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COMMUNICATIONS

Published on Web 09/29/2006

# Selective Homo- and Heterodehydrocouplings of Phosphines Catalyzed by Rhodium Phosphido Complexes

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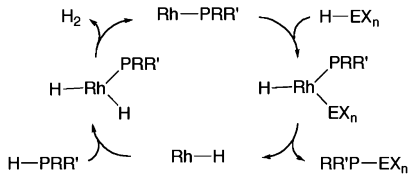
The increasing importance of phosphorus compounds in synthesis and biology has stimulated extensive studies on new phosphorus-element bond-forming reactions via transition metal catalysis.[1] Given the success of dehydrocouplings of silanes and related compounds,[2] similar metal-catalyzed reactions of phosphines should provide useful routes to phosphorus−element (P−E) bonded compounds, especially since such reactions produce hydrogen as the only byproduct (eq 1). However, to date, this strategy has met with limited success, perhaps because phosphine and phosphido ligands inherently form strong, relatively nonlabile interactions with unsaturated metal species.[2−4] Group 4 metallocene catalysts dehydrocouple primary phosphines to cyclic oligomers,[3a−c] and Cp*Rh($CH_2$=$CHSiMe_3$)$_2$ is a catalyst for the coupling of secondary phosphines to the corresponding diphosphanes.[3d] Recently, our

$$RR'P\text{-}H + H\text{-}EX_n \xrightarrow{\text{cat.}} RR'P\text{-}EX_n + H_2 \qquad (1)$$

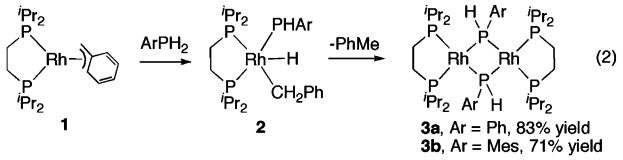
attention was attracted to the highly reactive (dippe)Rh (dippe = $^i$Pr$_2$PCH$_2$CH$_2$P$^i$Pr$_2$) fragment,[5] since we previously observed that a catalyst derived therefrom is active in promoting an intramolecular C−H/P−H dehydrocoupling.[6] This result suggested that related, intermolecular dehydrocouplings might be possible via the general mechanism of Scheme 1. Herein we communicate our preliminary

***Scheme 1***

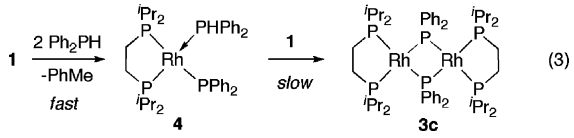



results on efficient dehydrodimerizations of primary and secondary phosphines and the first heterodehydrocoupling of a phosphine with a thiol.

When $PhPH_2$ (0.29 mmol) was added to a solution of the benzyl rhodium complex (dippe)Rh($\eta^3$-$CH_2$Ph)[5a] (**1**, 0.29 mol) in benzene-$d_6$ (2 mL) at room temperature, the color of the solution immediately turned from orange to red. A $^1$H NMR spectrum after 0.5 h revealed the formation of toluene and a rhodium hydride species **2** (br s, $\delta$ −8.27) bearing a benzyl group (br s, $\delta$ 3.35, *C*$H_2$Ph). This complex, presumed to be the oxidative addition product (dippe)Rh(H)(PHPh)-($CH_2$Ph),[7] was observed to be part of a product mixture that also included diastereomers of the phosphido derivative **3a** (**3a′** and **3a″**), observed as broad signals shifted to high field in the $^{31}$P NMR spectrum, at −119.5 (**3a′**) and −125.2 (**3a″**) (eq 2; **3a′**/**3a″**/**2** ratio = 3/3/1). As indicated by $^1$H and $^{31}$P NMR spectroscopies, the hydride **2** gradually transformed to **3a** at room temperature. Concentration and cooling of the reaction mixture gave a brown solid of the binuclear phosphido-bridged rhodium **3a** as a 1/1 mixture of diastereoisomers of **3a′** and **3a″**.[8] The above results are therefore consistent with the sequence of reactions shown in eq 2. Similar results were observed for the reaction of **1** with $MesPH_2$, which gave **3b** as a red solid in 71% yield. The dimeric nature of this product was confirmed by X-ray crystallography.[9]




