Supporting information B707320H

C_{α},C_{ortho}-Dimetalated Phosphazene Complexes

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General. All reactions and manipulations were carried out in a dry N_2 gas atmosphere using standard procedures. THF and THF-d_8 were distilled from sodium/benzophenone immediately prior to use. Commercial reagents were purchased from Acros. Thin-layer chromatography (TLC) was performed on aluminum-backed Merck plates coated with silica gel 60 F_{254}. Silica gel 60 (40-63 μm) or activated alumina (neutral, 70-290 mesh) from Scharlau was used for column chromatography. Melting points are uncorrected. Mass spectra were determined by APCI technique. Phosphazene **3a** was prepared as described elsewhere.[1]

NMR studies. NMR experiments were conducted on two spectrometers working at proton frequencies of 300 MHz (B_0= 7 T) and 500 MHz (B_0= 11.74 T). Two 5-mm probe heads were used: a QNPZ probe (^{1}H, ^{13}C, ^{15}N, ^{31}P) for B_0=7 T, and a direct triple probe ^{1}H/^{31}P, BB (^{31}P–^{109}Ag) for B_0= 11.74 T. Both probes included a z-gradient coil. The 500 MHz instrument was equipped with a third radio frequency channel. Frequencies, pulse widths for the 90° pulses and the attenuation levels applied are given in Table S1. The spectral references used were internal tetramethylsilane for ^{1}H and ^{13}C, external 85% H_3PO_4 for ^{31}P, 1 M LiBr in D_2O for ^{7}Li, Me_4Sn (saturated solution in $CDCl_3$) for ^{119}Sn, and Me_2Hg (neat liq.; Ξ = 17.910822 MHz) for ^{199}Hg. A set of two complementary ^{31}P/^{7}Li-selective band pass/stop frequency filters was used for the measurement of NMR spectra involving ^{31}P and ^{7}Li nuclei.

Table S1. Pulse widths for 90º pulses (μs) and attenuation levels (dB, in brackets) used.

Field (Tesla)	**^{1}H**	**^{1}H-dec**	**^{7}Li**	**^{7}Li-dec**	**^{13}C**	**^{31}P**	**^{31}P-dec**	**^{119}Sn**	**^{199}Hg**
7.05	8.8 (-2)	95 (20)	-	-	8.0 (-3)	9.7 (-6)	-	-	-
Freq (MHz)	300.13	300.13			75.47	121.49			
11.74	9.2 (-4)	85 (15)	15.7 (0)	88 (15)	7.5 (0)	31 (0)	100 (8.4)	28 (-2)	7.5 (0)
Freq (MHz)	500.13	500.13	194.37	194.37	125.72	202.46	202.46	(186.5)	(89.58)

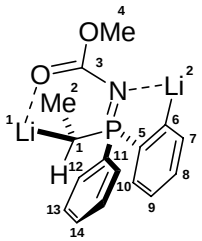
NMR samples of **6** were prepared according to the following protocol: to a solution of 26 mg (91 mmol) of **3a** in dry THF-d_8 (0.3 mL) prepared in a dried 5-mm NMR tube at -70 ºC were added 132 μL (0.199 mmol) of *s*BuLi (1.3 M solution in *n*-hexane). The sample was transferred to the magnet with the probehead previously cooled to –90 ºC. The extra signals shown in the spectra correspond to the solvent of the organolithium base, which was not eliminated. This procedure reproduces faithfully the same reaction conditions used in bulk. The NMR spectra of neutral compounds were measured in $CDCl_3$ solutions. Unless otherwise stated, standard Bruker software routines were used for the 1D and 2D NMR measurements.

Selected spectral parameters were as follows: ^{7}Li NMR (194.32 MHz): 16 *K* data points; spectral width 1400 Hz; exponential multiplication with a line broadening factor of 1 Hz. ^{31}P NMR (202.4 MHz): 32 *K*

1 J. M. Álvarez-Gutiérrez, E. Peralta-Pérez, I. Pérez-Álvarez and F. López-Ortiz, *Tetrahedron*, 2001, **57**, 3075.

data points; spectral width 6000 Hz; exponential multiplication with a line broadening factor of 1 Hz. Resolution enhancement processing parameters are given at the caption of the appropriated figure. The assignment of the proton signals was based on the analysis of chemical shifts and the multiplicity patterns in the ^{1}H NMR spectra. For compound **6** the assignment was completed through the correlations observed in a 2D COSY45 spectrum acquired at –90 ºC. The assignment of the carbon signals was deduced from the correlations observed in the HMQC spectrum measured at –90 ºC and the magnitude of the chemical shifts.

Numbering scheme for **6**:

