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Preparation and Properties of Kinetically Stabilized Phosphaethene Derivatives Carrying the Methylsulfanyl Group

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1-Methylsulfanyl-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithiums, prepared from (*Z*)-2-bromo-2-methylsulfanyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene, displayed an *E*/*Z* isomerization upon warming to room temperature. The copper-mediated coupling reaction afforded (*Z*,*Z*)-2,3-bis(methylsulfanyl)-1,4-diphosphabuta-1,3-diene. The reaction of the phosphaethenyllithiums with dimethyl disulfide and iodomethane gave the corresponding bis(methylsulfanyl)phosphaethene and a methylated *E*-isomer, respectively. On the other hand, the latter methylated *Z*-isomer was alternatively prepared from (*Z*)-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene. Both methylated *E*- and *Z*-isomers were allowed to react with $W(CO)_5$(thf) to give the corresponding pentacarbonyltungsten(0) complexes, either of which was deprotonated to give the 3-phospha-2-propenyllithium derivative leading to the formation of a homocoupled (*Z*,*Z*)-1,6-diphosphahexa-1,5-diene complex. Some key compounds were analyzed by X-ray crystallography, revealing the effect of the methylsulfanyl group on the structures. A straightforward preparation of 1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene as well as its carbonyltungsten(0) complex is also described.

The kinetic stabilization method utilizing sterically encumbered substituents has been widely employed for stabilizing a number of multiple bonds of the heavier main-group elements.[1–3] We have continued to investigate stable multiple bonds of phosphorus[4,5] since we reported the first stable phosphorus-phosphorus double bond stabilized by the 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Mes*) group.[6] In the course of our study, we have become interested in sterically protected phosphaethenyllithium as a phosphorus analog of vinyllithium. For example, we have investigated properties of 1-halo-2-phosphaethenyllithiums **1** (Chart 1), which are recognized as phosphanylidene carbenoids, showing some intriguing reactions: [1,2]-rearrangement (Fritsch–Buttenberg–Wiechell rearrangement) reaction,[7,8] intramolecular C–H insertion,[9] copper-mediated coupling,[10] nucleophilic substitution,[11,12] and an unusual trimerization.[13] Moreover, we have studied 1-arylsulfanyl-2-phosphaethenyllithiums **2**, displaying the predominant stability of their *Z*-isomers[14,15] as well as the stabilizing effect of the sulfanyl group on the carbanion.[16]

On the other hand, we have been interested in phosphapropenyllithium derivatives as a novel synthetic intermediate for low-coordinated phosphorus compounds. Recently we have reported an isomerization of a 1-phosphaisopropenyllithium derivative affording a 3-phospha-2-propenyllithium compound **3** upon coordination and we prepared a 1,6-diphosphahexa-1,5-diene complex by copper-mediated oxidative coupling of **3**.[17] In this case, we did not observe the generation of η^3-phosphaallyl compounds.[4] Thus **3** is a promising reagent to introduce a 3-phospha-2-propenyl moiety and **3** indicates interconversion of the properties of negatively charged phosphaethene derivatives.

Taking the properties of some carbanion species containing unsaturated phosphorus atom(s) and sulfanyl groups into consideration, we have been interested in the effects of the methylsulfanyl group on low-coordinated phosphorus compounds. The methylsulfanyl group is an attractive chemical group because it might exert an influence electronically on molecules to stabilize the adjacent carbanion center,[16,18,19] as well as acting sometimes as an electron-donating substituent.[20] In this article we report preparation, properties, and reactions of the methylsulfanyl-substituted phosphaethenyllithiums **4** and 3-phospha-2-propenyllithiums **5**, utilizing the coordination with the carbonyltungsten(0) moiety. Additionally, we describe a facile synthesis of 1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene and its carbonyltungsten complexes from the prerequisite 2-bromo-1-phosphapropene compounds.

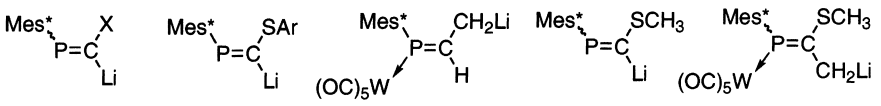


Chart 1.

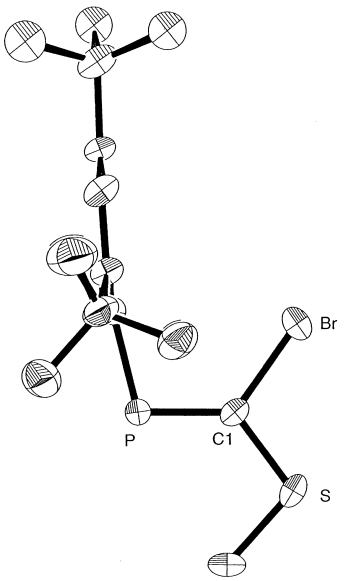


Fig. 1. An ORTEP drawing of **7** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. The *p*-*t*-butyl group is disordered and one of them, refined isotropically, is shown. Selected bond lengths (Å) and angles (°): P–C1 1.70(1), P–Mes* 1.82(1), C1–S 1.71(1), S–CH_3 1.74(1), C1–Br 1.90(1), Mes*–P–C1 103.8(5), P–C1–S 126.5(7), P–C1–Br 125.2(6), Br–C1–S 108.3(6), C1–S–CH_3 101.7(6).

Results and Discussion

Preparation and Properties of 1-Methylsulfanyl-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (4). 2,2-Dibromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**6**)[21] was allowed to react with butyllithium, followed by quenching with dimethyl disulfide in THF at −78 °C to afford (*Z*)-2-bromo-2-methylsulfanyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**7**). This was analyzed by X-ray crystallography, as shown in Fig. 1, revealing almost a planar P=C–S–Me skeleton. A cissoid staggered conformer of **7** was confirmed, which corresponds to the theoretical investigation for methyl vinyl sulfide.[22,23] The intermolecular Br···P distance is 3.35 Å, which is shorter than the sum of the van der Waals radii (P, 1.90 Å; Br, 1.95 Å).[24]

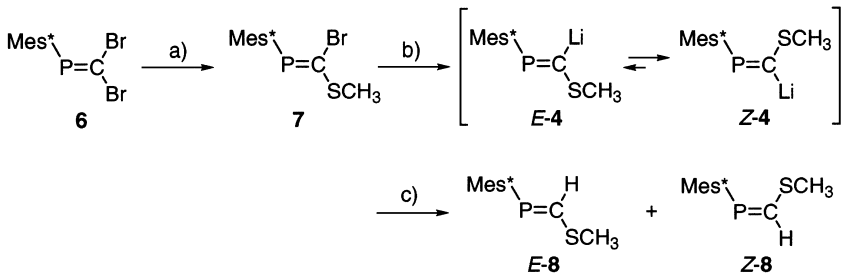
Phosphaethene **7** was allowed to react with *n*- or *t*-butyllithium at low temperature to generate **4**, which was quenched with methanol to afford the corresponding phosphaethene **8** as a mixture of the *E*/*Z* isomers. The *E*/*Z* ratio of **8** depended upon the quenching temperature with methanol as shown in Table 1. That is, at −100 °C, the *E*/*Z* ratio of **8** was 10:1 and this ratio did not change in the reaction at −78 °C. In the reaction at −40 °C or 0 °C, the isomerization of **4** was still slow and at 20 °C *Z*-**8** was predominantly afforded. Thus, *E*/*Z* isomerization of **4** was slower than that of arylsulfanyl-substituted phosphaethenyllithiums **2**, showing the facile *E*/*Z* isomerization even at −100 °C.[14,15] The slow rate of *E*/*Z* isomerization of **4** is due to a higher-energy level for the transition state compared to the case of **2**.

