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2,4,6-Tri-*tert*-butylphenyl and 2,4-Di-*tert*-butyl-6-methylphenyl Groups: Look Similar, React Differently

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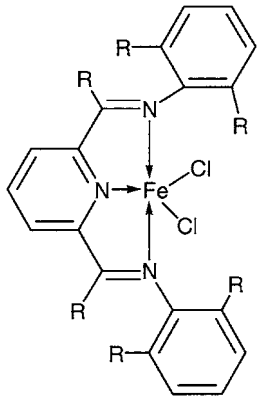
ABSTRACT: *The crystal structures of molecules with two phosphaalkene groups have been determined. Differences in the stabilization of the P=C π-bond by the 2,4,6-tri-*tert*-butylphenyl and 2,4-di-*tert*-butyl-6-methylphenyl groups were observed. It has been found that lithium supermesityl(trimethylsilyl)phosphide could be a very efficient base to remove a proton from acetonitrile.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:662–666, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10083

INTRODUCTION

The past decade has witnessed tremendous advances in the design and application of organometallic complexes as alpha-olefin polymerization catalysts; many are now reaching the early stages of commercialization [1]. Some of the most recent additions to the small but growing number of highly active nonmetallocene polymerization catalysts are the 2,6-bis(α-iminoalkyl)pyridine iron(II) complexes A [2,3].



A

Phosphorus is homologous to nitrogen and could increase the electron density on the metal center. Therefore, it can make the complex more stable and extend the lifetime of the catalyst in the polymerization. In order to replace nitrogen atoms in the tridentate [N,N,N] ligand in A by phosphorus atoms, we had to deal with low-coordinated phosphorus. Some synthetic methods to stabilize such molecules bearing 2,4,6-tri-*tert*-butylphenyl groups at the phosphorus atom have been published [4–8]. Our task was to make the low-coordinated phosphorus tridentate [P,N,P] ligands with additional steric hindrance near the imino functions of the pyridine ring, or the above kind of ligands with less steric hindrance at the phosphorus atom. In some cases, building additional bulk could facilitate the dissociation of the formed catalyst-product, and thus, lead to an enhancement of the reaction rates [9].

Dedicated to Professor Louis D. Quin on the occasion of his 74th birthday.

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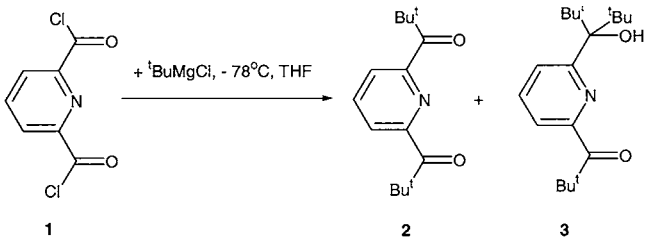
RESULTS AND DISCUSSION

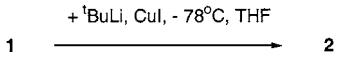
The preparation for the nitrogen backbone of the ligand was the first step. From the commercially available 2,6-pyridinedicarbonyl dichloride (**1**) and *tert*-butylmagnesium chloride, the corresponding diketone **2** could be made but with substantial amounts of the tris-adduct **3**.



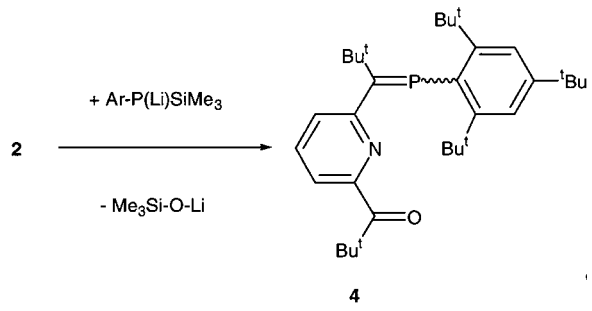
1 **2** **3**

Compounds **2** and **3** could be easily identified by GC/MS with *m/z* 247 for **2** and *m/z* 305 for **3**. The ratio between **2** and **3** was 4:1.

