

Rhodium-Catalyzed Insertion Reaction of PhP Group of Pentaphenylcyclopentaphosphine with Acyclic and Cyclic Disulfides

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Supporting Information

ABSTRACT: Organophosphorus compounds with a phosphorus atom attached to a phenyl group and two organothio/organoseleno $Ph \sim P^{-P} \sim Ph$ groups were synthesized using the rhodium-catalyzed insertion $Ph \sim P^{-P} \sim Ph$ reaction of the PhP group of pentaphenylcyclopentaphosphine (PhP)5 with acyclic disulfides and diselenides. The method was



applied to the synthesis of heterocyclic compounds containing the S-P-S group by the reaction of (PhP), and cyclic disulfides such as 1,2-dithietes, 1,2-dithiocane, 1,4,5-dithiopane, and 1,2-dithiolanes.

ligomeric organophosphanes $(RP)_n$ possessing P atoms attached to one organo moiety and two P atoms are an interesting group of polyphosphorus compounds that exhibit notable chemical properties, because of the P-P-P group.¹ It was considered that chemical reactions of such compounds could provide synthetic routes to various organophosphorus compounds containing X-P-X groups if two P-P bonds of P atoms could be efficiently converted to P-X bonds. It is then crucial to understand and control the chemical reactivity of P-P-P bond systems, and a transition-metal-catalyzed reaction of $(RP)_n$ compounds is considered an attractive approach.

Among various $(RP)_n$ compounds, pentaphenylcyclopentaphosphine $(PhP)_{5}$ (1) can readily be synthesized by the reaction of dichlorophenylphosphine and magnesium.² However, its chemical reactivity has not been significantly examined, except for a few examples: alkylation of 1 with alkyllithium gave mixtures of oligophosphide $Li(PhP)_n R (n = 1-4);^3$ substitution of 1 with 1,2-dichlorobenzene in the presence of a stoichiometric amount of potassium provided 1,2,3-triphenyl-1,2,3-triphosphaindan;⁴ addition of 1 to diphenylacetylene at 240 °C gave a mixture of 1,2-diphenyl-1,2-diphosphetene and pentaphenyltriphospholene;⁵ and carbene-phosphinidene adducts formed via the addition of 1 to carbene such as Nheteroacyclic carbenes and bicyclic (alkyl)(amino)carbene.⁶ Woollins reagent obtained from 1 and selenium powder are also used in organic synthesis.⁷ The insertion reaction of the PhP group into a single bond was reported for bis-(trifluoromethyl) disulfide at 120 °C to give phenylphosphonodithious acid bis(trifluoromethyl) ester.^{8a} The PhP group in 1 was also inserted to hexa(pentafluorophenyl)digermane.^{8b} A transition-metal-catalyzed reaction of 1 was not reported, although the complexation of a transition metal and 1 was known.

Essentially, all organophosphorus compounds are now synthesized from P4, which is converted to phosphorus trichloride (PCl₃) or phosphoryl chloride (POCl₃). Substitution of chloride with various groups in the presence of bases provides organophosphorus compounds, which are accompanied by the formation of stoichiometric amounts of inorganic metal halides. We consider that (i) the direct transformation of P₄ is preferable for the synthesis of organophosphorus compounds, in terms of saving energy and resources,¹⁰ and (ii) chemical studies of the $(RP)_n$ compounds are critical for such purpose.

We previously developed the addition reaction of diphosphines to unsaturated organic compounds and the single-bond metathesis reaction of diphosphines with diphosphines, disulfides, alcohols, 1-organothioalkynes, and acyl compounds, which involved P-P bond cleavage under rhodium- and palladium-catalyzed conditions.¹¹ A P atom of a diphosphine possesses one P-P bond and two C-P bonds, and the reactivity of $(RP)_n$ compounds with a P atom possessing two P-P bonds is of interest. Described here is the rhodiumcatalyzed synthesis of organophosphorus compounds, in which a P atom is attached to a phenyl group and two organothio groups by the reaction of acyclic disulfides and 1 (Scheme 1).

