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1,3-Diphosphorus Ylide Cyclopentadienylium Salts: Synthesis, Structures, and Application in Coupling Reactions

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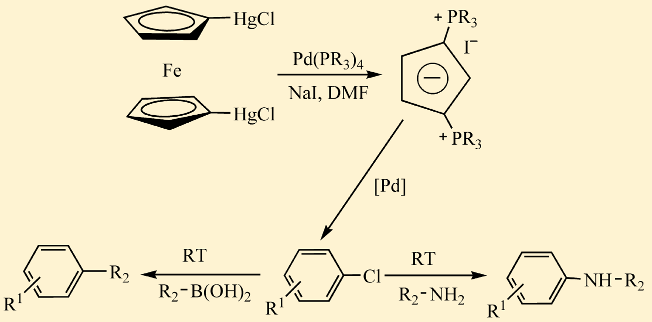
S *Supporting Information*

ABSTRACT: The 1,3-diphosphorus ylide cyclopentadienylium salts $(C_5H_3)(PPh_3)_2I$ (**1**) and $(C_5H_3)[P(4\text{-}CH_3\text{-}Ph)_3]_2I$ (**2**) have been prepared from the reaction of 1,1′-dichloromercurioferrocene with $Pd(PPh_3)_4$ and with $Pd[P(4\text{-}CH_3\text{-}Ph)_3]_4$, respectively. The molecular structure of **1** has been determined by X-ray diffraction analyses. The $Pd(OAc)_2$/**1** or **2**/K^tOBu system is highly efficient for the coupling reactions of aryl chlorides at room temperature.



As is known, the cyclopentadienyl anion $C_5H_5^-$ (Cp) is a classic example of aromaticity and will undergo electrophilic aromatic substitution readily. In 1957, Ramirez and Levy first reported tripenylphosphonium cyclopentadienylide **A** (Figure 1),[1] which is unusually inert, unlike normal ylides. They attributed this unusual stability to the charge delocalization implied by resonance structure **Ab**.[2] Because of difficulties in characterizing and synthesizing many phosphonium cyclopentadienylides, their reaction behaviors and donor properties have not been extensively explored.[3] Recently Baird and coworkers reported mixed alkyl−aryl cyclopentadienylidene derivatives which would be more amenable to characterize.[4] To the best of our knowledge, there is presently no report concerning the synthesis and structural characterization of diphosphorus ylide cyclopentadienylium salts **B**. In view of these findings and our continuous interest in the applications of chloromercurioferrocene,[5] we report a new method for the first direct synthesis of 1,3-diphosphorus ylide cyclopentadienylium salts (Scheme 1) and examined their catalytic activity in coupling reactions.

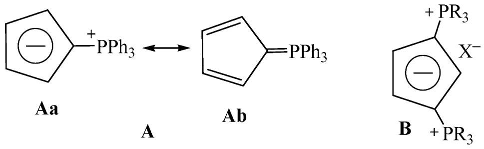


Figure 1. Structural motifs phosphonium cyclopentadienylides.

Scheme 1 illustrates our synthetic route to target compounds **1** and **2**. Heating a mixture of 1,1′-dichloromercurifoerrocene, $Pd(PPh_3)_4$, and NaI in DMF at 150 °C produced **1**, which was obtained by flash chromatography as the third band. The compounds of the first and second bands are $Pd(PPh_3)_2I_2$ and $Hg_2I_5PPh_4$, respectively (Figures S1 and S2; see the Supporting Information). Initially, we attempted the preparation of **1** starting from **A**; the expected product **1** was not obtained. We have investigated an alternative preparative scheme using chloromercurioferrocene as reagent; however, the target product was also not obtained. In addition, many attempts to synthesize **1** using Pd(II) complexes such as $Pd(PPh_3)_2Cl_2$ and $Ni(PPh_3)_4$ were unsuccessful. From these results, one possible reaction path (Scheme 1) is via electrophilic substitution of the Cp ring with PPh_3 catalyzed by a Pd(0) complex and demetalation of ferrocene; 1,1′-dichloromercurioferrocene plays an important role in promoting the demetalation.[6] To further extend the new method, the analogue **2** has also been successfully synthesized using $Pd[P(4\text{-}CH_3\text{-}Ph)_3]_4$ instead of $Pd(PPh_3)_4$.

