ARTICLE

OBC
www.rsc.org/obc

Preparation, structure and coordination properties of 3,3-bis(diisopropylamino)-3-thioxo-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene

Hongze Liang, Shigekazu Ito and Masaaki Yoshifuji *
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai, 980-8578, Japan. E-mail: yoshifj@mail.tains.tohoku.ac.jp

Received 9th May 2003, Accepted 24th July 2003
First published as an Advance Article on the web 6th August 2003

(*Z*)-1-Chloro-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium was allowed to react with bis(diisopropylamino)-phosphenium triflate to afford the corresponding 1,3-diphosphapropene which was converted to 3-thioxo-1,3-diphosphapropene [(*Z*)-Mes*P=C(Cl)–P(=S)(N^iPr_2)$_2$]. The coordination properties of 3-thioxo-1,3-diphosphapropene were investigated with carbonyltungsten(0) and dichloroplatinum(II) reagents, and the molecular structure of the chelate dichloroplatinum(II) complex was unambiguously determined by X-ray crystallography together with the free ligand. The dichloroplatinum(II) complex underwent intramolecular cyclisation involving C–H activation to give a 5,7-di-*tert*-butyl-3,3-dimethyl-1-(phosphinomethyl)-1-phosphaindane derivative as well.

Introduction

The chemistry of low-coordinated phosphorus compounds is of current interest.[1] At first, this interest most probably was triggered by questions raised regarding the classical double bond rule. Less was known about their catalytic properties in organic synthesis compared with the well-studied trivalent phosphines. Recently, increasing interest has been paid to the catalytic properties of the complexes containing low-coordinated phosphorus atoms.[2,3] Some palladium and platinum complexes coordinated to bidentate 3,4-diphosphinylidenecyclobutenes show several promising properties in catalytic reactions.[3] In the meantime, we are also interested in the molecular design and synthesis of new types of phosphaalkenes and their derivatives. 1,3-Diphosphapropenes contain two different types of phosphorus atoms, one in a low-coordinated state and the other in the normal state, and, therefore, they are potentially a new class of bidentate ligands. However, reports on the synthesis and coordination properties of 1,3-diphosphapropenes are limited.[4] Very recently, we have reported some results from our efforts to extend the P=C–P system to P=C–P=S. Our preliminary studies show that this type of new ligand system is a good chelating reagent towards transition metals as depicted in Chart 1.[5] Herein we report the synthesis and coordination reactivities of an amino- and sulfur substituted 1,3-diphosphapropene.

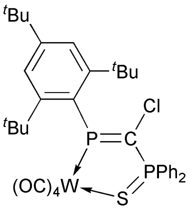
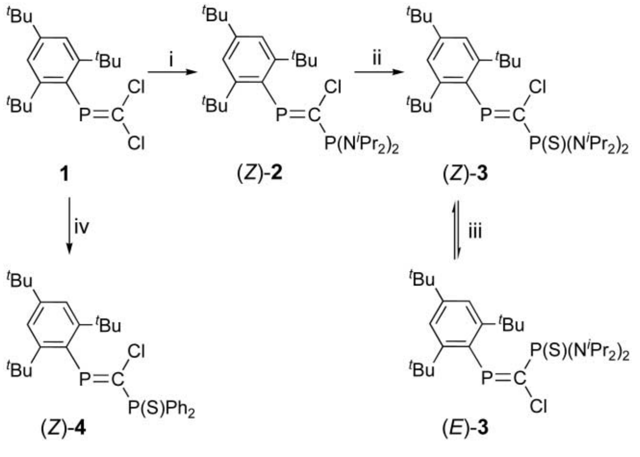


Chart 1 A chelating tungsten(0) complex from the P=C–P=S system.

Results and discussion

Synthesis, *E*–*Z* photoisomerisation and molecular structure of (*Z*)-3

2,2-Dichloro-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (**1**) was converted to 1-chloro-2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethenyllithium and was allowed to react with an equimolar amount of $(i\text{-}Pr_2N)_2P^+OTf^-$ to afford 2-chloro-3,3-bis(diisopropylamino)-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene, (*Z*)-**2**, which was, however, contaminated with some other unidentified species. As (*Z*)-**2** was not so stable in air, it was subsequently subjected, without purification, to a sulfurisation reaction with one equivalent of sulfur in refluxing toluene to give (*Z*)-**3** (Scheme 1). Like the sulfurisation of 2-chloro-3,3-diphenyl-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene,[5] this reaction proceeded regioselectively. The sp^3-phosphorus atom was sulfurised, whereas the sp^2-phosphorus atom remained unchanged. In contrast to the sulfurisation of diphosphenes and other phosphaalkenes, no disulfurisation product was obtained even if an excess of elemental sulfur was employed.[6] The results are understandable taking into account the fact that the sp^3-phosphorus atom is more basic than sp^2-phosphorus. A higher temperature was preferable in the sulfurisation, as separate experiments indicated that sulfurisation conducted at room temperature in toluene proceeded sluggishly. Photolysis of (*Z*)-**3** was also explored, and a mixture of (*Z*)-**3** and (*E*)-**3** with a ratio of 5 : 1 was observed when (*Z*)-**3** in THF was irradiated with a medium-pressure mercury lamp for 17 h.



