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Reactions of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide with alkyl halides and silicon and tin chlorides*

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Reactions of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide with primary alkyl bromides, secondary alkyl iodides, and silicon and tin chlorides gave stable 1-substituted 1,2-diphospholes. In a solution of 3,4,5-triphenyl-1-trimethylstannyl-1,2-diphosphacyclopenta-2,4-diene, the $\mathrm{Me_3Sn}$ group migrates between two phosphorus atoms.

Key words: sodium 1,2-diphosphacyclopentadienide, phospholes, alkyl halides, organosilicon chlorides, organotin chlorides.

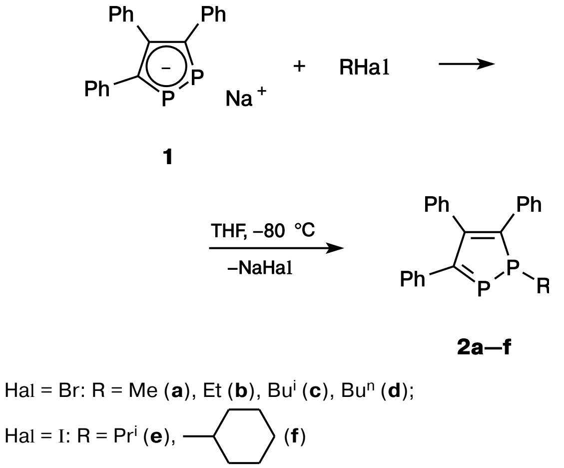
Phosphacyclopentadienes (phospholes), the phosphorus analogs of cyclopentadiene, are attractive synthons for the synthesis of phosphorus-containing polycyclic compounds, phosphacyclopentadienide anions, phosphametallocenes, phosphabenzene, *etc.*[1,2] Cycloaddition reactions involving phosphacyclopentadienes have been used to obtain novel chiral framework compounds of phosphorus, *viz.*, phosphanorbornenes and phosphanorbornadienes, which are employed as ligands for homogeneous, biphasic, and asymmetric catalysis of organic reactions such as the Heck reaction,[3] enantioselective hydrogenation,[4] *C*- and *N*-alkylation,[5] and hydroformylation of olefins.[6,7]

Among phospholes, the chemical behavior of monophosphacyclopentadienes is now best studied; for instance, their two tautomeric forms (1*R*- and 2*R*-phospholes) are known to differ greatly in reactivity and stability. Being thermally stable, 1*R*-phospholes are inert in cycloaddition reactions: only under harsh conditions do they react to give target products in low yields. In contrast, 2*R*-phospholes, which are formed from 1*R*-phospholes at high temperatures *via* *R*[1,5]-sigmatropic shift, contain the highly reactive P=C bond and easily react with both dienes and dienophiles.[8] Earlier,[9] we have demonstrated that 1-alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes (1-alkyl-1,2-diphospholes) combining the fragments of *1R*- and *2R*-phospholes are chemically similar to both tautomeric forms: they are thermally stable like 1*R*-phospholes and are highly reactive in cycloaddition reactions like 2*R*-phospholes.

In connection with this, for development of an approach to the synthesis of novel 1-substituted 1,2-diphospholes, it was interesting to study in more detail the reactivity of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) toward primary, secondary, and tertiary alkyl halides, as well as toward silicon(IV) and tin(IV) chlorides.

We found that sodium 1,2-diphosphacyclopentadienide **1** reacts with primary alkyl bromides in THF at –80 °C to form 1-alkyl-1,2-diphosphacyclopenta-2,4-dienes **2** in 50—60% yields (Scheme 1).

Scheme 1



Hal = Br: R = Me (**a**), Et (**b**), $\mathrm{Bu^i}$ (**c**), $\mathrm{Bu^n}$ (**d**);
Hal = I: R = $\mathrm{Pr^i}$ (**e**), (**f**)

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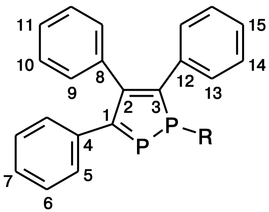
The structures of the obtained compounds were proved by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. For instance, the ^{31}P{^{1}H} NMR spectra of 1-alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes show two doublets at ~200 and ~70 ppm ($^1J_{\mathrm{P,P}} \approx 400$ Hz) characteristic of the sp^2- and sp^3-hybridized P atoms, respectively. In the ^{13}C NMR spectrum, the signal for the C(1) atom at the double P=C(1) bond appears as a doublet of doublets because of a coupling with two nonequivalent phosphorus nuclei.