The two ligands as red solids are very soluble in chloroform, dichloromethane, and acetone but insoluble in petroleum ether and *n*-hexane. They are not very stable in the air and turn black after several days. Therefore, they should be stored under argon. The NMR spectra of **1** and **2** were consistent with the proposed structures; the Cp protons are significantly shifted downfield, and the ^{13}C NMR chemical shifts for Cp also exhibit changes similar to those of the phosphorus ylide cyclopentadienylide.[3,4] The ^{31}P NMR spectra show signals at 14.2 and 13.3 ppm, respectively, for **1** and **2**. Furthermore, in the mass spectra of **1** and **2**, the most intense peaks were found at *m*/*z* 587.1 and 671.2, respectively, which was attributed to [M

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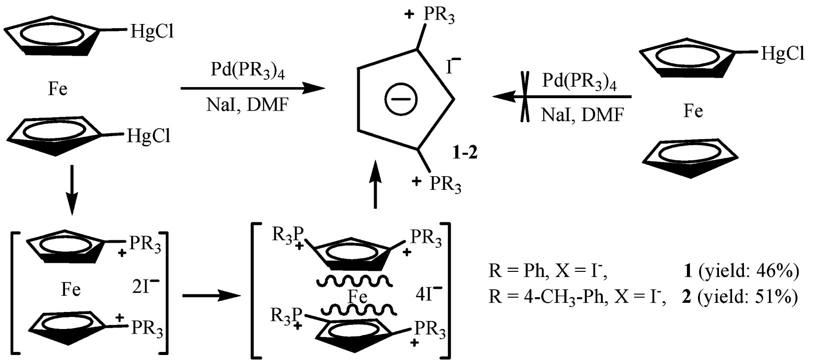
Scheme 1. Synthesis of 1 and 2



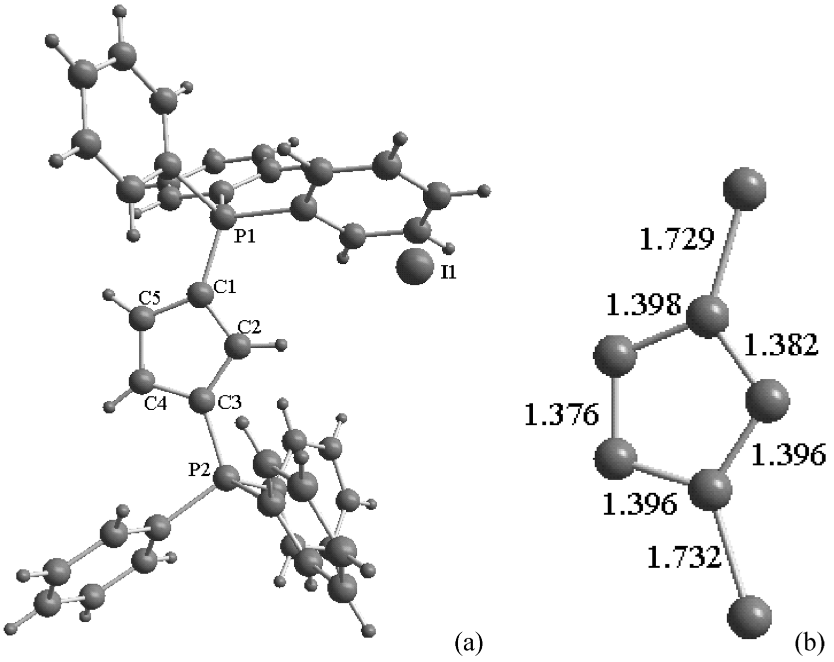


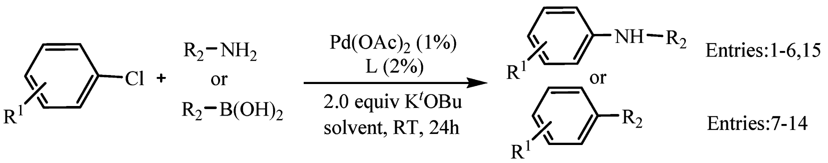
Figure 2. Molecular structure (a) of **1** and selected bond lengths (b).

