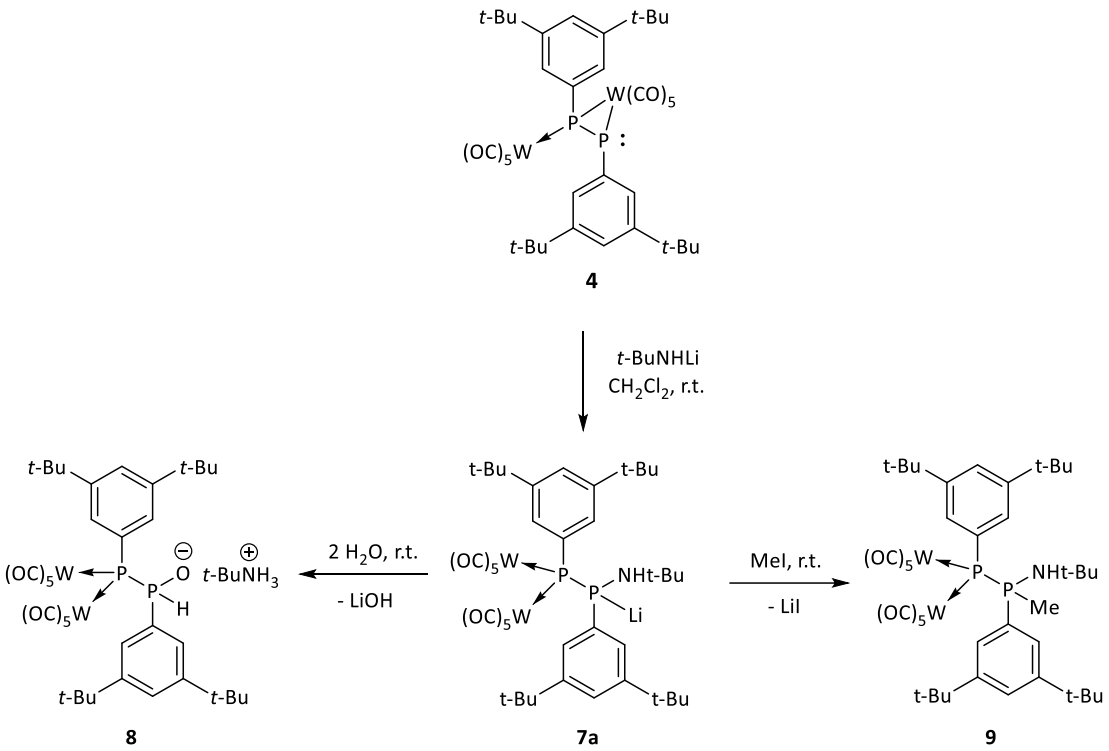


Figure S 12. *^{31}P NMR spectrum of **6** in THF-d_8.*

Complex 7a, 8 and 9



***Scheme S 4**. Reaction of complex **4** with t-BuNHLi in CH_2Cl_2 to yield complex **7a**. Hydrolysis of **7a** yielded complex **8**. Trapping reaction of **7a** with MeI to yield complex **9**.*

In a 10 mL Schlenk tube complex **4** (163 mg, 0.15 mmol, 1.00 eq.) was dissolved in 4 mL CH_2Cl_2 and *t*-BuNHLi (23.7 mg, 0.30 mmol. 2.00 eq.) was added as an excess. The reaction solution was stirred for 1 h and NMR sample was taken (see NMR). Then the solvent was removed under reduced pressure ($5 \cdot 10^{-2}$ mbar) and the residue was extracted with Et_2O. After removal of the solvent the crude product was washed with *n*-pentane (2 * 1 mL). After drying for 2 h under reduced pressure ($5 \cdot 10^{-2}$ mbar) the hydrolysis product **8** was obtained as colorless solid in 41 % yield (72.5 mg, 0.06 mmol).

^{1}H-NMR (400.1 MHz, 298 K, $CDCl_3$): δ /ppm = 1.11 (s, 18H, tBu), 1.32 (s, 18H, tBu), 1.51 (s, 9H, tBuN), 7.03 (d, $^{3}J_{PH}$ = 13.1 Hz, 2H, *ortho*-H), 7.33 (br s, 1H, *para*-H), 7.43 (br s, 1H, *para*-H), 7.51 (br s, 3H, NH_3), 7.74 (d, $^{3}J_{PH}$ = 10.3 Hz, 2H, *ortho*-H), 8.39 (dd, $^{1}J_{PH}$ = 449.8 Hz, $^{2}J_{PH}$ = 24.0 Hz, 1H, PH).

^{13}C{^{1}H}-NMR (100.6 MHz, 298 K, $CDCl_3$): δ / ppm = 28.1 (s, tBuN), 31.4 (s, tBu), 31.6 (s, tBu), 35.1 (s, tBu), 35.3 (s, tBu), 54.3 (s, tBuN), 123.1 (s, *para*-C), 124.8 (d, $^{2}J_{PC}$ = 10.8 Hz, *ortho*-C), 126.6 (s, *para*-C), 131.3 (m, *ortho*-C), 127.3 (dd, $^{2}J_{PC}$ = 11.1 Hz, $^{3}J_{PC}$ = 2.6 Hz, *ortho*-C), 150.4 (d, $^{3}J_{PC}$ = 7.4 Hz, *meta*-C), 151.0 (d, $^{3}J_{PC}$ = 11.5 Hz, *meta*-C), 199.6 (m, *cis*-CO), 200.8 (m, *cis*-CO), 201.4 (d, $^{2}J_{PC}$ = 15.9 Hz, *trans*-CO), 202.4 (d, $^{2}J_{PC}$ = 14.4 Hz, *trans*-CO).

^{31}P-NMR (162.0 MHz, 298 K, $CDCl_3$): δ / ppm = -77.2 (dm_{sat}, $^{1}J_{PP}$ = 188.5 Hz, $^{1}J_{WP}$ = 165.7 Hz, PW), 47.5 (ddt, $^{1}J_{PP}$ = 188.5 Hz, $^{1}J_{PH}$ = 449.2 Hz, $^{3}J_{PH}$ = 13.0 Hz, PH).

MS (EI, 70 eV): m/z (%) = 1104.9 (0.4) $[M\text{-}tBuNH_3]^+$, 490.0 (100) $[M\text{-}tBuNH_3\text{-}W(CO)5\text{-}Ar]^+$.

IR (ATR Diamant): ν /cm^{-1} = 3302 (w, NH), 3254 (w, NH), 3196 (w, NH), 2307 (w, PH), 2067 (m, CO), 2053 (s, CO), 1896 (vs, CO), 1864 (vs, CO).

Melting point: 128 °C.

Elemental analysis: cal. C 42.72, H 4.70, N 1.19; found C 42.10, H 5.18, 1.27.

With a different approach complex **7a** was trapped with MeI at ambient temperature (19 µL, 0.30 mmol, 2.00 eq.) to yield complex **9**. The solvent was removed under reduced pressure (5·10^{-2} mbar) and the residue was extracted with *n*-pentane. After removal of the solvent the crude product was washed with *n*-pentane (3 * 2 mL). After drying for 2 h under reduced pressure (5·10^{-2} mbar) the complex **9** was obtained as colorless solid in 52 % yield (91.7 mg, 0.08 mmol).

^{1}H-NMR (400.1 MHz, 298 K, C_6D_6): δ /ppm = 0.94 (s, 9H, tBuN), 1.09 (s, 18H, tBu), 1.35 (s, 18H, tBu), 2.15 (dd, $^{3}J_{PH}$ = 11.4 Hz, $^{2}J_{PH}$ = 3.6 Hz, 3H, CH_3), 3.10 (d, $^{2}J_{PH}$ = 9.2 Hz, 1H, NH), 7.24 (dd, $^{3}J_{PH}$ = 13.2 Hz, $^{4}J_{HH}$ = 1.7 Hz, 2H, *ortho*-H), 7.47 (m, 1H, *para*-H), 7.54 (m, 1H, *para*-H), 8.05 (dd, $^{3}J_{PH}$ = 11.2 Hz, $^{4}J_{HH}$ = 1.7 Hz, $^{4}J_{PH}$ = 1.7 Hz, 2H, *ortho*-H).

^{13}C{^{1}H}-NMR (100.6 MHz, 298 K, C_6D_6): δ / ppm = 14.7 (dd, $^{1}J_{PC}$ = 50.3 Hz, $^{2}J_{PC}$ = 6.7 Hz, PCH_3), 31.1 (s, tBu), 31.6 (s, tBu), 32.0 (d, $^{3}J_{PC}$ = 3.4 Hz, tBuN), 35.2 (s, tBu), 35.5 (s, tBu), 56.5 (d, $^{2}J_{PC}$ = 10.8 Hz, NtBu), 124.6 (s, *para*-C), 126.4 (d, $^{2}J_{PC}$ = 10.5 Hz, *ortho*-C), 128.4 (s, *para*-C), 132.0 (dd, $^{2}J_{PCs}$ = 5.6 Hz, $^{3}J_{PC}$ = 12.8 Hz, *ortho*-C), 151.2 (dd, $^{3}J_{PC}$ = 7.7 Hz, $^{4}J_{PC}$ = 1.6 Hz, *meta*-C), 151.2 (dd, $^{3}J_{PC}$ = 11.8 Hz, *meta*-C), 199.7 (m, *cis*-CO), 200.3 (m, *trans*-CO).

^{31}P-NMR (162.0 MHz, 298 K, C_6D_6): δ / ppm = -28.7 (br d_{sat}, $^{1}J_{PP}$ = 290.3 Hz, $^{1}J_{WP}$ = 171.5 Hz, PW), 42.3 (d, $^{1}J_{PP}$ = 290.3 Hz, PN).

MS (LIFDI): m/z (%) = 1174.9 (100) $[M]^{+\cdot}$.

IR (ATR): ν /cm^{-1} = 3387 (w, NH), 2966 (m, CH), 2069 (s, CO), 2056 (s, CO), 1975 (m, CO), 1892 (vs, CO).

Melting point: 88-92 °C.

Elemental analysis: cal. C 43.94, H 4.72, N 1.19; found C 43.91, H 4.75, N 1.08.

