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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Design, Synthesis, and Application of Phosphaalkenes to Unique Palladium and Gold Catalysts

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## Design, Synthesis, and Application of Phosphaalkenes to Unique Palladium and Gold Catalysts

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*A 2-silyl-1,3-diphosphapropene was utilized as an asymmetrical P2 ligand of stable palladium(II) catalysts. Several phosphaalkene ligands were utilized for synthesis of novel gold(I) complexes which exhibited unique catalytic activity in 1,6-enyne cycloisomerization, indicating effects of P = C double bond, Au–Au contact, and sulfanyl group.*

**Keywords** Catalysts; gold; palladium; phosphaalkenes

## INTRODUCTION

Phosphaalkenes (methylenephosphines,  $\text{--P=C<}$ ) have recently been recognized as promising ligands to develop novel transition-metal catalysts for unique molecular transformations, especially due to a characteristic low-lying  $\pi^*$  LUMO of the  $\text{P}=\text{C}$  moiety.<sup>1,2</sup> In this paper we describe novel properties of 1,3-diphosphapropenes<sup>3</sup> in relation to palladium chemistry and of phosphaalkene-gold complexes showing specific catalytic activity.

## RESULTS AND DISCUSSION

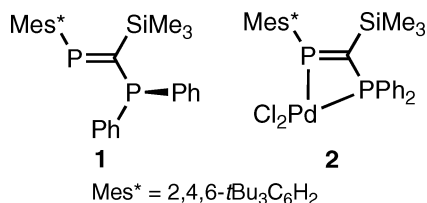
### 2-Silyl-1,3-diphosphapropenes for Palladium Chemistry

A stable 2-silyl-1,3-diphosphapropene **1** was prepared by employing a 1-silyl-2-phosphaethenyllithium and its structure was characterized

We thank Mr. Sou Hashino, Tohoku University, for conducting the reaction of **6** to **8** in the presence of **4** and Prof. Noboru Morita for his helpful comments and suggestions.

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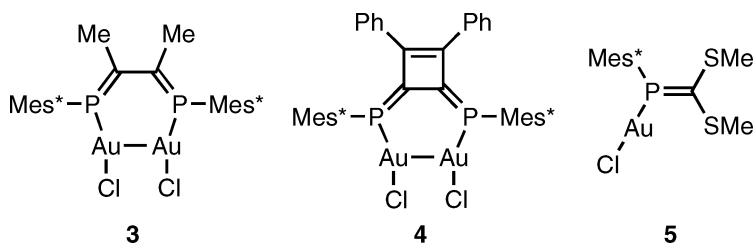
by the  $^{31}\text{P}$  NMR spectroscopic, X-ray crystallographic, and theoretical data. The unsymmetrical P2 ligand **1** afforded the corresponding dichloropalladium(II) chelate complex **2** (Chart 1), which is stable in dichloromethane and it showed considerable catalytic activity in Sonogashira cross-coupling reactions with an aryl iodide and phenylacetylene (57–96% yields).<sup>4,5</sup>



**CHART 1**

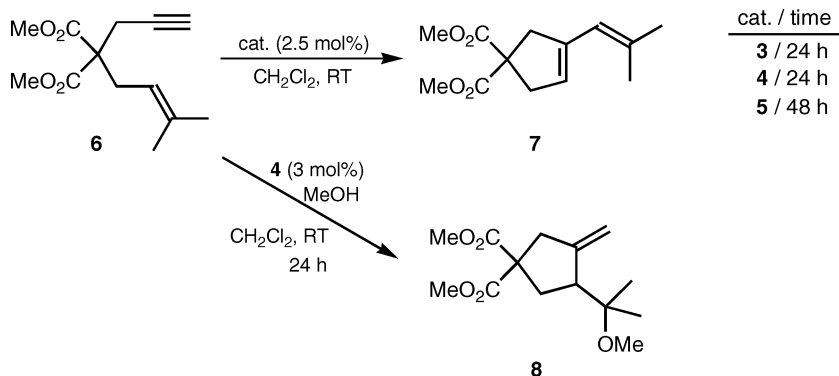
## Phosphaethenes for Gold Catalysts

Taking the  $\pi$ -electron accepting property of  $\text{P}=\text{C}$  double bond into account, phosphaalkenes are expected as a suitable ligand for gold catalysts which might show high electrophilic affinity for unsaturated carbon-carbon bonds. We successfully found that digold(I) complexes **3**, **4**, and a monogold(I) complex **5** (Chart 2) catalyze cycloisomerization of 1,6-enyne **6** to vinylcyclopentene **7** without using any silver additives for activation and regardless of attention to air/moisture. This indicates that the  $\text{P}=\text{C}$  structure, the aurophilic gold-gold contact, and the sulfur atom may increase electrophilicity of the gold center (Scheme 1).<sup>6</sup> Furthermore, in the presence of a catalytic amount of a DPCB-digold(I) complex **4**,<sup>6,7</sup> 1,6-enyne **6** and methanol afforded the corresponding methylenecyclopentane derivative **8**<sup>8</sup> almost quantitatively after stirring the mixture for 24 h at room temperature (Scheme 1). On the other hand, a 1,3-diphosphapropene-digold(I) complex  $[\text{Mes}^*\text{P}=\text{C}(\text{Me})-$



**CHART 2**

$\text{PPh}_2[\text{AuCl}]_2$  served as a catalyst for the cycloisomerization of **6** in the presence of co-catalytic  $\text{AgSbF}_6$ .<sup>6</sup>



SCHEME 1

## EXPERIMENTAL

### Reaction of **6** to **8**

A solution of **6** (0.92 mmol), methanol (4.6 mmol), and **4** (0.028 mmol) in dichloromethane (3 mL) was stirred at room temperature for 24 h. The volatiles were removed in vacuo and the residue was extracted with hexane. The solution was concentrated to afford **8** (0.92 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.02 (1H, s, =CH), 4.96 (1H, s, =CH), 3.71 (3H, s,  $\text{CO}_2\text{Me}$ ), 3.70 (3H, s,  $\text{CO}_2\text{Me}$ ), 2.90–2.81 (3H, m, CH), 2.58–2.52 (1H, m, CH), 1.99 (1H, dd,  $J = 13.4, 9.3$  Hz, CH), 1.16 (3H, s, Me), 1.10 (3H, s, Me).

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