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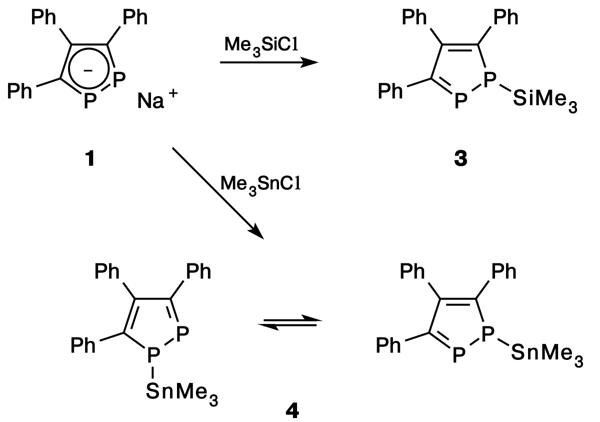
However, sodium 1,2-diphosphacyclopentadienide **1** does not react with secondary alkyl bromides under similar conditions: the starting reagents were recovered unchanged from the reaction mixture. Only the use of secondary alkyl iodides allowed us to obtain novel 1-alkyl-1,2-diphospholes **1e,f** in 40—45% yields. Note that *tert*-butyl iodide is unable to alkylate compound **1**; *i.e.*, the reaction is sensitive to the bulkiness of the electrophilic reagent.

An interesting goal in the context of these investigations was to obtain 1,2-diphospholes containing the Me$_3$Si (or Me$_3$Sn) group at the P atom, since such phospholes seem to be convenient reagents for introduction of a 1,2-diphosphacyclopentadienide ligand into transition metal complexes. We found that chlorotrimethylsilane reacts with sodium 1,2-diphosphacyclopentadienide **1** in THF at −80 °C to give 3,4,5-triphenyl-1-trimethylsilyl-1,2-diphosphacyclopenta-2,4-diene (**3**) (Scheme 2). The ^{31}P{^{1}H} NMR spectrum of compound **3** exhibits two doublets at 212 and 67 ppm with $^1J_{\mathrm{P,P}} = 413.5$ Hz.

Scheme 2



Trimethyltin chloride shows similar reactivity in a reaction with compound **1**. The ^{31}P{^{1}H} NMR spectrum of 3,4,5-triphenyl-1-trimethylstannyl-1,2-diphosphacyclopenta-2,4-diene (**4**) at ~20 °C contains a broad singlet at 116 ppm (the half-width of the signal is 41.7 Hz) with two satellites arising from couplings between the P and Sn nuclei. The ^{119}Sn NMR spectrum at ~20 °C shows a triplet with a central signal at 51 ppm ($^1J_{\mathrm{Sn,P}} = 276$ Hz). This suggests dynamic processes in a solution of compound **4** that are associated with the migration of the Me$_3$Sn group between the phosphorus atoms. Earlier, similar fluctuations of the trimethylstannyl group have been observed for tin derivatives of 1,2,4-triphosphacyclopenta-2,4-diene.[10,11]

Additional evidence for the fluctuations of the Me$_3$Sn group was obtained in the study of the temperature dependence of the ^{31}P{^{1}H} NMR spectrum of compound **4** in THF-d$_8$ (Fig. 1).

For instance, the signal disappears from the spectrum at 183 K, thus suggesting the coalescence temperature is reached. The calculated[12] Gibbs energy of activation of the Me$_3$Sn exchange between two P atoms is $\Delta G^{\neq} = 34.9 \pm 1$ kJ mol^{-1}, which is comparable with the energy of activation for tin derivatives of 1,2,4-triphosphacyclopenta-2,4-diene (31.5 kJ mol^{-1}).[10] At 165 K, the spectrum exhibits two broad signals at ~220 and ~30 ppm because of the stabilization of one tautomeric form. Unfortunately, freezing of the solvent upon further cooling precluded the determination of the coupling constant.

Additional evidence for the fluctuating character of the P—Sn bond was obtained in the attempted synthesis of dimethylbis(3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dien-1-yl)stannane (**6**). We found that a reaction of Me$_2$SnCl$_2$ with two equivalents of compound **1** gives a mixture of mono- (**5**) and disubstituted products (**6**), in which the Cl atoms are replaced by the 3,4,5-triphenyl-1,2-diphosphacyclopentadienyl fragments (Scheme 3).