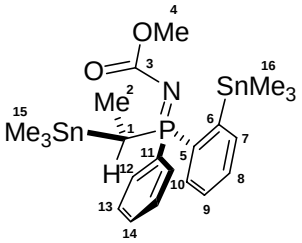


NMR data for 6 in THF-d_8: ^{1}H NMR (500.13 MHz, -90 ºC) δ 0.4 (bs, H1), 1.34 (dd, H2, J_{PH}= 20.5, J_{HH}= 8.2 Hz), 3.55 (s, H4), 6.70 (bt, H8, J_{PH}= 2.0, J_{HH}= 6.8 Hz), 6.72 (q, H9, J_{PH}= J_{HH}= 6.8 Hz), 7.24 (m, H13), 7.25 (m, H14), 7.4 (dd, H10, J_{PH}= 10.9, J_{HH}= 6.8 Hz), 7.69 (m, H12), 7.95 (d, H7, J_{HH}= 6.8 Hz). ^{13}C NMR (125.76 MHz, -95 ºC) δ 1.83 (dq, C1, J_{PC}= 51.9, J_{CLi}= 17.0 Hz), 11.58 (C2), 51.45 (C4), 121.3 (d, C9, J_{PC}= 16.0 Hz), 124.5 (C8), 127.62 (C10), 127.79 (d, C13, J_{PC}= 9.0 Hz), 128.87 (d, C14, J_{PC}= 3.1 Hz), 131.0 (d, C12, J_{PC}= 7.5 Hz), 140.06 (d, C11, J_{PC}= 81.8 Hz), 142.28 (d, C7, J_{PC}= 24.9Hz), 145.44 (d, C5, J_{PC}= 110.7 Hz), 165.08 (C3), 209.27 (m, C6, J_{CLi}= 30.3 Hz). ^{31}P NMR (202.46, -100 ºC) δ 43.81. ^{7}Li NMR (194.37 MHz, -100 ºC) δ 1.2 (d, Li2, J_{PLi}= 3.2 Hz), 2.3 (d, Li1, J_{PLi}= 7.1 Hz). Key: bs: broad singlet, bt: broad triplet, m: multiplet.

Synthesis of the tin(IV) complexes 7, 8, and 9.

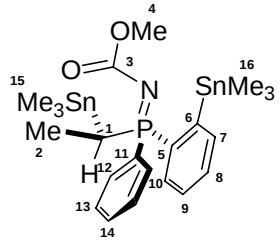
To a solution of **3a** (6.64×10^{-4} mol) in THF (15 mL) was added a solution of *t*BuLi (0.86 mL of a 1.7 M solution in cyclohexane, 1.46×10^{-3} mol) at –70 ºC. After 30 min of metalation was added chlorotrimethyltin (1.33×10^{-3} mol). The reaction mixture was stirred at –95 ºC for 15 h and then quenched with water. After aqueous workup, the organic layers were dried over Na_2SO_4 and concentrated in vacuo. ^{1}H, ^{1}H{^{31}P}, and ^{31}P NMR spectra of the crude reaction were measured in order to determine the distribution of products. The crude mixture was purified by flash column chromatography (eluent: ethyl acetate:hexane, ratio of 1:4) affording the compounds **7**, **8**, and **9** (order of elution). Yields after chromatography were 63% for **7** (white solid, 93.8 ºC), 3% for **8** (yellow oil), and 10% for **9** (white solid, 132.5 ºC).

Numbering scheme for **7**:



NMR data for 7 in $CDCl_3$: ^{1}H NMR (500.13 MHz, 25 ºC) δ 0.05 (s, H15), 0.36 (s, H16), 1.33 (dd, H2, J_{PH}= 18.7, J_{HH}= 7.4 Hz), 2.46 (dq, H1, J_{PH}= 13.7, J_{HH}= 7.4 Hz), 3.62 (s, H4), 7.37 (ddt, H9, J_{PH}= 3.4, J_{HH}= 7.6 Hz, J_{HH}= 1.4 Hz), 7.48 (m, H8, H13 y H14), 7.56 (dddd, H10, J_{PH}= 12.6, J_{HH}= 7.6 Hz, J_{HH}= 1.4 Hz, J_{HH}= 0.5 Hz), 7.68 (m, H12), 7.89 (dddd, H7, J_{PH}= 2.8, J_{HH}= 7.6 Hz, J_{HH}= 1.4 Hz, J_{HH}= 0.5 Hz). ^{13}C NMR (125.76 MHz, 25 ºC) δ -7.02 (d, C15, J_{PC}= 1.4 Hz), -3.08 (d, C16, J_{PC}= 0.9 Hz), 10.85 (d, C2, J_{PC}= 4.3 Hz), 13.28 (d, C1, J_{PC}= 47.4 Hz), 51.98 (d, C4, J_{PC}= 3.4 Hz), 127.97 (d, C9, J_{PC}= 14.3 Hz), 128.67 (d, C13, J_{PC}= 11.3 Hz), 130.27 (d, C8, J_{PC}= 3.4 Hz), 130.91 (d, C10, J_{PC}= 18.2 Hz), 131.26 (d, C12, J_{PC}= 9.1 Hz), 131.53 (d, C14, J_{PC}= 2.8 Hz), 131.55 (d, C11, J_{PC}= 83.3 Hz), 134.07 (d, C5, J_{PC}= 117.6 Hz), 137.55 (d, C7, J_{PC}= 14.3 Hz), 151.75 (d, C6, J_{PC}= 11.1 Hz), 162.32 (d, C3, J_{PC}= 3.5 Hz). ^{31}P NMR (202.46, 25 ºC) δ 31.88, $^{2}J_{SnP}$= 30.1, $^{3}J_{SnP}$= 11.1 Hz. ^{119}Sn NMR (186.5, 25 ºC) δ 7.59 (d, $^{2}J_{SnP}$= 30.1 Hz, *Sn*C1), -72.91 (d, $^{3}J_{SnP}$= 11.1 Hz, *Sn*C6). MS (APCI-ES) *m/z* 616 (M+1). Calcd (%) for $C_{22}H_{34}NO_2PSn_2$: C, 43.11; H, 5.59; N, 2.29. Found: C, 43.09; H, 5.63; N, 2.27.