Scheme 1 Sulfurisation of phosphinophosphaalkene. *Reagents and conditions:* i, *n*-BuLi then $(i\text{-}Pr_2N)_2P^+OTf^-$; ii) 1/8 S_8; iii) *hν*; iv) *n*-BuLi then $Ph_2P(S)Cl$.

DOI: 10.1039/b305216h

Table 1 Crystallographic data and collection parameters for (*Z*)-**3**, (*Z*)-**3Pt** and **5**

	(*Z*)-**3**	(*Z*)-**3Pt**	**5**·½C_7H_8
Formula	$C_{31}H_{57}ClN_2P_2S$	$C_{31}H_{57}Cl_3N_2P_2SPt$	$C_{34.5}H_{61}Cl_3N_2P_2PtS$
Formula weight	587.27	853.26	899.33
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1 (#2)	*P*2$_1$/*a* (#14)	*P*2$_1$/*n* (#14)
a/Å	14.2800(2)	11.0215(6)	20.7395(7)
b/Å	25.481(2)	21.108(1)	16.5550(5)
c/Å	10.8300(3)	16.2925(5)	11.8561(6)
α/deg	92.549(8)	90	90
β/deg	111.862(2)	92.524(2)	90.060(2)
γ/deg	85.841(9)	90	90
V/Å^3	3647.0(3)	3786.6(3)	4070.7(3)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.069	1.497	1.467
T/K	296	296	296
Scan method	Multi-scan	Multi-scan	Multi-scan
2*θ*/deg	55.0	55.0	55.0
Reflections collected	25003	17979	31362
Ind. reflections	4876	6348	9148
R(int)	0.057	0.035	0.060
Goodness-of-fit	1.758	1.571	1.466
R_1	0.137	0.041	0.056
R_w	0.185	0.054	0.065

In contrast to its precursor (*Z*)-**2**, (*Z*)-**3** was stable in air. Finally, the structure of (*Z*)-**3** was confirmed by X-ray crystallography. Two independent molecules were observed in the unit cell, and Fig. 1 shows one of them. The crystallographic data and collection parameters of (*Z*)-**3** are given in Table 1 and the selected bond lengths and angles are listed in Table 2. The P=C(Cl)–P=S system is similar in shape to that found in 2-chloro-3,3-diphenyl-3-thioxo-1,3-diphosphapropene (*Z*)-**4**. The bond distances of P(1)–C(1) and P(2)–S(1) are within the normal ranges of P=C and P=S bonds, respectively,[1*a*,7] and are comparable to those of (*Z*)-**4**.[5]

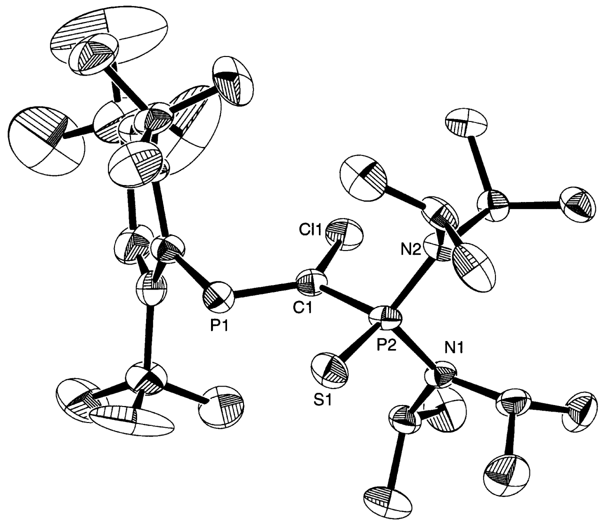
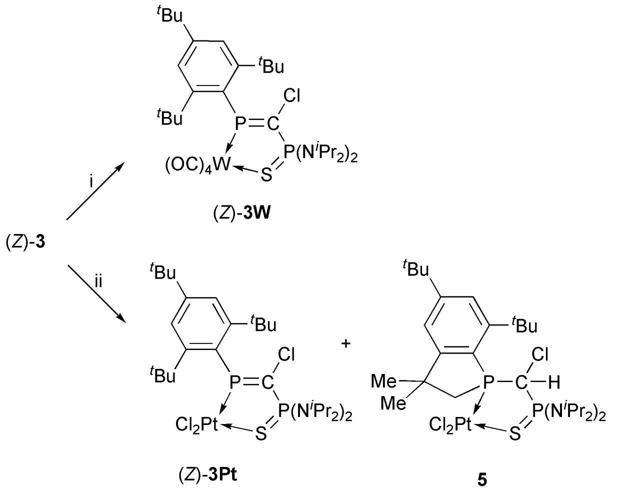


Fig. 1 Molecular structure of (*Z*)-**3**. Hydrogen atoms are omitted for clarity.

Reactions of (*Z*)-3 with W(CO)$_5$(THF) and W(CO)$_4$(COD)

We investigated the coordination properties of (*Z*)-**3** with tungsten(0) reagents as performed in the case of (*Z*)-**4**.[6] Compound (*Z*)-**3** reacted with W(CO)$_5$(THF) very slowly, even in refluxing THF, to give (*Z*)-**3W** in 9% isolated yield after workup (Scheme 2). In contrast to the reaction of (*Z*)-**4** with W(CO)$_5$(THF),[5] no intermediary mono-coordinated complex *via* the sulfur atom was observed in the case of (*Z*)-**3**. The reaction of (*Z*)-**3** with W(CO)$_4$(COD) proceeded rather smoothly, and the yield of the product greatly increased to 71%. The similarities in the spectra between (*Z*)-**3W** and the corresponding complex of (*Z*)-**4**[5] and elemental analysis are in good agreement with the chelate-type structure.[8]



Scheme 2 Reactions of (*Z*)-**3** with tungsten(0) carbonyls and platinum(II) chloride. *Reagents and conditions:* i, W(CO)$_5$(THF) or W(CO)$_4$(COD); ii, PtCl$_2$(COD).

