

1,3-Diphosphapropenes for novel chemistry of metal complexes

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Received 28 June 2004; accepted 20 September 2004

Available online 1 February 2005

Abstract

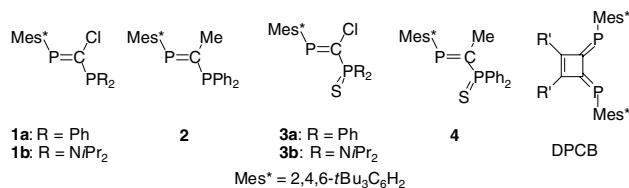
2-Methyl-3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropene was obtained as a chelate ligand for palladium(II) and platinum(II) complexes. Sulfurization of 2-methyl-1,3-diphosphapropene mainly gave 3-thio-1,3-diphosphapropene which bears a P=C–P=S skeleton and was used as a ligand of transition-metal complexes. A doubly-sulfurized product of the 1,3-diphosphapropene, 1,3-dithio-1,3-diphosphapropene, was isolated and characterized. The palladium(II) complexes containing the ligated 1,3-diphosphapropenes were used for catalytic reactions such as cross-couplings and direct conversion of allyl alcohol to allylaniline. © 2004 Elsevier B.V. All rights reserved.

Keywords: Diphosphapropenes; Transition metal complexes; Sulfurization; Catalytic reactions; Coupling reactions

1. Introduction

Chemistry of low-coordinated phosphorus compounds has greatly developed in the past decades [1] and we have reported a number of phosphathenes kinetically stabilized by bulky 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Mes*) groups [2]. Previously we reported the preparation of 2-chloro-1,3-diphosphapropenes **1**, which were used as ligands for transition-metal complexes [3]. Basically **1** takes the *Z* configuration to avoid steric congestion, which is advantageous to act as a chelate ligand. The 1,3-diphosphapropene skeleton behaves like an unsymmetrical chelating ligand containing two kinds of phosphorus atoms, and will display unique coordinating properties to metals [3]. Utilization of low-coordinated phosphorus compounds as ligands of synthetic catalysts is one of the recent topics of phosphorus chemistry, and we [4] and others [5] have used several low-coordinated phosphorus compounds such

as 3,4-diphosphanylidenecyclobutenes (DPCB) as ligands of catalysts. It prompted us to explore 1,3-diphosphapropene derivatives which afford the corresponding palladium or platinum complexes of catalytic activity. We here describe that 3-methyl-3,3-diphenyl-1,3-diphosphapropene **2** afforded the corresponding chelate palladium(II) and platinum complexes. Additionally, we recently established extension of the P=C–P system to P=C–P=S by utilizing the regioselective sulfurization of 1,3-diphosphapropenes **1** affording **3** [6]. Thus, we report the preparation of 2-methyl-3-thio-1,3-diphosphapropene **4** from sulfurization of **2**, and **4** was used as a chelating ligand for several transition-metal complexes. Catalytic activity of several palladium(II) complexes was investigated as an application of metal complexes.



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2. Results and discussion

2.1. Preparation of 2-methyl-1,3-diphosphapropene derivatives

(*Z*)-2-Bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene [7] was allowed to react successively with butyllithium and chlorodiphenylphosphine to give (*E*)-2-methyl-1,3-diphosphapropene **2** in a moderate (66%) yield, including the *E/Z* isomerization in the P=C moiety [8]. 1,3-Diphosphapropene **2** was allowed to react with an equivalent amount of sulfur (1/8 S₈) in refluxing toluene for 20 h to afford the corresponding sulfurized compound **4** in an excellent yield (91%) (Scheme 1) [9]. Compounds **2** and **4** were an air- and moisture-stable colorless solids, and the structures were characterized by spectroscopic data. Reaction of **2** with an excess amount of sulfur (3/8 S₈) afforded **5**, where both of the sp²-type phosphorus and the phosphino group are sulfurized, together with **4**. Reaction of **4** with sulfur in the presence of DBU (=1,8-diazabicyclo[5.4.0]undec-7-ene) gave **5** together with unidentified products [10]. The structure of **5** was confirmed by X-ray crystallography as displayed in Fig. 1. The structural parameters of **5** indicate a normal molecular framework of both methyl-ethioxophosphorane [1] and phosphine sulfide. The torsion angle of P1–C1–P1–S2 is 138.3(3)°, which is in contrast to the reported 3-thio-1,3-diphosphapropenes **3** revealing an almost planar P=C–P=S skeleton [6].