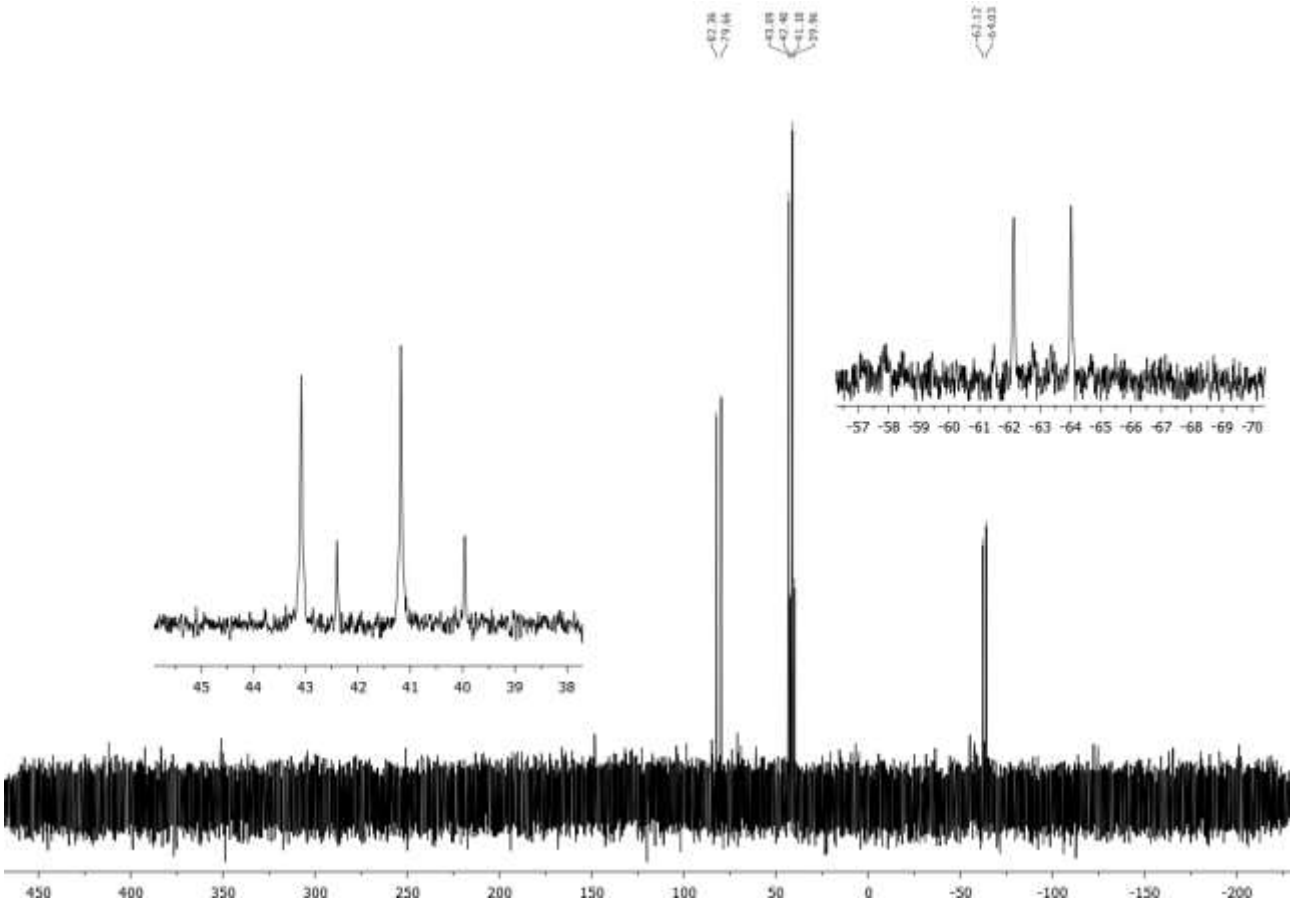


Figure S 13. *$^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution towards complex **7a** and **7b** in CH_2Cl_2.*