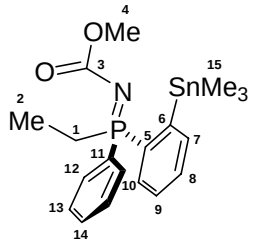
Numbering scheme for **8**:



NMR data for 8 in $CDCl_3$: ^{1}H NMR (300.13 MHz, 25 ºC) δ 0.02 (s, H15), 0.30 (s, H16), 1.54 (dd, H2, J_{PH}= 18.9, J_{HH}= 7.5 Hz), 2.53 (dq, H1, J_{PH}= 12.4, J_{HH}= 7.5 Hz), 3.62 (s, H4), 7.43 (m, H8, H9, H13 and H14), 7.62 (ddd, H10, J_{PH}= 11.8, J_{HH}= 7.6 Hz, J_{HH}= 1.5 Hz), 7.70 (m, H12), 7.85 (ddd, H7, J_{PH}= 2.7, J_{HH}= 7.6 Hz, J_{HH}= 1.4 Hz, J_{HH}= 0.5 Hz). ^{13}C NMR (75.47 MHz, 25 ºC) δ -8.62 (d, C15, J_{PC}= 1.4 Hz), -3.36 (C16), 11.72 (d, C2, J_{PC}= 4.6 Hz), 16.46 (d, C1, J_{PC}= 48.1 Hz), 52.0 (d, C4, J_{PC}= 3.3 Hz), 127.84 (d, C9, J_{PC}= 13.6 Hz), 128.59 (d, C13, J_{PC}= 11.5 Hz), 130.45 (d, C8, J_{PC}= 3.0 Hz), 130.55 (d, C11, J_{PC}= 82.7 Hz), 131.0 (d, C10, J_{PC}= 16.5 Hz), 131.23 (d, C14, J_{PC}= 2.9 Hz), 131.51 (d, C12, J_{PC}= 9.5 Hz), 134.18 (d,

C5, J_{PC}= 120.3 Hz), 137.84 (d, C7, J_{PC}= 14.3 Hz), 151.18 (d, C6, J_{PC}= 12.0 Hz), 162.32 (d, C3, J_{PC}= 3.5 Hz). ^{31}P NMR (121.49, 25 ºC) δ 31.15, $^{2}J_{SnP}$= 27.9, $^{3}J_{SnP}$= 16.7 Hz. ^{119}Sn NMR (186.5, 25 ºC) δ 18.6 (d, $^{2}J_{SnP}$= 27.9 Hz, *Sn*C1), -69.24 (d, $^{3}J_{SnP}$= 16.7 Hz, *Sn*C6). MS (APCI-ES) *m/z* 616 (M+1). Calcd (%) for $C_{22}H_{34}NO_2PSn_2$: C, 43.11; H, 5.59; N, 2.29. Found: C, 43.13; H, 5.65; N, 2.31.

Numbering scheme for **9**:

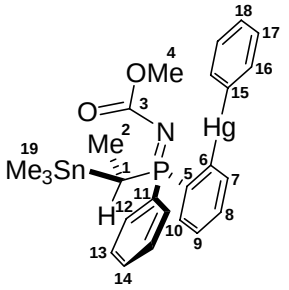


NMR data for 9 in $CDCl_3$: ^{1}H NMR (500.13 MHz, 25 ºC) δ 0.37 (s, H15), 1.05 (dt, H2, J_{PH}= 18.3 Hz, J_{HH}= 7.5 Hz), 2.41 (ddq, H1, J_{PH}= 8.4 Hz, J_{HH}= 15 Hz, J_{HH}= 7.5 Hz), 3.18 (tq, H1, J_{PH}= J_{HH}= 15 Hz, J_{HH}= 7.5 Hz), 3.61 (s, H4), 7.38 (m, H9), 7.45 (m, H13), 7.51 (m, H), 7.69 (m, H12) y 7.92 (m, H-7). ^{13}C NMR (125.76 MHz, 25 ºC) δ -3.33 (C15), 5.59 (d, C2, J_{PC}= 4.0 Hz), 18.34 (d, C1, J_{PC}= 57.9 Hz), 52.15 (d, C4, J_{PC}= 3.4 Hz), 128.11 (d, C9, J_{PC}= 14.6 Hz), 128.73 (d, C13, J_{PC}= 11.5 Hz), 130.75 (d, C5, J_{PC}= 119.6 Hz), 130.87 (d, C8, J_{PC}= 3.6 Hz), 131.03 (d, C11, J_{PC}= 86.9 Hz), 131.37 (d, C10, J_{PC}= 18.6 Hz), 131.41 (d, C12, J_{PC}= 9.1 Hz), 131.96 (d, C14, J_{PC}= 2.7 Hz), 152.50 (d, C6, J_{PC}= 11.9 Hz), 162.31 (d, C3, J_{PC}= 2.5 Hz). ^{31}P NMR (202.46, 25 ºC) δ 27.93, $^{3}J_{SnP}$= 13.4 Hz. ^{119}Sn NMR (186.5, 25 ºC) δ -73.42 (d, $^{3}J_{SnP}$= 13.4 Hz, *Sn*C6). MS (APCI-ES) *m/z* 452 (M+1). Calcd (%) for $C_{19}H_{26}NO_2PSn$: C, 50.70; H, 5.82; N, 3.11. Found: C, 50.72; H, 5.79; N, 3.13.

Synthesis of the Hg(II), tin(IV) complexes 10, 11, and Hg(II) complex 12.

A solution of **3a** ($6.64x10^{-4}$ mol) in THF (15 mL) was treated with a solution of *t*BuLi (0.86 mL of a 1.7 M solution in cyclohexane, $1.46x10^{-3}$ mol) at –70 ºC for 30 min. Chlorophenylmercury ($6.64x10^{-4}$ mol) was then introduced at –90 ºC to the reaction mixture, which was stirred for 15 h. Subsequently, chlorotrimethyltin ($6.64x10^{-4}$ mol) was added at –90 ºC and the reaction mixture was stirred for an additional period of 4 h. After aqueous workup, the organic layers were dried over Na_2SO_4 and concentrated in vacuo. ^{1}H, ^{1}H{^{31}P}, and ^{31}P NMR spectra of the crude reaction were measured in order to determine the distribution of products. The crude mixture was purified by flash column chromatography (eluent: ethyl acetate:hexane, ratio of 1:5; adsorbent: alumina) affording the compounds **10**, **11**, and **12** (order of elution). Yields after chromatography were 40% for **10** (white oil), 8% for **11** (yellow oil), and 4% for **12** (white foam).