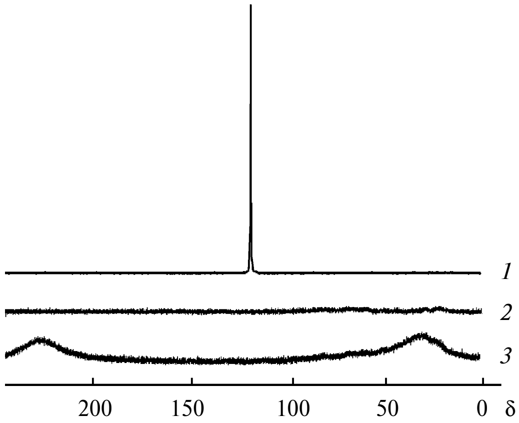
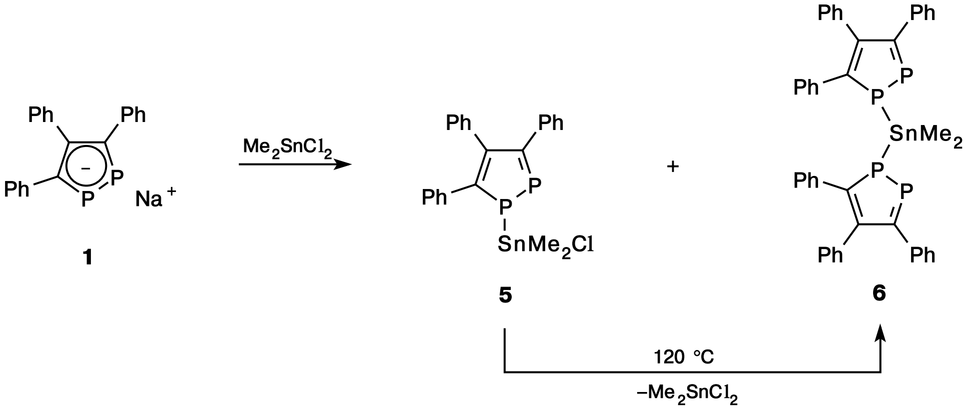


Fig. 1. ^{31}P NMR spectra of 3,4,5-triphenyl-1-trimethylstannyl-1,2-diphosphacyclopentadiene (**4**) at 298 (*1*), 183 (*2*), and 165 K (*3*).

Scheme 3



Our numerous attempts to separate this mixture failed. Nevertheless, the yield of product **6** was increased to 60% upon heating its mixture with compound **5** *in vacuo* at 120 °C with simultaneous removal of Me_2SnCl_2.

To sum up, we demonstrated that the reactions of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide with primary alkyl bromides, secondary alkyl iodides, chlorotrimethylsilane, and trimethyltin chloride afford 1-substituted 1,2-diphospholes. In 1-trimethylstannyl-1,2-diphosphole **4**, the P—Sn bond is labile, which is evident from the tautomeric shift of the Me_3Sn fragment between the phosphorus atoms.

Experimental

All manipulations for the preparation of the starting reagents and the synthesis and isolation of products were carried out in an inert atmosphere using standard Schlenk techniques. All solvents were distilled over Na/benzophenone immediately before use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (400 (^{1}H), 100.6 (^{13}C), and 161.975 MHz (^{31}P)) for 10—20% solutions in inert solvents (C_6D_6, $CDCl_3$) with Me_4Si as the internal standard (^{1}H and ^{13}C) and with 85% H_3PO_4 as the external standard (^{31}P).

Sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) was prepared according to a known procedure.[13] Bromomethane, bromoethane, 1-bromo-2-methylpropane, 1-bromobutane, 2-iodopropane, iodocyclohexane, chlorotrimethylsilane, and trimethyltin chloride were commercial reagents used without further purification.

1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopentadienides (2) (general procedure). An appropriate alkyl halide (1.2 mmol) was added at –80 °C to a solution of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (1 mmol) in THF (30 mL). The reaction mixture was stirred at ~20 °C for 3 h. The solvent was removed and the product was extracted from the residue with hexane (2×30 mL). The extract was filtered, concentrated, and dried *in vacuo*. No further purification of the target product was required.