Table 1. Reaction of **4** with Methanol

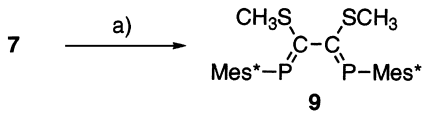
Temp/°C	Yield of **8**/%	*E*:*Z* Ratio of **8**
−100[a)]	> 99	10:1
−40[a)]	94	2:1
0[b)]	92	1:1
20[b)]	73	1:10

a) *n*-Butyllithium was used for preparation of **4**.
b) *t*-Butyllithium was used for preparation of **4**.

In the ^{31}P NMR spectrum, both of the isomers of **4** were observed at −80 °C in THF-d_8 [*Z*-**4**: δ_P = 138.1; *E*-**4**: δ_P = 227.2]. Although **4** slowly decomposed at 20 °C, which might be responsible for the lower yield of **8** as shown in Table 1, it was stable below 0 °C, which indicates quite high stability in comparison with **1**. Compared to **8**, the ^{31}P nucleus in *Z*-**4** is considerably shielded ($\Delta\delta_P$ = −80.7 to *Z*-**8**), whereas in *E*-**4** it is deshielded ($\Delta\delta_P$ = 21.3 to *E*-**8**), which corresponds to the nature of **1** except for the magnitudes of $\Delta\delta_P$ values.[9,25] The ^{6}Li-labeled *Z*-**4** was investigated by ^{13}C NMR spectroscopy. In THF-d_8 at −80 °C, the sp^2-hybridized ^{13}C nucleus was observed at δ_C = 232.5 with $^1J_{PC}$ 133 Hz. Compared to *Z*-**8**, the ^{13}C nucleus in the P=C part of *Z*-**4** is deshielded ($\Delta\delta$ = 65.6) with a larger $^1J_{PC}$ [$\Delta(^1J_{PC})$ = 80 Hz], which is similar to **1a**.[25] The ^{13}C(sp^2)–^{6}Li coupling in *Z*-**4** was 6 Hz with the 1:1:1 triplet multiplicity and the triplet peak disappeared above −60 °C. The $^1J_{C^6Li}$ value of *Z*-**4** is smaller than that of **1a** (14.1 Hz).[25] This might indicate the presence of a weak C–Li covalent bond in a monomeric structure, or an aggregated structure in the solution.[26] The ^{7}Li nucleus in *Z*-**4** was observed at $\delta_{^7Li}$ 0.52, which is similar to that of **1a** ($\delta_{^6Li}$ 0.55).[25] Attempts to crystallize *Z*-**4** from THF, DME, or Et_2O have not been successful (Scheme 1).



Scheme 1. Preparation of methylsulfanyl-substituted phosphaethenes. *Reagents and conditions*: a) (1) *n*-BuLi/THF/−78 °C, (2) $(CH_3S)_2$/−78 °C; b) *n*-BuLi or *t*-BuLi/THF; c) MeOH.



Scheme 2. Copper-mediated coupling reaction. *Reagents and conditions*: a) (1) *n*-BuLi/THF/−78 °C, (2) $CuCl_2$/−78 °C, (3) O_2/−78 °C.

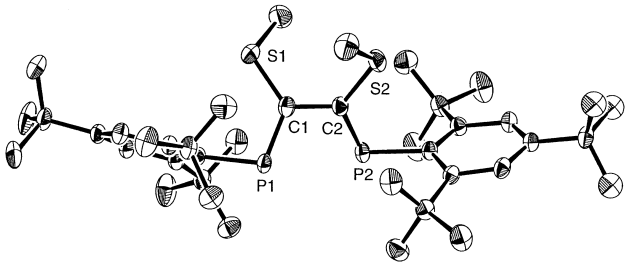
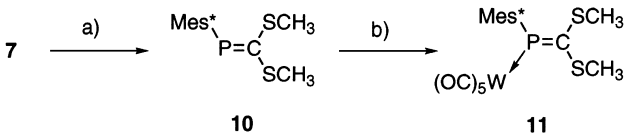


Fig. 2. An ORTEP drawing of **9** with 30% probability ellipsoids. The hydrogen atoms and the solvent (toluene) are omitted for clarity. The *p*-*t*-butyl group in the P2-side is disordered and the atoms with predominant occupancy factors (0.56), refined isotropically, are shown. Selected bond lengths (Å) and angles (°): P1–C1 1.702(6), P2–C2 1.694(5), P1–Mes* 1.852(5), P2–Mes* 1.848(4), C1–C2 1.456(6), C1–S1 1.754(5), C2–S2 1.757(5), S1–CH_3 1.801(8), S2–CH_3 1.802(8), C1–P1–Mes* 104.3(2), C2–P2–Mes* 105.0(2), P1–C1–C2 113.3(4), P1–C1–S1 123.4(3), P2–C2–C1 113.6(3), P2–C2–S2 123.9(3), S1–C1–C2 123.2(4), S2–C2–C1 122.5(3), C1–S1–CH_3 104.6(3), C2–S2–CH_3 103.9(3).

Copper-Mediated Coupling Reaction of 1-Methylsulfanyl-2-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethenyllithium (4). We studied copper-mediated homocoupling reaction of **4**, as has been previously described.[10,14,15] 1-Bromo-1-methylsulfanyl-2-phosphaethene **7** was allowed to react with butyllithium and subsequently treated with copper(II) chloride and oxygen to afford the corresponding 1,4-diphosphabuta-1,3-diene derivative **9**. The yield was moderate (41%), probably due to an undesired oxidation causing decomposition of the substrate or the product. Compound **9** was characterized by spectroscopic methods and only (*Z*,*Z*)-isomer was obtained, probably through an isomerization during the reaction and workup procedure (Scheme 2). The structure of **9** was confirmed by X-ray crystallography as shown in Fig. 2, indicating a twisted *s*-cis (gauche) conformation. The dihedral angle between the two P=C–S planes is 44.9° and other structural parameters of **9** are similar to those of 2,3-bis(arylsulfanyl)-1,4-diphosphabuta-1,3-dienes.[14,15]

Preparation and Coordination Chemistry of 2,2-Bis(methylsulfanyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (10). Phosphaethene **7** was allowed to react with butyllithium, followed by quenching with dimethyl disulfide to afford 2,2-bis(methylsulfanyl)-1-phosphaethene **10** in 35% yield as a pale yellow oil (Scheme 3), which can be regarded as a thioketal of 1-phosphaketene.[27] A small amount of **10** was formed in preparing **7**, as mentioned in Scheme 1.

