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Preparation and Coordination Properties Including Catalytic Activities of a Bulky 2-Methyl-3-thioxo-1,3-diphosphapropene

Hongze Liang, Shigekazu Ito, and Masaaki Yoshifuji*

Department of Chemistry, Graduate School of Science, Tohoku University,
Aoba, Sendai 980-8578, Japan

yoshifj@mail.tains.tohoku.ac.jp

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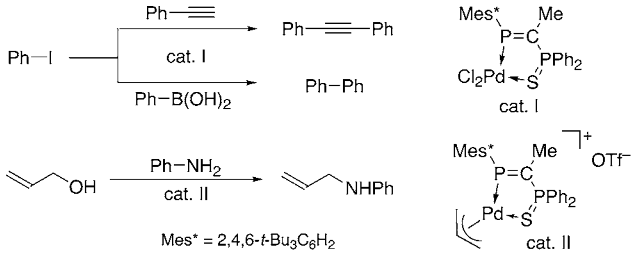
ABSTRACT



2-Methyl-3,3-diphenyl-3-thioxo-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene, which bears a P═C–P═S skeleton, was prepared and used as a ligand of transition-metal complexes. The palladium complexes containing the ligated 3-thioxo-1,3-diphophapropene were stable and used for catalytic reactions such as cross-couplings and direct conversion of allyl alcohol to allylaniline.

Chemistry of the low-coordinated phosphorus compounds has greatly developed in the past decades,[1] and we have reported a number of phosphaethenes kinetically stabilized by a bulky 2,4,6-tri-*tert*-butylphenyl (hereafter abbreviated to Mes*) group.[2] Previously we reported preparation of the 1,3-diphosphapropene derivatives **1** and **2**, which were used as ligands for transition-metal complexes.[3] Compounds **1** and **2**, both carrying a low-coordinated sp^2 phosphorus atom and a normal sp^3 phosphino group, displayed a stepwise coordination pattern by way of a monodentate to a chelation mode.[3,4] Moreover, a palladium complex containing the ligated **2** displayed a catalytic activity for the Sonogashira cross-coupling reaction.[3b] Recently, low-coordinated phosphorus compounds have been utilized for synthetic catalysts,[5,6] and especially, transition-metal complexes containing the ligated 3,4-diphosphinidenecyclobutene (DPCB) derivatives have been available for several unique catalytic reactions.[7] These results prompted us to develop novel low-coordinated phosphorus compounds which can be used as ligands for synthetic catalytic reactions. Previously, we reported sulfurizations of **1** affording the corresponding 3-thioxo-1,3-diphosphapropenes **3** that consist of the P═C−P═S skeleton, and indeed, **3** behaved as *P,S*-chelating ligands

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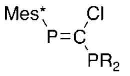
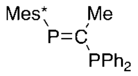
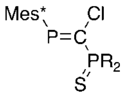
for transition-metal complexes.[8] In this paper, we report preparation of a bulky 2-methyl-3-thioxo-1,3-diphosphapropene **4** from sulfurization of **2**. Compound **4** was used as a chelating ligand for several transition-metal complexes, and the palladium complexes were employed for catalytic reactions.



