Copper-mediated Coupling Reaction of Kinetically Stabilized 1-Methyl-2-phosphaethenyllithiums Involving an Isomerization to a 3-Phospha-2-propenyllithium Derivative[1]

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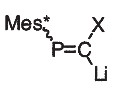
Copper-mediated coupling reaction of 1-methyl-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithiums afforded 1,4-diphosphabuta-1,3-diene or 1,6-diphosphahexa-1,5-diene derivatives, depending upon non-coordinated or coordinated to W(CO)$_5$, which facilitates an isomerization to a 3-phospha-2-propenyllithium.

We and others have reported various types of stable multiple bonds of phosphorus by utilizing the kinetic stabilization method.[2] Phosphaethenyllithiums **1** bearing the 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Mes*) group are suitable reagents for synthesis of some low-coordinated phosphorus compounds, and we have studied copper-mediated coupling reactions of **1**, where X=Cl, Br, SPh, and STol, i. e. lithium phosphanylidene carbenoids, affording 1,4-diphosphabuta-1,3-diene derivatives **2** as a conjugated system involving the P=C moieties.[2,3] Recently, a considerable attention has been paid to coordination chemistry of multiple-bonded phosphorus compounds to develop a novel class of synthetic catalyst,[4] and we expected to utilize **2** for a ligand of metal complexes as an analog of 3,4-diphosphanylidenecyclobutene derivatives **3**.[4c–f,5] Although **2** displayed quite low reactivity to the transition metal such as tungsten or chromium, or undesirable reactivity to some palladium or platinum reagents, an alternative method was employed to synthesize phosphaethenyllithiums in a transition-metal complex form exemplified such as **4**.[6] In this paper we report copper-mediated coupling reaction of a bulky 1-methyl-2-phosphaethenyllithium in a free form (**5**) or a coordinated form on the tungsten metal (**5w**).



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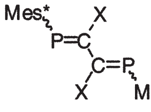

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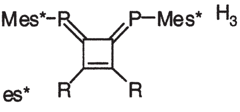

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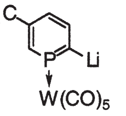

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Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

(*Z*)-2-Bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene (**6**) was allowed to react with butyllithium to afford 2-lithio-1-phosphapropene **5**,[7] which was treated with copper(II) chloride and oxygen at −78 °C to give 2,3-dimethyl-1,4-diphosphabuta-1,3-diene **7** as a mixture of three isomers (*EE*-, *ZZ*-, and *EZ*-**7**) almost quantitatively (Scheme 1). The ratio of the isomers was *EE* : *ZZ* : *EZ* = 1 : 1 : 3, which was determined by ^{31}P NMR spectroscopy.[8] The mixture **7** was irradiated by a medium-pressure mercury lamp through a Pyrex filter ($\lambda > 300$ nm) or heated in refluxing toluene to afford the single isomer (*EE*-**7**), whereas (*EZ*)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphosphabuta-1,3-diene was reported to afford the *ZZ*-isomer by irradiation or heating by Appel et al.[9] The structure of *EE*-**7** was confirmed by X-ray crystallography revealing a planar *s*-trans conformation with a torsion angle of 174.6(1)° in the P=C–C=P system (Figure 1).[8] The P=C bond lengths [1.703(2) and 1.699(2) Å] and the (P)C–C(P) bond length [1.465(3) Å] are slightly longer than the corresponding distances for **2** (X=Cl) [P=C 1.691(4) Å; C–C 1.445(7) Å],[3a] probably due to an electron donating effect of the methyl groups.

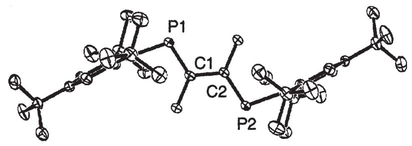
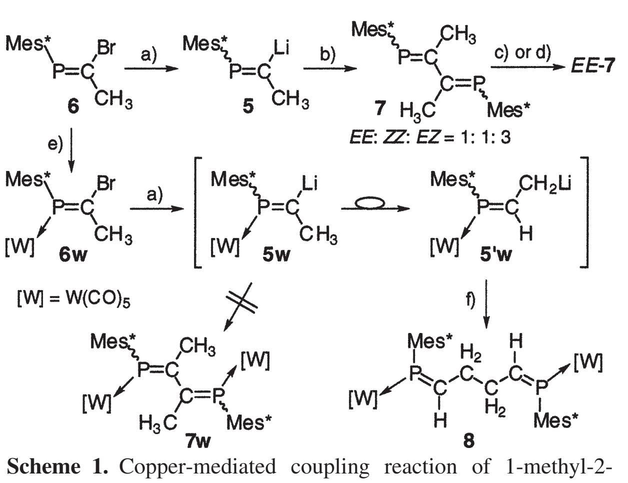


Figure 1. Molecular structure of *EE*-**7**.