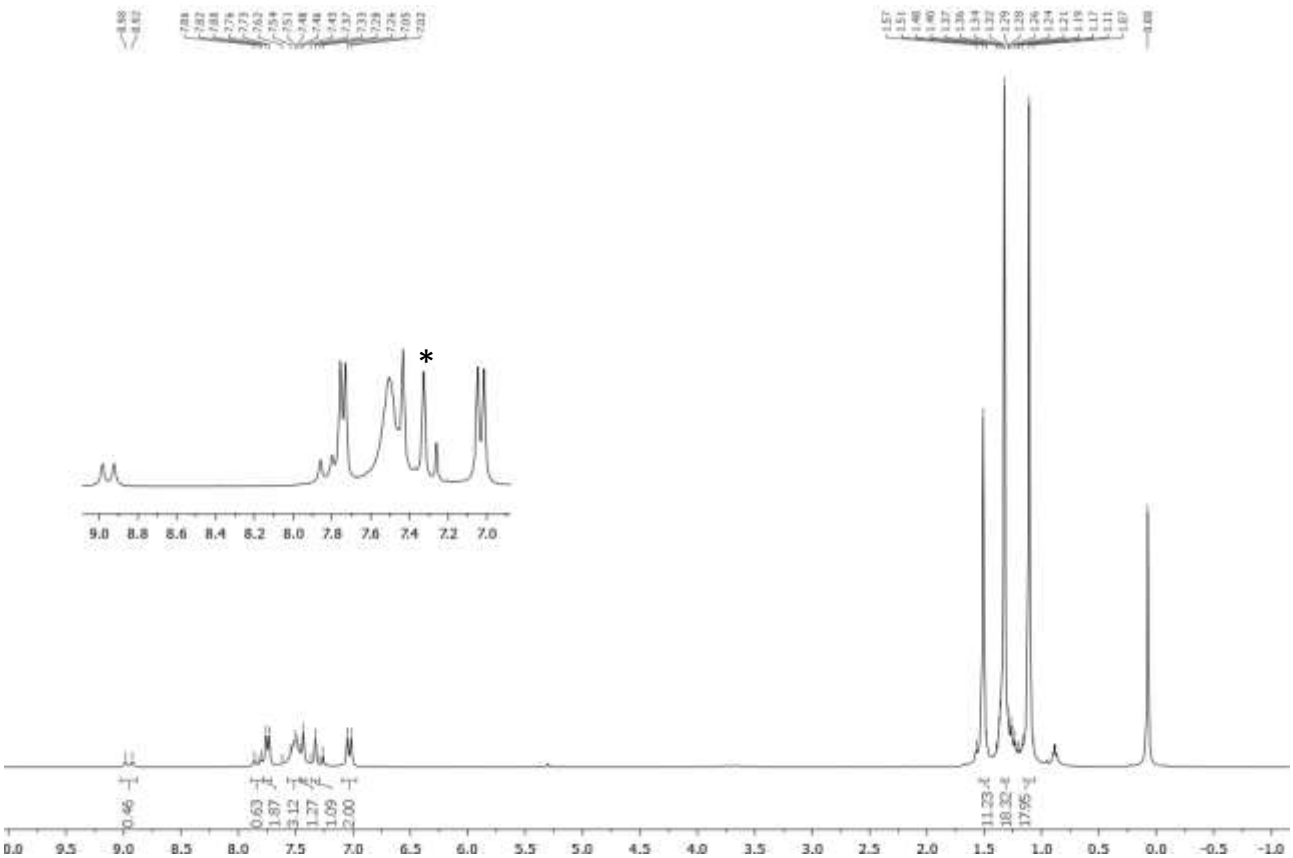


Figure S 14. *^{1}H NMR spectrum of **8** (*$CDCl_3$).*

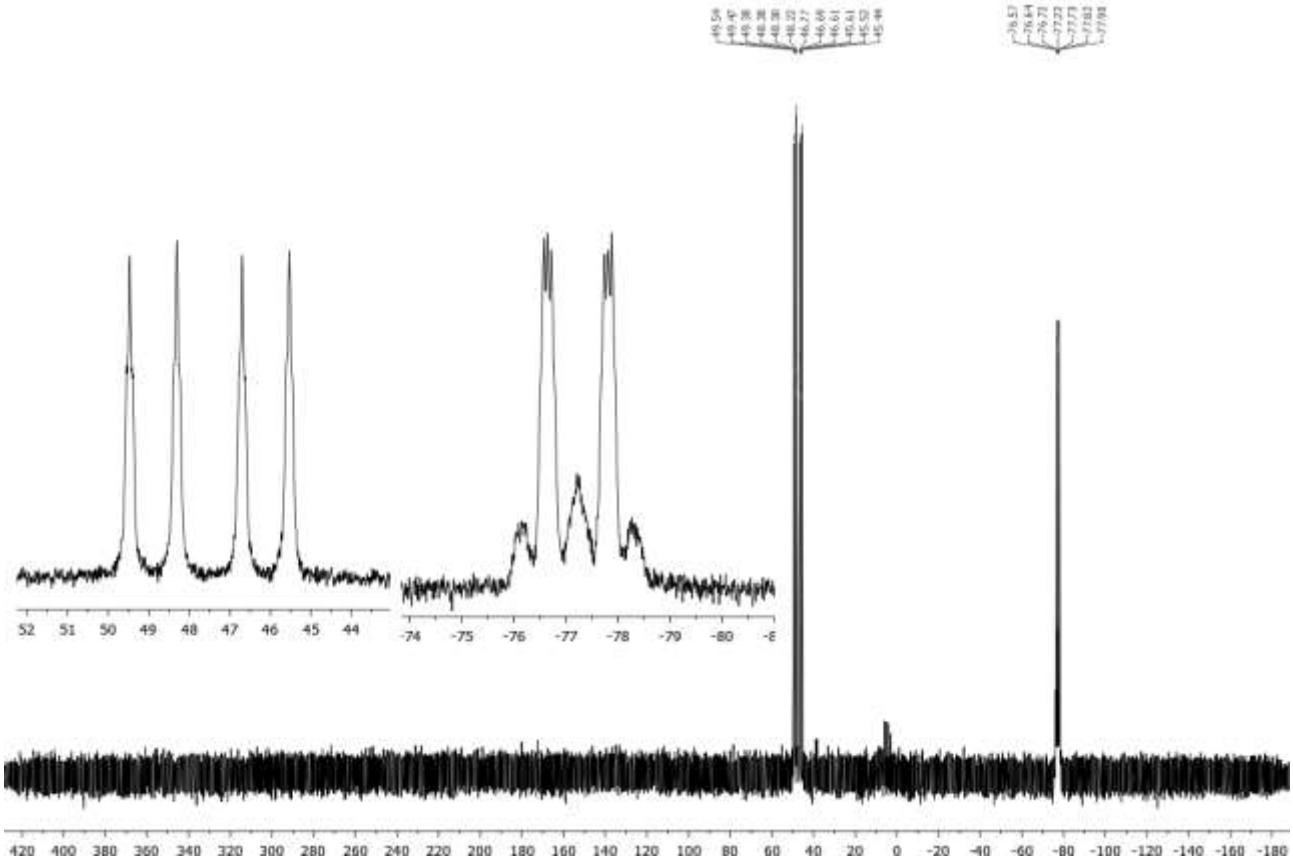


Figure S 15. *^{31}P NMR spectrum of **8** in $CDCl_3$.*

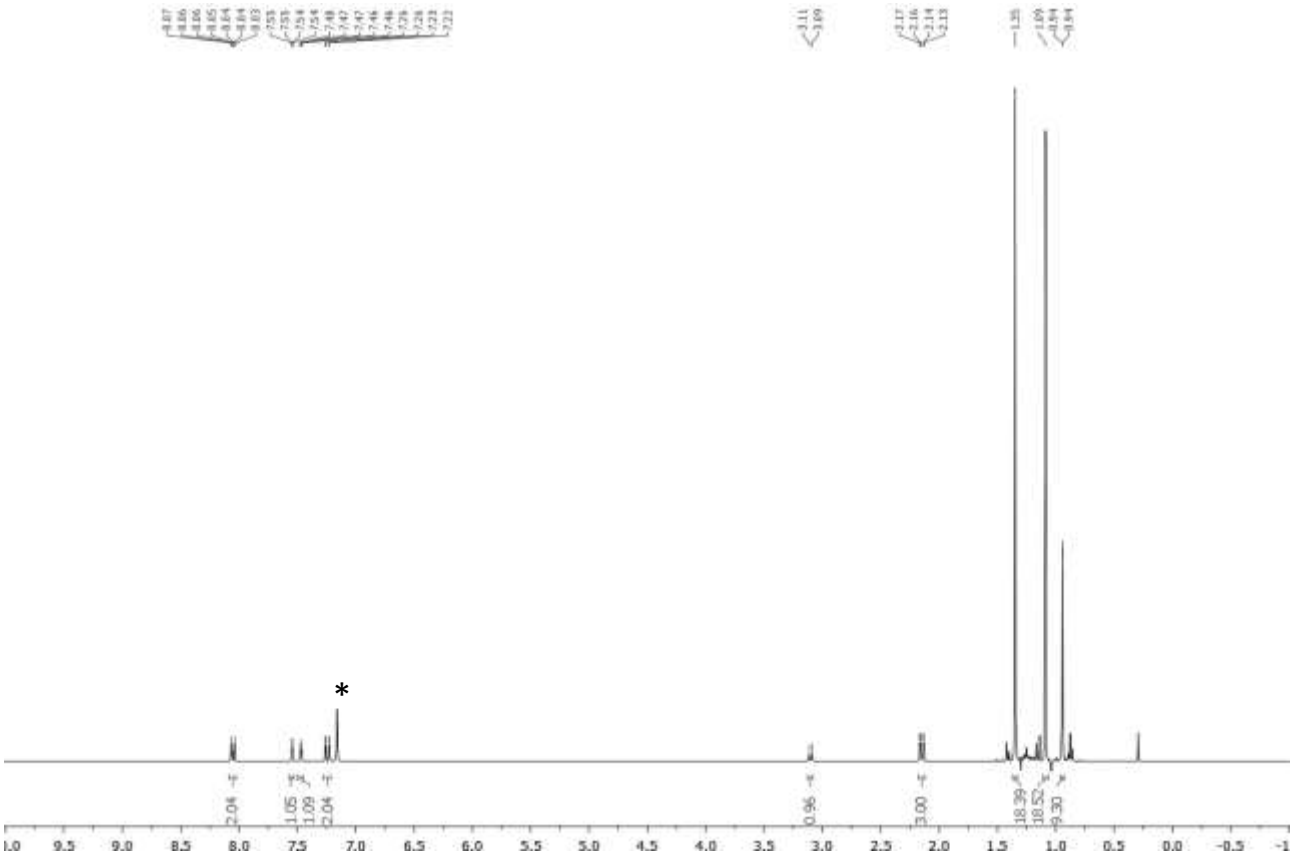


Figure S 16. *^{1}H NMR spectrum of **9** (*C_6D_6).*

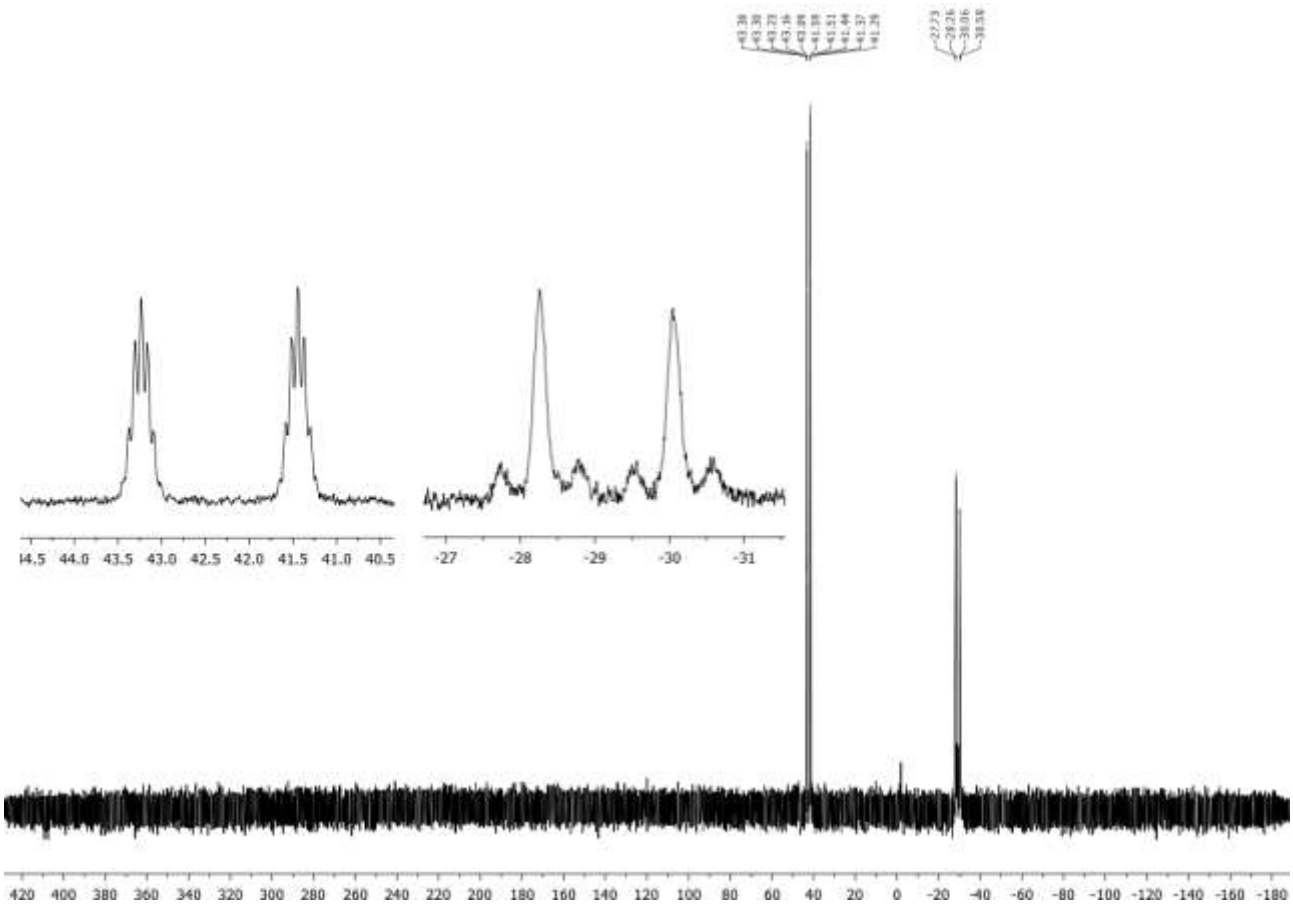


Figure S 17. *^{31}P NMR spectrum of **9** in C_6D_6.*

3. Crystallographic Data for 4, 5b, 6, 8 and 9

	Complex 4	**Complex 5b**	**Complex 6**
Temperature/K	100	100	100
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
a/Å	14.0133(16)	9.8761(18)	12.8111(6)
b/Å	12.7833(14)	10.9209(19)	20.0384(6)
c/Å	23.791(3)	12.138(2)	22.5678(7)
α/°	90	67.727(5)	100.106(3)
β/°	105.431(4)	66.395(5)	98.870(4)
γ/°	90	70.170(5)	99.627(3)
Volume/Å^3	4108.1(8)	1082.7(3)	5521.8(4)
Z	4	1	4
ρ_{calc}g/cm^3	1.760	1.717	1.639
μ/mm^{-1}	5.726	5.435	4.286
F(000)	2112.0	546.0	2712.0
Crystal size/mm^3	0.26 × 0.24 × 0.04	0.21 × 0.06 × 0.02	0.25 × 0.15 × 0.08
Absorption correction	empirical	empirical	empirical
Tmin; Tmax	0.4330; 0.7461	0.4878; 0.7461	0.3853; 0.7460
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.032 to 55.998°	4.98 to 56°	3.09 to 50.5°
Completeness to theta	0.999	0.998	1.000
Index ranges	-18 ≤ h ≤ 18, -16 ≤ k ≤ 16, -31 ≤ l ≤ 31	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -24 ≤ k ≤ 24, -27 ≤ l ≤ 27
Reflections collected	88750	30838	126588
Independent reflections	9901 [R_{int} = 0.1234, R_{sigma} = 0.0690]	5213 [R_{int} = 0.1006, R_{sigma} = 0.0675]	19977 [R_{int} = 0.1852, R_{sigma} = 0.0949]
Data/restraints/parameters	9901/42/512	5213/6/263	19977/590/1310
Goodness-of-fit on F^2	1.025	1.044	1.244
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.0856	R_1 = 0.0420, wR_2 = 0.0880	R_1 = 0.1337, wR_2 = 0.2269
Final R indexes [all data]	R_1 = 0.0585, wR_2 = 0.0954	R_1 = 0.0561, wR_2 = 0.0944	R_1 = 0.1588, wR_2 = 0.2383
Largest diff. peak/hole / e Å^{-3}	1.62/-2.00	2.25/-1.97	7.02/-5.37

	Complex 8	**Complex 9**
Temperature/K	123	100
Crystal system	triclinic	orthorhombic
Space group	P-1	$P2_12_12_1$
a/Å	10.9081(5)	9.5701(14)
b/Å	12.0080(5)	22.718(3)
c/Å	21.9058(10)	24.433(3)
α/°	78.880(4)	90
β/°	82.328(4)	90
γ/°	72.568(3)	90
Volume/Å^3	2677.3(2)	5312.1(12)
Z	2	4
ρ_{calc} g/cm^3	1.553	1.561
μ/mm^{-1}	4.406	4.441
F(000)	1244.0	2476.0
Crystal size/mm^3	0.36 × 0.33 × 0.18	0.36 × 0.06 × 0.03
Absorption correction	integration	empirical
Tmin; Tmax	0.3896; 0.6399	0.4928; 0.7462
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.646 to 50.498°	5.314 to 55.996°
Completeness to theta	0.979	0.998
Index ranges	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26	-12 ≤ h ≤ 12, -29 ≤ k ≤ 30, -32 ≤ l ≤ 32
Reflections collected	17719	83420
Independent reflections	9493 [R_{int} = 0.0323, R_{sigma} = 0.0249]	12809 [R_{int} = 0.1622, R_{sigma} = 0.1086]
Data/restraints/parameters	9493/52/621	12809/66/586
Goodness-of-fit on F^2	1.035	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0219, wR_2 = 0.0550	R_1 = 0.0522, wR_2 = 0.1002
Final R indexes [all data]	R_1 = 0.0251, wR_2 = 0.0562	R_1 = 0.0867, wR_2 = 0.1154
Largest diff. peak/hole / e Å^{-3}	1.12/-0.90	1.58/-2.85

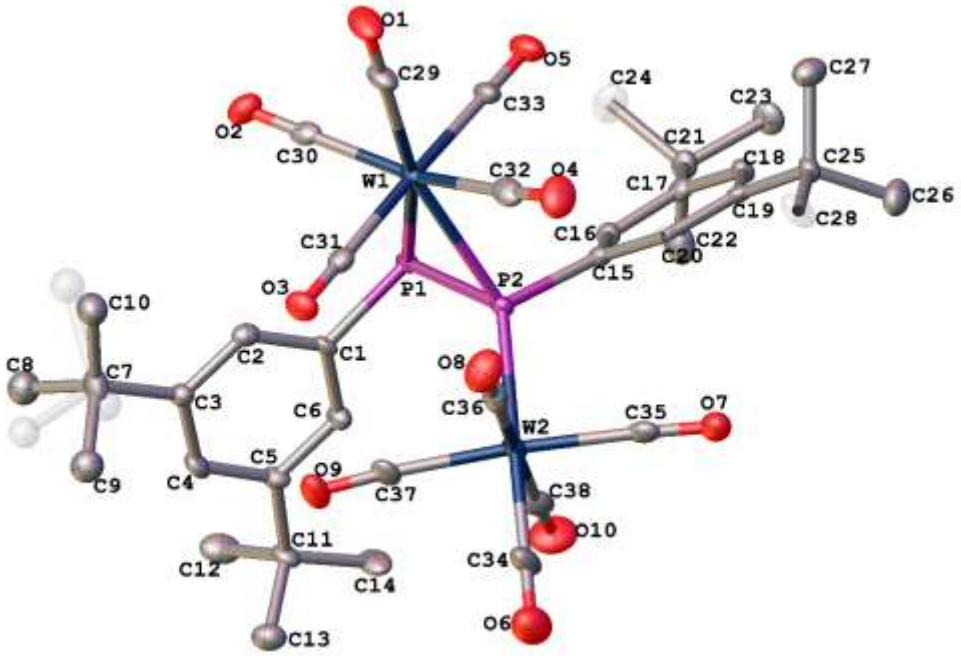


Figure S 18. *Molecular structure of* ***4****. All hydrogen atoms are omitted for clarity. The thermal ellipsoids are set at 50 % probability.*

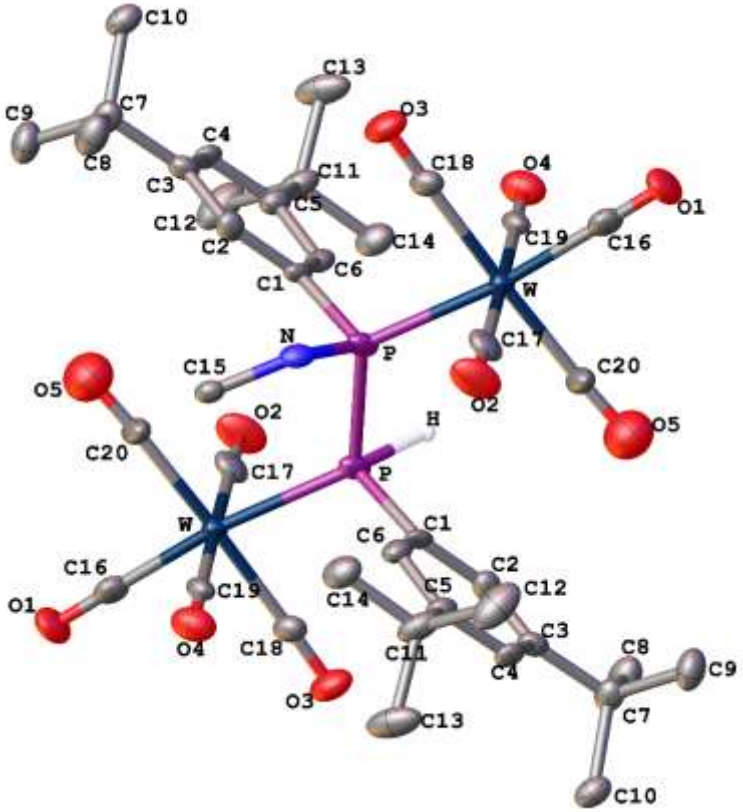


Figure S 19*. Molecular structure of* ***5b****. All hydrogen atoms are (except P-H) omitted for clarity. The thermal ellipsoids are set at 50 % probability.*