2.2. Complexation with carbonyl tungsten(0) moieties

Compound **2** was allowed to react with W(CO)₅(thf) to afford monocoordinated complex **6** in 70% yield together with a small amount (3% yield) of chelate complex **7** [8]. Furthermore **6** was irradiated to afford **7** by releasing one CO ligand in 2% yield based on **6** (Scheme 2) [8]. When **4** was allowed to react with W(CO)₅(thf) in THF, both the monocoordinated complex **8** and the chelate complex **9** were obtained as a mixture (**6**: 42%; **7**: 15%) (Scheme 3) [9]. Isolation and characterization of **9** was successful, whereas attempts to purify **8** failed.

2.3. Pd and Pt complexes bearing ligated 1,3-diphosphapropenes

Compound **2** functioned as a chelate ligand for palladium(II) and platinum(II) complexes: **2** was allowed to

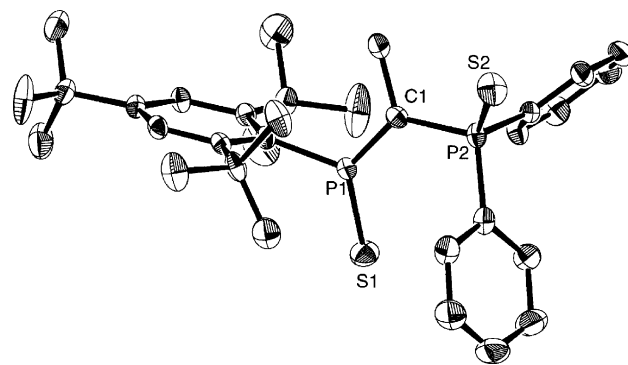
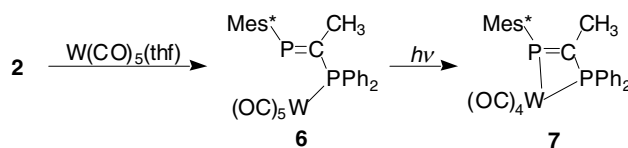
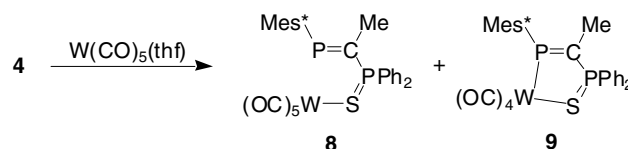


Fig. 1. An ORTEP presentation of the molecular structure of **5** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–S1 1.916(2), P2–S2 1.951(2), P1–C1 1.651(5), P1–C_{Mes*} 1.820(4), P2–C1 1.811(5), C1–Me 1.535(7) and S1–P1–C1 128.1(2), S1–P1–C_{Mes*} 118.1(2), C1–P1–C_{Mes*} 113.7(2), S–P2–C1 110.1(2), P1–C1–P2 125.6(3), P1–C1–Me 120.4(3), P2–C1–Me 114.0(3).



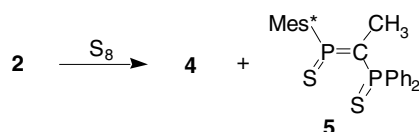
Scheme 2.