1-Methyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (2a) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (0.81 g, 1.31 mmol) and bromomethane (0.15 g, 1.57 mmol, 20% excess). The yield of compound **2a** was 0.27 g (61%), light yellow oil. Found (%): C, 76.89; H, 5.33; P, 17.79. $C_{22}H_{18}P_2$. Calculated (%): C, 76.74; H, 5.27; P, 17.99. ^{1}H NMR (C_6D_6), δ: 1.41 (m, 3 H, Me); 6.74—7.16 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 218.44 (d, $^{1}J_{P,P}$ = = 4108.36 Hz); 47.09 (d, $^{1}J_{P,P}$ = 410.36 Hz). ^{13}C NMR (C_6D_6), δ: 15.35 (dd, Me, $^{1}J_{C,P}$ = 44.23 Hz, $^{2}J_{C,P}$ = 13.34 Hz); 125.87 (s, C(11)); 126.32 (s, C(15)); 126.47 (s, C(7)); 127.12 (s, C(6)); 127.98 (s, C(10)); 128.26 (s, C(14)); 128.69 (dd, C(5), $^{3}J_{C,P}$ = = 13.13 Hz, $^{4}J_{C,P}$ = 1.58 Hz); 129.62 (d, C(13), $^{3}J_{C,P}$ = 10.45 Hz); 132.38 (t, C(8), $^{3}J_{C,P}$ = 7.92 Hz); 137.66 (d, C(9), $^{4}J_{C,P}$ = = 4.12 Hz); 139.45 (dd, C(4), $^{2}J_{C,P}$ = 11.33 Hz, $^{3}J_{C,P}$ = 3.69 Hz); 144.07 (d, C(12), $^{2}J_{C,P}$ = 17.88 Hz); 151.67 (t, C(2), $^{2}J_{C,P}$ = = 17.38 Hz); 166.23 (dd, C(3), $^{1}J_{C,P}$ = 11.12 Hz, $^{2}J_{C,P}$ = 5.04 Hz); 197.37 (dd, C(1), $^{1}J_{C,P}$ = 59.28 Hz, $^{2}J_{C,P}$ = 11.19 Hz).

1-Ethyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (2b) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (3.81 g, 6.16 mmol) and bromoethane (0.80 g, 7.34 mmol, 20% excess). The yield of compound **2b** was 1.30 g (59%), light yellow oil. Found (%): C, 76.89; H, 5.22; P, 17.89. $C_{23}H_{20}P_2$. Calculated (%): C, 77.09; H, 5.63; P, 17.29. ^{1}H NMR (C_6D_6), δ: 0.94 (dt, 3 H, CH_3, $^{3}J_{H,H}$ = 7.34 Hz, $^{3}J_{H,P}$ = 14.51 Hz); 2.13 (m, 2 H, CH_2); 7.34 (d, $^{3}J_{H,H}$ = 7.34 Hz); 6.96 (t, 4 H, $^{3}J_{H,H}$ = 6.36 Hz); 7.00 (d, 4 H, $^{3}J_{H,H}$ = 4.89 Hz); 7.03 (d, 2 H, $^{3}J_{H,H}$ = 5.87 Hz); 7.07 (d, 4 H, $^{3}J_{H,H}$ = 7.34 Hz); 7.23 (d, 2 H, $^{3}J_{H,H}$ = 5.38 Hz); 7.31 (t, 1 H, $^{3}J_{H,H}$ = 8.31 Hz). ^{31}P NMR (C_6D_6), δ: 209.47 (d, $^{1}J_{P,P}$ = 408.88 Hz); 73.08 (d, $^{1}J_{P,P}$ = 408.88 Hz). ^{13}C NMR (C_6D_6), δ: 13.98 (d, CH_3, $^{2}J_{C,P}$ = 2.89 Hz); 17.87 (dd, CH_2, $^{1}J_{C,P}$ = 16.13 Hz, $^{2}J_{C,P}$ = = 5.79 Hz); 126.37 (s, C(11)); 126.52 (s, C(15)); 126.88 (s, C(7)); 127.52 (s, C(6)); 128.03 (s, C(10)); 128.26 (s, C(14)); 128.65 (dd, C(5), $^{3}J_{C,P}$ = 11.17 Hz, $^{4}J_{C,P}$ = 2.48 Hz); 129.23 (d, C(13), $^{3}J_{C,P}$ = 9.32 Hz); 131.38 (t, C(8), $^{3}J_{C,P}$ = 9.10 Hz); 137.34 (d, C(9), $^{4}J_{C,P}$ = 5.38 Hz); 138.33 (dd, C(4), $^{2}J_{C,P}$ = 10.34 Hz, $^{3}J_{C,P}$ = = 4.14 Hz); 142.89 (d, C(12), $^{2}J_{C,P}$ = 19.02 Hz); 150.28 (t, C(2), $^{2}J_{C,P}$ = 15.09 Hz); 164.14 (dd, C(3), $^{1}J_{C,P}$ = 10.75 Hz, $^{2}J_{C,P}$ = = 4.55 Hz); 191.90 (dd, C(1), $^{1}J_{C,P}$ = 56.86 Hz, $^{2}J_{C,P}$ = 14.27 Hz).

