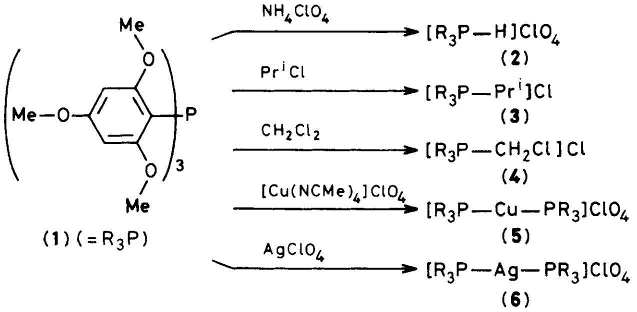
A Highly Basic Triphenylphosphine, $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$

Masanori Wada* and Shogo Higashizaki
Department of Applied Chemistry, Osaka University, Suita, Osaka 565, Japan

Tris(2,4,6-trimethoxyphenyl)phosphine was found to be highly basic (pK_a, 11.2).



Triphenylphosphine is useful as a reagent or catalyst in organic chemistry and as a ligand in inorganic chemistry.[1] Its basicity is low, and *para*-substitution of the phenyl groups results in only a small increase in basicity.[2] Compared to these phosphines, tris(2,4,6-trimethoxyphenyl)phosphine, (**1**), is expected to show either higher basicity owing to the multi methoxy substitutions (mesomeric effect) or lower basicity owing to the bulkiness of the aryl group (B-strain). We report here that (**1**) has a very high basicity; probably the highest known for tertiary phosphines.[3]

Phosphine (**1**) is easily prepared from $P(OPh)_3$ and 2,4,6-trimethoxyphenyl-lithium in diethyl ether at 0°C to room temperature and can be recrystallized from ethanol in air as colourless crystals in 60—70% yield,† m.p. 158—160 °C, ^{1}H n.m.r. ($CDCl_3$, 100 MHz) δ 3.47 (s, 2,6-MeO), 3.76 (s, 4-MeO), and 6.03 (d, J 3 Hz, 3,5-H).

Phosphine (**1**) reacts with perchloric acid in ethanol to give the tertiary phosphonium salt, (**2**), m.p. 186 °C (decomp.), ^{1}H n.m.r. ($CDCl_3$) δ 3.69 (s, 2,6-MeO), 3.89 (s, 4-MeO), 6.17 (d, J 5 Hz, 3,5-H), and 8.35 (d, J 541 Hz, P–H). The same salt was obtained in 88% yield by treating (**1**) (1 mmol) with NH_4ClO_4 (1.5 mmol) in ethanol (50 cm^3), suggesting that (**1**) has a higher basicity than NH_3 (pK_a, 9.21). Compound (**2**) can be recrystallized from ethanol containing an excess of Bu^n_3P (pK_a, 8.43), which is one of the most basic tertiary phosphines,[3] and even from ethanol containing NEt_3 (pK_a, 10.75).

The basicity of (**1**) was studied further by examining the ^{1}H n.m.r. spectra of a mixture of (**2**) and a suitable amine in acetone in the region of the 2,6-MeO proton resonance. It was found to be a stronger base than Et_2NH (pK_a, 11.0), comparable to piperidine (pK_a, 11.2), but weaker than 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (pK_a, 11.5).

A series of methoxy substituted triphenylphosphines‡ was also prepared from $PPhCl_2$ or PPh_2Cl and 2,4,6-trimethoxyphenyl-lithium or 2,6-dimethoxyphenyl-lithium.

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† The preparation of (**1**) from 1,3,5-$(MeO)_3C_6H_3$, PCl_3, and $ZnCl_2$ has been reported (ref. 4).

‡ All new compounds including (**1**) have been fully characterized by elemental (C, H, Cl) and spectral analyses.

Their basicities were compared in a similar manner as their tertiary phosphonium perchlorates.‡ The results can be summarized as follows [abbreviations: (2,4,6) = 2,4,6-$(MeO)_3C_6H_2$ and (2,6) = 2,6-$(MeO)_2C_6H_3$]: DBU (pK_a, 11.5) > (**1**) *ca.* = piperidine (11.2) > NEt_2H (11.0) > NEt_3 (10.75) > $P(2,6)_3$ > $PPh(2,4,6)_2$ > γ-collidine (7.4) > $PPh(2,6)_2$ > pyridine > $PPh_2(2,4,6)$ > $PPh_2(2,6)$ > PPh_3 (2.3[2] or 2.73[3]).

Apparently, the basicity of the triphenylphosphines increased as the level of methoxy substitution increased even though the bulkiness also increased. Noteworthy is the higher basicity of $P(2,6)_3$ than $PPh(2,4,6)_2$, suggesting that 2,6-methoxy groups have a greater effect than 4-methoxy groups on the increase in basicity.

Phosphine (**1**) reacted under mild conditions with a variety of alkyl halides including chlorides to give the quaternary phosphonium salts. In spite of the bulkiness of its aryl groups, (**1**) (1 mmol) reacted with isopropyl bromide (1 cm^3) in less than 1 h in ethanol (20 cm^3) at 65 °C, and even reacted with the chloride (2 cm^3) in 15 h to give the isopropyl phosphonium salt, (**3**).

While triphenylphosphine is stable in dichloromethane for a prolonged period, (**1**) reacted rapidly at room temperature ($t_{1/2}$ < 15 min in neat CH_2Cl_2) to give the chloromethyl phosphonium salt, (**4**). The relative reactivity of the other methoxyphenylphosphines with dichloromethane decreased in the same order as the basicity.

While triphenylphosphine forms 4:1 complexes with Cu^I and Ag^I,[5] (**1**) gave the stable 2:1 complexes, (**5**) and (**6**), in agreement with its large cone angle (184°).

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