Numbering scheme for **10**:



NMR data for (2-((R*)-*N*-(methoxycarbonyl)-*P*-phenyl-*P*-((R*)-1-(trimethylstannyl)-ethyl)phosphorimidoyl)phenyl)-(phenyl)mercury 10 in THF-d_8: ^{1}H NMR (300.13 MHz, 25 ºC) δ 0.01 (s, H19), 1.40 (dd, H2, J_{PH}= 19, J_{HH}= 7.5 Hz), 2.59 (dq, H1, J_{PH}= 12.1, J_{HH}= 7.5 Hz), 3.48 (s, H4), 7.14 (m, H18), 7.33 (m, H9 and H17), 7.47 (m, H8, H13 and H14), 7.65 (m, H16), 7.69 (m, H7) and 7.85 (m, H10 and H12). ^{13}C NMR (75.47 MHz, 25 ºC) δ -7.61 (d, C19, J_{PC}= 1.5 Hz), 9.81 (d, C2, J_{PC}= 4.2 Hz), 13.04 (d, C1, J_{PC}= 46.6 Hz), 50.92 (d, C4, J_{PC}= 3.5 Hz), 126.53 (d, C9, J_{PC}= 14.5 Hz), 126.54 (C18), 127.30 (C17), 128.51 (d, C13, J_{PC}= 11.5 Hz), 129.84 (d, C8, J_{PC}= 3.3 Hz), 131.45 (d, C10, J_{PC}= 18.6 Hz), 130.95 (d, C12, J_{PC}= 9.2 Hz), 131.30 (d, C14, J_{PC}= 2.7 Hz), 132.35 (d, C11, J_{PC}= 88.1 Hz), 135.76 (d, C5, J_{PC}= 116.1 Hz), 138.49 (C16), 139.28 (d, C7, J_{PC}= 14.2 Hz), 162.27 (d, C3, J_{PC}= 4.6 Hz), 167.21 (d, C15, J_{PC}= 4.8 Hz) and 177.28 (d, C6, J_{PC}= 11.9 Hz). ^{31}P NMR (121.49, 25 ºC) δ 35.34 ($^{3}J_{HgP}$= 90.5 Hz, $^{2}J_{SnP}$= 32.8). ^{199}Hg NMR (89.58, 25 ºC) δ -701.87 (d, $^{3}J_{HgP}$= 90.5 Hz). ^{119}Sn NMR (186.50, 25 ºC) δ 7.55 (d, $^{2}J_{SnP}$= 32.8). Calcd (%) for $C_{25}H_{30}HgNO_2PSn$: C, 41.31; H, 4.16; N, 1.93. Found: C, 41.35; H, 4.11; N, 1.94.

