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Synthesis and Application of New Dipyrido-annulated *N*-Heterocyclic Carbene with Phosphorus Substituents

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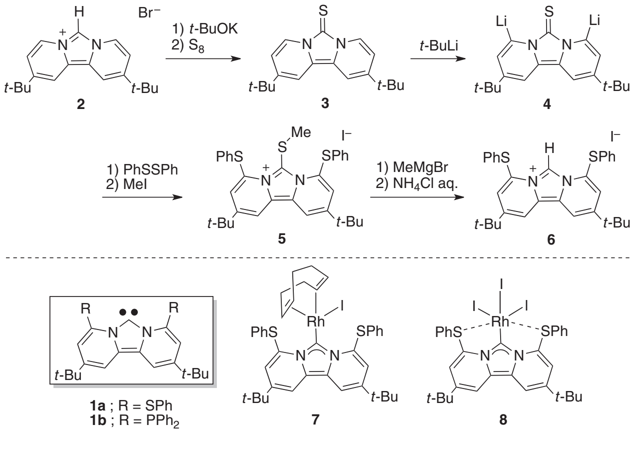
A new dipyrido-annulated *N*-heterocyclic carbene with phosphorus substituents at the 4 and 8 positions and the corresponding Rh(I) and Rh(III) complexes prepared from the carbene are reported. The X-ray structure of the Rh(I) complex **11** suggested the presence of strong interactions between the phosphorus atoms and Rh(I), in contrast to the previously reported sulfur-substituted system. The new carbene ligand shows promise as a useful carbene-centered pincer ligand with a fixed scaffold for other metal complexes.

The versatility and efficiency of *N*-heterocyclic carbenes (NHCs) as ligands for transition-metal catalysts and low-valent main-group element species have helped establish them as indispensable entities.[1,2] Thus, it is no surprise that the chemistry of pincer ligands with carbene centers has become a growing research field.[3–6] Among these tridentate ligands, however, there was no precedence of those with a rigid backbone until our recently disclosed **1a** (R = SPh).[5b] Our method for introducing SPh groups to the *ortho* positions involved the sequence shown in Scheme 1 starting from previously known **2**.[7] The carbene **1a** could be generated by treating the precursor **6a** with a base such as NaHMDS (HMDS: hexamethyldisilazane), and the corresponding Rh complexes were prepared thereof. It is interesting to note that the ligand could serve either as a monodentate **7** or a tridentate **8** based on the oxidation state of the central Rh moiety. Phosphorus-based ligands have been most widely utilized for late-transition metals; therefore, for wider application as pincer ligands for transition metals, phosphorus-substituted carbene ligands are highly desirable.[8] Herein, we report on the preparation of a new dipyrido-annulated NHC **1b** with phosphorus substituents at the 4 and 8 positions, thereby providing the first carbene-centered phosphorus-flanking tridentate ligand with a rigid backbone. Rh^I and Rh^{III} derivatives are also reported.

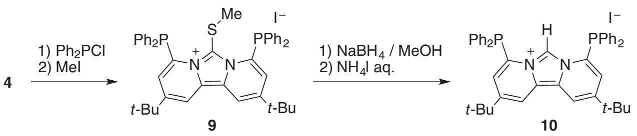


Scheme 1. Procedure for the introduction of substituents at the 1 and 8 positions.

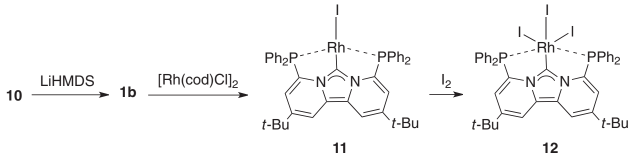
Imidazolium salt **10**, the precursor of carbene **1b**, was prepared as shown in Scheme 2. Electrophilic addition of Ph_2PCl to **4**, generated from **3**, followed by methylation afforded **9**. Because crude **9** was sufficiently pure after workup, it was used for the next step without further purification. To our surprise, desulfurization did not proceed at all by the use of the procedure (1.1 equiv of MeMgBr in THF) successful for **5a**. Reaction with MeLi, *t*-BuLi, and $LiAlH_4$ were equally unsatisfactory, resulting in either no reaction or a complex mixture. However, $NaBH_4$ in MeOH afforded the expected **10** in 59% yield under the optimized conditions after treatment with saturated aqueous NH_4I (Scheme 2).[9] Although **10** gradually underwent oxidation under aerobic conditions, it was thermally stable and could be purified by recrystallization from acetone.