Reaction of (*Z*)-3 with PtCl$_2$(COD) and the crystal structure of (*Z*)-3Pt and 5

The reaction of (*Z*)-**3** with PtCl$_2$(COD) also proceeded in a mixture of THF and dichloromethane to afford the corresponding platinum(II) complex (*Z*)-**3Pt** in 37% isolated yield. This reaction proceeded slowly in THF alone. On the other hand, no complex was obtained in the reaction of (*Z*)-**4** with PtCl$_2$(COD), forming a sharp contrast to the present (*Z*)-**3**. The ^{31}P NMR spectrum indicated that the P=C phosphorus atom coordinates to the platinum in an end-on form [the large J_{PPt} coupling constant (4562 Hz) together with the chemical shift (δ_P 234.0)].[9] Additionally, another product **5** was also observed and isolated in 14% yield as a compound indicating the same molecular weight as that of (*Z*)-**3Pt**.

The structures of red (*Z*)-**3Pt** (37% yield) and yellow **5** (14% yield) were characterised unambiguously by X-ray crystallography. The crystallographic data and collection parameters of (*Z*)-**3Pt** and **5** are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Fig. 2 shows the molecular structure of (*Z*)-**3Pt**. The geometry of the structure of (*Z*)-**3Pt** is almost the same as those

Table 2 Selected bond lengths (Å) and angles (°) for (*Z*)-**3**, (*Z*)-**3Pt** and **5**

(*Z*)-**3**			
P(1)–C(1)	1.68(1)	Cl(1)–C(1)	1.77(1)
P(2)–C(1)	1.836(10)	P(2)–S(1)	1.969(5)
P(1)–C$_{\text{Mes*}}$	1.84(1)	P(2)–N(1)	1.674(8)
P(2)–N(2)	1.651(8)		
P(1)–C(1)–P(2)	117.7(6)	P(1)–C(1)–Cl(1)	125.7(6)
C(1)–P(2)–S(1)	106.0(4)	P(2)–C(1)–Cl(1)	116.6(6)
C(1)–P(1)–C$_{\text{Mes*}}$	101.8(5)		
(*Z*)-**3Pt**			
Pt(1)–Cl(2)	2.328(2)	Pt(1)–Cl(3)	2.318(2)
Pt(1)–P(1)	2.172(1)	Pt(1)–S(1)	2.301(2)
P(1)–C(1)	1.666(5)	Cl(1)–C(1)	1.726(5)
P(2)–C(1)	1.810(6)	P(2)–S(1)	2.046(2)
P(1)–C$_{\text{Mes*}}$	1.816(5)	P(2)–N(1)	1.638(5)
P(2)–N(2)	1.636(5)		
Cl(2)–Pt(1)–Cl(3)	90.21(7)	Cl(2)–Pt(1)–S(1)	86.38(7)
Cl(2)–Pt(1)–P(1)	176.58(7)	Cl(3)–Pt(1)–S(1)	176.21(6)
Cl(3)–Pt(1)–P(1)	92.98(6)	Pt(1)–P(1)–C(1)	116.2(2)
Pt(1)–S(1)–P(2)	105.60(7)	P(1)–C(1)–P(2)	117.0(3)
C(1)–P(2)–S(1)	104.8(2)	P(1)–Pt(1)–S(1)	90.39(5)
C(1)–P(1)–C$_{\text{Mes*}}$	110.5(2)	Pt(1)–P(1)–C$_{\text{Mes*}}$	133.2(2)
5			
Pt(1)–Cl(2)	2.314(2)	Pt(1)–Cl(3)	2.341(2)
Pt(1)–S(1)	2.288(2)	Pt(1)–P(1)	2.197(2)
P(1)–C(1)	1.869(8)	P(1)–C(2)	1.825(7)
P(1)–C(19)	1.823(7)	C(1)–Cl(1)	1.778(7)
P(2)–C(1)	1.836(8)	P(2)–S(1)	2.029(3)
P(2)–N(1)	1.653(6)	P(2)–N(2)	1.645(6)
Cl(2)–Pt(1)–Cl(3)	90.67(8)	Cl(2)–Pt(1)–S(1)	176.38(7)
Cl(2)–Pt(1)–P(1)	89.89(7)	Cl(3)–Pt(1)–P(1)	178.97(7)
P(1)–Pt(1)–S(1)	93.72(7)	Pt(1)–S(1)–P(2)	107.41(10)
Pt(1)–P(1)–C(1)	107.7(2)	Pt(1)–P(1)–C(2)	125.6(2)
Pt(1)–P(1)–C(19)	114.1(2)	C(1)–P(1)–C(2)	106.1(3)
C(1)–P(1)–C(19)	106.2(3)	C(2)–P(1)–C(19)	95.4(3)
P(1)–C(1)–P(2)	111.5(4)	P(1)–C(1)–Cl(1)	112.8(4)
P(2)–C(1)–Cl(1)	115.3(4)	C(1)–P(2)–S(1)	102.1(2)
S(1)–P(2)–N(1)	112.7(2)	S(1)–P(2)–N(2)	111.8(2)