Scheme 1. Rhodium-Catalyzed Synthesis of Cyclic and Acyclic Organophosphorus Compounds with S-P-S Bonds Using (PhP)₅ (1) and Disulfides



The reaction was also employed for the efficient synthesis of heterocycles containing S and P atoms when applied to cyclic disulfides. 1 reacted with diphenyl diselenide and dibutyl diselenide. The rhodium complex effectively inserts a PhP group of 1 into group 16 heteroatom-heteroatom single bonds.

It was initially confirmed that the P-P bond of 1 can be cleaved and the PhP group can be inserted into the S-S bond

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of acyclic disulfides by rhodium catalysis (see Scheme 2). When 1 (1 equiv atom) was reacted with di(hexyl) disulfide (2a) in

Scheme 2. Rhodium-Catalyzed Reaction of Disulfides/ Diselenides and 1



the presence of RhH(dppe)₂ (5 mol %) in refluxing THF for 15 min, phenylphosphonodithious acid di(hexyl) ester (3a) was obtained in 94% yield. It was noted that five PhP groups of 1 were effectively inserted into the S–S bond. No reaction occurred in the absence of RhH(dppe)₂. RhH(PPh₃)₄ in the presence of dppe exhibited similar reactivity, whereas RhCl-(PPh₃)₃, [Rh(OAc)]₂, Rh(acac)₃, and Pd(OAc)₂ were inactive. Aliphatic disulfides with triethylsilyloxy and methoxycarbonyl groups also reacted effectively (2b and 2c). The reaction of 1 and diphenyl disulfide 2d gave phenylphosphonodithious acid diphenyl ester 3d (90%). 1 reacted with diphenyl diselenide 4a and dibutyl diselenide 4b, and the products 5a and 5b were isolated after air oxidization. Using the rhodium complex, two P–P bonds of 1 were cleaved, and the PhP group was inserted into the S–S and Se–Se bonds.

The reaction of 1 was applied to four-membered cyclic disulfides. When 1 was reacted with 3-(t-butyl)-4-phenyl-1,2-dithiete (6a)¹² (1 equiv) in the presence of RhH(dppe)₂ (5 mol %) in refluxing THF for 0.5 h, 2-phenyl-4-(t-butyl)-5-phenyl-1,3,2-dithiaphosphole (7a) was obtained in 77% yield (see Scheme 3). The structure of 7a was determined by X-ray





crystal structure analysis (see Figure 1). 3-(*t*-Butyl)-4-(4-tolyl)-1,2-dithietes (**6b**) also gave 1,3,2-dithiophospholes (7**b**) in 73% yield. The 1,3,2-dithiophospholes obtained here are new compounds. The reaction of 1 and 1,2-dithietes, which, in turn, are readily obtained from alkynes and S₈,¹¹ can be a novel efficient synthetic method for 1,3,2-dithiophospholes from alkynes.¹³

The reaction of 1 and five-, seven-, and eight-membered cyclic disulfides was conducted (see Table 1). 1,2-Dithiocane (8a) reacted with 1, giving the corresponding ring-expanded



Figure 1. ORTEP view of 7a.

 Table 1. Rhodium-Catalyzed Synthesis of 1,3,2-Dithiaphosphorus Derivatives



^{a)}Yield of **9a**' was calculated on the basis of **8a**. A mixture (R^*, R^*) -**9a**': (R^*, S^*) -**9a**' = 1:1 was obtained.

compound 9a, along with cyclic dimers 9a' $[(R^*,R^*)-9a': (R^*,S^*)-9a' = 1:1]$. The PhP group was efficiently inserted into the S–S bond of 1-oxa-4,5-dithiepane (8b), 1,2-dithiolane-3-pentanoic acid methyl ester (8c), and 3H-1,2-benzodithiol-3-one dioxide (8d), and the corresponding ring-expanded compounds 9b–9d were obtained in high yields. A rhodium complex can be used for the synthesis of the heterocyclic compound possessing S–P–S bonds via the cleavage of two

P–P bonds in (PhP)₅ and the S–S bond in disulfides. As an exception, 3H-1,2-benzodithiol-3-one (8e) gave 2-phenyl-1,2-benzoisothiaphosphole-3(2*H*)-one (9e) with desulfurization. All cyclic organophosphorus products obtained here are new compounds.