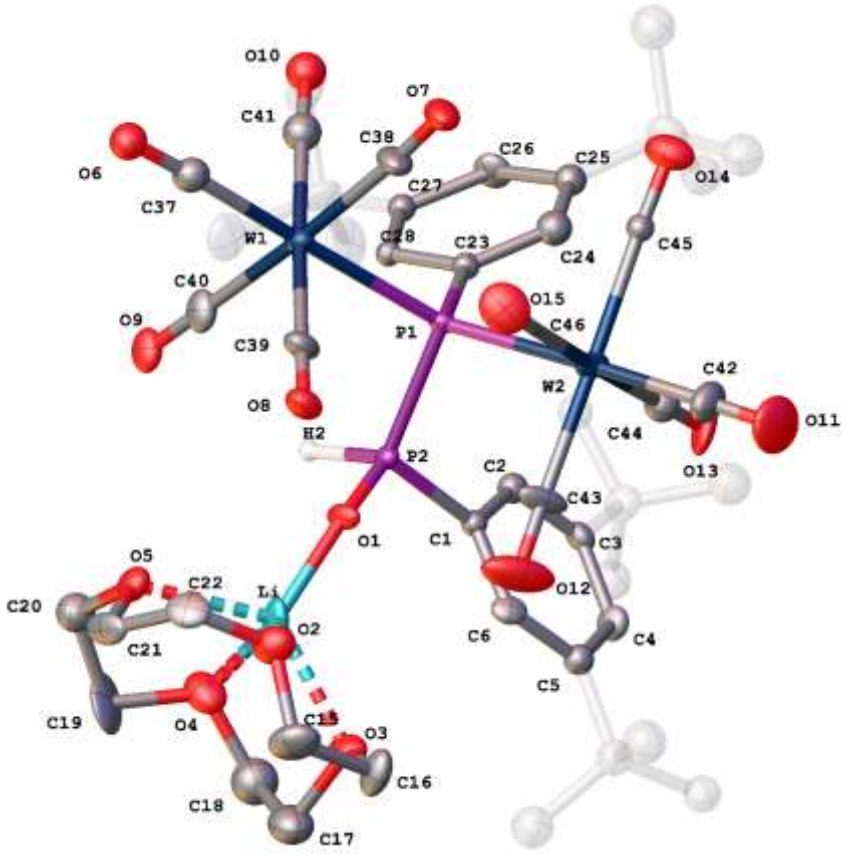


***Figure S 20**. Molecular structure of **6**. All hydrogen atoms (except P-H) are omitted for clarity and the t-Bu groups are presented transparently.*

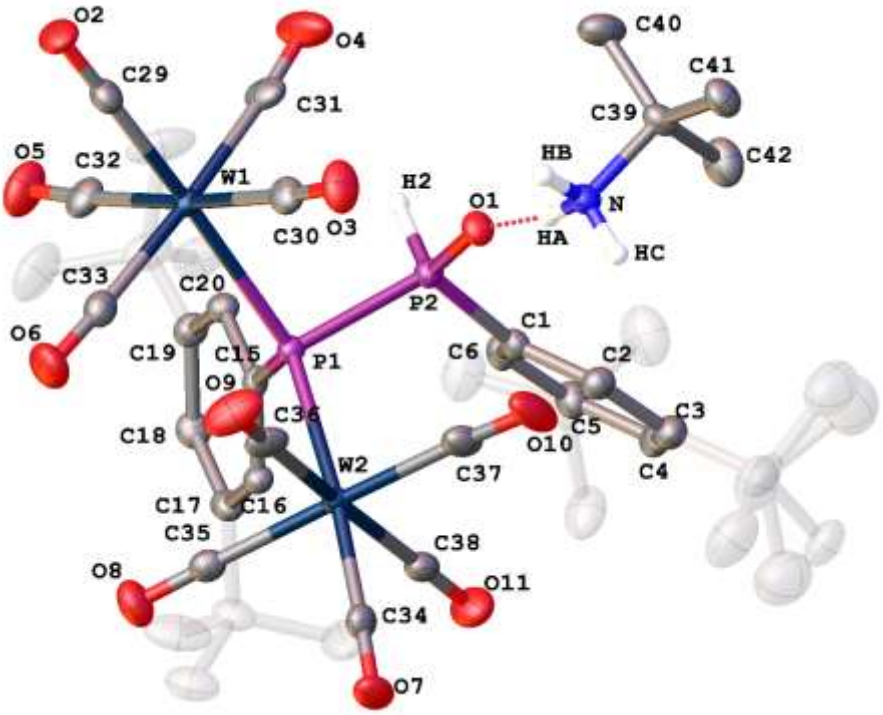


***Figure S 21**. Molecular structure of **8**. All hydrogen atoms (except P-H and N-H) are omitted for clarity and the t-Bu groups are presented transparently.*

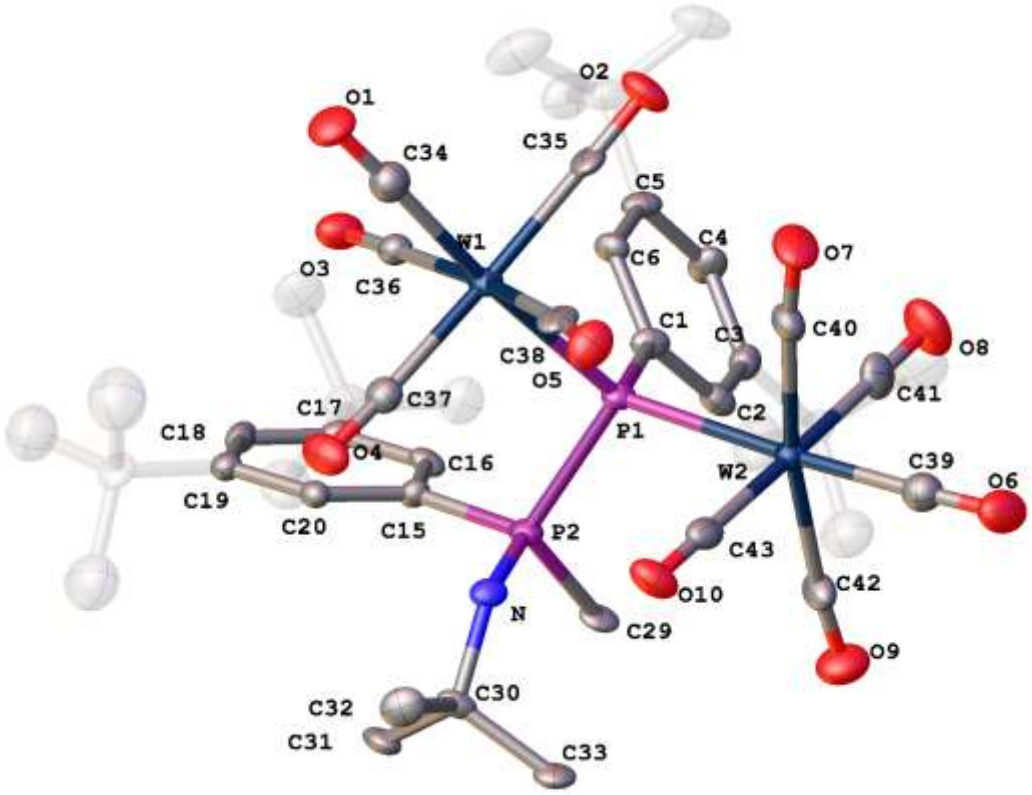
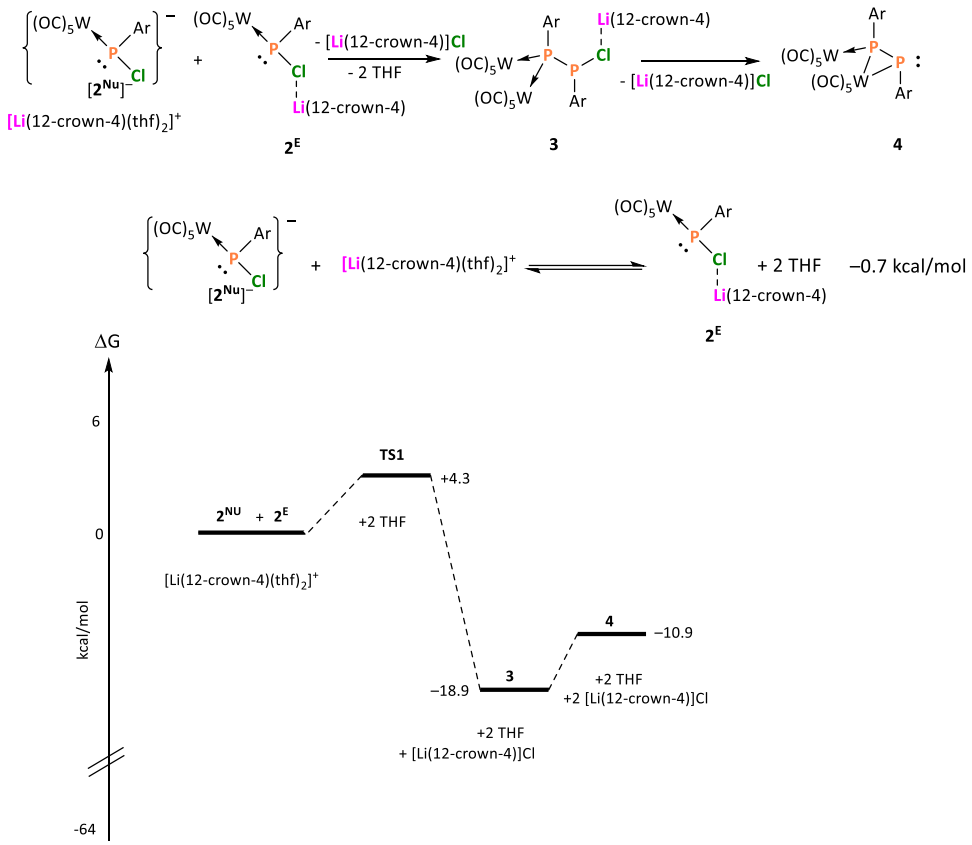


***Figure S 22**. Molecular structure of **9**. All hydrogen atoms are omitted for clarity and the t-Bu groups are presented transparently.*