The reaction of **10** with LiHMDS in deuterated solvents such as THF-d_8 or C_6D_6 resulted in a color change from a yellow suspension to a clear brown solution, suggesting the formation of carbene **1b**. This was confirmed by ^1H NMR measurements that revealed that the imidazolium proton of **10** at 8.73 ppm in $CDCl_3$ was absent. The poor solubility of **1b** hampered ^{13}C NMR measurements and the carbenic ^{13}C chemical shift could not be determined. The trapping of in situ generated **1b** with $[Rh(cod)Cl]_2$ provided indirect support for the generation of **1b** by affording **11**, a species gradually oxidized under aerobic conditions. Sequential one-pot treatment of **11** with I_2 afforded the expected Rh^{III} complex [Rh(**1b**)I_3] (**12**) as an air-stable species (Scheme 3).

The identity of **11** was established by X-ray diffraction analysis (Figure 1). In stark contrast to the corresponding Rh^I complex **7** of the sulfur series, the 1,5-cyclooctadiene (COD)



Scheme 2. Preparation of phosphorus-substituted imidazolium salt **10**.



Scheme 3. Generation of the carbene and introduction of Rh.

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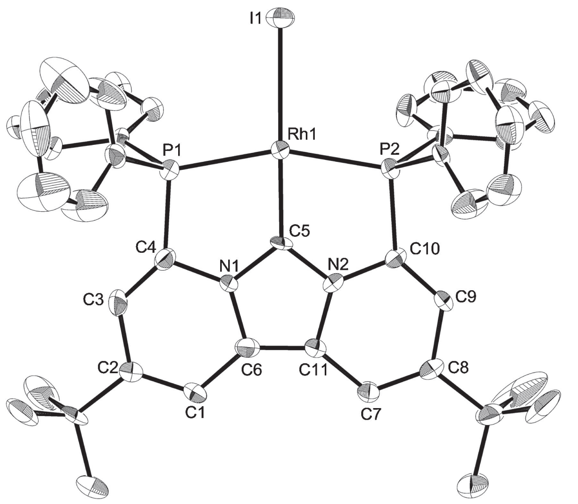

Figure 1. ORTEP drawing of **11** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms and the solvent molecule (THF) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–I1 = 2.6913(14), Rh1–P1 = 2.293(2), Rh1–P2 = 2.273(2), Rh1–C5 = 1.905(6), P1–C4–N1 = 107.6(5), P2–C10–N2 = 108.0(5).

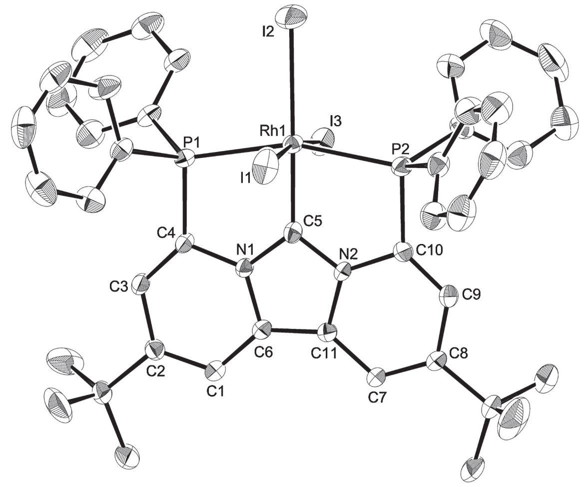

Figure 2. ORTEP drawing of **12** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms and the solvent molecule (dichloromethane) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–I1 = 2.6574(7), Rh1–I2 = 2.7240(7), Rh1–I3 = 2.6981(7), Rh1–P1 = 2.379(1), Rh1–P2 = 2.396(1), Rh1–C5 = 1.904(4). P1–C4–N1 = 109.3(3), P2–C10–N2 = 109.4(3).