The methylsulfanyl group can act as a π-donating group to some π-electron systems such as ethylene moiety[28] and this



Scheme 3. Preparation of bis(methylsulfanyl)-substituted phosphaethenes. *Reagents and conditions*: a) (1) *n*-BuLi/THF/−78 °C, (2) $(CH_3S)_2$/−78 °C; b) $W(CO)_5$(thf).

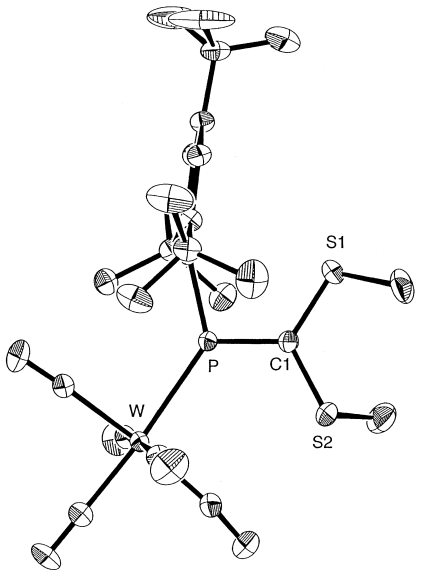


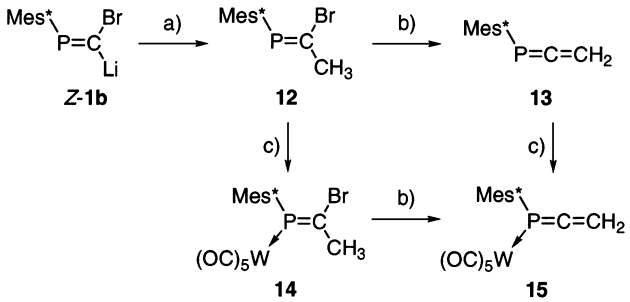
Fig. 3. An ORTEP drawing of **11** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W–P 2.550(1), P–C1 1.687(6), P–Mes* 1.849(5), C1–S1 1.747(6), C1–S2 1.738(6), S1–CH_3 1.805(6), S2–CH_3 1.796(10), W–P–C1 124.2(2), W–P–Mes* 133.5(2), Mes*–P–C1 102.3(3), P–C1–S1 122.4(4), P–C1–S2 117.9(3), S1–C1–S2 119.8(3).

fact prompted us to study coordination chemistry of **10** toward transition metal. Phosphaethenes can act as a good π-acceptor in coordinating on metal[29–31] and thus we were interested in the π-donating effect of methylsulfanyl groups on the P=C moiety. Here we report the coordinating property of **10** toward the carbonyltungsten(0) moiety.

Phosphaethene **10** was allowed to react with $W(CO)_5$(thf) in THF at room temperature to afford the corresponding complex **11** as green-yellow prisms (Scheme 3). In its IR spectrum, **11** displays the CO stretching bands at ν = 2069, 1950, 1934, and 1913 cm^{-1}, which are lower frequencies compared to those of $W(CO)_5(PPh_3)$ [2075, 1944 cm^{-1}].[32] Thus the phosphaethene ligand **10** may donate electrons effectively in complex **11** to promote electron transfer from the metal to the CO ligands. The structure of **11** was confirmed by X-ray crystallography, as shown in Fig. 3. The W–P distance of 2.550(1) Å is the longest among the $W(CO)_5$ complexes of phosphaethenes and still longer than that of $W(CO)_5(PPh_3)$ [2.545(1) Å].[33] In general, P–W distances in the pentacarbonyltungsten(0) complexes of phosphaethene (P=C) ligands are shorter than those of the PR_3 ligands, due to the π-accepting properties of phosphaethenes.[29–31] Thus, the elongated P–W distance in **11** represents effective π-electron donating ability of the methylsul-

Table 2. Bond Lengths (Å) of the Carbonyl Groups for **11**

W–C_{ax}	1.982(7)	C_{ax}–O_{ax}	1.143(8)
W–$C_{eq}1$	2.043(7)	$C_{eq}1$–$O_{eq}1$	1.131(8)
W–$C_{eq}2$	2.034(7)	$C_{eq}2$–$O_{eq}2$	1.130(8)
W–$C_{eq}3$	2.023(7)	$C_{eq}3$–$O_{eq}3$	1.139(8)
W–$C_{eq}4$	2.047(8)	$C_{eq}4$–$O_{eq}4$	1.139(8)



Z-**1b** **12** **13** **14** **15**

Scheme 4. Reactions of 2-bromo-1-phosphapropenes. *Reagents and conditions*: a) (1) *n*-BuLi/THF/−78 °C, (2) CH_3I/−78 °C; b) *t*-BuOK/THF; c) $W(CO)_5$(thf).

fanyl groups, which would be responsible for the shorter W–C_{ax} and the longer C_{ax}–O_{ax} distances than the bond lengths of CO_{eq} moieties as shown in Table 2. Coordination of the sulfur atom on the tungsten was not observed.

Preparation and Coupling of Bulky 2-Methylsulfanyl-3-phospha-2-propenyllithium Intermediates 5. In our recent communication, we described how lithiated 1-phosphapropene derivatives could afford a 1,4-diphosphabuta-1,3-diene and a 1,6-diphosphahexa-1,5-diene compound.[17] Such a result indicates that 1-phosphapropenes would be a promising reagent for low-coordinated phosphorus compounds. For example, 2-bromo-1-phosphapropene **12** was allowed to react with a base such as potassium *t*-butoxide to afford 1-phosphaallene **13** almost quantitatively. Although **13** was previously reported, the synthetic schemes were not excellent enough in view of the yields and the experimental procedure.[34] Coordination chemistry of **13** with a carbonyltungsten(0) moiety was also studied and thus complex **15** was prepared from **13** or complex **14**[17] as described in Scheme 4.