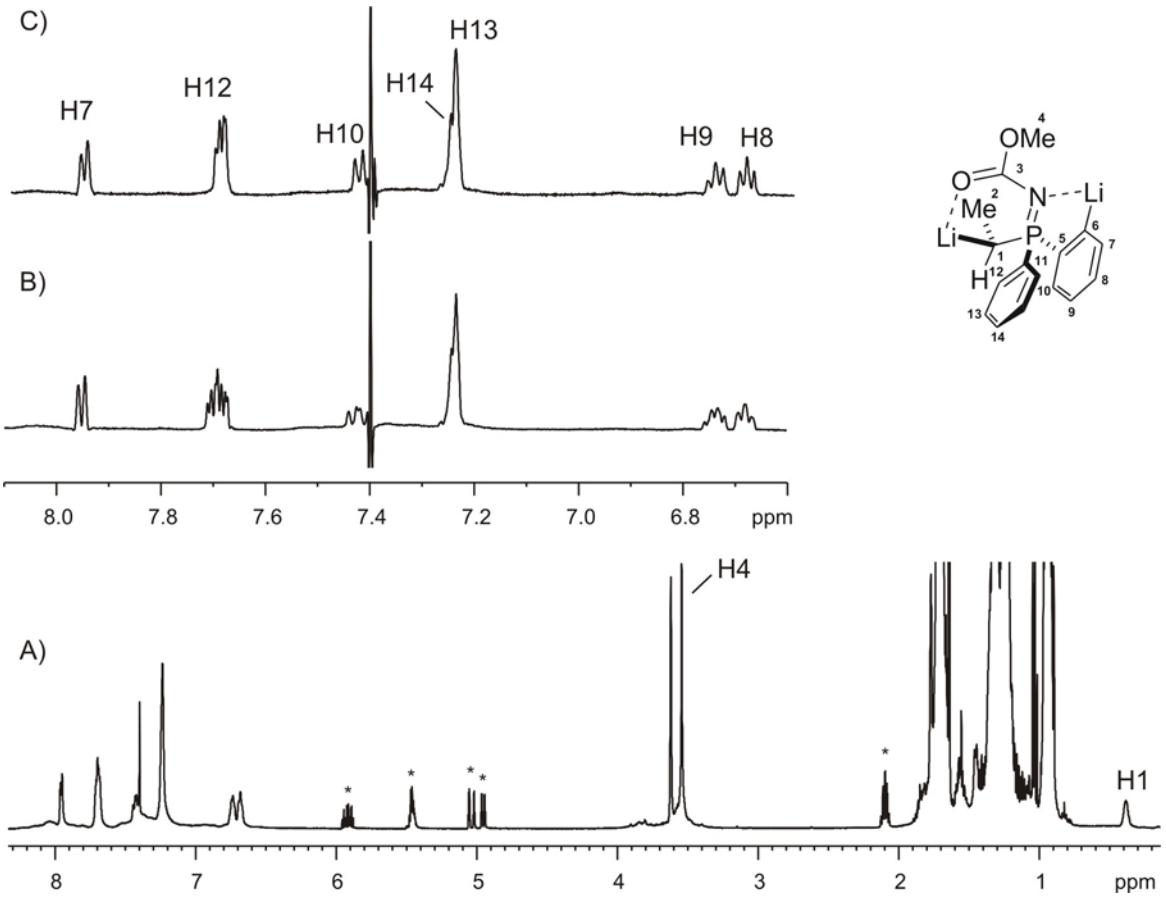


Figure S1. ^{1}H NMR spectra (500.13 MHz) of **6** in THF-d_8 measured at –90 ºC: (A) standard. (B) Expansion of the aromatic region of (A), processed with resolution enhancement (Gaussian, LB= –5, GB= 0.1). (C) The same as (B) with ^{31}P decoupling. *The olefinic proton signals and some of the signals appearing in the high field region correspond to impurities present in the *s*BuLi solution.[2]

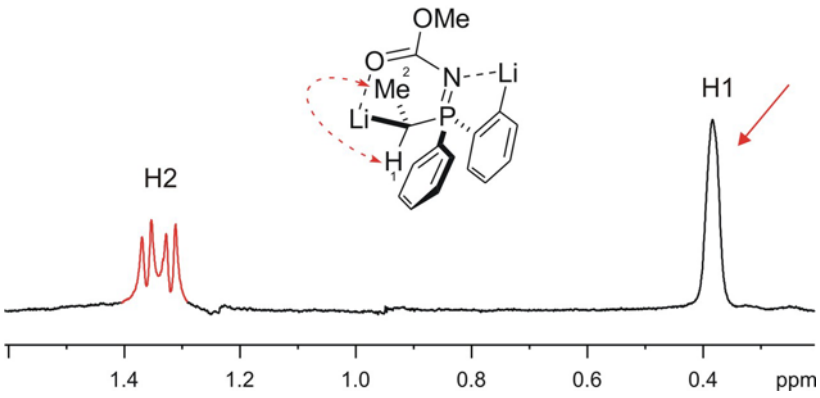


Figure S2. Expansion of the 1D gTOCSY of **6** in THF-d_8 measured at –90 ºC. The arrow indicates the proton being selectively excited.

2 T. R. Hoye, B. M. Eklov and M. Voloshim, *Org. Lett*., 2004, **6**, 2567.

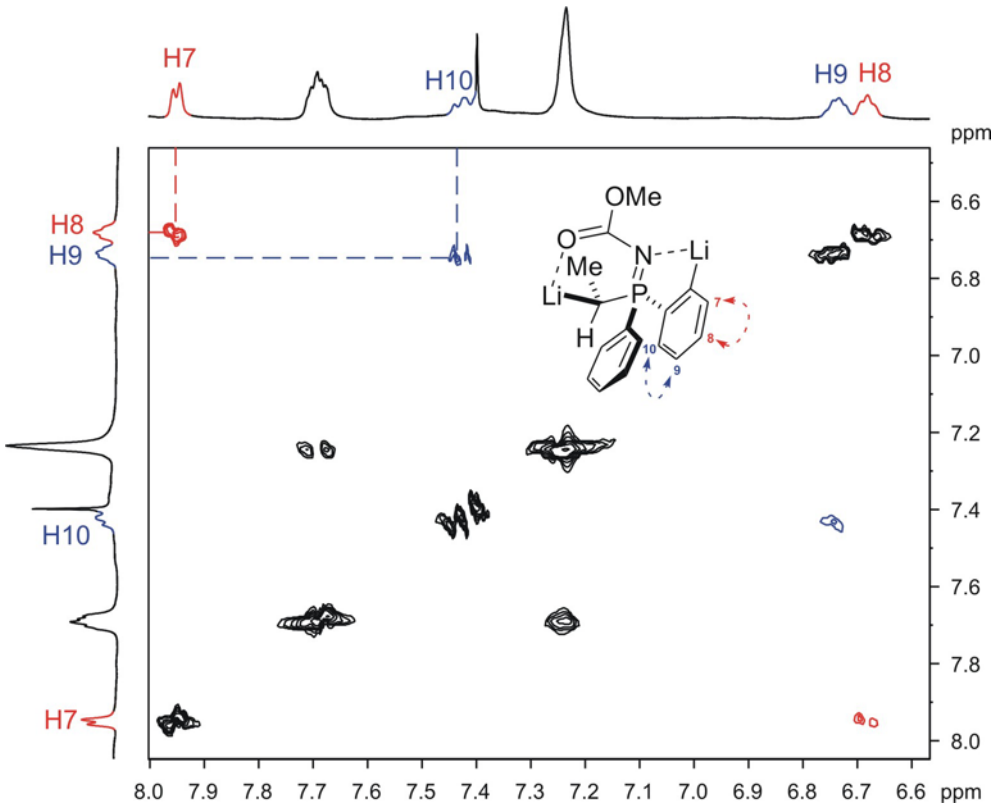


Figure S3. Expansion of the 2D gCOSY45 spectrum (500.13 MHz) of **6** in THF-d_8 measured at –95 ºC. Only the aromatic region is shown.