moiety is used up, thereby indicating that the coordination scheme has completely changed to incorporate the flanking phosphine substituents, whereas the sulfur substituents in **7** were innocent bystanders. This significant difference should be due to the stronger coordinating ability of the phosphorus atom compared with the corresponding sulfur atom. This alteration is also reflected in the distances between the phosphorus atoms and $\mathrm{Rh^{I}}$ in **11** that were 2.273(2) and 2.293(2) Å, while the corresponding distances between the sulfur atoms and $\mathrm{Rh^{I}}$ in **7** were as long as 3.056(3) Å on average. The distances of **11** are comparable with the P–Rh distances of analogous flexible tridentate systems, an *o*-phenylene-bridged NHC diphosphine $[(i\text{-}\mathrm{Pr_2PCP}i\text{-}\mathrm{Pr_2})\mathrm{Rh^{I}Cl}]$ complex **13a**[8z] with values of 2.2910(13) and 2.3042(14) Å, and a 2,3-dihydroperimidine-cored NHC diphosphine $[(\mathrm{Ph_2PCPPh_2})\mathrm{Rh^{I}Cl}]$ complex **13b**[8ab] with values of 2.247(1) and 2.2545(1) Å. The ^{31}P NMR of **11** shows one sharp signal, suggesting that the complex is symmetric in solution, as one might expect. The low-field chemical shift of 49.5 ppm is also indicative of the strong coordination of the phosphorus atoms, and the coupling constant of $^{1}J_{\mathrm{Rh-P}} = 157$ Hz is similar to that of **13b** ($\delta_{\mathrm{P}} = 22.9$, $^{1}J_{\mathrm{Rh-P}} = 153$ Hz), suggesting that the interatomic interaction is approximately the same, regardless of whether the phosphorus atoms are fixed or not.

As for the structure of **12** (Figure 2), the distances between the phosphorus atoms and $\mathrm{Rh^{III}}$ were 2.379(1) and 2.396(1) Å. Here again, the distances are comparable with those of an analogous flexible tridentate system, an ethyl-bridged NHC diphosphine $[(\mathrm{Ph_2PCPPh_2})\mathrm{Rh^{III}Cl_3}]$ complex (**13c**)[8k] with values of 2.3714(18) and 2.3589(19) Å. Although the distances of **12** are similar to those between the sulfur atoms and $\mathrm{Rh^{III}}$ in **8** (2.386(3) Å), the interaction between P and Rh in **12** should be stronger based on the difference in the covalent radii between S (1.04 Å) and P (1.10 Å).[10] Furthermore, the Rh–I2 distance (2.7240(7) Å) in **12** is slightly longer than that of **8** (2.712(2) Å); other bonds around the Rh atom show similar elongations. In addition, the deviation from the ideal value of 120° of the P1–C4–N1 (109.3(3)°) and P2–C10–N2 (109.4(3)°) angles in **12** are larger than those of the corresponding angles (111.5(6)°) of **8**, which is consistent with the discussion on coordination strength between S and P. The coupling constant of $^{1}J_{\mathrm{Rh-P}} = 92$ Hz is also similar to that of **13c** ($\delta_{\mathrm{P}} = 1.7$, $^{1}J_{\mathrm{Rh-P}} = 89$ Hz), again suggesting comparable interaction. The resemblance in bond lengths (from X-ray structures) and the implicated similarity of coordination strength (from NMR) for both $\mathrm{Rh^{I}}$ and $\mathrm{Rh^{III}}$ (which can be considered as thermodynamically stable model species of a catalytic cycle involving this ligand system) with the corresponding flexible tridentate systems is an indication that although our ligand system is rigid, it may perhaps retain sufficient adjustable nature required for efficient catalysis.[6]

In conclusion, we have developed a method for the preparation of a new dipyrido-annulated NHC carbene with phosphorus substituents at the 4 and 8 positions. The corresponding Rh complexes from the carbene are also reported, where the ligand serves as a tridentate for both $\mathrm{Rh^{I}}$ and $\mathrm{Rh^{III}}$, in contrast to our previously reported sulfur-substituted complexes. The features of the complexes suggest that our new ligand is promising for transition-metal catalysis. The introduction of other transition metals and low-valent main-group elements, in addition to the preparation of other *ortho*-substituted derivatives, is in progress.[11]

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