Coordination chemistry of **7** is of interest, because compound **3**, including the 1,4-diphosphabuta-1,3-diene skeleton, has been utilized as ligands for synthetic catalysts.[4] But the coordinating property of **7** on transition metals turned out to be very poor by the fact that **7** did not coordinate on the transition-metals such as group 6 or group 10 metals. Thereupon we attempted to couple **5** on a transition metal. Compound **6** was allowed to react with pentacarbonyl(tetrahydrofuran)tungsten(0) to afford the corresponding complex **6w** in a moderate yield (60%).[10] In an attempt to obtain complex **7w**, **6w** was allowed to react with butyllithium and copper(II) chloride, but the product was not **7w** but **8** in 30% yield as purple crystals,[11] indicating a [1,2]-hydrogen rearrangement to leading to the 1,6-diphosphahexa-1,5-diene skeleton through an intermediate (**5′w**) (Scheme 1). Oxygen was not used in this coupling reaction to prevent decomplexation of **6w**. The structure of **8** was confirmed by X-ray crystallography as shown in Figure 2,[11] displaying a *ZZ* configuration. The P=C length



Scheme 1. Copper-mediated coupling reaction of 1-methyl-2-phosphaethenyllithiums. Reagents and conditions: a) *n*-BuLi, THF, −78 °C; b) CuCl$_2$, O$_2$, −78 °C; c) Medium pressure Hg lamp (100 W), benzene, 0 °C; d) toluene, reflux; e) W(CO)$_5$(thf), rt; f) CuCl$_2$.

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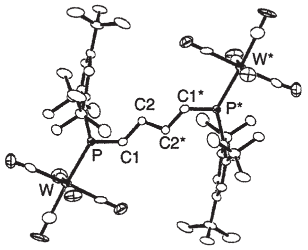
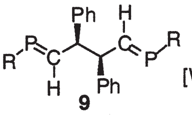


Figure 2. Molecular structure of **8**.

[1.660(7) Å] is comparable to the corresponding value of **9** [1.635(4) Å],[12] and the P–W bond length [2.539(2) Å] is similar to that of the pentacarbonyltungsten(0) complex of 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene [2.531(2) Å].[13] The C1–C2 and C2–C2* distances are 1.478(9) and 1.54(1) Å, respectively.

To verify the [1,2]-hydrogen shift of **5w**, we examined the reaction of **6w** as follows: **6w** was allowed to react with 1 eq of butyllithium and quenched with methanol-d_4 at −78 °C to give (*Z*)-3-deuterio-1-phosphapropene complex *Z*-**10** in an 80%-D ratio, (*E*)-1-phosphapropene complex *E*-**11**, and 1-phosphaallene complex **12** in a 6 : 3 : 1 ratio almost quantitatively.[10] Formation of *Z*-**10** indicates the [1,2]-rearrangement leading to a 3-phospha-2-propenyllithium intermediate (**5′w**). Compound *E*-**11** might have been generated by proton abstraction of **5w** from **6w**, indicating slow rate of the halogen-metal exchange to generate **5w**, and **12** might have been formed by an elimination of hydrogen bromide from **6w**. It indicates a facile [1,2]-hydrogen shift of **5w** proceeds to afford the 3-phospha-2-propenyllithium derivative (Z-**5′w**).



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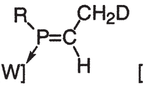
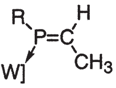
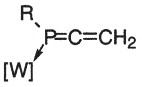


Z-**10**



E-**11**



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R = Mes*

As for **5w**, coordination of the pentacarbonyltungsten(0) group might increase the acidity of the methyl group, which resembles in the property of (η^6-arene)transition metal complexes.[14] Moreover, we assume that steric congestion around the "solvated" lithium atom might facilitate the [1,2]-rearrangement. Although the detailed reaction mechanism for the facile [1,2]-rearrangement of **5w** has not been clarified, it is interesting to note that the reactivity of **5** changes upon coordination.

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References and Notes

1 This paper is dedicated to Prof. Dr. Dieter Seebach at Eidgenössische Technische Hochschule Zürich on the occasion of his 65th birthday.