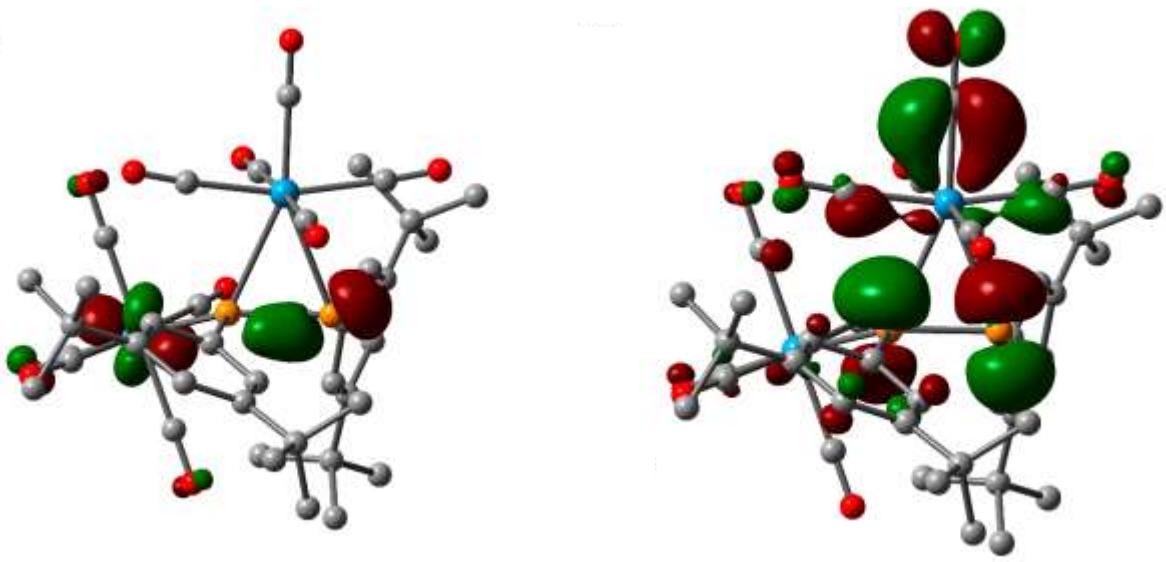
4. Computational details

The energies of all complexes included in this study were fully optimized at the B3LYP-D3/def2-TZVP level of theory. The calculations have been performed by using the program TURBOMOLE version 7.0.[4] For the calculations we have used the DFT-D functional with the latest available correction for dispersion (D3).[5] This level of theory is a good compromise between the accuracy of the results and the size of the systems (> 100 atoms). In order to reproduce solvent effects, we have used the conductor-like screening model COSMO,[6] which is a variant of the dielectric continuum solvation models.[7] We have used THF as solvent. The minimum or transition state nature of the compounds has been confirmed by doing frequency calculations. Due to the size of the systems, IRC have not been computed. However, we have checked that the negative frequency corresponds to the transition from the starting points to the products.

Scheme S1 shows the species that are used to compute the relative energies of each point of Scheme 1 discussed the main text, in order to be stoichiometrically consistent.



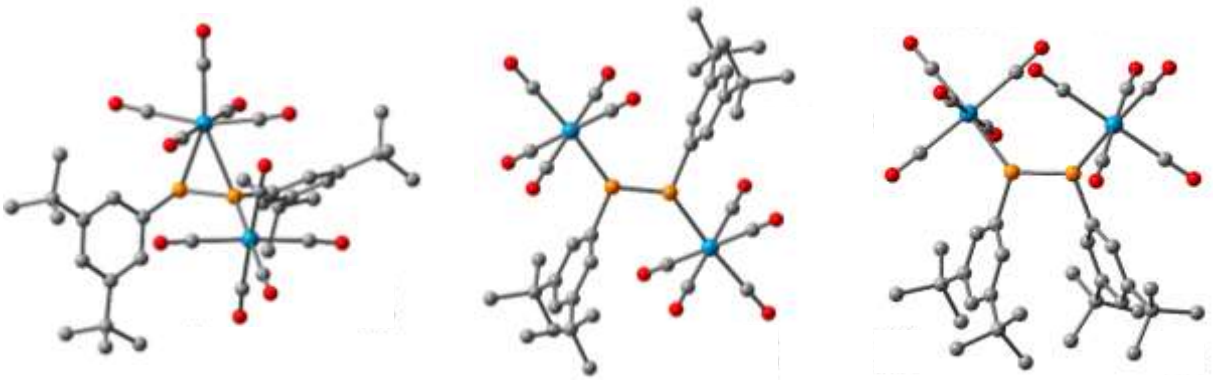
Scheme S1. Energetic profile and equations used to evaluate the mechanism analyzed in this work



HOMO
-6.079 eV

LUMO
-3.021 eV

***Figure S 23**. HOMO and LUMO orbital of complex **4** with the corresponding energies (B3LYP-D3/def2-TZVP).*

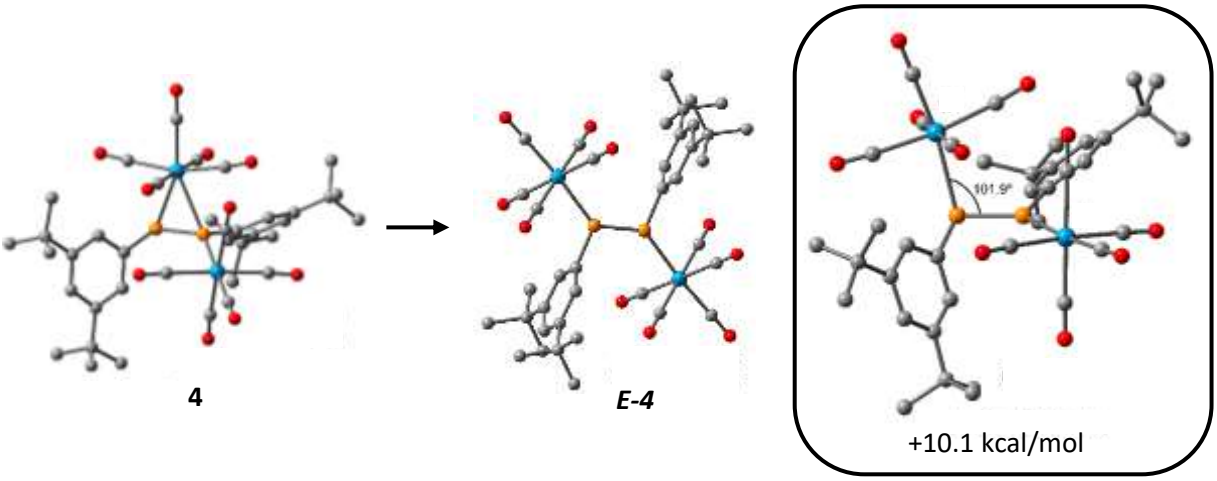


4
0.0 kcal/mol

***E*-4**
+2.9 kcal/mol

***Z*-4**
+3.5 kcal/mol

Figure S 24*. Geometry optimized complex **4** and the corresponding E-isomer **E-4** and Z-isomer **Z-4** (B3LYP-D3/def2-TZVP). Energy differences between the isomers and complex **4** (B3LYP-D3/def2-TZVP).*



4

E-4

+10.1 kcal/mol

Figure S 25*. Isomerization of complex **4** towards **E-4** and the corresponding transition state (B3LYP-D3/def2-TZVP).*

Figure S26 shows the energy profile for the nucleophillic attack of hydroxyl to compound **6**. The transition energy barrier is low (4.0 kcal/mol) and the TS connects the staring material to an intermediate (INT), where both W atoms are coordinated to the same P-atom, thus indicating that the η^2-coordinated W-atom in **4** changes to a monocoordination mode during the reaction coordinate (nucleophillic attack). The reaction is exergonic with the intermediate that is 25.8 kcal/mol lower in energy than the starting materials. The final product resulting from the [1,2]proton shift is 8.8 kcal/mol lower in energy than the intermediate. Finally, the coordination of 6 to Li(12-Crown-6) is also very exergonic –40.2 kcal/mol (not shown in Figure S26) thus explaining the X-ray form.

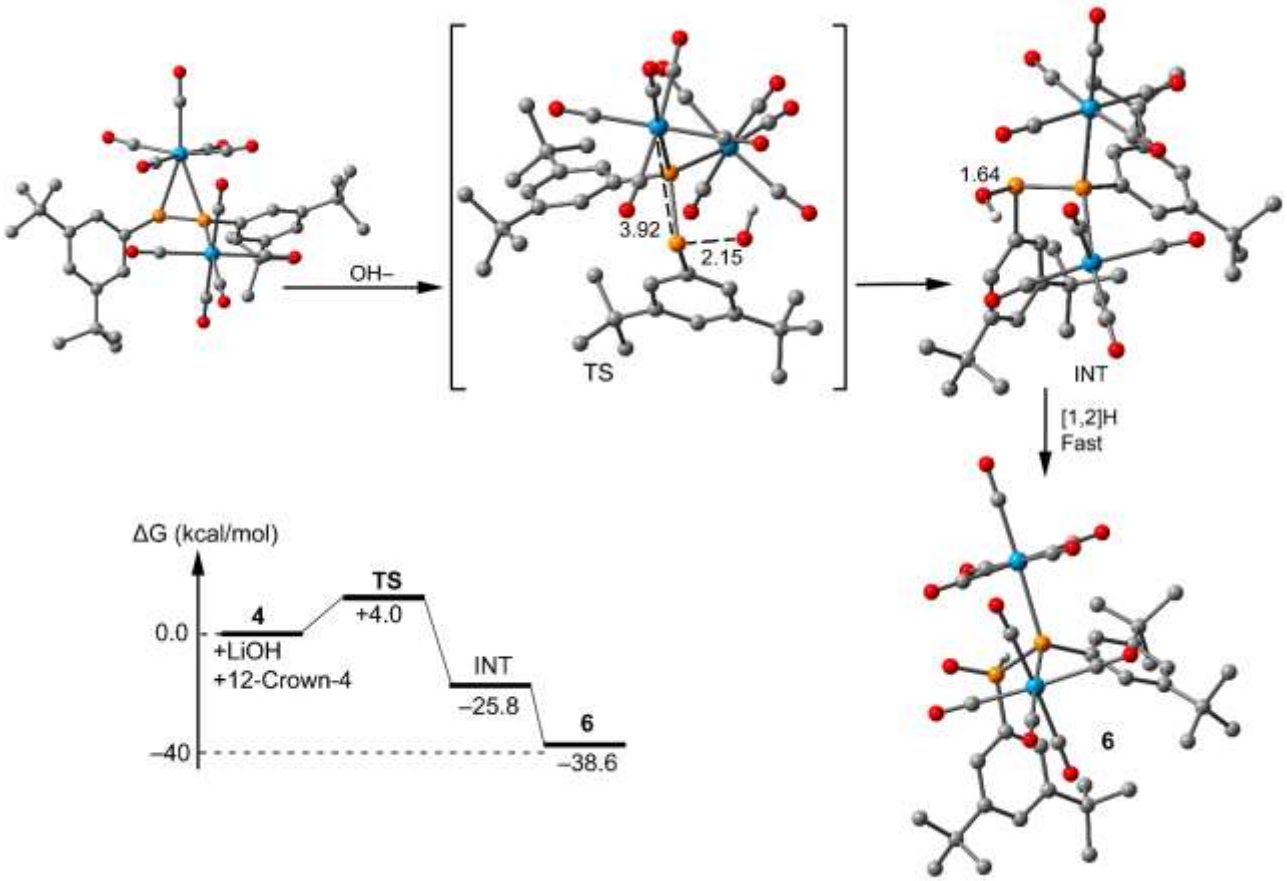


Figure S 26. Proposed mechanism for the formation of **6** from **4.** Bottom left: energetic profile of the reaction sequence (energies in kcal/mol). The optimized geometry of all compounds have been performed at the B3LYP-D3/def2-TZVP level of theory (H-atoms omitted for clarity, distances in Å).