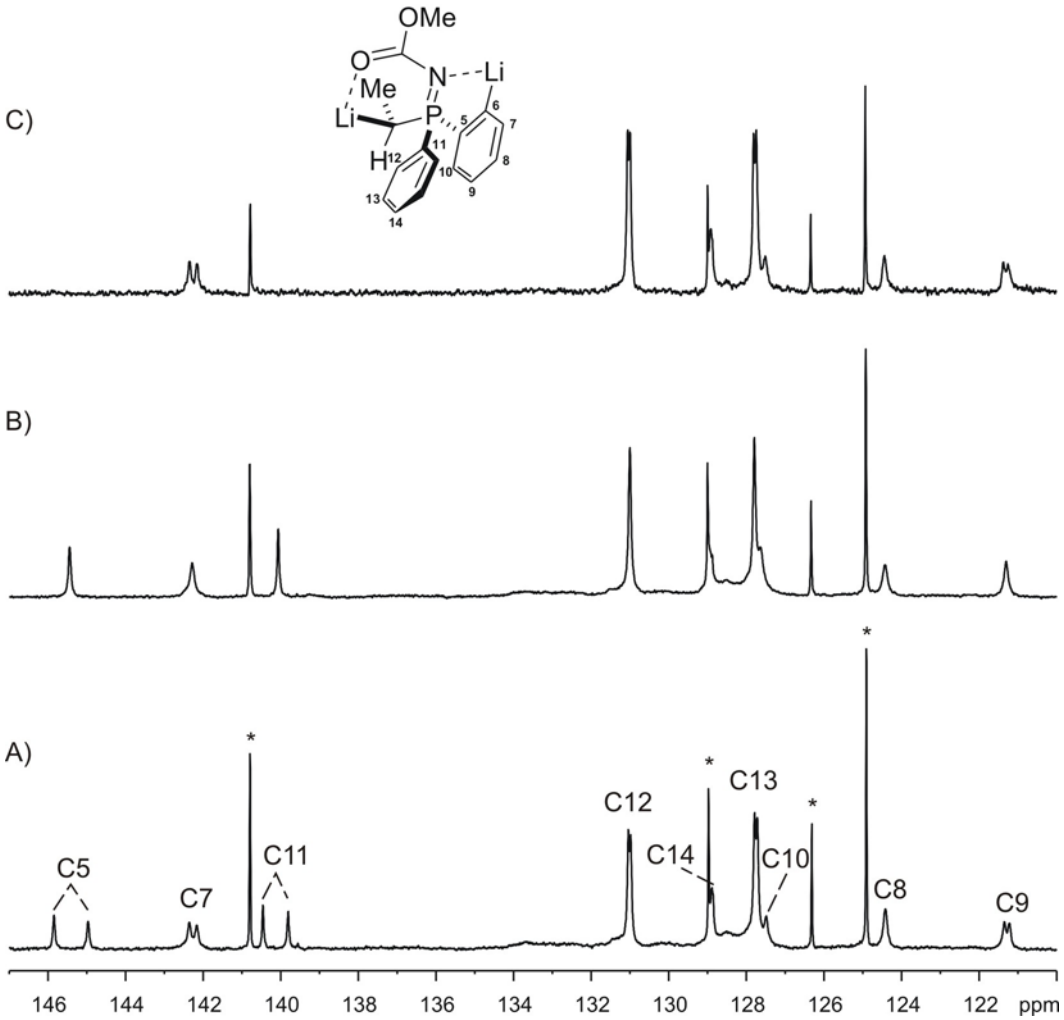


Figure S4. Aromatic region of the ^{13}C NMR spectra (125.76 MHz) of **6** in THF-d_8 measured at –95 ºC: (A) $^{13}C\{^{1}H\}$. (B) $^{13}C\{^{31}P,^{1}H\}$. (C) DEPT135. *Olefinic carbon signals are assigned to impurities present in the *s*BuLi solution.[2]

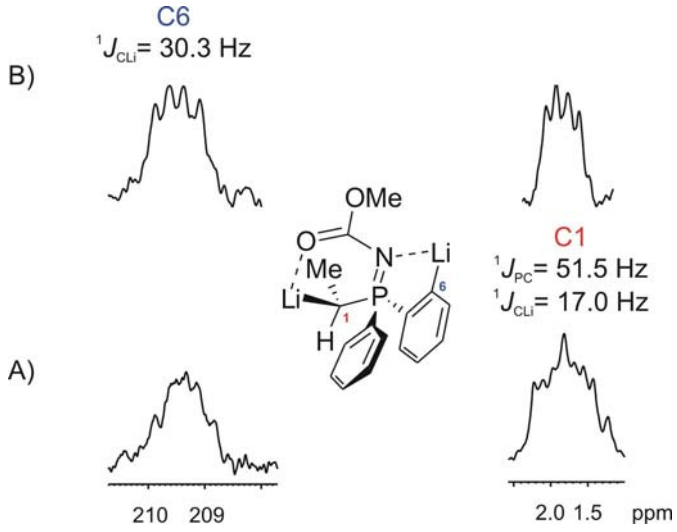


Figure S5. Expansions of the C1 and C6 carbon signals (125.76 MHz) of **6** measured at –95 ºC: (A) $^{13}C\{^{1}H\}$ NMR spectrum. (B) $^{13}C\{^{31}P,^{1}H\}$ NMR spectrum.

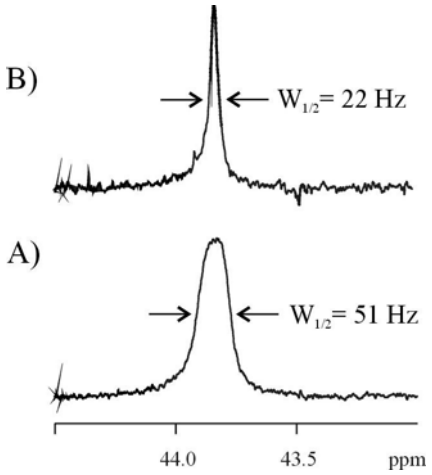


Figure S6. $^{31}P\{^{1}H\}$ NMR spectra (202.46 MHz) of **6** measured at –100 ºC processed with exponential multiplication (LB: 2): (A) Standard. (B) With ^{7}Li decoupling. The arrows indicate the line width at half height.