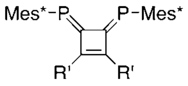
1a: R = Ph
1b: R = N*i*Pr$_2$



2



3a: R = Ph
3b: R = N*i*Pr$_2$

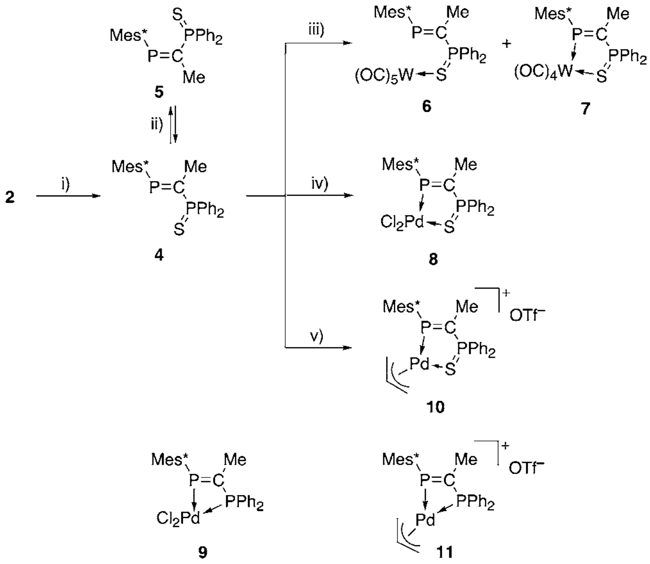


DPCB

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

As described in our previous paper on the sulfurization,[8] 1,3-diphosphapropene **2**[3b] was allowed to react with an equivalent amount of sulfur (1/8 S$_8$) in refluxing toluene for 20 h to afford the corresponding sulfurized compound **4** in an excellent yield (91%) (Scheme 1).[9] Compound **4** was an air- and moisture-insensitive colorless solid, and the structure was characterized by the spectroscopic data.[9] Similarly to the case of **3**,[8] *E*/*Z* isomerization of **4** was observed upon irradiation (medium-pressure Hg lamp, $\lambda > 300$ nm, in THF) resulting in the formation of a mixture of **4** and **5** in a 5:1 ratio after 21 h [**5**: δ_P 331.3, 41.2, ${}^2J_{PP} = 58$ Hz].

Scheme 1 [a]



[a] Reagents and conditions: (i) 1/8 S$_8$, toluene, reflux, 20 h; (ii) medium-pressure Hg lamp (100 W), THF, 21 h; (iii) W(CO)$_5$(THF), THF, rt, 16 h; (iv) PdCl$_2$(MeCN)$_2$, CH$_2$Cl$_2$, rt, 0.5 h; (v) [(allyl)PdCl]$_2$, AgOTf, CH$_2$Cl$_2$, rt, 2 h.

To evaluate the properties of **4** as a ligand, at first, preparation of carbonyltungsten(0) complexes was performed. When compound **4** was allowed to react with W(CO)$_5$(thf) in THF, both of the monocoordinated complex **6** and the chelate complex **7**[10] were obtained as a mixture (**6**: 42%; **7**: 15%) (Scheme 1). Attempts to isolate **6** [δ_P 329.4, 55.8, ${}^2J_{PP}$ 121 Hz] by recrystallization were not successful, probably due to the instability of **6** in solution. On the other hand, **6** afforded **7** by release of a CO ligand together with several desulfurized and/or decomplexed compounds such as **2** and **4** in solutions.

We next focused on the coordination chemistry of **4** with palladium reagents for the purpose of obtaining catalysts including a 3-thioxo-1,3-diphosphapropene [P═C−P═S] framework. Compound **4** was allowed to react with PdCl$_2$(MeCN)$_2$ in dichloromethane at room temperature for 30 min to give **8** in 84% yield (Scheme 1).[11] Complex **8** was an air- and moisture-insensitive solid and displayed no decomposition in solutions for several weeks, whereas a palladium complex of **2** (**9**) reacted with water in solutions to afford the complexes including a 1-hydroxy-1,3-diphosphapropane derivative.[3b] Attempts to obtain a platinum(II) complex from **4** and PtCl$_2$(cod) (cod = cycloocta-1,5-diene) were not successful. The structure of **8** was characterized by the spectroscopic data and confirmed by X-ray crystallography (Figure 1), revealing a planar structure around the palladium atom.[12] The Pd−Cl1 distance is close to the Pd−Cl2 length, indicating a similar trans effect of the P1 and S atoms. The P1−C1 distance is within the phosphorus−carbon double