Interestingly, the reaction of $Ph_2PH$ with **1** takes a somewhat different course, to initially form **4**, which contains a diphenylphosphine ligand. When **1** and $Ph_2PH$ were combined in a 1:1 ratio, half of **1** was left unreacted (by NMR spectroscopy) after 50 min. Thereafter, **4** reacted slowly with the remaining amount of **1** to give **3c** after 2 days. Both **3c** and **4** are red solids that were isolated in 91% and 87% yields, respectively, from reactions using 1 and 2 equiv of $Ph_2PH$.[10,11]




The phosphido complexes **3a**−**c** and **4** exhibit catalytic activity (5 mol % in benzene) in the selective dehydrocoupling of phosphines to the corresponding diphosphanes. With **3a** as a catalyst, 13% of $PhPH_2$ was converted to PhHP−PHPh after 20 h at 20 °C, and **3b** provided a 51% conversion of $MesPH_2$ to the corresponding diphosphane after 2 h at 110 °C. Whereas **3c** did not produce diphosphane from reaction with $Ph_2PH$ over 10 h at 70 °C, **4** gave a 92% yield of $Ph_2P$−$PPh_2$ under the same conditions. The latter results, and the influence of ancillary ligands and substrates suggest that the active catalyst is mononuclear (vide infra).

Higher catalytic activities are exhibited by complex **1**, used as an isolated compound or generated in situ from the reaction of (1,4-cod)Rh($\eta^3$-$CH_2$Ph)[5a] with dippe (Table 1).[12] When 5 mol % of **1** was added to $PhPH_2$ in benzene at room temperature, gas evolution was immediately observed. After 3 h, PhHP−PHPh had selectively formed in 20% yield as a 52/48 meso/rac mixture (by NMR spectroscopy).[13] The yield of PhHP−PHPh slightly increased to 36% after 1 day; however, no further conversion was observed indicating deactivation of the catalyst. A similar result was obtained with **1**, generated in situ (run 2). It should be noted that the chelating diphosphine ligand is crucial for the success of this coupling reaction. Thus, (1,4-cod)Rh($\eta^3$-$CH_2$Ph) alone did not catalyze the dehydrocoupling, even at 70 °C. Although the corresponding ($Cy_2$-$PCH_2CH_2PCy_2$)Rh($\eta^3$-$CH_2$Ph) complex behaves similarly, giving a 32% yield of PhHP−PHPh under the reaction conditions of run


10.1021/ja065346+ CCC: $33.50 

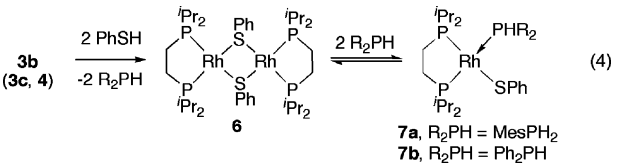
***Table 1.*** Dehydrocouplings of Phosphines Catalyzed by **1**

| run | phosphine | conditions | % yield[b] |
|---|---|---|---|
| 1 | $PhPH_2$ | 20 °C, 20 h (3 h) | 36 (20) |
| 2 | | 20 °C, 20 h[a] | 31 |
| 3 | | 5 mol % dippe, 20 °C, 20 h | 51 |
| 4 | 2-$EtC_6H_4PH_2$ | 20 °C, 20 h (3 h) | 74 (61) |
| 5 | 2-*i*-$PrC_6H_4PH_2$ | 20 °C, 20 h (3 h) | 80 (64) |
| 6 | $MesPH_2$ | 70 °C, 18 h (3 h); 110 °C 3 h | 68 (59); 81 |
| 7 | 2,4,6-*i*-$Pr_3C_6H_2PH_2$ | 70 °C, 18 h (3 h); 110 °C 3 h | 71 (66); 93 |
| 8 | $Ph_2PH$ | 70 °C, 8(3) h | 91 (76) |

[a] Catalyst generated in situ from a Rh(cod)Bz/dippe = 1/1 ratio mixture. [b] Estimated from $^{31}P$ NMR. All $(ArHP)_2$ are ca. 1/1 meso/rac mixtures (see Supporting Information for details).