1-(2-Methylpropyl)-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (2c) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (4.12 g, 6.65 mmol) and 1-bromo-2-methylpropane (1.09 g, 7.98 mmol, 20% excess). The yield of compound **2c** was 1.37 g (55%), light yellow oil. Found (%):

C, 77.82; H, 6.04; P, 16.14. $C_{25}H_{24}P_2$. Calculated (%): C, 77.71; H, 6.26; P, 16.03. ^{1}H NMR (C_6D_6), δ: 0.84 (d, 6 H, $^{3}J_{H,H}$ = 6.85 Hz); 1.48 (m, 1 H, CH); 1.74 (m, 2 H, CH_2); 6.70—7.20 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 207.47 (d, $^{1}J_{P,P}$ = 420.73 Hz); 62.78 (d, $^{1}J_{P,P}$ = 420.73 Hz). ^{13}C NMR (C_6D_6), δ: 23.54 (d, CH_3, $^{3}J_{C,P}$ = 7.86 Hz); 23.81 (d, CH_3, $^{3}J_{C,P}$ = 7.03 Hz); 27.24 (d, $^{2}J_{C,P}$ = 4.96 Hz); 33.57 (d, $^{2}J_{C,P}$ = 16.95 Hz); 126.29 (s, C(15)); 126.42 (s, C(7)); 126.45 (s, C(11)); 127.27 (s, C(6)); 127.92 (s, C(10)); 128.29 (s, C(14)); 128.67 (d, C(5), $^{3}J_{C,P}$ = 16.04 Hz); 129.44 (d, C(13), $^{3}J_{C,P}$ = 10.06 Hz); 133.24 (d, C(8), $^{3}J_{C,P}$ = 16.95 Hz); 137.46 (d, C(9), $^{4}J_{C,P}$ = 6.20 Hz); 138.24 (dd, C(4), $^{2}J_{C,P}$ = 10.34 Hz, $^{3}J_{C,P}$ = 3.72 Hz); 142.81 (d, C(12), $^{2}J_{C,P}$ = 19.44 Hz); 149.17 (t, C(2), $^{2}J_{C,P}$ = 15.51 Hz); 164.56 (dd, C(3), $^{1}J_{C,P}$ = 7.24 Hz, $^{2}J_{C,P}$ = 3.10 Hz); 188.82 (dd, C(1), $^{1}J_{C,P}$ = 57.07 Hz, $^{2}J_{C,P}$ = 14.89 Hz).

1-Butyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (2d) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (4.78 g, 7.71 mmol) and 1-bromobutane (1.26 g, 9.25 mmol, 20% excess). The yield of compound **2d** was 1.70 g (59%), light yellow powder. Found (%): C, 77.86; H, 6.14; P, 16.23. $C_{25}H_{24}P_2$. Calculated (%): C, 77.71; H, 6.26; P, 16.03. ^{1}H NMR (C_6D_6), δ: 0.59 (t, CH_3, 3 H, $^{3}J_{H,H}$ = 7.34 Hz); 1.02 (m, 2 H, CH_2); 1.36 (m, 2 H, CH_2); 2.02 (m, 2 H, CH_2); 6.85 (d, 4 H, $^{3}J_{H,P}$ = 3.42 Hz); 6.90 (d, 2 H, $^{3}J_{H,P}$ = 7.34 Hz); 6.96 (d, 4 H, $^{3}J_{H,P}$ = 6.85 Hz); 6.99 (m, 1 H, $^{3}J_{H,P}$ = 5.38 Hz); 7.20 (d, 2 H, $^{3}J_{H,P}$ = 7.34 Hz); 7.29 (d, 2 H, $^{3}J_{H,P}$ = 5.87 Hz). ^{31}P NMR (C_6D_6), δ: 211.73 (d, $^{1}J_{P,P}$ = 416.28 Hz); 68.68 (d, $^{1}J_{P,P}$ = 416.28 Hz). ^{13}C NMR (C_6D_6), δ: 17.54 (s, CH_3); 23.81 (d, CH_2, $^{3}J_{C,P}$ = 2.03 Hz); 24.19 (d, CH_2, $^{2}J_{C,P}$ = 6.12 Hz); 27.24 (dd, CH_2, $^{1}J_{C,P}$ = 34.96 Hz, $^{1}J_{C,P}$ = 8.23 Hz); 125.99 (s, C(11)); 126.17 (s, C(15)); 126.32 (s, C(7)); 127.45 (s, C(6)); 127.86 (s, C(10)); 128.39 (s, C(14)); 128.87 (dd, C(5), $^{3}J_{C,P}$ = 12.56 Hz, $^{4}J_{C,P}$ = 2.12 Hz); 129.45 (d, C(13), $^{3}J_{C,P}$ = 9.14 Hz); 131.49 (t, C(8), $^{3}J_{C,P}$ = 6.96 Hz); 136.89 (d, C(9), $^{4}J_{C,P}$ = 5.14 Hz); 139.67 (dd, C(4), $^{2}J_{C,P}$ = 12.13 Hz, $^{3}J_{C,P}$ = 2.98 Hz); 148.17 (d, C(12), $^{2}J_{C,P}$ = 15.89 Hz); 152.98 (t, C(2), $^{2}J_{C,P}$ = 19.12 Hz); 169.49 (dd, C(3), $^{1}J_{C,P}$ = 10.17 Hz, $^{2}J_{C,P}$ = 4.59 Hz); 195.19 (dd, C(1), $^{1}J_{C,P}$ = 51.17 Hz, $^{2}J_{C,P}$ = 10.07 Hz).