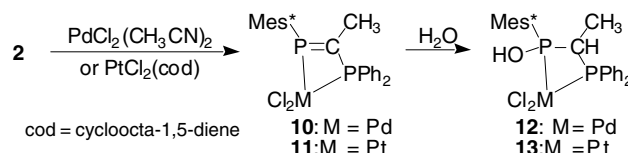
Scheme 3.

react with MCl₂(CH₃CN)₂ (M = Pd, Pt) to afford the corresponding palladium(II) and platinum(II) complexes **10** and **11** [8]. On the other hand, **1** afforded neither isolable Pd or Pt complex, suggesting that coordination properties of the 1,3-diphosphapropene ligand strongly depends on the substituents (Scheme 4) [11]. Whereas **10** and **11** are stable in the solid state and do not decompose in air, they reacted with water to afford **12** and **13**, respectively. Structures of **12** and **13** were confirmed by X-ray crystallography proving the *syn*-addition of water [8,12].

Compound **4** was allowed to react with PdCl₂(MeCN)₂ in dichloromethane at room temperature for



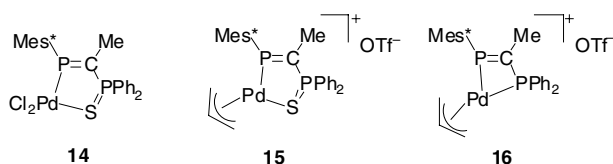
Scheme 1.



Scheme 4.

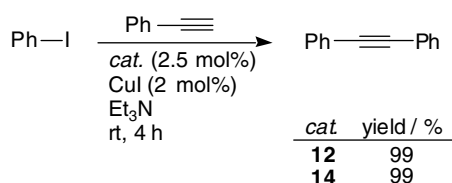
30 min to give **14** in 84% yield [9]. Complex **14** was air- and moisture-stable solid and displayed no decomposition in solution for several weeks. In fact, no hydrolysis occurred in the presence of water in solution, whereas **10** afforded **14** by hydrolysis. It is probably due to the greater stability of the five-membered chelate structure compared with the four-membered one. Alternatively, the electronic effect of sulfur would play a role in preventing the hydrolysis. Attempts to prepare a platinum(II) complex from **4** and $\text{PtCl}_2(\text{cod})$ (cod = cyclo-octa-1,5-diene) failed. The structure of **14** was characterized by the spectroscopic data and confirmed by X-ray crystallography revealing a planar structure around the palladium [9].

Moreover, **4** was used as a ligand of a π -allylpalladium(II) complex. Indeed, **4** was allowed to react with $[(\eta^3\text{-allyl})\text{PdCl}]_2$ and silver(I) triflate to afford the corresponding complex **15** almost quantitatively as an air and moisture stable compound, and the structure was characterized by the spectroscopic data [9]. Similarly, **2** was used as a ligand of a π -allyl complex and actually afforded **16**, but it decomposed in several hours even in an inert atmosphere.

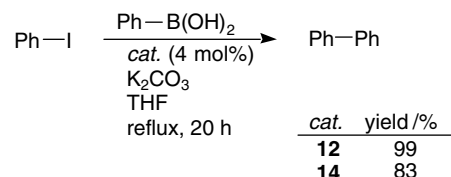


2.4. Catalytic reactions using Pd(II) complexes

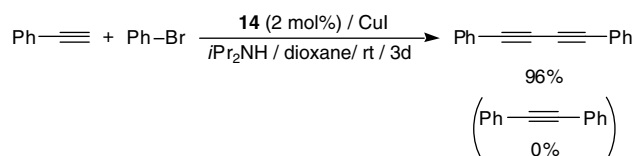
By using **12** and **14**, preliminary studies concerning catalytic cross-coupling reactions such as the Sonogashira [13] and the Suzuki [14] couplings were performed. As described in Schemes 5 and 6, iodobenzene was allowed to react with phenylacetylene and phenylboronic acid in the presence of **12** or **14** as catalyst, together with some other reagents, to afford diphenylacetylene and biphenyl in good yields, respectively [8,9]. Whereas these cross-coupling reactions smoothly proceeded in the case of iodobenzene, bromobenzene showed poor reactivity under these reactions. In the reaction of bromobenzene with phenylacetylene under the catalytic reaction conditions with **14**, diphenylbutadiyne was obtained almost quantitatively (96%) (Scheme 7) [9]. The low activity



Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

of **12** and **14** for the cross-coupling might be attributed to the descending electron-donating effect of the sp^2 -phosphorus atom preventing the oxidative-addition to the C–X bond [1,4,5].