$-$ I]$^+$. Finally, the structure of **1** has been confirmed by single-crystal X-ray diffraction.

Figure 2 shows clearly that **1** is a cyclopentadienium salt containing a new triphenylphosphonium cyclopentadinylide cation and a I$^-$ anion and the Cp ring is planar. The C−C−C bond angles (105.9(6)−110.0(6)°) of the Cp ring are very close to the 108° of a regular pentagon. The structure of the Cp ring exhibits alternating patterns of bond lengths, which are much shorter than a typical C−C single-bond length and are similar to those of benzene (1.3894 Å). More to the point, the P−Cp bond lengths (1.729(7) and 1.732(6) Å) are obviously shorter than the C−P single bonds in phenyl phosphonium ylides, while they are longer than the P═CH$_2$ bond in Ph$_3$P═CH$_2$ (1.66 Å).[7] These results are consistent with very significant contributions from both the uncharged and zwitterionic resonance structures.[4]

Recently, great progress has been obtained in coupling reactions by using bulky electron-rich phosphines[8] and N-heterocyclic carbene (NHCs) ligands.[9] However, palladium-catalyzed coupling reactions of aryl chlorides at room temperature have been less reported.[10] As the structures of 1,3-diphosphorus ylide cyclopentadienylium salts are similar to those of imidazolium salts, we were interested to see whether compounds **1** and **2** would be efficient ligands for coupling reactions. As a preliminary study, the catalytic activities of **1** and **2** were tested in the Buchwald−Hartwig reaction and Suzuki reaction (Table 1). Our initial exploration of the reactions focused on the coupling of chlorobenzene with aniline. The reaction was performed under a nitrogen atmosphere in dioxane in the presence of 2 equiv of K^{t}OBu as base at room temperature for 20 h. We are pleased to find that the Pd(OAc)$_2$/L(**1** or **2**) (1 mol %/2 mol %) system provided coupled products in excellent yields (entries 1 and 2). Under the same reaction conditions, similar to the results for chlorobenzene, good yields were also obtained in the case of 4-chlorotoluene and *p*-toluidine (entries 3 and 4). Reactions of electron-deficient aryl chlorides such as 4-chloronitrobenzene gave higher yields (entries 5 and 6). Moreover, their application to the Suzuki reaction was also investigated. However, under the above conditions, chlorobenzene with phenylboronic acid gave the coupled product in only a 43% yield (entry 7). When toluene was used as solvent, the yields increased significantly to 85% and 90% (entries 8 and 9). Similar to the results of chlorobenzene, good yields were also obtained in the case of 4-chlorotoluene and 4-methylphenylboronic acid (entries 10 and

Table 1. Coupling Reactions of Aryl Chlorides Catalyzed by Pd(OAc)$_2$/**1** or **2**[a]



entry	R$_1$	R$_2$	ligand	yield (%)[b]
1	H	Ph	**1**	86
2	H	Ph	**2**	93
3	4-CH$_3$	4-CH$_3$-Ph	**1**	83
4	4-CH$_3$	4-CH$_3$-Ph	**2**	91
5	4-NO$_2$	4-CH$_3$-Ph	**1**	90
6	4-NO$_2$	4-CH$_3$-Ph	**2**	97
7	H	Ph	**1**	43
8[c]	H	Ph	**1**	85
9[c]	H	Ph	**2**	90
10[c]	4-CH$_3$	4-CH$_3$-Ph	**1**	81
11[c]	4-CH$_3$	4-CH$_3$-Ph	**2**	87
12[c]	4-NO$_2$	Ph	**1**	94
13[c]	4-NO$_2$	Ph	**2**	99
14[c]	4-CH$_3$	4-CH$_3$-Ph	**A**	0
15	H	H	**A**	0

[a] Reaction conditions: Pd(OAc)$_2$ (1 mol %), ligand (2 mol %), aryl chloride (1.0 mmol), amine (1.2 mmol) or arylboronic acid (1.5 mmol), K^{t}OBu (2 mmol), dioxane (5 mL), room temperature, 20 h. [b] Isolated yields (average of two runs). [c] Toluene was used.

