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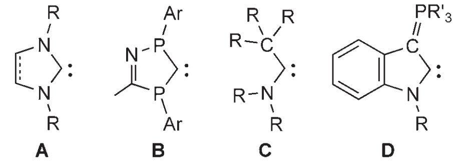
Generation and Coordinating Properties of a Carbene Bearing a Phosphorus Ylide: An Intensely Electron-Donating Ligand**

*Shin-ya Nakafuji, Junji Kobayashi, and Takayuki Kawashima**

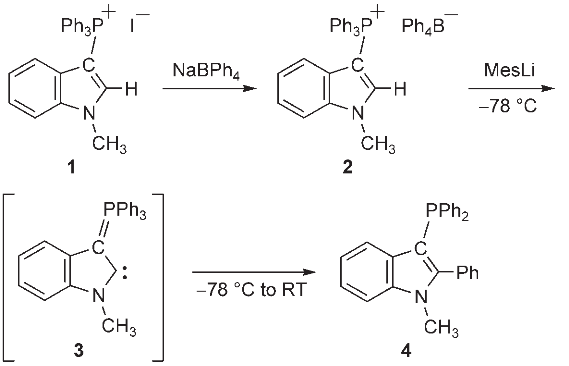
Dedicated to Professor Renji Okazaki on the occasion of his 70th birthday

Since the first synthesis of stable N-heterocyclic carbenes (NHCs) **A** (Scheme 1) was reported by Arduengo and co-workers in 1991,[1] their chemistry as stable carbene species has been extensively studied.[2] Furthermore, the spectacular success of NHCs as a new class of ligands for transition-metal complexes and their application to catalytic systems[3] have proved to be a tremendous advantage of using NHCs. One of the major features of NHCs is their high electron-donating ability to the metal center, by which catalytically active species are electronically stabilized and catalytic processes are accelerated. From this viewpoint, transition-metal complexes bearing a carbene with higher electron-donating ability are attractive target molecules. Modification of the scaffold is an important method to improve the donating ability of NHCs, and replacement of one or both nitrogen atoms adjacent to the carbene center with other main-group elements has provided a dramatic effect.[4] For example, Bertrand and co-workers recently reported diphosphinocarbenes (PHC) **B**[5] and alkylamino carbenes **C**,[6] which exhibit enhanced electron-donating ability. The electron-donating ability of carbenes is considered to be dominated by π-electron-donating ability and the electronegativities of the two adjacent atoms. To develop the electron-donating ability of NHCs, the neighboring substituents are required to have high π-donating ability and low electronegativity at the same time. Thus, we focused our attention on a phosphorus ylide moiety as a carbene-stabilizing substituent. Aminoylidecarbene (AYC) **D**[7] is expected to have a high σ-donating ability towards transition metals because the inductive effect of the phosphorus ylide moiety is smaller than that of the amino groups. In addition, π-donation of the ylide carbanion to the carbene center might stabilize a carbene similar to the case of amino groups in NHCs.[8] Although this unknown carbene **D** can be classified as a kind of cyclic alkylamino carbenes (CAAC),[6b,c] the substituent of an sp^2-hybridized anionic carbon atom, instead of an sp^3-hybridized neutral carbon atom, will enhance the donating ability of the carbene. Several complexes (Pt, Cr, Mo, W) of AYC (R = H) have already been reported by Michelin and co-workers.[9] These complexes were synthesized from the corresponding transition-metal isocyanide complexes bearing a phosphorus ylide at the *ortho* position through intramolecular cyclization; unfortunately, extension to a wide variety of transition-metal complexes is limited. Moreover, most of the complexes were obtained as an inseparable mixture with imido complexes; therefore, the unambiguous investigation of properties of carbene–metal complexes is difficult. Herein, we report the development of general synthetic methods for AYC (R = CH_3) and its complexes with Rh and Pd, along with their properties.



Scheme 1. Stabilized carbenes.

Phosphonium salt **1** was prepared according to a literature procedure.[10] To improve the solubility of **1** in THF, the counteranion of **1** was exchanged to tetraphenylborate (Scheme 2). Tetraphenylborate salt **2** was treated with mesityllithium (MesLi) at −78 °C, and the reaction mixture was allowed to warm to room temperature to give diphenylphosphine **4** as a major product. Formation of **4** suggested the



Scheme 2. Generation of AYC **3**. Mes = 2,4,6-trimethylphenyl.