1-Isopropyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (2e) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (1.93 g, 3.11 mmol) and 2-iodopropane (0.80 g, 4.67 mmol, 50% excess). The yield of compound **2e** was 0.46 g (40%), light yellow powder. Found (%): C, 76.56; H, 6.12; P, 16.03. $C_{24}H_{22}P_2$. Calculated (%): C, 77.41; H, 5.95; P, 16.64. ^{1}H NMR (C_6D_6), δ: 1.18 (dd, CH_3, 6 H, $^{3}J_{H,H}$ = 7.14 Hz, $^{3}J_{H,P}$ = 15.07 Hz); 2.49 (m, 1 H, CH); 6.90—7.40 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 209.28 (d, $^{1}J_{P,P}$ = 410.28 Hz); 94.47 (d, $^{1}J_{P,P}$ = 410.28 Hz). ^{13}C NMR (C_6D_6), δ: 14.48 (d, CH_3, $^{2}J_{C,P}$ = 7.02 Hz); 26.18 (dd, CH, $^{1}J_{C,P}$ = 19.29 Hz, $^{2}J_{C,P}$ = 4.93 Hz); 126.74 (s, C(11)); 126.77 (s, C(15)); 126.98 (s, C(7)); 127.29 (s, C(6)); 128.19 (s, C(10)); 128.51 (s, C(14)); 128.79 (dd, C(5), $^{3}J_{C,P}$ = 12.71 Hz, $^{4}J_{C,P}$ = 1.96 Hz); 129.94 (d, C(13), $^{3}J_{C,P}$ = 8.92 Hz); 132.84 (t, C(8), $^{3}J_{C,P}$ = 8.14 Hz); 136.98 (d, C(9), $^{4}J_{C,P}$ = 4.84 Hz); 139.83 (dd, C(4), $^{2}J_{C,P}$ = 11.83 Hz, $^{3}J_{C,P}$ = 5.03 Hz); 141.27 (d, C(12), $^{2}J_{C,P}$ = 18.67 Hz); 151.94 (t, C(2), $^{2}J_{C,P}$ = 17.21 Hz); 167.51 (dd, C(3), $^{1}J_{C,P}$ = 9.83 Hz, $^{2}J_{C,P}$ = 4.89 Hz); 197.88 (dd, C(1), $^{1}J_{C,P}$ = 51.67 Hz, $^{2}J_{C,P}$ = 12.65 Hz).