5. References

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6. Cartesian coordinates

```
1.
E (THF): -2441.59879622459 Ha
NIMAG=0
W     -3.6238394     2.2162704    -1.3355967
P     -2.8674156     0.4162141     0.2498156
```

O	-4.5584938	4.4946738	-3.3607455
O	-1.5226458	1.1767128	-3.5314004
O	-1.4556740	4.2493418	-0.1185003
O	-5.7850749	3.2457962	0.8216333
O	-5.8414741	0.2400653	-2.5837175
C	-1.1370069	-0.1365456	0.3222163
C	-0.1712159	0.6976019	-0.2227559
H	-0.4695602	1.6180203	-0.6994561
C	1.1862048	0.3620458	-0.1607683
C	1.5203523	-0.8376355	0.4546487
H	2.5595920	-1.1243991	0.5075930
C	0.5668317	-1.7044149	1.0150124
C	-0.7671602	-1.3328313	0.9482802
H	-1.5342035	-1.9622103	1.3708818
C	1.0285741	-3.0143402	1.6680315
C	1.7631702	-3.8737397	0.6177050
H	1.1035350	-4.1091203	-0.2199195
H	2.0952506	-4.8134009	1.0651288
H	2.6433148	-3.3665469	0.2200870
C	1.9873871	-2.6944473	2.8336621
H	2.8732339	-2.1554005	2.4951154
H	2.3226921	-3.6187546	3.3097936
H	1.4896899	-2.0829400	3.5891903
C	-0.1459340	-3.8341045	2.2225026
H	-0.6918974	-3.2888786	2.9949470
H	0.2316004	-4.7537579	2.6728086
H	-0.8500448	-4.1165174	1.4371336
C	-4.2254535	3.6768210	-2.6320596
C	-2.2677447	1.5442580	-2.7450525
C	-2.2284574	3.5199217	-0.5437905
C	-5.0161717	2.8764636	0.0642761
C	-5.0541622	0.9342188	-2.1374703
C	2.2237500	1.3203349	-0.7597575
C	3.6559780	0.7824770	-0.6323039
H	4.3539442	1.4960320	-1.0733921
H	3.9465529	0.6415705	0.4109854
H	3.7799306	-0.1672910	-1.1571346
C	2.1441415	2.6726825	-0.0199753
H	1.1594597	3.1324897	-0.1129060
H	2.3561097	2.5458661	1.0436173
H	2.8763406	3.3703968	-0.4330275
C	1.9190365	1.5359567	-2.2562987
H	1.9557061	0.5917338	-2.8026282
H	0.9327737	1.9720617	-2.4151508
H	2.6549260	2.2140207	-2.6942987
Cl	-3.2285943	0.8261943	2.2586694
Cl	-3.8878543	-1.3829655	0.0543713

2^{Nu} = 2+[Li(12-crown-4)$(THF)_2$]

2.
E(THF): -1981.5248860565 Ha
NIMAG=0

W	-3.6118437	1.5412749	-1.4124995
P	-2.7137251	1.3805554	1.1176497
O	-4.6446753	1.8951102	-4.3868718
O	-1.4824803	-0.7176080	-2.2480535
O	-1.3907670	3.8121774	-1.8428073
O	-5.6784225	3.7291447	-0.2905398
O	-5.7795686	-0.7778486	-0.8800728
C	-1.0969125	0.5195574	0.9343052
C	-0.0337120	1.3139571	0.4976064
H	-0.2142645	2.3673151	0.3142659
C	1.2360663	0.7860503	0.2660982
C	1.4339659	-0.5723038	0.5100928
H	2.4070136	-1.0077311	0.3373814
C	0.3987260	-1.3984544	0.9637341
C	-0.8568685	-0.8383547	1.1717313
H	-1.6817786	-1.4495756	1.5011733
C	0.6716626	-2.8959023	1.1771682
C	1.0888473	-3.5305324	-0.1661589
H	0.3023503	-3.3963811	-0.9114430
H	1.2723001	-4.6024497	-0.0433840
H	1.9989760	-3.0752264	-0.5591175
C	1.8072485	-3.0789766	2.2047527
H	2.7317367	-2.6038336	1.8736020
H	2.0132603	-4.1421682	2.3619363
H	1.5303733	-2.6379004	3.1649644
C	-0.5624933	-3.6499705	1.6955161
H	-0.9059628	-3.2510297	2.6516419
H	-0.3141305	-4.7048671	1.8401796

H	-1.3932589	-3.5961825	0.9901582
C	-4.2681238	1.7673165	-3.2976177
C	-2.2424247	0.0934550	-1.9596835
C	-2.1933036	2.9982378	-1.6901966
C	-4.9400580	2.9468751	-0.6980361
C	-5.0061897	0.0495756	-1.0606241
C	2.3478511	1.7022849	-0.2688949
C	3.6923008	0.9736582	-0.4171569
H	4.4476356	1.6698588	-0.7903437
H	4.0449419	0.5783953	0.5381356
H	3.6263868	0.1455102	-1.1261132
C	2.5549455	2.8893068	0.6935376
H	1.6462233	3.4813738	0.8025069
H	2.8449218	2.5353297	1.6856412
H	3.3431064	3.5503476	0.3203745
C	1.9350267	2.2364611	-1.6563598
H	1.7708556	1.4101385	-2.3514283
H	1.0134976	2.8155233	-1.6084845
H	2.7191802	2.8809548	-2.0660422
Cl	-3.8684363	-0.1424491	2.1177758

[Li(12-crown-4)(THF)$_2$]
E(THF): -1087.5662691371 Ha
NImag: 0

Li	-0.0051335	-0.4513968	-0.6329326
O	-1.1365938	-1.5448775	0.6600502
C	-0.2791052	-1.9369261	1.7401448
H	-0.5546741	-2.9290879	2.1091262
H	-0.3641719	-1.2180021	2.5600944
C	1.1522138	-1.9369110	1.2224320
H	1.8470983	-2.1791719	2.0331491
H	1.2792067	-2.6735012	0.4194906
O	1.3709584	-0.6196409	0.7266567
C	2.5569539	-0.3270953	-0.0135238
H	2.7040510	-1.0755306	-0.8018944
H	3.4381270	-0.3257929	0.6359507
C	2.3412023	1.0584193	-0.6034497
H	2.2357212	1.7844340	0.2045740
H	3.1881404	1.3328510	-1.2382631
O	1.1296761	1.0224941	-1.3760952
C	0.3250287	2.2135966	-1.3822167
H	0.5015598	2.7773372	-0.4649386
H	0.5710205	2.8336361	-2.2488408
C	-1.1332432	1.7856840	-1.4416384
H	-1.7852469	2.6638553	-1.4002090
H	-1.3474726	1.2328123	-2.3651462
O	-1.3303292	0.9400383	-0.3069471
C	-2.5393277	0.1982986	-0.1735403
H	-3.3867369	0.8530310	0.0537039
H	-2.7589719	-0.3484669	-1.0988220
C	-2.2937436	-0.7622404	0.9810136
H	-3.1633896	-1.4069898	1.1370576
H	-2.1100324	-0.1869885	1.8930190
C	-0.9212432	-2.8005483	-2.2862553
C	-0.4656415	-3.5053990	-3.5575687
H	-0.8224065	-3.3999260	-1.3827915
C	0.0357511	-2.3368352	-4.4133975
H	-1.2704869	-4.0697661	-4.0261812
H	-0.8035453	-1.8136449	-4.8769556
C	0.7069415	-1.4511347	-3.3746051
H	1.7362794	-1.7684610	-3.1820914
O	-0.0651204	-1.6321828	-2.1555553
H	0.7106813	-0.3898932	-3.6166719
H	0.7219380	-2.6428440	-5.2018956
H	0.3511467	-4.1967862	-3.3398743
H	-1.9574790	-2.4590280	-2.3646944
C	1.3363330	1.8913991	3.0776745
C	-0.8730492	2.4844555	3.7044938
C	0.5345481	2.3440582	4.2944481
H	2.3825212	2.2028240	3.1081490
H	1.3015751	0.8028887	2.9546436
H	-1.5219460	3.1413478	4.2828776
H	-1.3565230	1.5053818	3.6392117
H	0.8937357	3.3121879	4.6487593
H	0.5904114	1.6375570	5.1224310
O	0.7102834	2.5047041	1.9384734
C	-0.5766555	3.0299370	2.3088962
H	-1.3038872	2.7121263	1.5590239
H	-0.5269475	4.1237141	2.3114507

2^{E}
E(THF)= -2604.2753771179 Ha
NImag: 0

W	1.2838596	1.5982717	-2.5793165
P	-0.3018345	0.3545029	-0.8966173
O	3.0712097	3.2110013	-4.6559104
O	2.7434699	-1.1653036	-3.2675717
O	3.4195814	2.0665237	-0.2133905
O	-0.3073513	4.2639665	-1.7200089
O	-0.9182825	1.0166064	-4.8312206
C	-0.0535589	1.1313428	0.7491776
C	-0.9536578	2.1549456	1.0599373
H	-1.7421656	2.3887092	0.3535802
C	-0.8556398	2.8786185	2.2473139
C	0.1550330	2.5265354	3.1463034
H	0.2360398	3.0645667	4.0756879
C	1.0599099	1.4962686	2.8791695
C	0.9462180	0.8160931	1.6672879
H	1.6506005	0.0329248	1.4264647
C	2.1747398	1.0985653	3.8594690
C	3.5461083	1.2940587	3.1808419
H	3.6436688	0.6872952	2.2810002
H	4.3508928	1.0158650	3.8666608
H	3.6889091	2.3358819	2.8880576
C	2.1554930	1.9359501	5.1471457
H	2.3070477	2.9973626	4.9408373
H	2.9617725	1.6099372	5.8075711
H	1.2152311	1.8226753	5.6909334
C	2.0046335	-0.3841574	4.2503557
H	1.0393845	-0.5475212	4.7352848
H	2.7923231	-0.6863337	4.9455799
H	2.0566359	-1.0379928	3.3791955
C	2.4204117	2.6294182	-3.9036129
C	2.2340726	-0.1574992	-3.0296410
C	2.6571850	1.9089347	-1.0518292
C	0.2668007	3.3215474	-2.0281541
C	-0.1250667	1.2311742	-4.0228290
C	-1.8531358	4.0137744	2.5264613
C	-1.6166958	4.6846214	3.8881260
H	-2.3488848	5.4813056	4.0348729
H	-1.7263985	3.9779118	4.7135294
H	-0.6234166	5.1335526	3.9503548
C	-3.2902540	3.4523345	2.5158079
H	-3.5423437	3.0061853	1.5529892
H	-3.4115511	2.6847018	3.2834833
H	-4.0112658	4.2500609	2.7129668
C	-1.7167405	5.0905026	1.4307133
H	-0.7066470	5.5047918	1.4195705
H	-1.9147581	4.6881520	0.4376069
H	-2.4202091	5.9075649	1.6120926
Cl	0.6633969	-1.6191476	-0.4753389
Li	-0.2918294	-3.0222416	-2.1407377
O	-1.4355167	-1.8702002	-3.2818080
C	-1.2529080	-2.2208802	-4.6568466
H	-1.3704467	-1.3424191	-5.2948152
H	-1.9878462	-2.9807169	-4.9425940
C	0.1445615	-2.7970352	-4.7962780
H	0.3029582	-3.1602837	-5.8171877
H	0.9050972	-2.0487073	-4.5659041
O	0.2006203	-3.8744698	-3.8566879
C	1.4557115	-4.4679645	-3.5294738
H	2.1642032	-3.7033184	-3.1931667
H	1.8860857	-4.9929850	-4.3894031
C	1.1375173	-5.4595995	-2.4192348
H	0.4765138	-6.2388425	-2.8116663
H	2.0546120	-5.9257083	-2.0466706
O	0.4770476	-4.7471056	-1.3695445
C	-0.5867319	-5.4107466	-0.6801829
H	-1.0662006	-6.1326855	-1.3493569
H	-0.2036427	-5.9405098	0.1976591
C	-1.6060400	-4.3632288	-0.2575648
H	-2.4537143	-4.8499962	0.2376340
H	-1.1568675	-3.6396392	0.4302849
O	-2.0167492	-3.7147580	-1.4599001
C	-2.7382859	-2.4800920	-1.3619370
H	-3.7595230	-2.6506913	-1.0044191
H	-2.2279097	-1.7903529	-0.6835543
C	-2.7732169	-1.9054064	-2.7718393
H	-3.1914012	-0.8960802	-2.7518241
H	-3.3908697	-2.5403820	-3.4139699

TS 2-3
E(THF): -2604.2753771179 Ha
NImag=1 (-127 cm-1)