11). As expected, 4-chloronitrobenzene could provide excellent yields (entries 12 and 13).

To explore the role of **1** and **2** in the above coupling reactions, we performed control coupling reactions catalyzed by **A** (entries 14 and 15); the phosphorus ylide **A** was inactive under the same conditions, suggesting that **1** and **2** probably participated in the catalytic cycles as carbene precursors. However, numerous attempts to isolate the corresponding carbenes of **1** and **2** at low temperature failed because of their instability. Recently Kawashima and co-workers reported a carbene bearing a phosphorus ylide, which had the highest electron-donating ability of a carbene at the time.[11] Soon after, Fürstner and co-workers also reported the (amino)(ylide)-carbenes.[12] These ligands have high σ-donating ability because the inductive effect of the phosphorus ylide moiety is smaller than that of the amino group. From this viewpoint, the corresponding carbenes of diphosphorus ylides cyclopentadienylium salts **1** and **2** may have higher electron-donating ability.

To gain more insight into the origin of the donating property of the corresponding carbenes of **1** and **2**, theoretical calculations[13] were performed at the B3LYP/6-31G(d) level according to the literature.[11] The π-acceptor orbitals of the corresponding carbenes of **1** and **2** (LUMO+12, 1.70 eV; LUMO+12, 1.84 eV), which mainly consist of the p(π) orbital of the carbene center, are located at a higher energy level relative to that of a carbene bearing a phosphorus ylide (0.60 eV).[11] At the same time, the σ-donating HOMO orbital of the corresponding carbenes of **1** and **2** (HOMO, −3.58 eV; HOMO, −3.42 eV) are also higher than that of carbene bearing a phosphorus ylide (−4.4 eV)[11] (Figures 3 and 4 and Figures S3−S6 (Supporting Information)). The results suggest that the enhanced electron-donating ability of the corresponding carbenes of **1** and **2** is derived from both the high σ-donating ability and the low π-accepting ability. To the best of our knowledge, the corresponding carbene of **2** has the highest electron-donating ability among carbenes known to date, which is consistent with its high catalytic activity in the above coupling reactions.

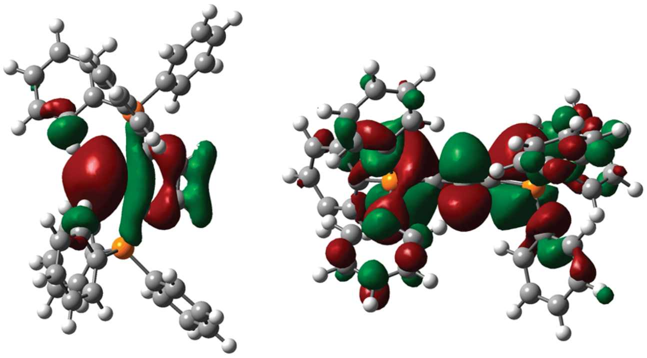


Figure 3. HOMO (left) and LUMO+12 (right) of the corresponding carbene of **1**.

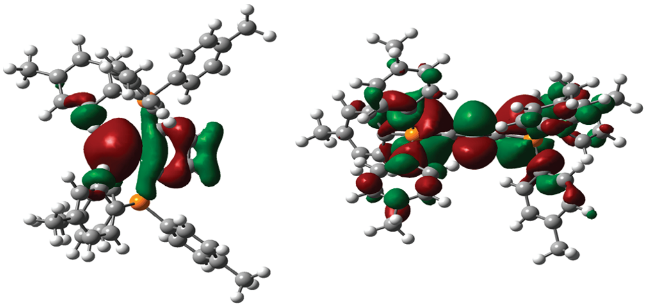


Figure 4. HOMO (left) and LUMO+12 (right) of the corresponding carbene of **2**.

In summary, we found a new method for the first direct synthesis of 1,3-diphosphorus ylide cyclopentadienylium salts. The Pd(OAc)$_2$/**1** or **2**/K^{t}OBu system is highly efficient for the coupling reactions of aryl chlorides at room temperature. The synthesis and application of these carbene complexes are currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and a CIF file giving experimental details, characterization data, details of the calculations, and X-ray crystal structure data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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