

Evaluation of σ -Donating Ability of a 9-Phosphatriptycene and Its Application to Catalytic Reactions

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(Received May 6, 2004; CL-040504)

The low σ -donating ability of 9-phosphatriptycene **1** was revealed by cyclic voltammetry and theoretical calculations. The tungsten complex of **1** was synthesized and the IR and NMR spectroscopic data of the complex also suggested the low σ -donating ability of **1**. **1** was shown to be effective as a ligand in the palladium-catalyzed reactions, the Stille coupling and the Heck reaction.

Phosphines have been known as useful ligands for transition metals and they have played an important role in several catalytic reactions.¹ The coordinating ability of a phosphine is controlled by steric factors (C–P–C angle and cone angle) and electronic factors (σ -donation and π -back donation). The structures and reactivities of the transition metal complexes are strongly influenced by these factors, thus organic chemists have made numerous efforts to develop novel phosphine ligands up to date.

9-Phosphatriptycene was first synthesized in 1974 by Bickelhaupt.² 9-Phosphatriptycenes have been expected to exhibit interesting properties as a ligand reflecting their unique structural and electronic characteristics. However, the metal complexes bearing a 9-phosphatriptycene have not been reported so far, probably because of the complex synthetic route to 9-phosphatriptycenes. Recently, we have reported a new and convenient synthetic route to 9-phosphatriptycene oxide **2** by utilizing ortho-lithiation of tris(3-methoxyphenyl)phosphine oxide as a key step.³ Here, we describe the σ -donating ability and the application to catalytic reactions of 9-phosphatriptycene **1** (δ_P –64.8), which was obtained by methylation of **2** followed by reduction with PhSiH₃ (Figure 1).⁴

X-ray crystallographic analyses of 9-phosphatriptycenes revealed that the C–P–C angles are narrowed because of ring strains.⁵ Such a unique structural feature promoted us to elucidate *s* character of the lone pair of **1**. As shown in Table 1, the oxidation potential of **1** was shifted to a more positive region than that of Ph₃P, indicating that the lone pair orbital of **1** is located at the lower energy level,⁶ which was supported by theoretical calculations as follows.⁷ Single-point calculation at DFT theory level revealed that the molecular orbitals of lone pair of Ph₃P and (2-furyl)₃P correspond to the HOMOs. On the other hand, the HOMO of **1** was the aromatic π orbital, and the lone pair was HOMO–5 which was located by 1.10 eV below the HOMO. The small C–P–C angle of **1** prevents the phosphorus atom from taking sp³ hybridization, and the *s* character of the lone pair is higher than those of usual triarylphosphines. The ¹J_{PSe} values of phosphine selenides are known to reflect the σ -donating ability of the corresponding phosphine.⁸ The ¹J_{PSe} value of 9-phosphatriptycene selenide **3** (δ_P 5.6, δ_{Se} –592) that was prepared by selenation of **1** showed the largest value among those of the other phosphine selenides,⁴ indicating that the σ -

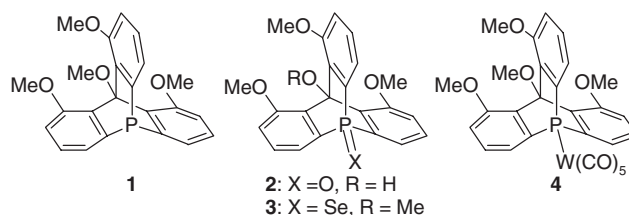


Figure 1.

Table 1. Comparison of σ -donating ability of **1**, Ph₃P, and (2-furyl)₃P

Ar ₃ P	<i>E</i> _{ox} /V ^a	Lone pair orbital ^b	¹ J _{PSe} value of Ar ₃ P=Se ^c /Hz
1	1.68	HOMO–5	828
Ph ₃ P	1.05	HOMO	736
(2-furyl) ₃ P	—	HOMO	788

^aIrreversible, peak potential, V vs Ag/Ag⁺ in CH₂Cl₂ with 0.10 M *n*-Bu₄N ClO₄, scan rate: 30 mV s^{–1}. ^bSingle-point calculations and geometry optimizations were performed at B3LYP/6-311G(d) for P, and 6-31G(d) for all other atoms. ^cIn CDCl₃.

donating ability of **1** is lower than that of Ph₃P and (2-furyl)₃P.

In a LW(CO)₅ complex, the *trans*-CO group respect to L is polarized in accordance with increase of the σ -donating ability of L. This polarization causes the low-field shift and the bathochromic shift in the ¹³C NMR spectra and infrared spectra, respectively. The tungsten complex **4** was isolated as air-stable yellow solids by the reaction of **1** with W(CO)₅(thf) in THF at room temperature quantitatively.^{9,10} In the ¹³C NMR spectrum of **4** the signal due to the *trans*-CO was shifted up-field, compared to those of Ph₃PnW(CO)₅, and the CO stretching frequency of **4** showed bathochromic shift compared to that of Ph₃PW(CO)₅ (Table 2). When these data were taken into consideration, the σ -donating ability of **1** is the weakest among phosphines and almost the same as that of Ph₃Sb.