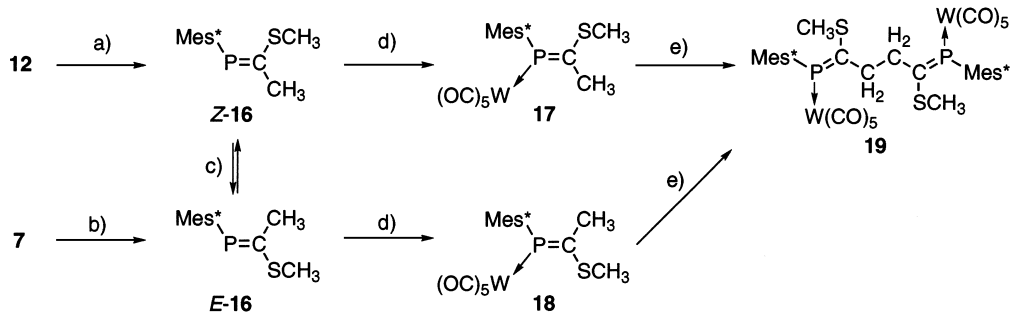
We performed a reaction of tungsten-coordinated 2-methylsulfanyl-3-phospha-2-propenyllithium species. The methylsulfanyl group can be expected to promote generation and stabilization of the carbanion. 2-Bromo-1-phosphapropene **12** was allowed to react with butyllithium and then with dimethyl disulfide to afford the corresponding product *Z*-**16**, whereas its isomer *E*-**16** was obtained by the reaction of **7** with butyllithium and iodomethane. The *E*/*Z* isomerization of **16** was observed upon irradiation of light to afford a 2:1 mixture of the *E*/*Z* isomers. 1-Phosphapropenes *Z*- and *E*-**16** were allowed to react with pentacarbonyl(tetrahydrofuran)tungsten(0) to afford the corresponding end-on complexes **17** and **18**, respectively. To generate **5**, **17** was deprotonated with butyllithium, followed by treatment with copper(II) chloride as described in the case of **3**[17] to afford the corresponding homocoupled product **19** in 30% yield. The proton abstraction of 1-phosphapropenes **16** failed, indicating the effect of the tungsten moiety to generate the carbanion.[17] The structure of **19** was characterized by spectroscopic methods, whereas X-ray structural determination was not completed due to the poor quality of the crystals. A typical feature to determine the configuration of **19** is that the ^3J(PCCH) value is large (26 Hz), indicating that the methylene is located on the same side of the $W(CO)_5$ group. On the other hand, a similar reaction for **18** also afforded **19**, indicating an isomerization to avoid steric congestion (Scheme 5).

Conclusion

1-Methylsulfanyl-2-phosphaethenyllithium **4** was prepared from 2-bromo-2-methylsulfanyl-1-phosphaethene **7** and characterized by the spectroscopic methods. Phosphaethenyllithium **4** displayed similar spectroscopic properties to those of phosphanylidene carbenoid **1**. As shown in arylsulfanyl-derivatives **2**, an *E*/*Z* isomerization of **4** was observed to afford the dominant *Z*-isomer. Phosphaethenyllithium **4** was utilized for preparation of several novel phosphaethenes. Structures of 2,3-bis(methylsulfanyl)-1,4-diphosphabuta-1,3-diene **9** and a carbonyltungsten(0) complex of 2,2-bis(methylsulfanyl)-1-phosphaethene **11** were confirmed by X-ray analysis to reveal some electronic effects of the methylsulfanyl groups. Several methylsulfanyl-substituted phosphapropenes were prepared and utilized for generation of 3-phospha-2-propenyllithiums upon coordination by carbonyltungsten moiety, affording 1,6-diphosphahexa-1,5-diene complex **19**.

Experimental

General. All the experiments described here were carried out under argon atmosphere with dry solvents, unless otherwise speci-



Scheme 5. Preparation of 2-methylsulfanyl-1-phosphapropenes. *Reagents and conditions*: a) (1) *n*-BuLi/THF/−78 °C, (2) $(CH_3S)_2$/−78 °C; b) (1) *n*-BuLi/THF/−78 °C, (2) CH_3I/−78 °C; c) medium pressure Hg lamp (100 W)/benzene/5 °C/4 h; d) $W(CO)_5$(thf); e) (1) *n*-BuLi/THF/−78 °C, (2) $CuCl_2$/−78 °C.

fied. Melting points were determined with a Yanagimoto micro melting-point apparatus MP-J3 and are not corrected. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200P or AVANCE400 spectrometer and ^{31}P NMR spectra were obtained with a Bruker AC200P or AVANCE400 spectrometer using 85% H_3PO_4 as an external standard. NMR spectra were recorded at 25 °C unless otherwise noted. MS spectra were taken on a JEOL HX-110 or a Hitachi M-2500S spectrometer. FT-IR and UV-vis spectra were taken on a Horiba FT-300 and a Hitachi U-3210 spectrometer, respectively. X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer (Table 3). All calculations for structure solutions were performed using the teXsan crystallographic software package.[35] Single crystals for X-ray crystallography were obtained by recrystallization from hexane at 20 °C (for **7** and **11**), or from toluene at 0 °C (for **9**·1/2C_7H_8).

Preparation of (*Z*)-2-Bromo-2-methylsulfanyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (7). To a solution of 2,2-dibromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**6**)[21] (201 mg, 0.449 mmol) in THF (15 mL) was added butyllithium (0.49 mmol; 1.4 M solution in hexane, 1 M = 1 mol dm^{-3}) at −78 °C. After the reaction mixture was stirred for 10 min, dimethyl disulfide (0.46 mmol) was added. The reaction mixture was stirred at −78 °C for 15 min and then warmed to room temperature. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane) to give 110 mg of **7** (59%). **7**: Colorless needles (MeOH), mp 102–104 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *p*-*t*-Bu), 1.50 (18H, d, $^{5}J_{PH}$ = 1 Hz, *o*-*t*-Bu), 2.57 (3H, d, $^{4}J_{PH}$ = 3 Hz, SCH_3), 7.41 (2H, d, $^{4}J_{PH}$ = 2 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 21.4 (d, $^{3}J_{PC}$ = 22 Hz, SMe), 31.3 (s, *p*-C*Me*$_3$), 32.4 (d, $^{4}J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 35.0 (s, *p*-*C*Me$_3$), 37.9 (d, $^{3}J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 122.1 (d, $^{3}J_{PC}$ = 1 Hz, *m*-arom.), 137.9 (d, $^{1}J_{PC}$ = 57 Hz, *ipso*-arom.), 151.1 (s, *p*-arom.), 153.4 (d, $^{2}J_{PC}$ = 3 Hz, *o*-arom.), 157.3 (d, $^{1}J_{PC}$ = 77 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 240.0; MS (70 eV, EI) *m*/*z* (rel intensity) 416 ([$C_{20}H_{32}{}^{81}$BrPS]$^+$; 44), 414 ([$C_{20}H_{32}{}^{79}$BrPS]$^+$; 41), 359 ([$C_{20}H_{32}{}^{81}$BrPS]$^+$–Bu; 100), 357 ([$C_{20}H_{32}{}^{79}$BrPS]$^+$–Bu; 95). Anal. Found: C, 57.65; H, 7.82; Br, 18.98%. Calcd for $C_{20}H_{32}$BrPS: C, 57.83; H, 7.76; Br, 19.23%.

