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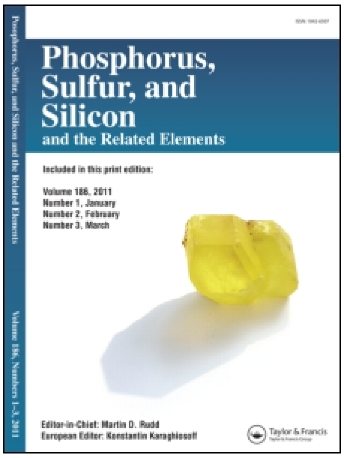

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Synthesis and Complexations of a Novel Stable Carbene Bearing a Phosphorus Ylide

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Synthesis and Complexations of a Novel Stable Carbene Bearing a Phosphorus Ylide

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*Rh complexes **5** and **6** were synthesized via the titled carbine **1**. In the IR spectrum of **6**, the carbonyl stretching frequency was observed at the lower wave number among all [(carbene)Rh(CO)$_2$Cl] complxes reported to date, including the highest electron-donating ability of carbene **1**.*

Keywords Carbene ligands; carbenes; phosphorus rhodium; ylides

Since the first report by Arduengo in 1991,[1] N-heterocyclic carbenes (NHCs) have been extensively studied. Through their successful application as ligands for transition metal catalysts, the tuning of electronic and structural properties of NHCs has become an important subject. One of the modification methods of NHCs is the replacement of amino groups adjacent to the carbene center to other π-donating substituents. Thus, we have focused our attention on carbene **1**, which has a phosphorus ylide moiety next to the carbene center. Due to π-donation ability of the ylide carbanion to the carbene center like an amino group and smaller electronegativity of carbon than that of nitrogen, **1** is expected to have a strong electron-donating ability to the metal center in its transition metal complexes. Although several transition metal (Pt, Cr, Mo, W) complexes of carbene **1** (R = H) were reported,[2] they were synthesized from the corresponding isocyanide complexes, and available metals were limited. Herein, we report the development of the general synthetic method of carbene **1** (R = CH_3) and its coordinating properties.

Reaction of phosphonium salt **2** with mesityllithium gave diphenylphosphine **3** as a major product. Diphenylphosphine **3** is

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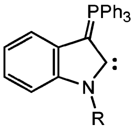
Address correspondence to Takayuki Kawashima, Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail:takayuki@chem.s.u-tokyo.ac.jp considered to be formed by 1,3-phenyl shift via carbene **1**. At lower temperature, however, carbene **1** could be trapped by elemental sulfur to give **4**, quantitatively.

To evaluate the ligand property of carbene **1**, rhodium complexes **5** and **6** were prepared. Both **5** and **6** are air stable in the solid state. Carbonyl stretching frequencies of **6** were observed at the lowest wave numbers among analogous carbene rhodium complexes, indicating that carbene **1** has a strong electron-donating ability.



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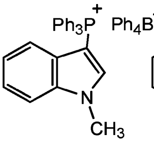

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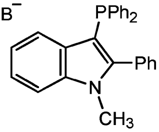

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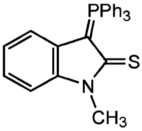

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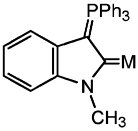

5 (M = Rh(cod)Cl)
6 (M = $Rh(CO)_2Cl$)

REFERENCES

[1] J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **113,** 361 (1991).
[2] R. A. Michelin, A. J. L. Pombeiro, and M. F. C. Guedes da Silva, *Coord. Chem. Rev.*, **218,** 75 (2001).