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C₅(α,ortho) Dimetalated Phosphazene Complexes
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**General.** All reactions and manipulations were carried out in a dry N₂ gas atmosphere using standard procedures. THF and THF-d₈ 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 F₂₅₄. 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 (B₀= 7 T) and 500 MHz (B₀= 11.74 T). Two 5-mm probe heads were used: a QNPZ probe (¹H, ¹³C, ¹⁵N, ³¹P) for B₀=7 T, and a direct triple probe ¹H/³¹P, BB (³¹P–¹⁰⁹Ag) for B₀= 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 ¹H and ¹³C, external 85% H₃PO₄ for ³¹P, 1 M LiBr in D₂O for ⁷Li, Me₂Sn (saturated solution in CDCl₃) for ¹¹⁹Sn, and Me₂Hg (neat liq.; Ξ= 17.910822 MHz) for ¹⁹⁹Hg. A set of two complementary ³¹P/⁷Li-selective band pass/stop frequency filters was used for the measurement of NMR spectra involving ³¹P and ⁷Li nuclei.

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

<table>
<thead>
<tr>
<th>Field (Tesla)</th>
<th>¹H</th>
<th>¹H-dec</th>
<th>⁷Li</th>
<th>⁷Li-dec</th>
<th>¹³C</th>
<th>³¹P</th>
<th>³¹P-dec</th>
<th>¹¹⁹Sn</th>
<th>¹⁹⁹Hg</th>
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<tr>
<td>7.05</td>
<td>8.8 (-2)</td>
<td>95 (20)</td>
<td>-</td>
<td>-</td>
<td>8.0 (-3)</td>
<td>9.7 (-6)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Freq (MHz)</td>
<td>300.13</td>
<td>300.13</td>
<td>75.47</td>
<td>121.49</td>
<td>15.7 (0)</td>
<td>88 (15)</td>
<td>7.5 (0)</td>
<td>31 (0)</td>
<td>100 (8.4)</td>
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<tr>
<td>11.74</td>
<td>9.2 (-4)</td>
<td>85 (15)</td>
<td>15.7 (0)</td>
<td>194.37</td>
<td>194.37</td>
<td>125.72</td>
<td>202.46</td>
<td>202.46</td>
<td>186.5 (186.5)</td>
</tr>
<tr>
<td>Freq (MHz)</td>
<td>500.13</td>
<td>500.13</td>
<td>194.37</td>
<td>194.37</td>
<td>125.72</td>
<td>202.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

NMR samples of 6 were prepared according to the following protocol: to a solution of 26 mg (91 mmol) of 3a in dry THF-d₈ (0.3 mL) prepared in a dried 5-mm NMR tube at -70 ºC were added 132 µL (0.199 mmol) of sBuLi (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 CDCl₃ solutions. Unless otherwise stated, standard Bruker software routines were used for the 1D and 2D NMR measurements.

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

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:

![Numbering Scheme](image)

NMR data for 6 in THF-$d_8$: $^1$H NMR (500.13 MHz, -90 ºC) $\delta$ 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) $\delta$ 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) $\delta$ 43.81. $^7$Li NMR (194.37 MHz, -100 ºC) $\delta$ 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 (6.64x10$^{-4}$ mol) in THF (15 mL) was added a solution of tBuLi (0.86 mL of a 1.7 M solution in cyclohexane, 1.46x10$^{-3}$ mol) at −70 ºC. After 30 min of metalation was added chlorotrimethyltin (1.33x10$^{-3}$ 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$_2$SO$_4$ 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:

![Numbering Scheme for 7]

NMR data for 7 in CDCl₃: ¹H NMR (500.13 MHz, 25 °C) δ 0.05 (s, H15), 0.36 (s, H16), 1.33 (dd, H2, J_PΗ= 18.7, J_HΗ= 7.4 Hz), 2.46 (dq, H1, J_PΗ= 13.7, J_HΗ= 7.4 Hz), 3.62 (s, H4), 7.37 (ddt, H9, J_PΗ= 12.6, J_HΗ= 7.6 Hz, J_HΗ= 1.4 Hz, J_HΗ= 0.5 Hz), 7.48 (m, H8, H13 and H14), 7.56 (dddd, H10, J_PΗ= 2.8, J_HΗ= 7.6 Hz, J_HΗ= 1.4 Hz, J_HΗ= 0.5 Hz). ¹³C NMR (125.76 MHz, 25 °C) 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). ³¹P NMR (202.46, 25 °C) δ 31.88, 2J_SnP= 30.1, 3J_SnP= 11.1 Hz. ¹¹⁹Sn NMR (186.5, 25 °C) δ 7.59 (d, 2J_SnP= 30.1 Hz, SnC1), -72.91 (d, 3J_SnP= 11.1 Hz, SnC6). MS (APCI-ES) m/z 616 (M+1). Calcd (%) for C₂₂H₃₄NO₂PSn₂: C, 43.11; H, 5.59; N, 2.29. Found: C, 43.09; H, 5.63; N, 2.27.