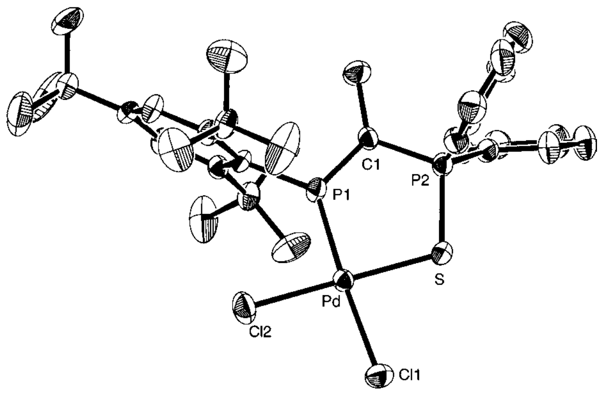


Figure 1. ORTEP representation of the molecular structure of **8** with 30% probability ellipsoids. Hydrogen atoms and the solvent molecules (dichloromethane) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−Cl1 2.319(3), Pd−Cl2 2.307(3), Pd−S 2.284(3), Pd−P1 2.186(3), P2−S 2.012(4), P1−C1 1.644(9), P1−Mes* 1.806(9), P2−C1 1.779(2), C1−Me 1.50(1), Cl1−Pd−Cl2 93.4(1), Cl1−Pd−S 86.0(1), Cl1−Pd−P1 174.6(1), Cl2−Pd−S 177.9(1), Cl2−Pd−P1 91.1(1), S−Pd−P1 89.60(10), Pd−S−P2 106.7(1), Pd−P1−C1 119.8(3), Pd−P1−Mes* 128.3(3), C1−P1−Mes* 112.0(4), S−P2−C1 110.0(3), P1−C1−P2 113.5(5), P1−C1−Me 126.2(7), P2−C1−Me 120.0(7).

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[9] **4**: colorless crystals; mp 67 °C; ${}^{31}P\{{}^1H\}$ NMR (162 MHz, CDCl$_3$) δ 314.8 (P═C), 50.9 (P═S), ${}^2J_{PP} = 123$ Hz.

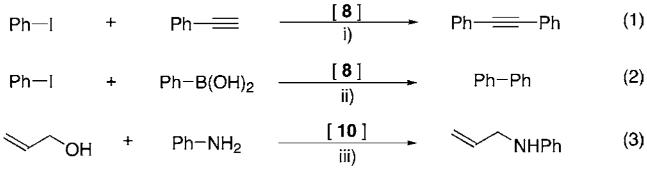
[10] **7**: brown solid; mp 143 °C dec; ${}^{31}P\{{}^1H\}$ NMR (162 MHz, CDCl$_3$) δ 324.6 (${}^1J_{PW} = 278$ Hz, P═C), 56.9 (P═S), ${}^2J_{PP} = 123$ Hz.

[11] **8**: yellowish-brown solid; mp 218−220 °C; ${}^{31}P\{{}^1H\}$ NMR (162 MHz, CDCl$_3$): δ 277.5 (P═C), 55.5 (P═S), ${}^2J_{PP} = 95$ Hz.

bond,[1] and an end-on coordination mode was established. In contrast to the previous report on the metal complexes including the ligated $P{=}C{-}P{=}S$ skeletons, which displayed envelope-type skeletons,[8] the five-membered ring in **8** is almost planar [Θ(Pd−P1−C1−P2) 0.4(6)°, Θ(S−Pd−P1−C1) 4.0(3)°].

Complex **8** was applied to catalytic cross-coupling reactions such as the Sonogashira and the Suzuki couplings.[13] As described in eqs 1 and 2 (Scheme 2), iodobenzene was allowed to react with phenylacetylene and phenylboronic acid in the presence of **8** and some other reagents to afford diphenylacetylene in 83% yield and biphenyl in almost quantitative yield,[14] respectively. In the case of the Sonogashira coupling, *p*-iodoanisole and phenylacetylene afforded the corresponding diarylacetylene in 65% yield, although the Suzuki coupling with *p*-iodoanisole gave a poor result (1% yield). Whereas these cross-coupling reactions smoothly proceeded in the case of iodobenzene, bromobenzene showed poor reactivity for these reactions. In the reaction of bromobenzene and phenylacetylene under the catalytic reaction conditions with **8**, diphenylbutadiyne was obtained almost quantitatively (96%). The low activity of **8** for the cross-coupling might be attributed to both descending electron-donating effect of the sp^2-phosphorus atom and enhancing oxidative-addition ability to the C−X bond.[1,3b,5]

Scheme 2 [a]



[a] Reagents and conditions: (i) **8** (2.5 mol %), CuI (2 mol %), Et_3N, rt, 4 h; (ii) **8** (4 mol %), K_2CO_3, THF, reflux, 20 h; (iii) **10** (2 mol %), $MgSO_4$, toluene, rt, 2 h.