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[*] S. Nakafuji, Dr. J. Kobayashi, Prof. Dr. T. Kawashima
Department of Chemistry
Graduate School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5800-6899
E-mail: takayuki@chem.s.u-tokyo.ac.jp

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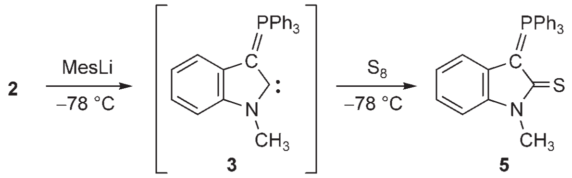
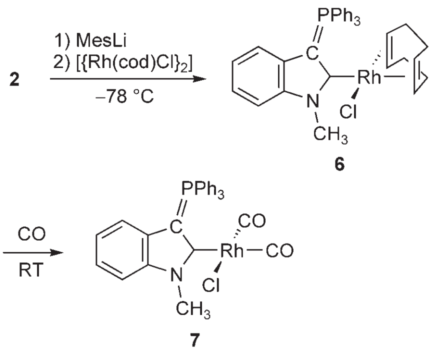
generation of AYC **3** and subsequent formal 1,3-phenyl rearrangement of **3** to **4**. However, numerous attempts to observe AYC **3** at low temperature failed because of its instability. In contrast, it was observed by ^{31}P NMR spectroscopy that treatment of the reaction mixture with elemental sulfur at −78 °C gave thioamide **5** quantitatively (Scheme 3), thus indicating AYC has sufficient stability to be trapped under the reaction conditions.



Scheme 3. Trapping of AYC **3** with S_8.

We synthesized transition-metal complexes of AYC **3** to investigate its coordinating properties. Treatment of **2** with MesLi at −78 °C and subsequent reaction with [{Rh(cod)Cl}$_2$] led to the formation of Rh complex **6** (Scheme 4), which was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and X-ray crystallographic analysis (Figure 1).[11] The ^{13}C NMR chemical shift for the carbene center of **6** was observed at $\delta_C = 200.6$ ppm ($^1J_{CRh}$, $^2J_{CP} = 40.8$, 40.3 Hz), which is slightly low-field shifted relative to benzimidazol-2-ylidene [Rh(cod)Cl] complexes ($\delta_C = 195$–196 ppm).[12] The Rh−C$_{carbene}$ bond length (2.036(2) Å) and other parameters around the Rh atom are within the range of those reported for [(NHC)Rh(cod)Cl].[13] The C$_{carbene}$−C bond length (1.417(3) Å) lies between those of single and double bonds, whereas the C$_{carbene}$−N bond length (1.378(3) Å) is slightly longer than those of [(NHC)Rh(cod)Cl] complexes (1.32–1.37 Å),[13] meaning that π-donation of the amino group to the carbene center is weaker than observed in other NHC complexes.



Scheme 4. Synthesis of Rh complexes. cod = 1,5-cyclooctadiene.

The carbonyl stretching frequencies of *cis*-[RhCl(CO)$_2$L] complexes are recognized as an index of the electron-donating properties of the ligand L. Complex **7** was obtained by bubbling CO through a solution of **6** in $CHCl_3$ (Scheme 4), and its structure was determined by X-ray crystallographic analysis (Figure 1). The average carbonyl stretching frequency of **7** (2012 cm^{-1}) was observed at the lowest wavenumber compared with IR data for known *cis*-[RhCl(CO)$_2$(carbene)] complexes (Table 1). This result indicated the high electron-donating ability of AYC.[14]

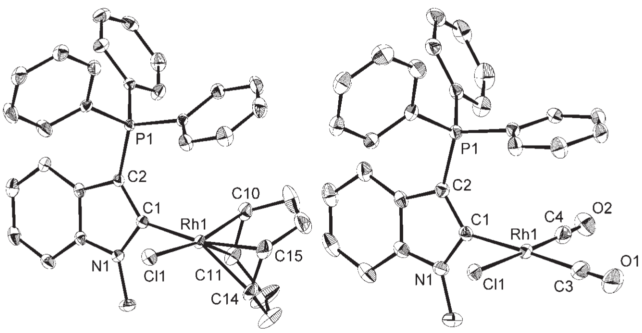
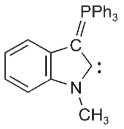
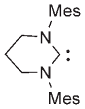
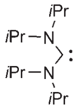
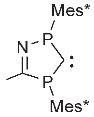
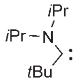
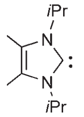
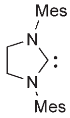


Figure 1. ORTEP drawings (50% probability) of **6** (left) and **7** (right) (H atoms are omitted). Selected bond lengths (Å) and angles (°), **6**: C1–C2 1.417(3), C2–P1 1.744(2), C1–N1 1.378(3), C1–Rh1 2.036(2), Rh1–Cl1 2.4258(6), Rh1–C10 2.097(2), Rh1–C11 2.101(2), Rh1–C14 2.202(2), Rh1–C15 2.231(2), N1-C1-C2 105.0(2), C2-C1-Rh1 137.70(18), Rh1-C1-N1 117.29(15); **7**: C1–C2 1.396 (3), C2–P1 1.740(2), C1–N1 1.370(3), C1–Rh1 2.075(2), Rh1–Cl1 2.4235(6), Rh1–C3 1.914(3), Rh1–C4 1.828(3), C3–O1 1.126(4), C4–O2 1.069(4), N1-C1-C2 105.7(2), C2-C1-Rh1 133.5(2), Rh1-C1-N1 120.72(18).