Since the low σ -donating ability of **1** was revealed, the palladium-catalyzed reactions, the Stille coupling and the Heck reaction, were examined to reveal the effectiveness of **1** as a ligand.¹²

Table 2. Spectral data of Ar₃PnW(CO)₅

Ar ₃ Pn ^a	δ_C^b	$\nu(\text{trans-CO})^c/\text{cm}^{-1}$
1	197.1	1946
Ph ₃ P	199.2	1943
Ph ₃ As ^d	199.0	1945
Ph ₃ Sb ^d	198.2	1947

^aPn = P, As, Sb. ^bIn CDCl₃. ^cIn hexane. ^dRef. 11.

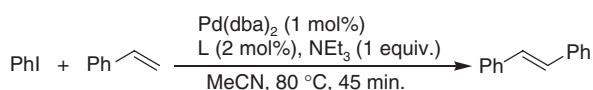
The results of the Stille coupling using **1** as a ligand are summarized in Table 3. The coupling of PhI using **1** proceeded faster than those using Ph₃P, (2-furyl)₃P, and Ph₃As, because of the lower σ -donating ability of **1**. It is known that in the Stille coupling weak σ donors exhibit the good catalytic activity and that (2-furyl)₃P and Ph₃As have about 10–10² times higher activity than Ph₃P.¹³ The trend was explained in the literature as follows. Such ligands decrease the electron density on the palladium atom and the transmetalation from the nucleophilic stannanes to the electrophilic palladium, the rate-determining step, is accelerated.

Table 3. The Stille coupling using **1** as a ligand

$\text{ArI} + (n\text{-Bu})_3\text{Sn} \text{---} \text{C}=\text{C} \xrightarrow[\text{THF, 50 }^\circ\text{C, 2 h}]{\text{Pd(dba)}_2 \text{ (2 mol \%), L (4 mol \%)}} \text{Ar} \text{---} \text{C}=\text{C}$					
L	ArI	Yield ^a /%	L	ArI	Yield ^a /%
1	PhI	95	Ph ₃ P	PhI	4
1	<i>p</i> -MeOC ₆ H ₄ I	64	(2-furyl) ₃ P	PhI	84
1	<i>p</i> -CF ₃ C ₆ H ₄ I	36	Ph ₃ As	PhI	76

^aEstimated by ¹H NMR spectroscopy.

The reaction of *p*-MeOC₆H₄I gave the lower yield, because its electron-rich nature decreased the rate of oxidative addition. Although the oxidative addition to electron-deficient ArX usually should proceed readily, the yield of the reaction of *p*-CF₃C₆H₄I was much lower than that of PhI, presumably because of the catalyst decomposition or generation of inactive complexes. As shown in Scheme 1, the Heck reaction using **1** as a ligand gave *trans*-stilbene in 53% yield, which was superior to the results of Ph₃P (6%),¹⁴ (2-furyl)₃P (13%), and Ph₃As (42%). The result is quite reasonable taking into account that the migratory-insertion of alkenes, the rate-determining step, is accelerated by weak σ donors in the Heck reaction.¹⁴



All yields were estimated by ¹H NMR spectroscopy.

Scheme 1.

In summary, we have succeeded in the synthesis of the first metal complex bearing a 9-phosphatriptycene. The low σ -donating ability of **1** was evaluated by various methods. On the basis of such an electronic property, **1** accelerated the Stille coupling and the Heck reaction of PhI compared with well-known weak σ donors, (2-furyl)₃P and Ph₃As.

This work was supported by Grant-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry (T. K.) and for Scientific Research (T. K.) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Tosoh Finechem Corporation and Shin-etsu Chemical Corporation for the generous gifts of alkylolithiums and phenylsilane, respectively.

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- 4 Compounds **1** and **3** were characterized by ¹H, ¹³C, ³¹P, and ⁷⁷Se NMR spectroscopy and high resolution mass spectrometry (HRMS). **1**: colorless solid, mp. 218–220 °C. ¹H NMR (400 MHz, CDCl₃) δ 3.87 (s, 9H), 3.89 (s, 3H), 6.86 (d, J = 7.6 Hz, 3H), 7.03 (td, J = 7.6, 2.0 Hz, 3H), 7.41 (dd, J = 11.1, 7.6 Hz, 3H).
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- 9 **4**: yellow solid, mp 421–423 °C (dec.). ¹H NMR (500 MHz, CDCl₃) δ 3.81 (s, 3H), 3.90 (s, 9H), 6.98 (d, J = 8.1 Hz, 3H), 7.19 (td, J = 7.6, 3.2 Hz, 3H), 7.63 (dd, J = 14.0, 7.3 Hz, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 56.69 (s), 59.01 (s), 90.91 (d, J = 8.6 Hz), 117.69 (s), 125.52 (d, J = 21.5 Hz), 126.79 (d, J = 15.6 Hz), 136.30 (s), 137.75 (d, J = 36.1 Hz), 157.09 (d, J = 23.3 Hz), 196.40 (d, ² J_{CP} = 7.6 Hz, ¹ J_{CW} = 124 Hz), 197.06 (d, ² J_{CP} = 25.5 Hz, ¹ J_{CW} = 140 Hz); ³¹P{¹H} NMR (202 MHz, CDCl₃) δ 11.6 (s, ¹ J_{PW} = 261 Hz); IR (KBr): ν (CO) 2075, 1963, 1913 cm⁻¹; IR (hexane): ν (CO) 2075, 1946 cm⁻¹; HRMS (FAB⁺): m/z Calcd. for C₂₈H₂₁O₉P¹⁸⁶W 718.0475; Found 718.0471 (M⁺).
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