observed for (*Z*)-**3** and (*Z*)-**4** except for the metal moiety. The *s-cis* conformation remained unchanged, and the P=C(Cl)–P=S skeleton and Pt formed a 5-membered ring with the torsion angles of Pt–P(1)–C(1)–P(2) of 3.2(4)° and S–P(2)–C(1)–P(1) of 18.6(4)°, respectively, taking an envelope form. The coordination geometry around the platinum atom can be described as square planar with angles P(1)–Pt(1)–Cl(2) of 176.58(7)° and S(1)–Pt(1)–Cl(3) of 176.21(6)°, respectively. The distance of P=C (1.666(5) Å) is smaller than that found in the free ligand (1.68(1) Å), but is comparable to that found in the reported 3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinylidene]cyclobutene–platinum complex (1.669(3) Å).[3d] The bond distance of P=S in (*Z*)-**3Pt** (2.046(2) Å) is elongated due to the coordination by the metal and, accordingly, the absorption of P=S in the IR spectrum shifts to 597 cm^{-1}, lower than 683 cm^{-1} found in (*Z*)-**3**.

The ^{31}P NMR signals of the complex **5** [δ_P 73.6, 25.9 ($^1J_{PPt}$ = 3550 Hz)] dramatically shifted to high field compared with those of the free ligand (*Z*)-**3** as well as the complex (*Z*)-**3Pt**. X-Ray crystallography of **5** revealed that the Mes*P moiety intramolecularly cyclises to construct the 1-phosphaindane skeleton with a spiro structure as shown in Fig. 3. One of the 5-membered rings results from the intramolecular methyl C–H activation of one of the *o-tert*-butyl groups and addition to the P=C bond. Accordingly, both P(1) and C(1) are now sp^3-hybridised, which is reflected in the elongation of the bond distance of P(1)–C(1) from 1.666(5) Å in (*Z*)-**3Pt** to 1.869(8) Å in **5**, falling into the normal range of the P–C single bond (1.82–1.87 Å).[10] The corresponding distances of C(1)–P(2) and C(1)–Cl(1) in **5** [1.836(8) Å and 1.778(7) Å] are also longer than those in (*Z*)-**3Pt** [1.810(6) Å and 1.726(5) Å]. The sum of bond angles of C(1) (Σ 339.6°) also reflects the sp^3 character of C(1) in **5**. The platinum centre coordinates to the skeleton of **5** to form another 5-membered ring. The distances of two Pt–Cl bonds in **5** are comparable to those of (*Z*)-**3Pt**, while the distance of the P(1)–Pt bond is 2.197(2) Å in **5**, slightly longer than that in (*Z*)-**3Pt** [2.172(1) Å]. Indeed, the P(1) signal appeared at δ 25.9 ($^1J_{PPt}$ = 3550 Hz) in the ^{31}P NMR spectrum, representing the sp^3-hybridised characteristics, and the resonance of sp^3 C(1) appearing at δ 55.2 in ^{13}C NMR spectroscopy showed a sharp contrast with that of the sp^2 C(1) in the free ligand (*Z*)-**3**. Interestingly, the 1,3-diphosphapropane skeleton in **5** is found to be the *meso* isomers (1*R*,2*S*) and (1*S*,2*R*), indicating that the C–H insertion occurs in an *anti* fashion. The (±)-isomer was not formed in this reaction as demonstrated by the NMR spectroscopy showing the single diastereomer.

Thermal- or photo-induced intramolecular C–H activation has been observed for phosphorus-containing compounds,[11]

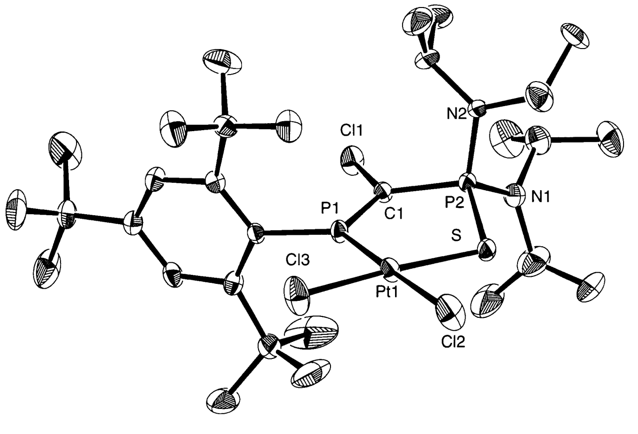


Fig. 2 Molecular structure of (*Z*)-**3Pt**. Hydrogen atoms are omitted for clarity.