Compound **4** was available for a ligand of a cationic π-allyl palladium(II) complex as described in Scheme 1. Indeed, **4** was allowed to react with $[(\eta^3\text{-allyl})PdCl]_2$ and silver(I) triflate[7a,b] to afford the corresponding complex **10** almost quantitatively, and the structure was characterized by the spectroscopic data.[15] Complex **10** did not decompose in air, whereas the π-allyl complex containing the ligated 1,3-diphosphapropene (**11**)[16] decomposed in several hours even in an inert atmosphere.

The cationic complex **10** was employed as a catalyst for the reaction of allyl alcohol with aniline.[7a] As described in eq 3 (Scheme 2), 2 mol % of **10** catalyzed the reaction of allyl alcohol with aniline in an 1:1 molar ratio at room temperature to afford *N*-(2-propenyl)aniline in 63% yield together with a small amount of *N*,*N*-di(2-propenyl)aniline (3%). Although a slightly larger amount of **10** was necessary for the reaction and the yield was not excellent compared with the results of catalysts bearing DPCB,[7a,b] **10** displayed a considerable catalytic ability for the direct conversion of allyl alcohol to allylaniline, which has been difficult by use of catalysts including normal phosphine ligands. The low-coordinated sp^2 phosphorus atom might enhance π-back-bonding due to the low-lying $P{=}C$ π^* orbital,[7a] and it might facilitate the C−O bond cleavage in allyl alcohol.

In conclusion, a novel 3-thioxo-1,3-diphosphapropene (**4**) was prepared and functioned as a monodentate and a chelating ligand. The dichloropalladium(II) complex **8** displayed higher stability than **9** and equivalent catalytic activities for the Sonogashira and Suzuki cross-coupling. On the other hand, the cationic allylpalladium(II) complex **10** was useful to the direct conversion of allyl alcohol, indicating the efficiency of low-coordinated phosphorus compounds as ligands for transition metal catalysts. Taking these easy procedures of preparation into consideration, the 3-thioxo-1,3-diphosphapropene skeleton would be widely used as a novel system of ligand as well as the 1,3-diphosphapropene system.

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Supporting Information Available: Experimental details for preparation of **4**, **6**−**8**, **10**, and **11**, with full characterization data. Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for **8**: $C_{32}H_{42}Cl_2P_2Pd{\cdot}1.5CH_2Cl_2$, $M_W = 825.40$, triclinic, *P*-1 (No. 2), $a = 13.0619(9)$ Å, $b = 14.127(2)$ Å, $c = 11.692(1)$ Å, $\alpha = 108.13(1)°$, $\beta = 109.703(5)°$, $\gamma = 77.28(1)°$, $V = 1914.2(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.432$ g cm^{-1}, $\mu_{MoK\alpha} = 0.994$ mm^{-1}, $F_{000} = 846$, $2\theta_{max} = 55.0°$, $T = 296$ °C, 13 145 measured reflections, 7794 unique reflections ($R_{int} = 0.055$), $R1 = 0.062$ ($I > 4\sigma(I)$ on F^2), $R_W = 0.163$ (all data), $S = 1.57$ (378 parameters).

(13) (a) Tykwinski, P. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566. (b) Li, C.-J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4856. (c) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998. (d) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(14) Complex **9** catalyzed the Suzuki coupling of iodobenzene and phenylboronic acid affording biphenyl almost quantitatively under a similar conditions in eq 2.

(15) **10**: yellow crystals; mp 125 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 289.2 ($P{=}C$), 61.0 ($P{=}S$), $^2J_{PP} = 126$ Hz.

(16) **11**: $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 249.8 ($P{=}C$), 12.4 (PPh_2), $^2J_{PP} = 11$ Hz.