Reaction of 1-Methylsulfanyl-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (4) with Methanol: at −100 °C. A solution of **7** (27 mg, 65 μmol) in THF (3 mL) was allowed to react with butyllithium (70 μmol) at −100 °C for 10 min. The reaction mixture was treated with methanol and warmed to room temperature. Silica-gel column chromatographic purification (hexane) afforded 22 mg of **8** in an *E*/*Z* ratio of 10:1 (quant.). **At −40 °C.** A solution of **7** (17 mg, 41 μmol) in THF (2 mL) was allowed to react with butyllithium (45 μmol) at −40 °C, followed by quenching with methanol to afford 13 mg of **8** in an *E*/*Z* ratio of 2:1 (94%). **At 0 °C.** A solution of **7** (36 mg, 87 μmol) in THF (4 mL) was allowed to react with *t*-butyllithium (175 μmol; 1.5 M solution in pentane) at −78 °C, followed by quenching with methanol at 0 °C to afford 27 mg of **8** in an *E*/*Z* ratio of 1:1 (92%). **At 20 °C.** A solution of **7** (32 mg, 77 μmol) in THF (3 mL) was allowed to react with *t*-butyllithium (155 μmol) at −78 °C and the reaction mixture was warmed to 20 °C. Methanol was added to the reaction mixture and the solvent was removed in vacuo. Silica-gel column chromatographic purification (hexane) afforded **8** in an *E*/*Z* ratio of 1:10 (73%). *E*-**8**: Colorless needles (MeOH), mp 111–112 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *p*-*t*-Bu), 1.52 (18H, s, *o*-*t*-Bu), 2.64 (3H, d, $^{4}J_{PH}$ = 4 Hz, SCH_3), 7.40 (2H, d, $^{4}J_{PH}$ = 1 Hz, arom.), 7.86 (1H, d, $^{2}J_{PH}$ = 21 Hz, P=CH); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 17.2 (d, $^{3}J_{PC}$ = 26 Hz, SMe), 31.3 (s, *p*-C*Me*$_3$), 33.7 (d, $^{4}J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 34.9 (s, *p*-*C*Me$_3$), 38.2 (d, $^{3}J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 121.6 (d, $^{3}J_{PC}$ = 1 Hz, *m*-arom.), 138.6 (d, $^{1}J_{PC}$ = 56 Hz, *ipso*-arom.), 149.4 (s, *p*-arom.), 154.3 (d,

Table 3. Crystal Data for **7**, **9**, and **11**

	7	**9**·1/2C_7H_8	**11**
Formula	$C_{20}H_{32}$BrPS	$C_{43.5}H_{68}P_2S_2$	$C_{26}H_{35}O_5PS_2W$
Formula weight	415.41	717.08	706.50
Crystal color, habit	colorless, prismatic	yellow, prismatic	yellow, prismatic
Crystal dimensions/mm	0.30 × 0.20 × 0.20	0.30 × 0.25 × 0.15	0.40 × 0.30 × 0.30
Temperature/K	288	288	288
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pnma* (#62)	$P\bar{1}$ (#2)	$P2_1/a$ (#14)
Lattice parameters			
a/Å	25.616(3)	10.462(7)	17.778(3)
b/Å	13.592(4)	19.610(6)	9.158(4)
c/Å	6.458(2)	11.512(10)	18.831(3)
α/°	90	75.30(3)	90
β/°	90	102.23(2)	101.66(1)
γ/°	90	103.72(4)	90
V/Å^3	2248.5(9)	2190(2)	3002(1)
Z	4	2	4
D_{calc}/g cm^{-3}	1.227	1.087	1.563
μ/mm^{-1}	1.996	0.221	4.075
Observed reflections	1801 [$I > 0.5\sigma(I)$]	4608 [$I > 2.0\sigma(I)$]	4452 [$I > 2.0\sigma(I)$]
No. of parameters	115	470	316
*R*1	0.086	0.079	0.039
R_w	0.200	0.190	0.104
Goodness of fit	1.30	1.86	1.29

$^2J_{PC}$ = 2 Hz, *o*-arom.), and 172.3 (d, $^1J_{PC}$ = 59 Hz, P=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 205.9. *Z*-**8**: Colorless plates (MeOH), mp 105–106 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (9H, s, *p*-*t*-Bu), 1.52 (18H, d, $^5J_{PH}$ = 1 Hz, *o*-*t*-Bu), 2.19 (3H, d, $^4J_{PH}$ = 1 Hz, SCH_3), 7.40 (2H, d, $^4J_{PH}$ = 1 Hz, arom.), 7.50 (1H, d, $^2J_{PH}$ = 35 Hz, P=CH); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 19.3 (s, SMe), 31.3 (s, *p*-C*Me*$_3$), 32.4 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 34.9 (s, *p*-*C*Me$_3$), 37.9 (s, *o*-*C*Me$_3$), 121.7 (d, $^3J_{PC}$ = 1 Hz, *m*-arom.), 135.8 (d, $^1J_{PC}$ = 46 Hz, *ipso*-arom.), 149.8 (s, *p*-arom.), 153.4 (d, $^2J_{PC}$ = 1 Hz, *o*-arom.), 166.9 (d, $^1J_{PC}$ = 53 Hz, P=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 218.8; MS (70 eV, EI) *m*/*z* (rel intensity) 336 (M^+; 35), 275 (Mes^*P^+-1; 100). HRMS Found: *m*/*z* 336.2044. Calcd for $C_{20}H_{33}PS$: *m*/*z* 336.2041.

Preparation of (*Z*,*Z*)-2,3-Bis(methylsulfanyl)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphosphabuta-1,3-diene (9). To a solution of **7** (150 mg, 0.36 mmol) in THF (5 mL) was added butyllithium (0.38 mmol) at −78 °C and the mixture was stirred for 5 min at −78 °C. Copper(II) chloride (0.82 mmol) was added to the reaction mixture at −78 °C and, after 1 h with stirring, oxygen (5 min, ca. 32 mmol) was bubbled through the mixture at −78 °C. The reaction mixture was treated with aqueous sodium sulfite and then warmed to room temperature. The reaction mixture was treated with ammonia (10% NH_3 in sat. NH_4Cl_{aq}) and extracted with ether. The organic layer was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane/toluene 5:1) to afford 54 mg of **9** (45%). **9**: Yellow prisms (xylene), mp 202–203 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (18H, s, *p*-*t*-Bu), 1.59 (36H, s, *o*-*t*-Bu), 2.11 (6H, s, SCH_3), 7.40 (2H, brs, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 16.7 (s, SMe), 31.4 (s, *p*-C*Me*$_3$), 32.7 (pt, ($^4J_{PC}$ + $^7J_{PC}$)/2 = 4 Hz, *o*-C*Me*$_3$), 35.0 (s, *p*-*C*Me$_3$), 37.9 (s, *o*-*C*Me$_3$), 121.7 (s, *m*-arom.), 137.9 (pt, ($^1J_{PC}$ + $^4J_{PC}$)/2 = 29 Hz, *ipso*-arom.), 150.1 (s, *p*-arom.), 154.2 (pt, ($^2J_{PC}$ + $^5J_{PC}$)/2 = 2 Hz, *o*-arom.), 177.7 (dd, $^1J_{PC}$ = 13 Hz, $^2J_{PC}$ = 8 Hz, P=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 235.0; UV (hexanes) λ_{max} (log ε) 250 (4.18), 319 (3.96), 396 (3.07) nm; FAB-MS *m*/*z* (rel intensity) 670 (M^+; 75), 275 (Mes^*P^+ − 1; 100). Anal. Found: C 71.77; H, 9.83%. Calcd for $C_{40}H_{64}P_2S_2$: C, 71.60; H, 9.62%.