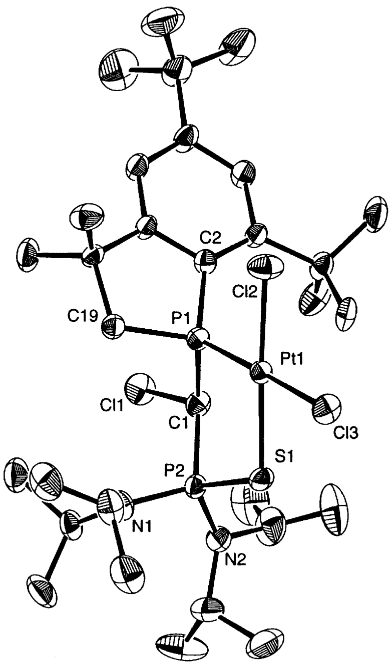


Fig. 3 Molecular structure of **5**. Hydrogen atoms are omitted for clarity.

and some intermediary species involving phosphenium ions,[11b] radicals,[11c] phosphinylidenes[11d] or phosphinylidene carbenes[11e] were proposed for such activation and insertion reactions. Although the reaction mechanism of the intramolecular C–H activation and insertion is not clear, it seems likely that platinum coordination to the ligand is a prerequisite. Without platinum, no product due to C–H activation and cyclisation was formed, and only the normal complex (*Z*)-**3Pt** was generated at the initial stage of the reaction. The yield of **5** almost doubled when the reaction was carried out for more than 3 days. Future work will be focused on an investigation into the effect of substitutions on such C–H activation and cyclisation.

Experimental

General

All manipulations were carried out under an argon atmosphere by means of the standard Schlenk techniques or in a glove box. All solvents employed were dried by appropriate methods. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AVANCE 400 spectrometer in CDCl$_3$ with Me$_4$Si (^{1}H, ^{13}C) and H$_3$PO$_4$ (^{31}P), respectively, as internal or external standard. IR spectra were measured on a Horiba FT-300 spectrometer as KBr pellets. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Mass spectra were recorded on a Bruker APEX3 spectrometer using fast atom bombardment (FAB). X-Ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer. Elemental analyses were performed in the Instrumental Analysis Center for Chemistry, Graduate School Science, Tohoku University.

Synthesis of (*Z*)-2-chloro-3,3-bis(diisopropylamino)-3-thioxo-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene (*Z*-3) and photo-isomerisation

Compound **1** was prepared according to the literature method.[12] To a stirred THF solution (15 mL) of **1** (1.712 g, 4.76 mmol) was added *n*-BuLi (1.56 M in hexane, 5.24 mmol) at −78 °C. This reaction mixture immediately turned yellowish–orange and was stirred at −78 °C for 10 min. Then, (i-Pr$_2$N)$_2$P$^+$OTf$^-$ (1.994 g, 5.24 mmol)[13] was added to the above solution at −78 °C and stirred for 30 min at the same temperature and then at room temperature for 1 h. THF was removed and the residue was extracted with hexane (50 mL) to give a brown oil of crude (*Z*)-**2** (δ_P 269.3, 71.0, $^{2}J_{PP}$ = 98 Hz). Without purification, crude (*Z*)-**2** was treated with sulfur (0.165 g, 5 mmol) in toluene (10 mL) and the mixture was refluxed overnight. The solvent was removed *in vacuo* to give a brown residue which was purified on silica gel (hexane : toluene = 3 : 1 to toluene), giving (*Z*)-**3** (0.934 g, 33% from **1**), pale yellow crystals, mp 144–146 °C. Found: C, 63.20; H, 9.68; N, 4.58. Calc. for C$_{31}$H$_{57}$ClN$_2$P$_2$S: C, 63.40; H, 9.80; N, 4.77%. IR (KBr, cm^{-1}): 683 (P=S); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 314.5 (P=C), 70.9 (P(S)Ph$_2$), $^{2}J_{PP}$ = 106 Hz; ^{1}H NMR (400 MHz; CDCl$_3$, δ): 7.44 (s, 2H, Ph), 3.93 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4H, NC*H*Me$_2$), 1.50 (s, 18H, *o*-^{t}Bu), 1.45 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{PH}$ = 2.4 Hz, 24H, NCHC*Me*$_2$), 1.36 (s, 9H, *p*-^{t}Bu); ^{13}C{^{1}H} (101 MHz, CDCl$_3$, δ): 164.3 (dd, $^{1}J_{PC}$ = 100.0 Hz, $^{1}J_{PC}$ = 85.1 Hz, P=*C*), 153.9 (s, *o*-Mes*), 150.9 (s, *p*-Mes*), 135.8 (dd, $^{1}J_{PC}$ = 67 Hz, $^{3}J_{PC}$ = 14 Hz, *ipso*-Mes*), 122.9 (s, *m*-Mes*), 48.7 (d, $^{2}J_{PC}$ = 5.6 Hz, N*C*HMe$_2$), 38.4 (s, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 33.6 (d, $^{4}J_{PC}$ = 7.2 Hz, *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 25.0 (s, NCH*Me*$_2$), 24.7 (d, $^{3}J_{PC}$ = 3.1 Hz, NCH*Me*$_2$).

A THF (0.3 mL) solution of (*Z*)-**3** (0.01g) in an NMR tube was irradiated with a medium-pressure Hg lamp (100 W) at 0 °C for 17 h. ^{31}P NMR spectrum indicated the formation of the (*E*)-**3** isomer (δ_P 329.2, 65.4, $^{2}J_{pp}$ = 60 Hz). The ratio of (*Z*)-**3** to (*E*)-**3** was 5 : 1, but no further attempt was made to separate them.