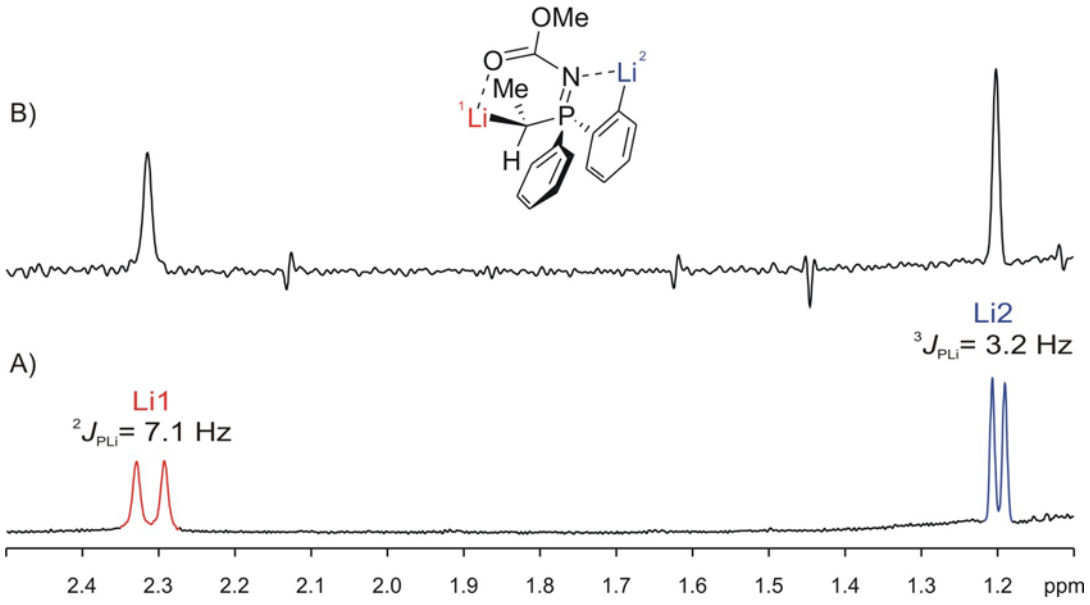


Figure S7. $^{7}Li\{^{1}H\}$ NMR spectra (194.37 MHz) of **6** measured at –100 ºC: (A) standard, processed with resolution enhancement (Gaussian multiplication of the FID, LB: -2.5, GB: 0.1). (B) Acquired with ^{31}P decoupling (Gaussian multiplication of the FID, LB: –2.5, GB: 0.3).

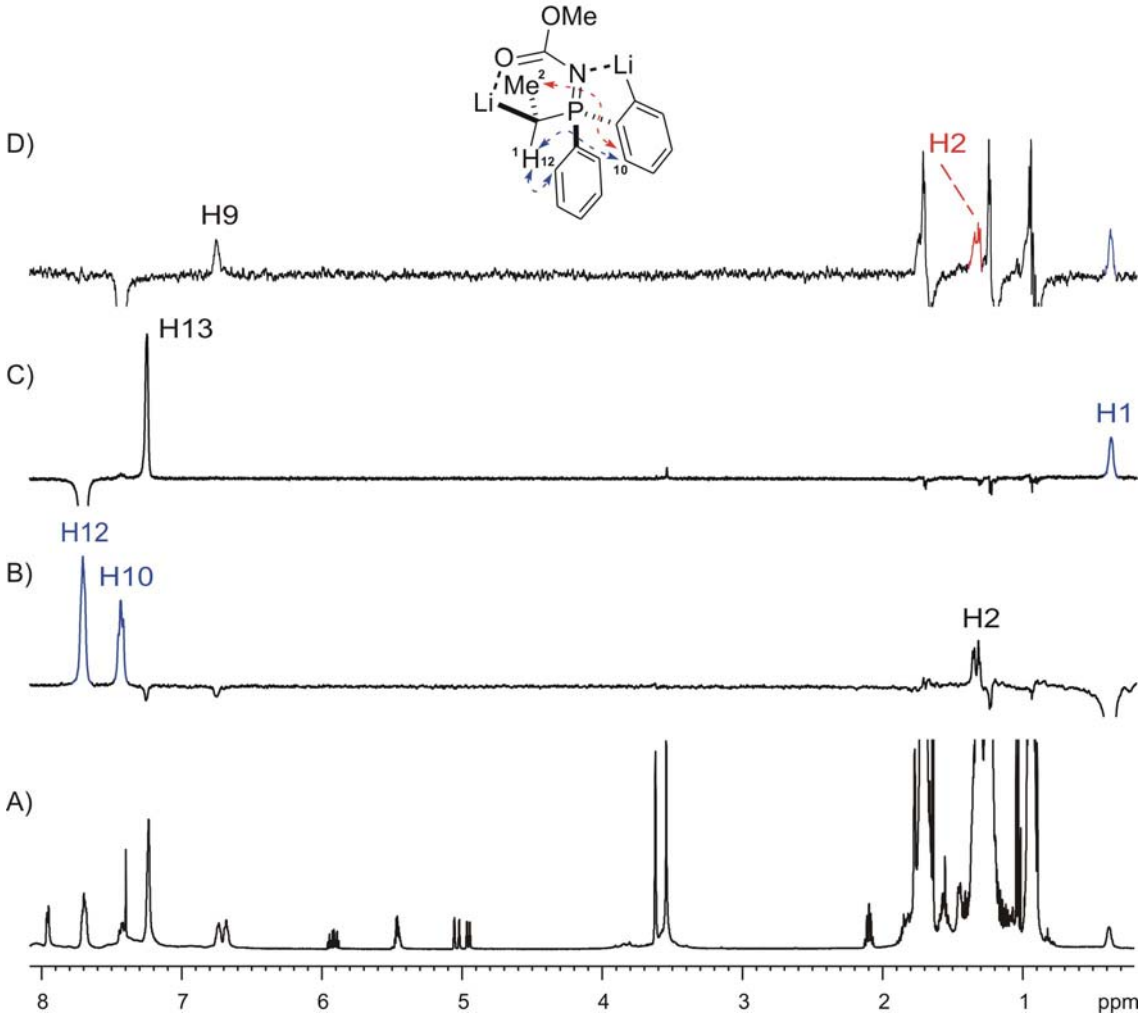


Figure S8. ^{1}H NMR spectra (500.13 MHz) of **6** in THF-d_8 measured at –90 ºC: (A) reference. (B), (C), and (D) 1D gROESY, mixing time of 200 ms.