Numbering scheme for 8:

![Numbering Scheme for 8]

NMR data for 8 in CDCl₃: ¹H NMR (300.13 MHz, 25 °C) δ 0.02 (s, H15), 0.30 (s, H16), 1.54 (dd, H2, J_PΗ= 18.9, J_HΗ= 7.5 Hz), 2.53 (dq, H1, J_PΗ= 12.4, J_HΗ= 7.5 Hz), 3.62 (s, H4), 7.43 (m, H8, H9, H13 and H14), 7.62 (dd, H10, J_PΗ= 11.8, J_HΗ= 7.6 Hz, J_HΗ= 1.5 Hz), 7.70 (m, H12), 7.85 (dd, H7, J_PΗ= 2.7, J_HΗ= 7.6 Hz, J_HΗ= 1.4 Hz, J_HΗ= 0.5 Hz). ¹³C NMR (75.47 MHz, 25 °C) 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 $^{2}$J_{SnP} = 27.9, 3 $^{3}$J_{SnP} = 14.3 Hz, 151.18 (d, C6, J_{PC} = 12.0 Hz), 162.32 (d, C3, J_{PC} = 3.5 Hz). $^{13}$C NMR (125.76 MHz, 25 ºC) δ -3.33 (C15), 5.59 (d, C2, J_{PC} = 4.0 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), 131.66 (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 $^{2}$J_{SnP} = 13.4 Hz. $^{119}$Sn NMR (186.5, 25 ºC) δ -73.42 (d, $^{3}$J_{SnP} = 13.4 Hz, C6). MS (APCI-ES) m/z 616 (M+1). Calcd (%) for C22H34NO2PSn2: C, 43.11; H, 5.59; N, 2.29. Found: C, 43.13; H, 5.65; N, 2.31.

Numbering scheme for 9:

![Numbering scheme for 9](image)

**NMR data for 9 in CDCl$_3$:** $^{1}$H NMR (500.13 MHz, 25 ºC) δ 0.37 (s, H15), 1.05 (dt, H2, $^{1}$J_{PH} = 18.3 Hz, $^{2}$J_{HH} = 7.5 Hz), 2.41 (ddq, H1, $^{1}$J_{PH} = 8.4 Hz, $^{2}$J_{HH} = 15 Hz, $^{1}$J_{HH} = 7.5 Hz), 3.18 (tq, H1, $^{1}$J_{PH} = $^{2}$J_{HH} = 15 Hz, $^{1}$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), 131.66 (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 $^{2}$J_{SnP} = 13.4 Hz. $^{119}$Sn NMR (186.5, 25 ºC) δ -73.42 (d, $^{3}$J_{SnP} = 13.4 Hz, C6). MS (APCI-ES) m/z 452 (M+1). Calcd (%) for C19H26NO2PSn: 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 tBuLi (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$_2$SO$_4$ 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).
NMR data for (2-((R*)-N-(methoxycarbonyl)-P-phenyl-P-((R*)-1-(trimethylstannyl)-ethyl)phosphorimidoyl)phenyl)-(phenyl)mercury 10 in THF-d₈: ¹H NMR (300.13 MHz, 25 °C) δ 0.01 (s, H19), 1.40 (dd, H2, Jₚₚ= 19, J_HH= 7.5 Hz), 2.59 (dq, H1, Jₚₚ= 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). ¹³C NMR (75.47 MHz, 25 °C) 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). ³¹P NMR (121.49, 25 °C) δ 35.34 (³J_HgP= 90.5 Hz, ²J_SnP= 32.8). ¹⁹⁹Hg NMR (89.58, 25 °C) δ -701.87 (d, ³J_HgP= 90.5 Hz). ¹¹⁹Sn NMR (186.50, 25 °C) δ 7.55 (d, ²J_SnP= 32.8). Calcd (%) for C₂₅H₉₀HgNO₂PSn: 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 °C: (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 sBuLi solution.2

Figure S2. Expansion of the 1D gTOCSY of 6 in THF-$d_8$ measured at −90 °C. The arrow indicates the proton being selectively excited.

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Figure S3. Expansion of the 2D gCOSY45 spectrum (500.13 MHz) of 6 in THF-$d_8$ measured at –95 °C. 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 °C: (A) $^{13}$C{$^1$H}. (B) $^{13}$C{$^31$P,$^1$H}. (C) DEPT135. *Olefinic carbon signals are assigned to impurities present in the sBuLi solution.*

Figure S5. Expansions of the C1 and C6 carbon signals (125.76 MHz) of 6 measured at –95 °C: (A) $^{13}$C{$^1$H} NMR spectrum. (B) $^{13}$C{$^31$P,$^1$H} NMR spectrum.
Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (202.46 MHz) of 6 measured at –100 °C processed with exponential multiplication (LB: 2): (A) Standard. (B) With $^7\text{Li}$ decoupling. The arrows indicate the line width at half height.

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