Reactions of (*Z*)-3 with W(CO)$_5$(THF) and W(CO)$_4$(COD)

A yellow THF (20 mL) solution of (*Z*)-**3** (0.0855 g, 0.146 mmol) and W(CO)$_5$(THF) (*ca.* 0.153 mmol, prepared from W(CO)$_6$ in THF by irradiation for 12 h with a medium-pressure 100 W Hg lamp at 0 °C) was refluxed overnight and the mixture turned black. Purification by column chromatography (hexane : toluene = 5 : 1) gave (*Z*)-**3W** (0.0118 g, 9%) together with the recovery of (*Z*)-**3** (0.044 g, 52%). (*Z*)-**3W**: Yellowish–black solid, mp 158 °C (decomp.). Found: C, 47.49; H, 6.38; N, 3.14. Calc. for C$_{35}$H$_{57}$ClN$_2$P$_2$SO$_4$W: C, 47.60; H, 6.51; N, 3.17%. IR (KBr, cm^{-1}): 2019, 1913, 1874 (CO), 605 (P=S); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 306.4 (P=C, $^{1}J_{PW}$ = 280 Hz), 77.3 (P(S)Ph$_2$), $^{2}J_{PP}$ = 145 Hz; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.51 (d, $^{4}J_{PH}$ = 2.4 Hz, 2H, Ph), 3.93 (sept, $^{3}J_{HH}$ = 7.2 Hz, 4H, NC*H*Me$_2$), 1.69 (s, 18H, *o*-^{t}Bu), 1.41 (s, 12H, NCHC*Me*$_2$), 1.39 (s, 12H, NCH*Me*$_2$), 1.38 (s, 9H, *p*-^{t}Bu); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$ δ): 209.8 (dd, $^{2}J_{PC}$ = 43.0 Hz, $^{3}J_{PC}$ = 6.6 Hz, CO$_{ax}$), 205.8 (d, $^{2}J_{PC}$ = 6.6 Hz, CO$_{eq}$), 202.7 (d, $^{2}J_{PC}$ = 9.3 Hz, CO$_{eq}$), 155.6 (s, *o*-Mes*), 152.9 (s, *p*-Mes*), 145.5 (dd, $^{1}J_{PC}$ = 121.2 Hz, $^{1}J_{PC}$ = 14.7 Hz, P=C), 130.1 (dd, $^{1}J_{PC}$ = 8.0 Hz, $^{3}J_{PC}$ = 3.6 Hz, *ipso*-Mes*), 123.4 (d, $^{3}J_{PC}$ = 6.2 Hz, *m*-Mes*), 49.0 (s, d, $^{2}J_{PC}$ = 5.6 Hz, N*C*HMe$_2$), 39.3 (s, *o*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 34.4 (s, *o*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 25.2 (d, $^{3}J_{PC}$ = 3.7 Hz, NCH*Me*$_2$), 25.0 (d, $^{3}J_{PC}$ = 3.2 Hz, NCH*Me*$_2$). The reaction of (*Z*)-**3** with W(CO)$_4$(COD) proceeded faster than that with W(CO)$_5$(THF). ^{31}P NMR spectrum indicated that more than 60% of (*Z*)-**3** was converted to the corresponding tungsten(0) complex (*Z*)-**3W** after the reaction mixture was stirred at room temperature for 4 h. The usual workup gave (*Z*)-**3W** in 71% yield.

Reaction of (*Z*)-3 with PtCl$_2$(COD)