1-Cyclohexyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (2f) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (3.33 g, 5.37 mmol) and 1-iodocyclohexane (1.69 g, 8.05 mmol, 50% excess). The yield of compound **2f** was 1.00 g (45%), light yellow powder. Found (%): C, 78.76; H, 6.27; P, 15.21. $C_{27}H_{26}P_2$. Calculated (%): C, 78.63; H, 6.35; P, 15.02. ^{1}H NMR (C_6D_6), δ: 1.4—1.7 (m, 10 H); 2.44 (m, 1 H, CH); 6.9—7.4 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 204.57 (d, $^{1}J_{P,P}$ = 413.46 Hz); 87.47 (d, $^{1}J_{P,P}$ = 413.46 Hz). ^{13}C NMR (C_6D_6), δ: 20.64 (s, CH_2); 22.14 (d, CH_2, $^{3}J_{C,P}$ = 6.86 Hz); 22.41 (d, CH_2, $^{2}J_{C,P}$ = 6.94 Hz); 23.17 (d, CH_2, $^{2}J_{C,P}$ = 13.43 Hz); 23.36 (d, CH_2, $^{2}J_{C,P}$ = 12.97 Hz); 28.78 (d, CH, $^{2}J_{C,P}$ = 17.03 Hz); 125.67 (s, C(15)); 125.87 (s, C(7)); 126.38 (s, C(11)); 127.67 (s, C(6)); 127.99 (s, C(10)); 128.14 (s, C(14)); 128.41 (d, C(5), $^{3}J_{C,P}$ = 14.93 Hz); 129.62 (d, C(13), $^{3}J_{C,P}$ = 9.06 Hz); 131.14 (t, C(8), $^{3}J_{C,P}$ = 6.89 Hz); 136.78 (d, C(9), $^{4}J_{C,P}$ = 5.26 Hz); 139.34 (dd, C(4), $^{2}J_{C,P}$ = 13.54 Hz, $^{3}J_{C,P}$ = 5.32 Hz); 143.67 (d, C(12), $^{2}J_{C,P}$ = 19.04 Hz); 150.67 (t, C(2), $^{2}J_{C,P}$ = 16.43 Hz); 166.48 (dd, C(3), $^{1}J_{C,P}$ = 8.96 Hz, $^{2}J_{C,P}$ = 4.33 Hz); 191.02 (dd, C(1), $^{1}J_{C,P}$ = 55.24 Hz, $^{2}J_{C,P}$ = 15.03 Hz).

3,4,5-Triphenyl-1-trimethylsilyl-1,2-diphosphacyclopenta-2,4-diene (3) was obtained from sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (1.93 g, 3.31 mmol) and chlorotrimethylsilane (0.51 g, 4.67 mmol, 50% excess). The yield of compound **3** was 0.87 g (65%), yellow oil. Found (%): C, 71.86; H, 6.19; P, 15.41. $C_{24}H_{24}P_2Si$. Calculated (%): C, 71.62; H, 6.01; P, 15.39. ^{1}H NMR (C_6D_6), δ: 0.15 (d, 9 H, Me, $^{3}J_{H,P}$ = 7.98 Hz); 6.14—7.45 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 212.26 (d, $^{1}J_{P,P}$ = 409.46 Hz); 67.10 (d, $^{1}J_{P,P}$ = 409.46 Hz). ^{13}C NMR (C_6D_6), δ: 5.35 (d, Me, $^{2}J_{C,P}$ = 14.15 Hz); 124.92 (s, C(11)); 126.41 (s, C(15)); 126.72 (s, C(7)); 127.33 (s, C(6)); 127.69 (s, C(10)); 128.31 (s, C(14)); 128.96 (d, C(5), $^{3}J_{C,P}$ = 12.83 Hz); 129.45 (d, C(13), $^{3}J_{C,P}$ = 9.32 Hz); 134.84 (t, C(8), $^{3}J_{C,P}$ = 6.88 Hz); 138.41 (d, C(9), $^{4}J_{C,P}$ = 3.89 Hz); 139.74 (dd, C(4), $^{2}J_{C,P}$ = 17.31 Hz, $^{3}J_{C,P}$ = 4.94 Hz); 147.32 (d, C(12), $^{2}J_{C,P}$ = 15.04 Hz); 155.03 (t, C(2), $^{2}J_{C,P}$ = 15.04 Hz); 169.92 (dd, C(3), $^{1}J_{C,P}$ = 14.34 Hz, $^{2}J_{C,P}$ = 4.67 Hz); 191.32 (dd, C(1), $^{1}J_{C,P}$ = 45.23 Hz, $^{2}J_{C,P}$ = 14.62 Hz).