W	-1.5942949	2.9933757	-2.1787842
W	-0.6870588	-2.9114930	1.3702068
P	-0.2834077	0.8545832	-1.1604679
P	0.2772424	-0.5014804	1.7590606
O	-2.7518254	5.6091644	-3.5286170
O	-3.9576383	3.3426938	-0.0595001
O	-3.6069643	1.1591493	-3.8834995
O	0.5010410	2.7408256	-4.6206028
O	0.3650416	4.7211407	-0.3136649
O	-1.8136053	-3.0214059	4.3718870
O	-1.9784487	-5.7857188	0.9996347
O	-3.4271109	-1.4428734	0.6345632
O	0.5271504	-3.4610270	-1.5540412
O	2.1091257	-4.0480333	2.4931485
C	-0.5207166	-0.4449763	-2.4398996
C	-1.7485208	-1.1212938	-2.4078266
H	-2.4746662	-0.8403277	-1.6588582
C	-2.0524762	-2.1216703	-3.3231634
C	-1.0888066	-2.4420353	-4.2879657
H	-1.3058212	-3.2230572	-4.9974193
C	0.1379206	-1.7887392	-4.3526423
C	0.4089793	-0.7907280	-3.4138730
H	1.3538840	-0.2691331	-3.4409980
C	1.2026049	-2.1298534	-5.4059683
C	2.4765475	-2.6249763	-4.6930866
H	2.8835362	-1.8626308	-4.0307057
H	3.2492605	-2.8826689	-5.4232967
H	2.2622373	-3.5070316	-4.0873388
C	0.7428224	-3.2265966	-6.3783804
H	0.5324375	-4.1638746	-5.8588052
H	1.5313188	-3.4216066	-7.1091185
H	-0.1540333	-2.9300994	-6.9269641
C	1.5321029	-0.8673066	-6.2289204
H	0.6427581	-0.5021220	-6.7471921
H	2.2993581	-1.0900508	-6.9760607
H	1.8998525	-0.0577549	-5.5982610
C	2.0140804	-0.2379232	1.2513978
C	2.6050998	0.9611219	1.6384918
H	2.0202276	1.6540914	2.2269033
C	3.9133478	1.2811790	1.2844911
C	4.6192089	0.3590350	0.5155415
H	5.6309938	0.5878897	0.2139113
C	4.0562103	-0.8519350	0.0943494
C	2.7522435	-1.1365629	0.4814051
H	2.2816565	-2.0549723	0.1748614
C	4.4822424	2.6470574	1.6924231
C	4.3311206	2.8430293	3.2153177
H	3.2858464	2.7966898	3.5218327
H	4.7288309	3.8176770	3.5135330
H	4.8729508	2.0676315	3.7615736
C	3.6911026	3.7479003	0.9560220
H	3.7741027	3.6292082	-0.1254416
H	4.0669935	4.7388483	1.2277021
H	2.6294266	3.7079511	1.1978017
C	5.9684922	2.7968163	1.3362985
H	6.5767197	2.0293526	1.8208374
H	6.3305763	3.7724838	1.6691913
H	6.1340047	2.7354614	0.2587095
C	4.8692488	-1.7958925	-0.8015215
C	5.2166799	-1.0603724	-2.1127510
H	4.3095916	-0.7098353	-2.6070261
H	5.7488254	-1.7269977	-2.7972242
H	5.8490577	-0.1900316	-1.9293909
C	6.1696345	-2.2090768	-0.0834736
H	6.7903474	-1.3451488	0.1610342
H	6.7595492	-2.8759055	-0.7188885
H	5.9434727	-2.7335578	0.8474725
C	4.0913324	-3.0721745	-1.1555200
H	3.8347025	-3.6463106	-0.2625773
H	4.7041475	-3.7093826	-1.7975474
H	3.1690803	-2.8518819	-1.6928033
C	-2.3397167	4.6473611	-3.0341162
C	-3.0730955	3.1696837	-0.7830292
C	-2.8762986	1.7960851	-3.2705555
C	-0.2134410	2.8306889	-3.7319495
C	-0.3181468	4.1053119	-1.0056227

C	-1.3953226	-2.9251551	3.3053439
C	-1.5093025	-4.7384127	1.1400134
C	-2.4288237	-1.9848342	0.8399454
C	0.0695546	-3.1698631	-0.5451040
C	1.1141537	-3.6525779	2.0869591
C	-3.3672791	-2.9137197	-3.2313232
C	-3.8031119	-3.4539836	-4.6063262
H	-4.7763608	-3.9430333	-4.5175431
H	-3.8922517	-2.6464089	-5.3364350
H	-3.1060581	-4.1950511	-5.0004375
C	-4.5180679	-2.0446468	-2.6914631
H	-4.3450868	-1.7210747	-1.6669009
H	-4.6614022	-1.1572878	-3.3095485
H	-5.4464023	-2.6221363	-2.6939179
C	-3.1416293	-4.1046696	-2.2771314
H	-2.3403771	-4.7507953	-2.6423901
H	-2.8572374	-3.7619613	-1.2824029
H	-4.0523210	-4.7037517	-2.1844037
Cl	1.7366774	1.4298714	-1.5365635
Cl	1.0287627	-0.7882072	4.0759267
Li	-0.6180479	0.9713867	3.7761803
O	0.4901981	2.7626459	3.8946615
C	-0.1273636	3.7463551	3.0504509
H	0.6309346	4.2886071	2.4793381
H	-0.6816407	4.4566509	3.6712152
C	-1.0882217	3.0511311	2.1058322
H	-1.6410488	3.7989057	1.5316062
H	-0.5574633	2.3973135	1.4087932
O	-1.9592272	2.2841812	2.9335669
C	-2.8430634	1.3630896	2.2898445
H	-2.2879145	0.7524042	1.5756506
H	-3.6412105	1.8841113	1.7589416
C	-3.4365673	0.5198526	3.4003078
H	-4.0741938	1.1492415	4.0296686
H	-4.0384679	-0.2874854	2.9741302
O	-2.3716242	-0.0141716	4.1916930
C	-2.6054482	-0.1145497	5.5925868
H	-3.3827777	0.6001600	5.8839419
H	-2.9323055	-1.1262922	5.8516805
C	-1.3179937	0.2150062	6.3323951
H	-1.5193621	0.2770861	7.4098951
H	-0.5620285	-0.5518813	6.1484722
O	-0.8834680	1.4730212	5.8212232
C	0.4290716	1.9153109	6.1418159
H	0.5013059	2.2116988	7.1969990
H	1.1577094	1.1255724	5.9387987
C	0.6871377	3.1260695	5.2593749
H	1.7093488	3.4897648	5.4142386
H	-0.0133167	3.9225208	5.5310254

3 (Scheme 1).
E(THF): -3502.7830046803 Ha
NImag=0

W	-0.1424282	0.6276204	-4.5418988
W	0.2871437	-2.9787818	-1.6258109
P	0.5690949	1.2731148	-1.9884124
P	-0.4748979	-0.5705891	-2.1130581
O	-0.3967827	1.0832682	-7.6810387
O	2.3629411	-1.3285351	-4.9958561
O	1.6056155	3.3266300	-4.7640538
O	-2.7724873	2.4037353	-3.9747348
O	-1.9900529	-1.8951205	-5.2720014
O	0.3628746	-3.9060678	-4.7041676
O	1.0902218	-5.9259748	-0.7795916
O	3.4566454	-2.4690992	-1.8861865
O	0.1534935	-2.3791882	1.5209120
O	-2.7613230	-3.9604155	-1.4582606
C	2.3150078	0.7868671	-1.6966113
C	3.3314310	0.9446889	-2.6364963
H	3.0857593	1.2414069	-3.6444427
C	4.6665042	0.7227974	-2.3032454
C	4.9548171	0.3438151	-0.9918533
H	5.9808777	0.1608465	-0.7207040
C	3.9648239	0.1916815	-0.0194785
C	2.6401129	0.4224280	-0.3862685
H	1.8502774	0.3481181	0.3502546
C	4.2897258	-0.1951978	1.4294203
C	3.4136868	-1.3905860	1.8515827
H	2.3595087	-1.1217981	1.8690636
H	3.6916916	-1.7170100	2.8564907

H	3.5480341	-2.2344243	1.1717785
C	5.7622005	-0.5883480	1.6154198
H	6.0372884	-1.4336929	0.9805487
H	5.9331761	-0.8814678	2.6536284
H	6.4382086	0.2403767	1.3957859
C	3.9769571	1.0069816	2.3448417
H	4.5786057	1.8733598	2.0602247
H	4.2089624	0.7536697	3.3829683
H	2.9223064	1.2786944	2.2918885
C	-2.1916006	-0.1309619	-1.6503914
C	-2.4518778	0.8454194	-0.6953264
H	-1.6301155	1.2937936	-0.1578589
C	-3.7675925	1.2268771	-0.4073621
C	-4.7972962	0.5746144	-1.0775633
H	-5.8186555	0.8590639	-0.8734260
C	-4.5686503	-0.4491117	-2.0079333
C	-3.2526602	-0.7890234	-2.2835566
H	-3.0387451	-1.5678492	-2.9958834
C	-4.0319044	2.3036680	0.6535141
C	-3.0201859	3.4596130	0.5139864
H	-2.0004770	3.1359155	0.7212987
H	-3.2639521	4.2507139	1.2275200
H	-3.0511527	3.8868259	-0.4906682
C	-3.8637649	1.6601289	2.0442951
H	-4.5847505	0.8515842	2.1885905
H	-4.0348538	2.4114863	2.8216169
H	-2.8607584	1.2513518	2.1695067
C	-5.4480567	2.8903660	0.5407363
H	-5.6297699	3.3091792	-0.4516536
H	-5.5711185	3.6920821	1.2718493
H	-6.2204200	2.1465542	0.7453239
C	-5.7572619	-1.1361303	-2.6935218
C	-6.6716911	-1.7659142	-1.6224300
H	-6.1247537	-2.5095943	-1.0395764
H	-7.5232872	-2.2609973	-2.0957835
H	-7.0637886	-1.0174688	-0.9322523
C	-6.5523992	-0.0881592	-3.4992437
H	-6.9393325	0.7063314	-2.8594718
H	-7.4021229	-0.5597261	-3.9989981
H	-5.9210856	0.3742208	-4.2608804
C	-5.3129779	-2.2493721	-3.6543804
H	-4.6913445	-1.8645342	-4.4650224
H	-6.1922208	-2.7129826	-4.1058098
H	-4.7539984	-3.0308430	-3.1364534
C	-0.3091253	0.9206403	-6.5518977
C	1.4959324	-0.6091791	-4.8171775
C	1.0025295	2.3661713	-4.6376717
C	-1.8388640	1.7799840	-4.1670166
C	-1.3395034	-1.0138829	-4.9505560
C	0.3305421	-3.5511427	-3.6174607
C	0.8035438	-4.8597835	-1.1018135
C	2.3235923	-2.5620079	-1.7788624
C	0.2171850	-2.5304094	0.3868245
C	-1.6848683	-3.5730591	-1.5232193
C	5.7541329	0.9015465	-3.3726126
C	7.1630345	0.6236329	-2.8282148
H	7.8967649	0.7701043	-3.6234138
H	7.4229200	1.2993476	-2.0108269
H	7.2635409	-0.4035187	-2.4715124
C	5.7189237	2.3517213	-3.8982904
H	4.7534275	2.5993627	-4.3415902
H	5.9071591	3.0622679	-3.0906687
H	6.4843868	2.4950039	-4.6650867
C	5.4899402	-0.0715796	-4.5389628
H	5.4662058	-1.1043600	-4.1869508
H	4.5377391	0.1306629	-5.0281811
H	6.2765190	0.0196065	-5.2924632
Cl	-0.0054947	1.0343617	2.0101472
Li	-0.1438717	0.0482476	4.0047026
O	-2.2096969	-0.1273570	4.4378005
C	-2.4948281	-1.4238232	4.9532428
H	-3.4424087	-1.7999275	4.5534450
H	-2.5621973	-1.3864206	6.0457039
C	-1.3505006	-2.3434515	4.5571286
H	-1.4847711	-3.3308304	5.0145683
H	-1.2951346	-2.4606203	3.4713242
O	-0.1804168	-1.6990581	5.0518028
C	1.1027565	-2.2661088	4.8044341
H	1.2610046	-2.4118370	3.7328655
H	1.2156149	-3.2295894	5.3152613