Preparation of 2,2-Bis(methylsulfanyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (10) and Reaction with Pentacarbonyl(tetrahydrofuran)tungsten(0). To a solution of **7** (46 mg, 0.11 mmol) in THF (5 mL) was added butyllithium (0.14 mmol) at −78 °C and the mixture was stirred for 10 min. After dimethyl disulfide (0.13 mmol) was added, the reaction mixture was stirred for 30 min. The reaction mixture was warmed to room temperature and the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography (hexane) to afford 15 mg of **10** (35%). **10**: Pale yellow solid, mp 93–95 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (9H, s, *p*-*t*-Bu), 1.51 (18H, d, $^5J_{PH}$ = 1 Hz, *o*-*t*-Bu), 2.22 (3H, d, $^4J_{PH}$ = 1 Hz, *Z*-SCH_3), 2.62 (3H, d, $^4J_{PH}$ = 3 Hz, *E*-SCH_3), 7.40 (2H, d, $^4J_{PH}$ = 1 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 16.3 (d, $^3J_{PC}$ = 3 Hz, *Z*-SMe), 19.3 (d, $^3J_{PC}$ = 30 Hz, *E*-SMe), 31.4 (s, *p*-C*Me*$_3$), 32.4 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 35.0 (s, *p*-*C*Me$_3$), 38.0 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 121.9 (d, $^3J_{PC}$ = 1 Hz, *m*-arom.), 135.8 (d, $^1J_{PC}$ = 58 Hz, *ipso*-arom.), 150.3 (s, *p*-arom.), 154.1 (d, $^2J_{PC}$ = 2 Hz, *o*-arom.), 177.0 (d, $^1J_{PC}$ = 74 Hz, P=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 206.9; MS (70 eV, EI) *m*/*z* (rel intensity) 382 (M^+; 62), 325 (M^+ − Bu; 100). To a solution of **10** (132 mg, 0.35 mmol) in THF (5 mL) was added ca. 0.54 mmol of $W(CO)_5$(thf), prepared from $W(CO)_6$ in THF (23 mL) by irradiation of a medium-pressure Hg lamp (100 W), and then the reaction mixture was stirred for 20 h. The solvent was removed in vacuo and the residue was treated with silica-gel column chromatography (hexane/toluene 1:1) to afford 203 mg of **11** (83%). **11**: Yellow green prisms (hexane), mp 137–140 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (9H, s, *p*-*t*-Bu), 1.59 (18H, s, *o*-*t*-Bu), 2.32 (3H, d, $^4J_{PH}$ = 3 Hz, *E*-SMe), 2.35 (3H, d, $^4J_{PH}$ = 2 Hz, *Z*-SMe), 7.51 (2H, d, $^4J_{PH}$ = 3 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 18.5 (d, $^3J_{PC}$ = 2 Hz, *Z*-SMe), 18.8 (d, $^3J_{PC}$ = 13 Hz, *E*-SMe), 31.1 (s, *p*-C*Me*$_3$), 34.6 (d, $^4J_{PC}$ = 1 Hz, *o*-C*Me*$_3$), 34.9 (s, *p*-*C*Me$_3$), 39.8 (d, $^3J_{PC}$ = 1 Hz, *o*-*C*Me$_3$), 124.9 (d, $^3J_{PC}$ = 7 Hz, *m*-arom.), 131.6 (m, *ipso*-arom.), 151.9 (d, $^4J_{PC}$ = 2 Hz, *p*-arom.), 152.8 (d, $^2J_{PC}$ = 2 Hz, *o*-arom.), 173.3 (d, $^1J_{PC}$ = 36 Hz, P=C), 197.9 (d, $^2J_{PC}$ = 10 Hz, CO_{ax}), 200.2 (m, CO_{eq}); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 215.4 ($^1J_{PW}$ = 286 Hz); IR (KBr) ν 2069, 1950, 1934, 1913 cm^{-1}. Anal. Found: C, 44.18; H, 4.99%; Calcd for $C_{26}H_{35}O_5PS_2W$: C, 44.20; H, 4.99%.

Preparation of 1-(2,4,6-Tri-*t*-butylphenyl)-1-phosphaallene (13). A solution of **12** (200 mg, 0.52 mmol)[17] and potassium *t*-butoxide (1.05 mmol) in THF (10 mL) was stirred at 0 °C for 30 min. The reaction mixture was warmed to room temperature and the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography (hexane) to afford 130 mg of **13** (83%). Physical data were identical to those in Ref. 34.

Preparation of the Pentacarbonyltungsten(0) Complex of 1-(2,4,6-Tri-*t*-butylphenyl)-1-phosphaallene (15). To a solution of **13** (150 mg, 0.50 mmol) in THF was added $W(CO)_5$(thf) (0.85 mmol) and the mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane) to afford 216 mg of **15** (70%). **15**: Yellow powder, mp 98–99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (9H, s, *p*-*t*-Bu), 1.71 (18H, s, *o*-*t*-Bu), 5.32 (2H, d, $^3J_{PH}$ = 51 Hz, P=C=CH_2), 7.47 (2H, d, $^4J_{PH}$ = 4 Hz, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 31.4 (s, *p*-C*Me*$_3$), 34.8 (d, $^4J_{PC}$ = 2 Hz, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 39.4 (s, *o*-*C*Me$_3$), 93.9 (d, $^2J_{PC}$ = 13 Hz, P=C=*C*), 123.5 (d, $^3J_{PC}$ = 8 Hz, *m*-arom), 125.7 (d, $^1J_{PC}$ = 7 Hz, *ipso*-arom), 152.6 (d, $^4J_{PC}$ = 2 Hz, *p*-arom), 155.8 (d, $^2J_{PC}$ = 3 Hz, *o*-arom), 197.1 (d, $^2J_{PC}$ = 9 Hz, CO_{eq}), 199.9 (d, $^2J_{PC}$ = 34 Hz, CO_{ax}), 244.6 (d, $^1J_{PC}$ = 85 Hz, P=*C*=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ 42.0 ($^1J_{PW}$ = 259 Hz); IR (KBr) ν 2073, 1986, 1943, 1926 cm^{-1}. HRMS Found: *m*/*z* 626.1413. Calcd for $C_{25}H_{31}O_5PW$: *m*/*z* 626.1419. Complex **15** was alternatively obtained from **14**[17] with potassium *t*-butoxide.