A pale yellow suspension of (*Z*)-**3** (0.1 g, 0.17 mmol) and PtCl$_2$(COD) (0.0637 g, 0.17 mmol) in THF (6 mL) was refluxed for 2 h. ^{31}P NMR spectrum indicated that a new species (δ_P 234.0, 67.0, $^{2}J_{PP}$ = 131 Hz) in a trace amount was formed together with the starting material. After addition of CH$_2$Cl$_2$ (12 mL) to this suspension, it became a clear yellowish–orange solution. This solution was then heated at 50 °C and monitored by ^{31}P NMR spectrum. The intensity of the first new species increased and the second new species (δ_P 74.2, 26.0, $^{2}J_{PP}$ = 52 Hz) then appeared after the solution was refluxed for 6 h. The reaction mixture gradually turned orange after refluxing overnight. Evaporation of the solvents afforded an orange–yellow residue and the residue was purified by column chromatography (toluene : hexane : THF = 3 : 3 :1) to yield (*Z*)-**3Pt** (0.054 g, 37%) and **5** (0.023 g, 14%) together with the recovered (*Z*)-**3** (0.04 g, 40%). (*Z*)-**3Pt**: Red crystals, mp 255 °C (decomp.). Found: C, 43.28; H, 6.56; N, 3.20. Calc. for C$_{31}$H$_{57}$Cl$_3$N$_2$P$_2$SPt: C, 43.64; H, 6.73; N, 3.28%; IR (KBr, cm^{-1}): 597 (P=S); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 230.9 (P=C, $^{1}J_{PPt}$ = 4562 Hz), 65.6 (P(S)Ph$_2$, $^{2}J_{PPt}$ = 57 Hz), $^{2}J_{PP}$ = 128 Hz; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.61 (d, $^{4}J_{PH}$ = 4.8 Hz, 2H, Ph), 3.91 (sept, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 6.8 Hz, 4H, NC*H*Me$_2$), 1.76 (s, 18H, *o*-^{t}Bu), 1.52 (d, $^{3}J_{HH}$ = 7.2 Hz, 12H, NCH*Me*$_2$), 1.47 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, NCH*Me*$_2$), 1.35 (s, 9H, *p*-^{t}Bu); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 156.1 (d, $^{1}J_{PC}$ = 4.2 Hz, *o*-Mes*), 155.2 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes*), 129.5 (dd, $^{1}J_{PC}$ = 110.2 Hz, $^{1}J_{PC}$ = 60.0 Hz, P=C), 125.7 (d, $^{3}J_{PC}$ = 10.6 Hz, *m*-Mes*), 114.8 (dd, $^{1}J_{PC}$ = 28.2 Hz, $^{3}J_{PC}$ = 9.2 Hz, *ipso*-Mes*), 49.6 (s, N*C*HMe$_2$), 49.5 (s, N*C*HMe$_2$), 39.9 (s, *o*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 35.0 (s, *o*-C*Me*$_3$), 31.4 (s, *p*-C*Me*$_3$), 24.8 (d, $^{3}J_{PC}$ = 3.4 Hz, NCH*Me*$_2$), 24.7 (d, $^{3}J_{PC}$ = 2.9 Hz, NCH*Me*$_2$). **5**: Yellow crystals, mp 178 °C (decomp.); Found: C, 49.81; H, 7.38; N, 2.75. Calc. for C$_{31}$H$_{57}$Cl$_3$N$_2$P$_2$SPt·1.5C$_7$H$_8$: C, 50.19; H, 7.00; N, 2.82%; IR (KBr, cm^{-1}): 606 (P=S); ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 73.6 (P=S), $^{2}J_{PPt}$ = 52 Hz, 25.9 (PCHCl, $^{1}J_{PPt}$ = 3550 Hz), $^{2}J_{PP}$ = 50 Hz; ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.57 (d, $^{4}J_{HP}$ = 6.0 Hz, 1H, Ph), 7.13 (s, 1H, Ph), 4.51 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, NC*H*Me$_2$), 3.89 (sept, $^{3}J_{HH}$ = 7.2 Hz, 2H, NC*H*Me$_2$), 3.76 (pseudo-t, ($^2J_{PH}$ + $^2J_{HH}$)/2 = 6.5 Hz, 1H, PC*H*Cl), 3.10 (d, $^2J_{HH}$ = 15.0 Hz, 1H, PC*H*$_2$), 2.77 (dd, $^2J_{HH}$ = 15.0 Hz, $^2J_{HP}$ = 11.6 Hz, 1H, PC*H*$_2$), 1.85 (s, 9H, *o*-^{t}Bu), 1.62 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NCH*Me*$_2$), 1.60 (s, 3H, C*Me*$_2$), 1.56 (d, $^3J_{HH}$ = 7.2 Hz, 6H, NCH*Me*$_2$), 1.52 (s, 3H, C*Me*$_2$), 1.48 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NCH*Me*$_2$), 1.43 (d, $^3J_{HH}$ = 7.2 Hz, 6H, NCH*Me*$_2$), 1.35 (s, 9H, *p*-^{t}Bu); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ): 161.8 (d, $^2J_{PC}$ = 23.6 Hz, *o*-Mes*), 157.0 (d, $^4J_{PC}$ = 2.4 Hz, *p*-Mes*), 154.1 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Mes*), 125.7 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Mes*), 119.5 (d, $^3J_{PC}$ = 12.3 Hz, *m*-Mes*), 116.4 (dd, $^1J_{PC}$ = 57.2 Hz, $^3J_{PC}$ = 8.1 Hz, *ipso*-Mes*), 55.2 (dd, $^1J_{PC}$ = 76.9 Hz, $^1J_{PC}$ = 12.6 Hz, P*C*HCl), 50.8 (d, $^2J_{PC}$ = 4.1 Hz, N*C*HMe$_2$), 49.8 (d, $^2J_{PC}$ = 3.9 Hz, N*C*HMe$_2$), 44.4 (s, P*C*H$_2$CMe$_2$), 39.1 (s, *o*-*C*Me$_3$), 35.8 (d, $^2J_{PC}$ = 3.9 Hz, PCH$_2$*C*Me$_2$), 35.6 (s, *p*-*C*Me$_3$), 34.4 (s, *o*-C*Me*$_3$), 31.5 (s, PCH$_2$C*Me*$_2$), 30.7 (s, *p*-C*Me*$_3$), 26.2 (d, $^3J_{PC}$ = 2.4 Hz, NCH*Me*$_2$), 24.7 (d, $^3J_{PC}$ = 2.9 Hz, NCH*Me*$_2$), 24.5 (d, $^3J_{PC}$ = 5.7 Hz, NCH*Me*$_2$), 24.0 (d, $^3J_{PC}$ = 2.4 Hz, NCH*Me*$_2$); *m/z* (FAB) 852 (M − H, relative intensity 20%), 782 (M − H − 2Cl, 100%).

X-Ray crystal data

Selected crystallographic data and collection parameters for (*Z*)-**3**, (*Z*)-**3Pt**, and **5** are listed in Table 1. CCDC reference numbers 206703–206705. See http://www.rsc.org/suppdata/ob/b3/b305216h/ for crystallographic data in .cif or other electronic format.

Acknowledgements

This work was supported in part by Grants-in-Aid for Scientific Research (No. 13303039 and 14044012) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. H. Liang is grateful to the Japan Society for the Promotion of Science for the Postdoctoral Fellowships for Foreign Researchers.