The activation mechanism of $(PhP)_5 \mathbf{1}$ with a $RhH(dppe)_2$ complex was investigated. $RhH(dppe)_2$ was reacted with $\mathbf{1}$ (2.0 equiv atom) in refluxing THF for 1 h, and the solvent was removed. As indicated by ³¹P NMR, a mixture was formed, containing $RhH(dppe)_2 \delta$ 57.0 (d, J = 133.0 Hz, 50%) and other rhodium complexes were observed at δ 56.2 (d, J = 143.9 Hz), 27.7 (d, J = 48.9 Hz), and 13.2 (d, J = 47.5 Hz). The residue was washed with hexane and chloroform, and $[Rh^+(dppe)_2]Cl^-$ complex **10** (73%) was formed (see Scheme 4).¹⁴ The Cl⁻ ion in **10** was derived from the chloroform used





to wash the complex. Because 10 did not contain 1, the elimination of the phosphorus group from rhodium metal was considered to be very rapid. Isocyanide was then added to stabilize the rhodium complex containing 1. $RhH(dppe)_2$ and 1-adamantlyisocyanide (4 equiv) were reacted with 1 (4 equiv atom) in refluxing THF for 1 h. The solvent was removed, and the mixture was washed with hexane, chloroform, and acetonitrile to give [Rh(PhP=PPh)(dppe)(AdNC)₂]Cl complex 11 in 59% yield as yellow crystals (Scheme 4). The structure was determined by liquid chromatography-mass spectroscopy (LC-MS) (electrospray ionization (ESI)) analysis, m/z 1039.3075, [Rh(PhP=PPh)(dppe)(AdNC)₂]⁺: calcd for 1039.3048. ³¹P NMR analysis showed two peaks at δ –28.4 (dt, J = 21.4, 19.8 Hz) and δ 42.1 (dt, J = 96.4, 19.9 Hz), which were assigned to the π -coordinated diphenyldiphosphene¹⁵ and the equatorial-coordinated dppe ligand, respectively. Infrared (IR) analysis showed an absorption of isocyanide at 2190 cm^{-1} . Two isocyanides were considered to be coordinated at two equatorial positions. The Cl⁻ ion in 11 was derived from chloroform used to wash the complex. The results indicated the formation of rhodium diphosphene complex 11 with a π coordinated P=P bond. When di(hexyl) disulfide (2a) was reacted with complex 11 in refluxing THF for 1 h, 3a was obtained in 16% yield. The lower yield of 3a in this reaction than in the reaction shown in Scheme 2 may be due to the presence of 1-adamantlyisocyanide. It is considered that an

active and unstable rhodium species with a structure related to 11 is formed. 16

A possible mechanism of this reaction is shown in Scheme 5. $RhH(dppe)_2$ and 1 react to provide a diphenyl diphosphene

Scheme 5. A Possible Mechanism



rhodium complex **A**. Then, rhodium intermediate **B** is formed via oxidative addition of rhodium complex **A** and the S–S bond, and the phosphide intermediate **C** was formed by the insertion of a PhP group. The organophosphorus compounds with the S-P(Ph)-S group were liberated by reductive elimination, and the rhodium catalyst was regenerated by insertion of **1**.

In summary, in the presence of a rhodium complex, PhP groups in $(PhP)_5$ 1 were inserted into the S–S bonds of cyclic and acyclic disulfides to give organophosphorus compounds containing the S–P–S group. A rhodium complex can effectively react with a polyphosphine containing a P atom with two P–P bonds. This reaction provides a useful synthetic method for the preparation of organophosphorus compounds with acyclic and cyclic structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b03825.

Experimental procedures and detailed characterizeation data for the compounds (PDF)

Accession Codes

CCDC 1816018 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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