C	2.0879449	-1.2571915	5.3713624
H	1.9363728	-1.1771885	6.4531126
H	3.1165707	-1.5828280	5.1830004
O	1.8312836	-0.0034346	4.7489693
C	2.0346164	1.1737690	5.5306855
H	1.9966261	0.9214562	6.5953286
H	3.0108163	1.6149244	5.3060767
C	0.9275424	2.1648185	5.2079591
H	1.0214403	3.0477751	5.8515685
H	0.9710079	2.4678124	4.1574251
O	-0.2914182	1.4689806	5.4674242
C	-1.5195359	2.0726555	5.0624638
H	-1.7601348	2.9372548	5.6930474
H	-1.4581563	2.3871241	4.0162877
C	-2.5754608	0.9953514	5.2406871
H	-3.5572654	1.3732451	4.9419174
H	-2.6133629	0.6998361	6.2944552

3···[Li(12-crown-4)] (Scheme 1).
E(THF): -4125.5326914388 Ha
NImag=0

W	-0.1424282	0.6276204	-4.5418988
W	0.2871437	-2.9787818	-1.6258109
P	0.5690949	1.2731148	-1.9884124
P	-0.4748979	-0.5705891	-2.1130581
O	-0.3967827	1.0832682	-7.6810387
O	2.3629411	-1.3285351	-4.9958561
O	1.6056155	3.3266300	-4.7640538
O	-2.7724873	2.4037353	-3.9747348
O	-1.9900529	-1.8951205	-5.2720014
O	0.3628746	-3.9060678	-4.7041676
O	1.0902218	-5.9259748	-0.7795916
O	3.4566454	-2.4690992	-1.8861865
O	0.1534935	-2.3791882	1.5209120
O	-2.7613230	-3.9604155	-1.4582606
C	2.3150078	0.7868671	-1.6966113
C	3.3314310	0.9446889	-2.6364963
H	3.0857593	1.2414069	-3.6444427
C	4.6665042	0.7227974	-2.3032454
C	4.9548171	0.3438151	-0.9918533
H	5.9808777	0.1608465	-0.7207040
C	3.9648239	0.1916815	-0.0194785
C	2.6401129	0.4224280	-0.3862685
H	1.8502774	0.3481181	0.3502546
C	4.2897258	-0.1951978	1.4294203
C	3.4136868	-1.3905860	1.8515827
H	2.3595087	-1.1217981	1.8690636
H	3.6916916	-1.7170100	2.8564907
H	3.5480341	-2.2344243	1.1717785
C	5.7622005	-0.5883480	1.6154198
H	6.0372884	-1.4336929	0.9805487
H	5.9331761	-0.8814678	2.6536284
H	6.4382086	0.2403767	1.3957859
C	3.9769571	1.0069816	2.3448417
H	4.5786057	1.8733598	2.0602247
H	4.2089624	0.7536697	3.3829683
H	2.9223064	1.2786944	2.2918885
C	-2.1916006	-0.1309619	-1.6503914
C	-2.4518778	0.8454194	-0.6953264
H	-1.6301155	1.2937936	-0.1578589
C	-3.7675925	1.2268771	-0.4073621
C	-4.7972962	0.5746144	-1.0775633
H	-5.8186555	0.8590639	-0.8734260
C	-4.5686503	-0.4491117	-2.0079333
C	-3.2526602	-0.7890234	-2.2835566
H	-3.0387451	-1.5678492	-2.9958834
C	-4.0319044	2.3036680	0.6535141
C	-3.0201859	3.4596130	0.5139864
H	-2.0004770	3.1359155	0.7212987
H	-3.2639521	4.2507139	1.2275200
H	-3.0511527	3.8868259	-0.4906682
C	-3.8637649	1.6601289	2.0442951
H	-4.5847505	0.8515842	2.1885905
H	-4.0348538	2.4114863	2.8216169
H	-2.8607584	1.2513518	2.1695067
C	-5.4480567	2.8903660	0.5407363
H	-5.6297699	3.3091792	-0.4516536
H	-5.5711185	3.6920821	1.2718493
H	-6.2204200	2.1465542	0.7453239
C	-5.7572619	-1.1361303	-2.6935218

C	-6.6716911	-1.7659142	-1.6224300
H	-6.1247537	-2.5095943	-1.0395764
H	-7.5232872	-2.2609973	-2.0957835
H	-7.0637886	-1.0174688	-0.9322523
C	-6.5523992	-0.0881592	-3.4992437
H	-6.9393325	0.7063314	-2.8594718
H	-7.4021229	-0.5597261	-3.9989981
H	-5.9210856	0.3742208	-4.2608804
C	-5.3129779	-2.2493721	-3.6543804
H	-4.6913445	-1.8645342	-4.4650224
H	-6.1922208	-2.7129826	-4.1058098
H	-4.7539984	-3.0308430	-3.1364534
C	-0.3091253	0.9206403	-6.5518977
C	1.4959324	-0.6091791	-4.8171775
C	1.0025295	2.3661713	-4.6376717
C	-1.8388640	1.7799840	-4.1670166
C	-1.3395034	-1.0138829	-4.9505560
C	0.3305421	-3.5511427	-3.6174607
C	0.8035438	-4.8597835	-1.1018135
C	2.3235923	-2.5620079	-1.7788624
C	0.2171850	-2.5304094	0.3868245
C	-1.6848683	-3.5730591	-1.5232193
C	5.7541329	0.9015465	-3.3726126
C	7.1630345	0.6236329	-2.8282148
H	7.8967649	0.7701043	-3.6234138
H	7.4229200	1.2993476	-2.0108269
H	7.2635409	-0.4035187	-2.4715124
C	5.7189237	2.3517213	-3.8982904
H	4.7534275	2.5993627	-4.3415902
H	5.9071591	3.0622679	-3.0906687
H	6.4843868	2.4950039	-4.6650867
C	5.4899402	-0.0715796	-4.5389628
H	5.4662058	-1.1043600	-4.1869508
H	4.5377391	0.1306629	-5.0281811
H	6.2765190	0.0196065	-5.2924632
Cl	-0.0054947	1.0343617	2.0101472
Li	-0.1438717	0.0482476	4.0047026
O	-2.2096969	-0.1273570	4.4378005
C	-2.4948281	-1.4238232	4.9532428
H	-3.4424087	-1.7999275	4.5534450
H	-2.5621973	-1.3864206	6.0457039
C	-1.3505006	-2.3434515	4.5571286
H	-1.4847711	-3.3308304	5.0145683
H	-1.2951346	-2.4606203	3.4713242
O	-0.1804168	-1.6990581	5.0518028
C	1.1027565	-2.2661088	4.8044341
H	1.2610046	-2.4118370	3.7328655
H	1.2156149	-3.2295894	5.3152613
C	2.0879449	-1.2571915	5.3713624
H	1.9363728	-1.1771885	6.4531126
H	3.1165707	-1.5828280	5.1830004
O	1.8312836	-0.0034346	4.7489693
C	2.0346164	1.1737690	5.5306855
H	1.9966261	0.9214562	6.5953286
H	3.0108163	1.6149244	5.3060767
C	0.9275424	2.1648185	5.2079591
H	1.0214403	3.0477751	5.8515685
H	0.9710079	2.4678124	4.1574251
O	-0.2914182	1.4689806	5.4674242
C	-1.5195359	2.0726555	5.0624638
H	-1.7601348	2.9372548	5.6930474
H	-1.4581563	2.3871241	4.0162877
C	-2.5754608	0.9953514	5.2406871
H	-3.5572654	1.3732451	4.9419174
H	-2.6133629	0.6998361	6.2944552

4.
E(THF): -3042.4375376366 Ha
NImag=0

W	-0.2184476	1.5967996	-2.6953490
W	0.5635100	-2.6475878	-0.9109316
P	0.3585211	1.5060127	-0.0532708
P	-0.4780892	-0.3089563	-0.7875152
O	-0.4991581	2.9331353	-5.5744919
O	2.4847019	0.1037514	-3.5838056
O	1.2791469	4.3822686	-2.0576642
O	-3.0216118	2.8661274	-1.7409461
O	-1.8111135	-0.7564098	-4.1929521
O	0.6689151	-2.6936235	-4.1248080
O	1.7321978	-5.5951090	-0.7614505
O	3.6480546	-1.7440827	-1.0638440

O	0.3762705	-2.5590561	2.2942913
O	-2.3245959	-4.0374786	-1.0399387
C	2.1246548	1.0859143	0.2070197
C	3.1623794	1.6158649	-0.5505408
H	2.9369273	2.2148765	-1.4197588
C	4.4970075	1.3809543	-0.2135812
C	4.7546378	0.6072460	0.9152880
H	5.7785534	0.4068036	1.1830525
C	3.7394909	0.0726383	1.7169788
C	2.4227215	0.3257246	1.3458921
H	1.6086306	-0.0687360	1.9366218
C	4.0718306	-0.8289828	2.9151352
C	4.1700132	-2.2829088	2.4055175
H	3.2258091	-2.6094114	1.9681344
H	4.4146926	-2.9595197	3.2280584
H	4.9424829	-2.3774695	1.6401061
C	5.4125760	-0.4361779	3.5626695
H	6.2604208	-0.6040988	2.8977544
H	5.5808980	-1.0430179	4.4543843
H	5.4154117	0.6142966	3.8612270
C	2.9846305	-0.7485444	4.0021305
H	2.8378140	0.2808744	4.3360695
H	3.2842901	-1.3455874	4.8657789
H	2.0270796	-1.1399765	3.6618825
C	-2.2357590	-0.2325245	-0.2788629
C	-2.6324812	0.3974814	0.8943625
H	-1.8891476	0.8754575	1.5157277
C	-3.9777812	0.4227209	1.2797309
C	-4.8996324	-0.2136414	0.4565305
H	-5.9417854	-0.2125471	0.7367223
C	-4.5323892	-0.8721627	-0.7266490
C	-3.1909130	-0.8715765	-1.0779873
H	-2.8717894	-1.3793321	-1.9730484
C	-4.3706711	1.1430028	2.5765372
C	-3.9567411	2.6261559	2.4761600
H	-2.8805201	2.7390413	2.3389425
H	-4.2339103	3.1579119	3.3895274
H	-4.4534252	3.1105614	1.6331262
C	-3.6416960	0.4842750	3.7660749
H	-3.9167763	-0.5686764	3.8547744
H	-3.9096737	0.9873930	4.6981592
H	-2.5577467	0.5385045	3.6585067
C	-5.8810997	1.0830455	2.8456826
H	-6.4541847	1.5606743	2.0481268
H	-6.1077324	1.6095864	3.7746541
H	-6.2331094	0.0551473	2.9554969
C	-5.6023420	-1.5770224	-1.5704947
C	-6.2279948	-2.7138238	-0.7352343
H	-5.4673485	-3.4410443	-0.4453280
H	-6.9933864	-3.2325381	-1.3173953
H	-6.6983989	-2.3350809	0.1734577
C	-6.6954105	-0.5642356	-1.9685153
H	-7.1899296	-0.1330086	-1.0973156
H	-7.4604027	-1.0551784	-2.5746714
H	-6.2708677	0.2546096	-2.5533843
C	-5.0229723	-2.1874973	-2.8557470
H	-4.5698022	-1.4288167	-3.4971507
H	-5.8232141	-2.6649195	-3.4241682
H	-4.2726986	-2.9495208	-2.6402255
C	-0.3994900	2.4535244	-4.5422380
C	1.5442143	0.6517833	-3.2462252
C	0.7622764	3.3829910	-2.2418561
C	-2.0260615	2.4236590	-2.0735031
C	-1.2474888	0.0480777	-3.6132959
C	0.6243094	-2.6734760	-2.9822148
C	1.3123012	-4.5289177	-0.8281573
C	2.5362747	-1.9871383	-0.9661031
C	0.4603687	-2.5929572	1.1524710
C	-1.3123280	-3.5051755	-0.9815717
C	5.6112382	1.9731729	-1.0876757
C	7.0126866	1.6062880	-0.5783700
H	7.7656671	2.0538638	-1.2295860
H	7.1886838	1.9788271	0.4330919
H	7.1736674	0.5264172	-0.5815405
C	5.4873502	3.5111013	-1.0953175
H	4.5247372	3.8399516	-1.4896040
H	5.5898917	3.9141051	-0.0854159
H	6.2699015	3.9496436	-1.7192118
C	5.4677273	1.4393349	-2.5273381
H	5.5101243	0.3490339	-2.5453055

H	4.5226991	1.7392704	-2.9796557
H	6.2737286	1.8276443	-3.1546433