Preparation of (*Z*)-2-Methylsulfanyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene (*Z*-16) and the Pentacarbonyltungsten(0) Complex (17). To a solution of **12** (200 mg, 0.52 mmol) in THF (20 mL) was added butyllithium (0.57 mmol) at −78 °C. After stirring for 10 min, an excess amount of dimethyl disulfide was added and the mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and the volatile materials were removed in vacuo. Silica-gel column chromatography (hexane) afforded 165 mg of *Z*-**16** (90%). *Z*-**16**: Colorless crystals, mp 97–99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (9H, s, *p*-*t*-Bu), 1.54 (18H, s, *o*-*t*-Bu), 2.13 (3H, d, $^4J_{PH}$ = 1 Hz, SCH_3), 2.38 (3H, d, $^3J_{PH}$ = 24 Hz, CH_3), 7.42 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 15.7 (d, $^3J_{PC}$ = 2 Hz, SMe), 24.6 (d, $^2J_{PC}$ = 43 Hz, P=C–*C*H_3), 31.9 (s, *p*-C*Me*$_3$), 32.7 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.5 (s, *o*-*C*Me$_3$), 122.2 (s, *m*-arom.), 137.0 (d, $^1J_{PC}$ = 53 Hz, *ipso*-arom.), 150.4 (s, *p*-arom.), 154.1 (s, *o*-arom.), 178.2 (d, $^1J_{PC}$ = 52 Hz, P=C), $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ 204. MS (70 eV, EI) *m*/*z* (rel intensity) 350 (M^+; 37), 293 (M^+-t-Bu; 100). HRMS Found: *m*/*z* 350.2200. Calcd for $C_{21}H_{35}PS$: *m*/*z* 350.2197. Compound *Z*-**16** was allowed to react with an excess

amount of $W(CO)_5$(thf) at room temperature to afford complex **17** as yellow crystals almost quantitatively. A small amount of the isomer (**18**) was also formed during the reaction. **17**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (9H, s, *p*-*t*-Bu), 1.64 (18H, s, *o*-*t*-Bu), 2.29 (3H, d, $^4J_{PH}$ = 3 Hz, SCH_3), 2.46 (3H, d, $^3J_{PH}$ = 32 Hz, CH_3), 7.54 (2H, d, $^4J_{PH}$ = 3 Hz, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 17.5 (s, SMe), 24.4 (d, $^2J_{PC}$ = 16 Hz, P=C–*Me*), 32.0 (s, *p*-C*Me*$_3$), 34.5, (s, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 40.2 (s, *o*-*C*Me$_3$), 125.2 (d, $^3J_{PC}$ = 7 Hz, *m*-arom.), 130.4 (d, $^1J_{PC}$ = 11 Hz, *ipso*-arom.), 152.3 (d, $^4J_{PC}$ = 2 Hz, *p*-arom.), 154.3 (s, *o*-arom.), 179.7 (d, $^1J_{PC}$ = 37 Hz, P=C), 197.3 (d, $^2J_{PC}$ = 10 Hz, CO_{eq}), 200.0 (d, $^2J_{PC}$ = 31 Hz, CO_{ax}); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ 159.0 ($^1J_{PW}$ = 267 Hz). HRMS Found: *m*/*z* 674.1456. Calcd for $C_{26}H_{35}O_5PSW$: *m*/*z* 674.1453.

Preparation of (*E*)-2-Methylsulfanyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene (*E*-16) and the Pentacarbonyltungsten(0) Complex (18). To a solution of **7** (200 mg, 0.48 mmol) in THF (20 mL) was added butyllithium (0.53 mmol) at −78 °C; after stirring for 10 min, an excess amount of iodomethane was added and the mixture was stirred for 1 h. The reaction mixture was warmed to room temperature and the volatile materials were removed in vacuo. Silica-gel column chromatography (hexane) afforded 153 mg of *E*-**16** (91%). *E*-**16**: Colorless crystals, mp 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (9H, s, *p*-*t*-Bu), 1.42 (3H, d, $^3J_{PH}$ = 11 Hz, CH_3), 1.50 (18H, s, *o*-*t*-Bu), 2.68 (3H, d, $^4J_{PH}$ = 3 Hz, SCH_3), 7.43 (2H, s, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 18.4 (d, $^3J_{PC}$ = 4 Hz, SMe), 25.3 (d, $^2J_{PC}$ = 14 Hz, P=C–*C*H$_3$), 31.8 (s, *p*-C*Me*$_3$), 32.8 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.5 (s, *o*-*C*Me$_3$), 122.1 (s, *m*-arom.), 137.0 (d, $^1J_{PC}$ = 59 Hz, *ipso*-arom.), 150.3 (s, *p*-arom.), 154.7 (s, *o*-arom.), 182.1 (d, $^1J_{PC}$ = 60 Hz, P=C); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ 194. Compound *E*-**16** was allowed to react with an excess amount of $W(CO)_5$(thf) at room temperature to afford complex **18** as yellow crystals almost quantitatively. A small amount of the isomer (**17**) was also formed during the reaction. **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (9H, s, *p*-*t*-Bu), 1.61 (18H, s, *o*-*t*-Bu), 1.71 (3H, d, $^3J_{PH}$ = 24 Hz, CH_3), 2.38 (3H, d, $^4J_{PH}$ = 2 Hz, SCH_3), 7.55 (2H, d, $^4J_{PH}$ = 2 Hz, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 17.3 (d, $^3J_{PC}$ = 1 Hz, SMe), 25.2 (d, $^2J_{PH}$ = 9 Hz, P=C–*Me*), 31.6 (s, *p*-C*Me*$_3$), 35.0 (s, *o*-C*Me*$_3$), 35.7 (s, *p*-*C*Me$_3$), 40.1 (s, *o*-*C*Me$_3$), 124.5 (d, $^4J_{PC}$ = 7 Hz, *m*-arom.), 131.2 (brs, *ipso*-arom.), 152.4 (s, *p*-arom.), 154.9 (s, *o*-arom.), 180.2 (d, $^1J_{PC}$ = 40 Hz, P=C), 197.7 (d, $^2J_{PC}$ = 9 Hz, CO_{eq}), 200.5 (d, $^2J_{PC}$ = 33 Hz, CO_{ax}); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ 182.1 ($^1J_{PW}$ = 264 Hz).