The π -allyl complex **15** was employed as a catalyst for the reaction of allyl alcohol with aniline [9]. As described in Scheme 8, 2 mol% of **15** catalyzed the reaction of allyl alcohol with aniline 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 large amount of **15** was necessary for the reaction and the yield was not good compared with the results of catalysts bearing DPCB ligands [4], **15** displayed a considerable catalytic ability for the direct conversion of allyl alcohol to allylaniline, which has been rather difficult by use of catalysts containing normal phosphine ligands. The low-coordinated sp^2 phosphorus atom might enhance π -backbonding due to the low-lying $\text{P}=\text{C}$ π^* orbital, and it might facilitate the C–O bond cleavage in allyl alcohol [9].

3. Conclusion

Novel 2-methyl-1,3-diphosphapropenes (**2**, **4**) were prepared and found to function as a monodentate and/or a chelating ligand of several transition-metal complexes. The dichloropalladium(II) complexes **12** and **14** displayed catalytic activities for the Sonogashira and Suzuki cross-coupling, although the activity was not as high as well-defined ligands with high activity. On the

other hand, the π -allylpalladium(II) complex **15** was useful for the direct conversion of allyl alcohol. The 1,3-diphosphapropene derivatives could be widely employed as a novel ligand system of metal complexes. Compound **5**, generated through sulfurization of **2**, was structurally characterized and expected to function as a novel S2-ligand.

4. Experimental section

4.1. Preparation of **4** and **5**

A solution of **2** (0.720 g, 1.47 mmol) and sulfur (4.5 mmol as S) in toluene (25 mL) was refluxed for 24 h. The solution was allowed to cool to room temperature and the solvent was removed in vacuo. Compounds **4** and **5** were obtained after silica gel column chromatography (hexane/AcOEt 20:1) of the residue. **4**: 0.40 g (52% yield); the physical data were identical to our previous report [9]. **5**: 0.10 g (12% yield); Colorless prisms (hexane) m.p. 185–188 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 188.6 [P(S)=C], 46.2 [P(Ph)₂=S], $^2J_{\text{PP}} = 21$ Hz; ^1H NMR (400 MHz, CDCl_3): δ 8.06 (m, 4H, Ph), 7.56 (d, $^4J_{\text{PH}} = 2.2$ Hz, 2H, Mes*), 7.52–7.48 (m, 6H, Ph), 1.69 (s, 18H, *o*-*t*-Bu), 1.57 (dd, $^3J_{\text{PH}} = 11.2$ Hz, $^3J_{\text{PH}} = 3.5$ Hz, 3H, CH₃), 1.32 (s, 9H, *p*-*t*-Bu); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 154.6 (d, $^4J_{\text{PC}} = 3.5$ Hz, *p*-Mes*), 153.8 (d, $^2J_{\text{PC}} = 7.1$ Hz, *o*-Mes*), 132.6 (d, $^2J_{\text{PC}} = 10.3$ Hz, *o*-Ph), 131.8 (d, $^3J_{\text{PC}} = 2.9$ Hz, *p*-Ph), 128.7 (d, $^3J_{\text{PC}} = 12.9$ Hz, *m*-Ph), 133.1 (dd, $^1J_{\text{PC}} = 88.3$ Hz, $^3J_{\text{PC}} = 3.2$ Hz, *ipso*-Ph), 132.5 (d, $^2J_{\text{PC}} = 10.7$ Hz, *o*-Ph), 125.7 (dd, $^1J_{\text{PC}} = 72.3$ Hz, $^3J_{\text{PC}} = 5.7$ Hz, *ipso*-Mes*), 124.7 (d, $^3J_{\text{PC}} = 13.2$ Hz, *m*-Mes*), 121.3 (dd, $^1J_{\text{PC}} = 101.9$ Hz, $^1J_{\text{PC}} = 69.1$ Hz, P=C), 39.9 (d, $^3J_{\text{PC}} = 2.6$ Hz, *o*-CMe₃), 35.7 (s, *p*-CMe₃), 34.1 (s, *o*-CMe₃), 31.4 (s, *p*-CMe₃), 21.5 (d, $^2J_{\text{PC}} = 5.8$ Hz, CH₃); IR (KBr): ν 690, 652 cm^{-1} (P=S). Anal. Calc. for C₃₂H₄₂P₂S: C, 69.53; H, 7.66; S, 11.60%. Found: C, 69.24, H, 7.71, S, 11.88%.