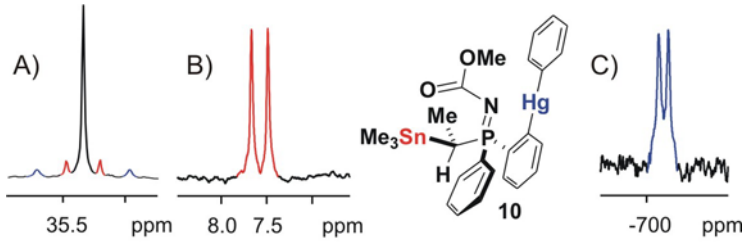


Figure S9. Selection NMR spectra of **10** in THF-d_8: (A) ^{31}P{^{1}H} NMR spectrum (121.49 MHz) of **10** in THF-d_8 (LB: 2). (B) ^{119}Sn, ^{1}H INEPT spectrum (186.50 MHz) of **10** in THF-d_8 (LB: 4). (C) ^{199}Hg{^{1}H} NMR spectrum (89.58 MHz) of **10** in THF-d_8 (LB: 5).

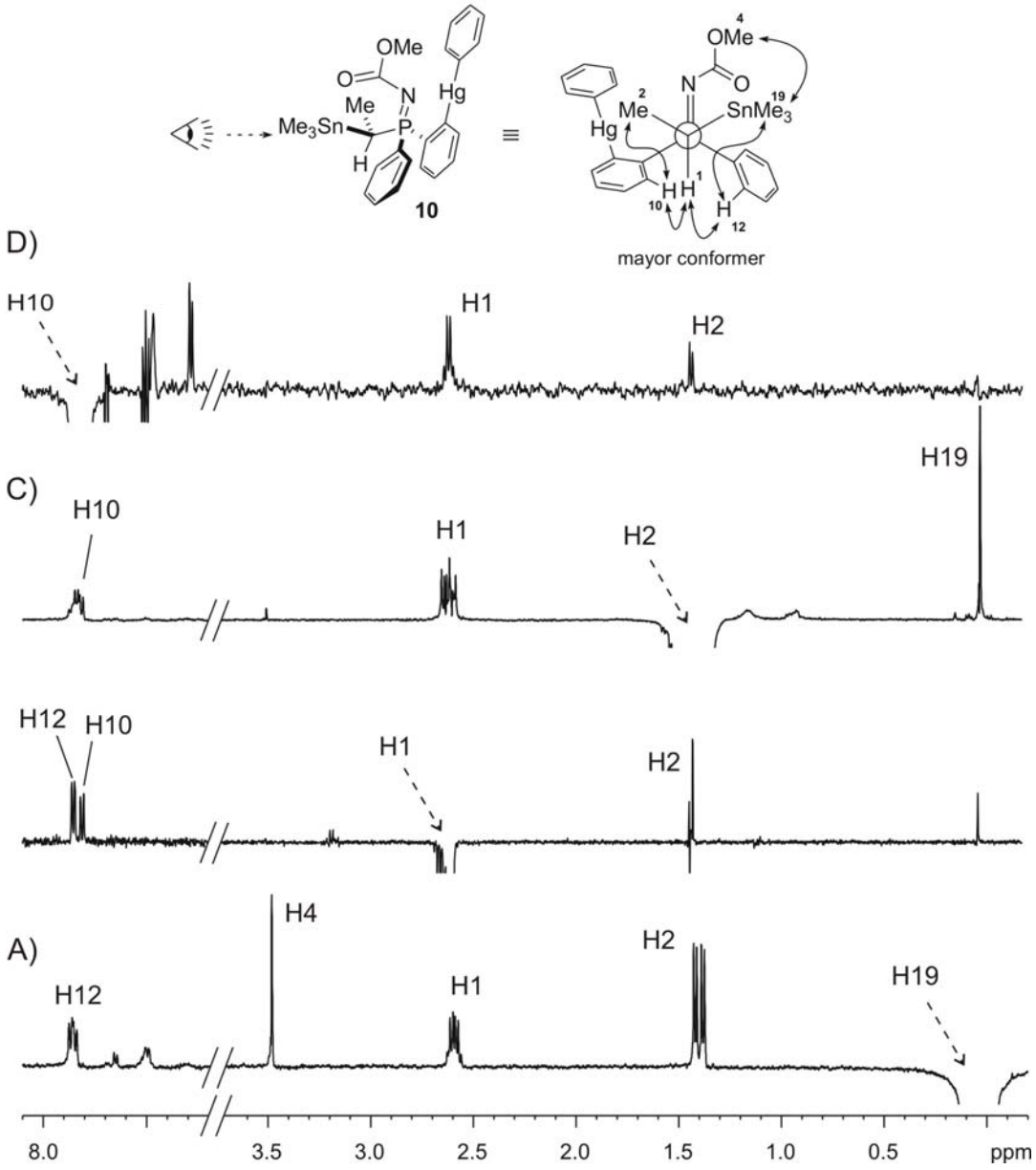


Figure S10. 1D gNOESY spectra (500.13 MHz) of **10** in THF-d_8, mixing time of 500 ms: (A) and (C); (B) and (D) acquired with ^{31}P decoupling.