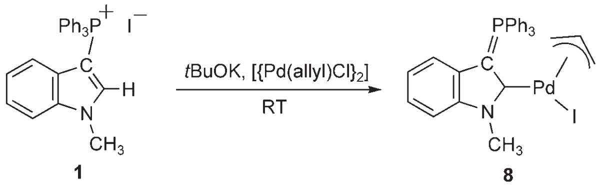
Table 1: IR carbonyl frequencies [cm^{-1}] of *cis*-[(carbene)Rh(CO)$_2$Cl] complexes.[a]

	ν(CO) I	ν(CO) II	Average	Ref.
	2062	1962	2012	this work
	2062	1976	2018	[13a]
	2057	1984	2021	[13b]
	2059	1985	2022	[5a]
	2070	1989	2030	[6a]
	2076	1996	2036	[13d]
	2081	1996	2039	[13b]

[a] Mes* = 2,4,6-$tBu_3C_6H_2$.

To gain more insight into the origin of the donating property of the carbene, theoretical calculations were performed on AYC **3** and several NHCs.[15] The donor and acceptor molecular orbitals of AYC and other NHCs are shown in the Supporting Information. The π-acceptor orbital of **3** (0.60 eV), which mainly consists of the p(π) orbital of the carbene center, is not located at a higher energy level relative to those of NHCs (−0.24 eV to 1.69 eV). In contrast, the σ-donating HOMO orbital of **3** (−4.4 eV) is higher than those of NHCs (−5.8 eV to −5.2 eV). These results suggest that the enhanced electron-donating ability of the present carbene is derived from high σ-donating ability, not from low π-accepting ability.

Among transition-metal complexes bearing NHCs, palladium complexes are particularly useful for various catalytic reactions.[3f] We could obtain Pd complex **8** as a 2:1 mixture of stereoisomers by using phosphonium salt **1** (Scheme 5). These stereoisomers were also found in the crystallographic analysis as a disordered structure (Figure 2). The chlorine atom on the palladium atom was replaced by iodine, derived from the counteranion of phosphonium salt **1**. In the [(NHC)Pd(allyl)X] complexes, the halogen-exchange reaction Pd−Cl→Pd−I is well known to be thermodynamically favored.[16] As a preliminary investigation, the catalytic reactivity of **8** was tested in the Buchwald–Hartwig reaction. The reaction was completed to give the desired product quantitatively, as analyzed by GC–MS (Scheme 6).



Scheme 5. Synthesis of Pd complex **8**.

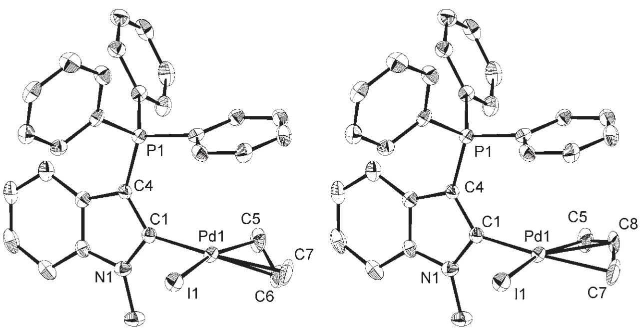
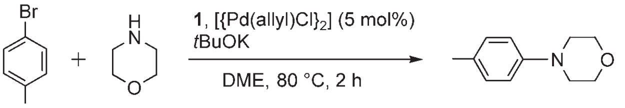


Figure 2. ORTEP drawings (50% probability) of **8** (major isomer: left, minor isomer: right) (H atoms are omitted). Selected bond lengths (Å), C1–C4 1.404(5), C4–P1 1.734(3), C1–N1 1.379(4), C1–Pd1 2.036(3), Pd1–I1 2.6524(8).

In summary, we have synthesized and characterized novel Rh and Pd complexes **6–8** containing AYC **3** as a ligand, and shown that AYC has the highest electron-donating ability among carbenes known to date. Such a high donating ability promises a good catalytic activity in transition-metal-catalyzed systems and further catalytic reactions are now under investigation.



Scheme 6. Arylation of morpholine with Pd complex **8**. DME = 1,2-dimethoxyethane.

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[14] CV measurements of Cr complexes of carbenes with a phosphorus ylide showed that they are stronger net electron donors than usual alkylamino carbenes.[9f]

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