Coupling Reaction of 17. To a solution of **17** (100 mg, 0.15 mmol) in THF (10 mL) at −78 °C was added butyllithium (0.17 mmol); after 10 min, copper(II) chloride (0.5 mmol) was added and the mixture was stirred for 1 h. This reaction mixture was warmed to room temperature and treated with ammonia as described in preparation of **9**, and then extracted with ether. The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane) to afford 60 mg of the homocoupling product **19** (30%). **19**: Green yellow amorphous solids, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (18H, s, *p*-*t*-Bu), 1.64 (36H, s, *o*-*t*-Bu), 2.41 (6H, s, SCH_3), 3.17 (4H, d, $^3J_{PH}$ = 26 Hz, CH_2), 7.55 (4H, d, $^4J_{PH}$ = 2 Hz, arom.); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 203.0 ($^1J_{PW}$ = 272 Hz); IR (KBr) ν 2071, 1986, 1940 cm^{-1}. Anal. Found: C, 44.13; H 4.91%. Calcd for $C_{52}H_{68}O_{10}P_2S_2W_2 \cdot 4H_2O$: C, 44.03; H, 5.40%. A similar reaction of **18** also afforded **19** in 30% yield.

X-ray Analytical Data. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre. No. CCDC-197683 (**7**), 197684 (**9**), and 197685 (**11**).

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References

1 P. P. Power, *Chem. Rev.*, **99**, 3463 (1999).
2 M. Yoshifuji, *J. Organomet. Chem.*, **611**, 210 (2000).
3 N. Tokitoh, *J. Organomet. Chem.*, **611**, 217 (2000).
4 M. Regitz and O. J. Scherer, "Multiple Bonds and Low Coordination in Phosphorus Chemistry," Georg Thieme Verlag, Stuttgart (1990).
5 K. B. Dillon, F. Mathey, and J. F. Nixon, "Phosphorus: The Carbon Copy," Wiley, Chichester (1998).
6 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); **104**, 6167 (1982).
7 M. Yoshifuji, T. Niitsu, and N. Inamoto, *Chem. Lett.*, **1988**, 1733; M. Yoshifuji, H. Kawanami, Y. Kawai, K. Toyota, M. Yasunami, T. Niitsu, and N. Inamoto, *Chem. Lett.*, **1992**, 1053; R. Appel and M. Immenkeppel, *Z. Anorg. Allg. Chem.*, **553**, 7 (1987).
8 V. D. Romanenko, M. Sanchez, T. V. Sarina, M.-R. Mazierès, and R. Wolf, *Tetrahedron Lett.*, **33**, 2981 (1992); H. Jun, V. G. Young Jr., and R. J. Angelici, *Organometallics*, **13**, 2444 (1994).
9 S. Ito, K. Toyota, and M. Yoshifuji, *Chem. Commun.*, **1997**, 1637.
10 S. Ito, K. Toyota, and M. Yoshifuji, *Chem. Lett.*, **1995**, 747; S. Ito, K. Toyota, and M. Yoshifuji, *J. Organomet. Chem.*, **553**, 135 (1998).
11 M. Yoshifuji, S. Ito, K. Toyota, and M. Yasunami, *Bull. Chem. Soc. Jpn.*, **68**, 1206 (1995); See also M. van der Sluis, F. Bickelhaupt, N. Veldman, H. Kooijman, A. L. Spek, W. Eisfeld, and M. Regitz, *Chem. Ber.*, **128**, 465 (1995).
12 E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, and W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, **34**, 555 (1995).
13 S. Ito, H. Sugiyama, and M. Yoshifuji, *Angew. Chem., Int. Ed.*, **39**, 2781 (2000).
14 S. Ito and M. Yoshifuji, *Chem. Lett.*, **1998**, 651.
15 S. Ito and M. Yoshifuji, *Chem. Lett.*, **2000**, 1390.
16 D. Seebach, J. Gabriel, and R. Hässig, *Helv. Chim. Acta*, **67**, 1083 (1984).
17 S. Ito, S. Kimura, and M. Yoshifuji, *Chem. Lett.*, **2002**, 708.
18 J.-M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **98**, 7498 (1976).
19 K. B. Wiberg and H. Castejon, *J. Am. Chem. Soc.*, **116**, 10489 (1994).
20 P. Lareginie, E. Zaballos-Garcia, V. A. Lokshin, A. Samat, R. Guglielmetti, S. M. Aldoshin, and O. S. Filipemko, *Mendeleev Commun.*, **1997**, 16.
21 R. Appel, C. Casser, and M. Immenkeppel, *Tetrahedron Lett.*, **26**, 3551 (1985); S. J. Goede and F. Bickelhaupt, *Chem. Ber.*, **124**, 2677 (1991); S. J. Goede, M. A. Dam, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **113**, 278 (1994).
22 J. Cao, *J. Am. Chem. Soc.*, **100**, 4685 (1978).
23 J. Cao, C. Eyermann, E. Southwick, and D. Leister, *J. Am. Chem. Soc.*, **107**, 5323 (1985).
24 J. Emsley, "The Elements, 3rd ed," Oxford Univ. Press (1998).

25 E. Niecke, M. Nieger, O. Schmidt, D. Gudat, and W. W. Schoeller, *J. Am. Chem. Soc.*, **121**, 519 (1999).

26 A.-M. Sapse and P. v. R. Schleyer, "Lithium Chemistry: A Theoretical and Experimental Overview," John Wiley & Sons, NY (1995).

27 R. Appel and W. Paulen, *Angew. Chem., Int. Ed. Engl.*, **22**, 785 (1983).

28 F. Bernardi, A. Mangini, N. D. Epiotis, J. R. Larson, and S. Schaik, *J. Am. Chem. Soc.*, **99**, 7465 (1977).

29 J. Deberitz and H. Nöth, *J. Organomet. Chem.*, **49**, 453 (1973); H. Vahrenkamp and H. Nöth, *Chem. Ber.*, **106**, 2227 (1973); J. H. Weinmaier, H. Tautz, A. Schmidpeter, and S. Pohl, *J. Organomet. Chem.*, **185**, 53 (1980).

30 T. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, and A. van Herk, *J. Organomet. Chem.*, **210**, 211 (1981).

31 L. Weber, *Angew. Chem., Int. Ed.*, **41**, 563 (2002).

32 R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, **6**, 65 (1972).

33 M. J. Aroney, I. E. Buys, M. S. Davies, and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, **1994**, 2827.

34 G. Märkl and S. Reitinger, *Tetrahedron Lett.*, **29**, 463 (1988); M. Yoshifuji, M. Shibata, K. Toyota, I. Miyahara, and K. Hirotsu, *Heteroat. Chem.*, **5**, 195 (1994).

35 "TeXsan: Crystal Structure Analysis Package," Molecular Structure Corporation, The Woodlands, TX (1985 and 1999).