References and Notes

1 (*a*) M. Regitz and O. J. Scherer, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Georg Thieme Verlag, Stuttgart, 1990; (*b*) K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley & Sons, Chichester, 1998; (*c*) M. Yoshifuji, *J. Chem. Soc., Dalton Trans.*, 1998, 3343–3349.

2 L. Weber, *Agnew. Chem., Int. Ed.*, 2002, **41**, 563–572 . See also M. Doux, N. Mézailles, M. Melaimi, L. Ricard and P. Le Floch, *Chem. Commun.*, 2002, 1566–1567; O. Daugulis, M. Brookhart and P. S. White, *Organometallics*, 2002, **21**, 5935–5943; A. Ionkin and W. Marshall, *Chem. Commun.*, 2003, 710–711.

3 (*a*) F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami and M. Yoshifuji, *J. Am. Chem. Soc.*, 2002, **124**, 10968–10969; (*b*) T. Minami, H. Okamoto, S. Ikeda, R. Tanaka, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2001, **40**, 4501–4503; (*c*) F. Ozawa, S. Yamamoto, S. Kawagishi, M. Hiraoka, S. Ikeda, T. Minami, S. Ito and M. Yoshifuji, *Chem. Lett.*, 2001, 972–973; (*d*) S. Ikeda, F. Ohhata, M. Miyoshi, R. Tanaka, T. Minami, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2000, **39**, 4512–4513; (*e*) K. Toyota, K. Masaki, T. Abe and M. Yoshifuji, *Chem. Lett.*, 1995, 221–222.

4 (*a*) S. Ito and M. Yoshifuji, *Chem. Commun.*, 2001, 1208–1209; (*b*) R. Appel and W. Schuhn, *J. Organomet. Chem.*, 1987, **329**, 179–185; (*c*) R. Appel, W. Schuhn and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 420–421.

5 S. Ito, H. Liang and M. Yoshifuji, *Chem. Commun.*, 2003, 398–399.

6 (*a*) K. Toyota, H. Takahashi, K. Shimura and M. Yoshifuji, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 141–145; (*b*) M. Yoshifuji, K. Shibayama and N. Inamoto, *Heterocycles*, 1984, **22**, 681–686; (*c*) M. Yoshifuji, K. Ando, K. Shibayama, N. Inamoto, K. Hirotsu and T. Higushi, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 418–419; (*d*) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 1983, 862–863.

7 K. M. Pietrusiewicz, M. Kuznikowski, W. Wieczorek and A. Brandi, *Heteroat. Chem.*, 1992, **3**, 37–40.

8 X-Ray analysis for (*Z*)-**3W** was performed. Although the data were not good due to the poor quality of the single crystal, the chelating coordination pattern was observed.

9 (*a*) H. W. Kroto, J. F. Nixon, M. J. Taylor, A. A. Frew and K. W. Muir, *Polyhedron*, 1982, **1**, 89–95; (*b*) T. A. van der Knaap, F. Bickelhaupt, J. G. Kraaykamp, G. van Koten, J. P. Bernards, H. T. Edzes, W. S. Veeman, E. de Boer and E. J. Baerends, *Organometallics*, 1984, **3**, 1804–1811.

10 G. Becker, W. A. Herrman, W. Kalcher, G. W. Kriecbaum, C. Pahl, C. T. Wagner and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 413.

11 (*a*) A. J. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek and K. Lammertsma, *Chem. Eur. J.*, 2003, **9**, 2200; (*b*) K. Lammertsma and M. J. M. Vlaar, *Eur. J. Org. Chem.*, 2002, **7**, 1127–1138; (*c*) M. E. García, V. Riera, M. A. Ruiz, D. Sáez, J. Vaissemann and J. C. Jeffery, *J. Am. Chem. Soc.*, 2002, **124**, 14304–14305; (*d*) C.-H. Tsang, C. A. Rohrick, T. S. Saini, B. O. Patrick and D. P. Gates, *Organometallics*, 2002, **21**, 1008–1010; (*e*) S. Shah, M. C. Simpson, R. C. Smith and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 2001, **123**, 6925–6926; (*f*) K. Tsuji, S. Sasaki and M. Yoshifuji, *Heteroat. Chem.*, 1998, **9**, 607–613; (*g*) S. Ito, K. Toyota and M. Yoshifuji, *Chem. Commun.*, 1997, 1637–1638; (*h*) M. Yoshifuji, T. Sato and N. Inamoto, *Chem. Lett.*, 1988, 1735–1738; (*i*) A. H. Cowley and M. Pakulski, *Tetrahedron Lett.*, 1984, **25**, 2125–2126; (*j*) M. Yoshifuji, I. Shima, K. Ando and N. Inamoto, *Tetrahedron Lett.*, 1983, **24**, 933–936; (*k*) M. Freytag, P. J. Dyson, L. Ernst, P. G. Jones and R. Schmutzler, *Inorg. Chem. Commun.*, 2002, **5**, 808–810.

12 (*a*) S. J. Goede and F. Bickelhaupt, *Chem. Ber.*, 1991, **124**, 2677–2684; (*b*) S. J. Goede, M. A. Dam and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, 1994, **113**, 278–282; (*c*) R. Appel, C. Cassser and M. Immenkeppel, *Tetrahedron Lett.*, 1985, **26**, 3551–3554.

13 M. R. Maziéres, C. Roques, M. Sanchez and J. P. Majoral, *Tetrahedron*, 1987, **43**, 2109–2118.