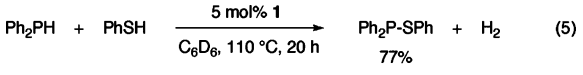
2, other phosphines, both monodentate $R_3P$ (R = Et, *t*-Bu, Ph) and bidentate $R_2PCH_2CH_2PR_2$ (R = Me, Ph), did not produce the coupling product at all (20 °C, overnight). The nature of the rhodium precursor complex also seems critical, as the $[Rh(cod)Cl]_2$/dippe combination exhibited no catalytic activity. This presumably results from the inability of this system to form a phosphido complex upon addition of the phosphine substrate. Interestingly, in the presence of an additional dippe ligand (run 3), the yield of PhHP−PHPh was improved from 36% to 51%.[13] The dehydrocoupling reaction is highly sensitive to the nature of ortho substituents on the aryl ring of the phosphine substrate. Thus, the introduction of 2-Et (run 4) and 2-$^i$Pr (run 5) groups to the aryl ring of a primary phosphine greatly increased the reactivity, resulting in high yields of the coupling products even at room temperature. With more hindered aryl substituents (runs 6 and 7), however, the dehydrocoupling did not proceed at room temperature and heating was required. The dehydrocoupling of the secondary phosphine $Ph_2PH$ proceeds sluggishly at room temperature. Upon heating at 70 °C, however, a high yield of the product was obtained (run 8).

Significantly, the application of this new rhodium catalyst system is not restricted to homodehydrocouplings. Investigations on the possibility of phosphorus−sulfur coupling began with examination of reactions of phosphido rhodium complexes with PhSH, which proceed readily with elimination of the phosphine (eq 4). Thus, when an excess of PhSH (3 equiv) was added to a suspension of **3b** in benzene at 25 °C, the formation of $MesPH_2$ (−156.8 ppm) and **6** (88.3 ppm)[16] occurred as shown by $^{31}P$ NMR spectroscopy. After 2 h at 70 °C, **3b** was completely consumed to give a transparent orange solution containing **6**, **7a**, (−86.4 ppm, Rh-*P*HMes) and $MesPH_2$ in a ratio of 3/60/37. Reactions of PhSH with **3c** and **4** occurred similarly, to produce the complex analogous to **7a** (**7b**). However in this case, unlike for **7a**, the equilibrium greatly favors formation of the monorhodium complex, and this facilitated its isolation. Furthermore, the catalytic dehydrocoupling of $Ph_2PH$




(4)

with PhSH was observed to readily form $Ph_2PSPh$ (eq 5).[15]




(5)

In summary, a simple and versatile catalyst system has been found for dehydrocoupling reactions of hydrophosphines. These catalytic reactions appear to involve intermediate, mononuclear Rh phosphido species which operate by the general mechanism depicted in Scheme 1. Ongoing studies focus on the optimization and scope of these reactions and on further characterization of the mechanism.

**Acknowledgment.** The authors thank the National Science Foundation for support of this work. L.-B.H. was on leave from the National Institute of Advanced Industrial Science and Technology, and thanks a JSPS Overseas Research Fellowship for the support of his visit.

**Supporting Information Available:** Full characterization data for **3a**−**c**, **4**, **5**, **6**, **7b**, and NMR spectra of related Rh intermediates; detailed reaction conditions and identification of the coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) We thank B. V. Mork for performing this X-ray analysis (unpublished).

(10) Complex **4** was not regenerated from a mixture of **3c** and additional $Ph_2PH$ at room temperature.

(11) Complexes **3a**−**c** are stable to 110 °C for 10 h. However, when heated to 70 °C for 3 h, **4** decomposed to free $Ph_2PH$, PhHPPHPh and a hydrido rhodium complex, presumably $[(dippe)Rh]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$ (**5**). Complex **3c** was not detected as a product. Note that **5** does not catalyze the dehydrocoupling of $Ph_2PH$.

(12) The generated catalyst in situ showed higher catalytic activity than **3a**−**c**, but activity similar to that of **4**.

(13) The product PhHPPHPh was identified by comparison of its $^1H$ and $^{31}P$ NMR data with those reported (ref 3c). When the reaction was carried out at higher temperatures, further reaction of PhHPPHPh took place to give a complicated mixture (see Supporting Information for details).

(14) We have confirmed that $PhPH_2$ can replace dippe from complex **3a**. Once dippe is replaced the catalyst loses its activity. The addition of excess dippe presumably delays this deactivation process.

(15) For a related rhodium-catalyzed dehydrocoupling of silanes with thiols, see Baruah, J. B.; Osakada, K.; Yamamoto, T. *Organometallics* **1996**, *15*, 456.

(16) Complex **6** was separately generated via reaction of **1** with PhSH (see Supporting Information).

JA065346+