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8 a) To a solution of **6** (0.13 mmol) in THF (6 mL) was added butyllithium (0.15 mmol), and in 5 min copper(II) chloride (0.25 mmol) was added at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and oxygen was bubbled for 5 min (ca. 32 mmol). After treatment with aqueous sodium sulfite and warming up to room temperature, the mixture was treated with ammonia (10% NH_3 in saturated aqueous NH_4Cl) and extracted with ether. The organic layer was concentrated in vacuo, and the residue was purified by silica-gel column chromatography (hexane/toluene 5 : 1) to afford 37 mg of **7** (97% yield) as yellow solids. b) *EE*-**7**: Yellow crystals, mp 233–234 °C; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 1.35$ (18H, s, *p*-*t*Bu), 1.50 (36H, s, *o*-*t*Bu), 1.55 (m, 6H, Me), 7.41 (4H, brs, arom); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 183.9$ (dd, $^1J_{PC} = 13$ Hz, $^2J_{PC} = 3$ Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) $\delta = 232$; HRMS calcd for $C_{40}H_{64}P_2$, 606.4483; found, 606.4488. c) *ZZ*-**7**; $\delta_P = 237$; *EZ*-**7**; $\delta_P = 240$, 288 (AB_q, $^3J_{pp} = 154$ Hz). d) Crystal data for *EE*-**7**; $C_{40}H_{64}P_2$ $M = 606.89$, triclinic, $P\bar{1}$ (no. 2), $a = 18.524(3)$, $b = 18.564(2)$, $c = 6.237(6)$ Å, $\alpha = 98.23(2)$, $\beta = 93.72(2)$, $\gamma = 64.40(1)°$, $V = 1914(1)$ Å^3, $Z = 2$, $\rho = 1.053$ g cm^{-3}, μ(Mo Kα) $= 0.138$ mm^{-1}, $T = 150$ K, 5428 reflections measured ($2\theta_{max} = 50.0°$), 5426 observed [$I > 1.0\sigma(I)$], $R1 = 0.047$ [$I > 2.0\sigma(I)$]. $R_w = 0.108$ (all data). CCDC-181946.

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10 ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) **6w**: $\delta = 210$ ($^1J_{PW} = 270$ Hz); *Z*-**10**: $\delta = 208$ ($^1J_{PW} = 262$ Hz); *E*-**11**: $\delta = 199$ ($^1J_{PW} = 259$ Hz); **12**: $\delta = 42$ ($^1J_{PW} = 259$ Hz).

11 a) To a solution of **6w** (0.14 mmol) in THF (10 mL) at −78 °C was added butyllithium (0.15 mmol) and in 10 min copper(II) chloride (0.29 mmol). The reaction mixture was stirred for 1 h and warmed to room temperature. The reaction mixture was treated with ammonia as described in the case of **7**, and extracted with ether. The organic layer was concentrated in vacuo, and the residue was purified by silica gel column chromatography (hexane/toluene 5 : 1) from recrystallization in hexane to afford 26 mg of **8** (30% yield) together with *E*/*Z*-**11** and their decomplexed products. **8**: mp 228–231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.03$ (4H, m, CH_2), 1.33 (18H, s, *p*-*t*Bu), 1.58 (36H, s, *o*-*t*Bu), 6.80 (2H, dt, $^2J_{PH} = 20$ Hz, $^3J_{HH} = 7$ Hz, P=CH), 7.42 (4H, d, $^4J_{PH} = 3$ Hz, arom); ^{31}P NMR (162 MHz, $CDCl_3$) $\delta = 202$ (dt, $^2J_{PH} = 20$ Hz, $^3J_{PH} = 20$ Hz; $^1J_{PW} = 259$ Hz); IR (KBr) $\nu = 2073$, 1990, 1932 cm^{-1}; FAB-MS *m*/*z* 1254 (M^+). Anal. Calcd for $C_{50}H_{64}O_{10}P_2W_2$: C, 47.84; H, 5.14. Found: C, 48.11; H, 5.14. b) Crystal data for **8**•$1/2C_7H_8$: $C_{53.5}H_{68}O_{10}P_2W_2$, $M = 1300.73$, monoclinic, $P2_1/c$ (no. 14), $a = 13.320(8)$, $b = 15.838(2)$, $c = 14.112(3)$ Å, $\beta = 102.65(2)$, $V = 2904(1)$ Å^3, $Z = 2$, $\rho = 1.540$ g cm^{-3}, μ(Mo Kα) $= 4.070$ mm^{-1}, $T = 150$ K, 4936 reflections measured ($2\theta_{max} = 50.0°$), 4714 observed [$I > 2.0\sigma(I)$], $R1 = 0.050$ [$I > 2.0\sigma(I)$]. $R_w = 0.064$ (all data). CCDC-181947.

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