Reactions of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (1) with tin chlorides

3,4,5-Triphenyl-1-trimethylstannyl-1,2-diphosphacyclopenta-2,4-diene (4). Solid Me_3SnCl (1.08 g, 5.4 mmol) was added at −78 °C to a suspension of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (1.9 g, 5.4 mmol) in toluene (25 mL). The reaction mixture was stirred at ~20 °C for 2 h. The solvent was removed and the product was extracted with hexane (3×25 mL). The extract was filtered, concentrated, and dried *in vacuo*. The yield of compound **4** was 1.57 g (59%), a light yellow oil that crystallizes on storage. Found (%): C, 58.35; H, 5.41; P, 13.21. $C_{25}H_{27}P_2Sn$. Calculated (%): C, 59.09; H, 5.36; P, 12.19; Sn, 23.36. ^{1}H NMR (C_6D_6), δ: −0.005 (s, 9 H, Me, $^{2}J_{Sn,H}$ = 53.8 Hz); 6.89 (t, 4 H, C_p, Ph, $^{3}J_{H,H}$ = 3.18 Hz); 6.94—7.02 (m, 8 H, Ph); 7.24 (d, 4 H, C_o, Ph, $^{3}J_{H,H}$ = 6.36 Hz). ^{31}P NMR (C_6D_6), δ: 116.39 (s). ^{13}C NMR (C_6D_6), δ: 0.37 (s, Me—Sn); 127.30 (C_p, Ph); 127.57 (C_p, Ph); 128.76 (C_m, Ph); 128.86 (C_m, Ph); 130.28 (C_o, Ph); 132.20 (C_o, Ph); 140.04 (s, C_{ipso}, Ph); 142.92 (t, C_{ipso}, Ph, $^{2}J_{C,P}$ = 7.03 Hz); 154.65 (t, C(2), $^{2}J_{C,P}$ = 4.96 Hz); 181.06 (t, C(1), $^{1}J_{C,P}$ = 21.71 Hz). ^{119}Sn NMR ($CDCl_3$), δ: 50.8 (t, $^{1}J_{Sn,P}$ = 276 Hz).

Dimethylbis(3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dien-1-yl)stannane (6). Solid Me_2SnCl_2 (1.19 g, 5.4 mmol) was added at −78 °C to a suspension of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**1**) (3.8 g, 10.8 mmol) in toluene (40 mL). The reaction mixture was stirred at ~20 °C for 2 h. The solvent was removed and the product was extracted with hexane (3×25 mL). The extract was filtered, concentrated, and dried *in vacuo* to give a light yellow oil (3.8 g) consisting of 1-(chlorodimethylstannyl)-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (**5**) and dimethylbis(3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dien-1-yl)stannane (**6**) (according to ^{1}H and ^{31}P NMR spectra).

Compound 5. ^{1}H NMR (C_6D_6), δ: –0.42 (s, 6 H, Me, $^2J_{\mathrm{Sn,H}}$ = = 52.8 Hz); 6.9—7.3 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 108.4 (s, $^1J_{\mathrm{P,Sn}}$ = 388.1 Hz).

Compound 6. ^{1}H NMR (C_6D_6), δ: –0.04 (s, 6 H, Me, $^2J_{\mathrm{Sn,H}}$ = = 58.6 Hz); 6.9—7.3 (m, 15 H, Ph). ^{31}P NMR (C_6D_6), δ: 112.9 (s, $^1J_{\mathrm{P,Sn}}$ = 372 Hz).

Heating of a mixture of compounds **5** and **6** *in vacuo* at 120 °C for 3 h with simultaneous removal of Me_2SnCl_2 followed by recrystallization from hexane at –80 °C gave dimethylbis(3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dien-1-yl)stannane (**6**) (2.61 g, 60%), light yellow powder, m.p. 87 °C (decomp.). Found (%): C, 63.71; H, 4.24; P, 15.07. $C_{44}H_{36}P_4Sn$. Calculated (%): C, 65.46; H, 4.49; P, 15.35. ^{13}C NMR (C_6D_6), δ: 0.55 (s, Me—Sn); 127.1 (C_p, Ph); 127.5 (C_p, Ph); 128.1 (C_m, Ph); 128.9 (C_m, Ph); 130.8 (C_o, Ph); 131.8 (C_o, Ph); 141.1 (s, C_{ipso}, Ph); 142.4 (t, C_{ipso}, Ph, $^2J_{\mathrm{C,P}}$ = 6.5 Hz); 151.7 (t, C(2), $^2J_{\mathrm{C,P}}$ = 4.6 Hz); 184.5 (t, C(1), $^1J_{\mathrm{C,P}}$ = 21.4 Hz). ^{119}Sn NMR ($CDCl_3$), δ: 54.8 (t, $^1J_{\mathrm{Sn,P}}$ = 372 Hz).

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