4.2. X-ray crystallography of **5**

X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer. The structure was solved by direct methods (SIR92) [15] and expanded using Fourier techniques (DIRDIF94) [16]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put on the calculated positions. Structure solution, refinement, and graphical representation were carried out using the teXsan package [17]. Crystal data of **5**: C₃₂H₄₂P₂S₅, $M = 552.75$, triclinic, $P\bar{1}$ (#2), $a = 10.6640(2)$, $b = 16.0652(9)$, $c = 10.6455(7)$ Å, $\alpha = 104.276(4)$, $\beta = 115.560(2)$, $\gamma = 76.308(1)^\circ$,

$V = 1576.7(2)$ Å³, $Z = 2$, $2\theta_{\text{max}} = 55.0^\circ$, $T = 296$ K, $\rho = 1.164$ g cm⁻³, $\mu = 0.289$ mm⁻¹, 12608 collected reflections, 4305 unique reflections ($R_{\text{int}} = 0.042$), $R1 = 0.081$ ($I > 2\sigma(I)$), $R_w = 0.095$ (all data), $S = 1.70$ (325 parameters). Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Date Centre as supplementary publication number CCDC-242211. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.3. The sonogashira coupling with **14**

Complex **14** was prepared according to [9]. A mixture of iodobenzene (1.0 mmol), phenylacetylene (1.0 mmol), **14** (0.025 mmol), copper(I) iodide (0.025 mmol), and triethylamine (4 mL) was stirred under argon at room temperature for 4 h. The solvent was removed in vacuo and the residue was extracted with ether. The solution was concentrated and the residue was chromatographed over silica gel (hexane) to afford 0.18 g of diphenylacetylene (99% yield).

4.4. The suzuki coupling with **14**

A solution of iodobenzene (2.00 mmol), phenylboric acid (3.00 mmol), **14** (0.080 mmol), potassium carbonate (6.00 mmol) in THF (10 mL) was refluxed for 20 h and after being allowed to cool to room temperature 10 mL of ether and 10 mL of water were added. The extracted organic layer was dried over MgSO₄. The solution was concentrated and silica gel column chromatography of the residue (hexane) afforded 0.26 g of biphenyl (83% yield based on iodomethane).

4.5. Synthesis of allylanilines with **15**

Complex **15** was prepared according to [9]. A solution of allyl alcohol (1.00 mmol), aniline (2.00 mmol), **15** (0.020 mmol), and MgSO₄ (2.00 mmol) in toluene (3 mL) was stirred at room temperature for 2 h. The solution was filtered through Celite and the filtrate was concentrated. The residual material was treated by silica gel column chromatography (hexane/AcOEt) to afford 74 mg of allylaniline (63% yield) and 5.1 mg of bis(allyl)aniline (3% yield).

Acknowledgements

This work was supported in part by Grants-in-Aid for Scientific Research (No. 13304049 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. The authors thank Prof. Fumiuyuki Ozawa, Institute of Chemical Research, Kyoto University, for his helpful suggestions.

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