The formation of tris-adduct **3** was a well-known complication for this kind of reaction. To overcome this complication cuprate chemistry was employed in the manner of polysilylcuprate [10]. By using *tert*-butyl cuprate, the diketone **2** was isolated with a 70% yield after chromatography.



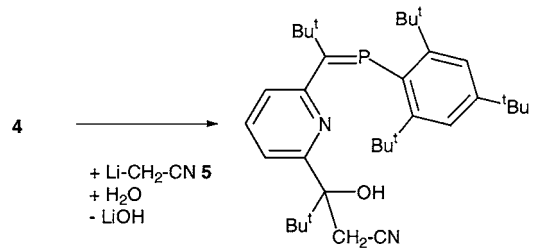
The synthesis of the phosphorus part of the ligand was the second step. Initially, lithium trimethylsilylphosphide bearing the 2,4,6-tri-*tert*-butylphenyl group was prepared [11]. Coupling the diketone **2** with it at room temperature led to the monosubstituted phosphaalkene **4**.



4

The phosphaalkene **4** is stable enough to pass through a GC column and give the molecular ion at 507. Compound **4** has a typical downfield chemical shift $\delta^{31}P = 256.0$. There are two downfield signals in the ^{13}C NMR spectrum proving a crucial bonding sequence in the molecule: $\delta = 205.5$ (carbonyl sp^2-carbon) and 191.7 (doublet, $^1J_{PC}$ 53.7 Hz, phosphaalkene sp^2-carbon).

Since 1 equiv of unreacted basic lithium trimethylsilyl(2,4,6-tri-*tert*-butylphenyl)phosphide was left in the reaction mixture, and taking into account work [12] about the addition of lithium aryl phosphides to the triple bond between the carbon and nitrogen in acetonitrile to form phosphaalkenes, we added a controlled amount of acetonitrile to the reaction mixture. To our surprise, we did not detect any amino-substituted phosphaalkenes in the reaction mixture. Instead, lithium trimethylsilyl(2,4,6-tri-*tert*-butylphenyl)phosphide behaved as a highly efficient base toward the weak acidic protons of the acetonitrile and lithiated it. The indication that lithium trimethylsilyl(2,4,6-tri-*tert*-butylphenyl)phosphide can be an efficient base has been discussed in reports of the synthesis of phosphasilenes [13,14]. The in situ formed lithium methylene nitrile **5** added to the carbonyl group of **4**. The formed adduct was purified by column chromatography, with the isolation of the corresponding alcohol **6** containing also the phosphaalkene moiety.



6

A crystal of **6** suitable for X-ray analysis was obtained from pentane and its ORTEP drawing is shown in Fig. 1. ^1H and ^{31}P NMR spectral data are in

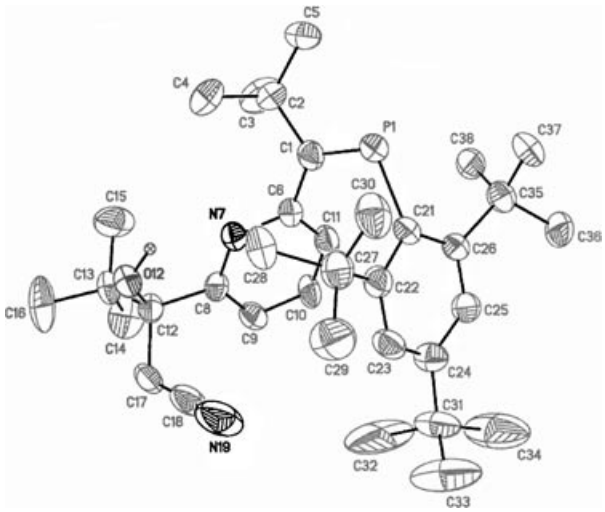
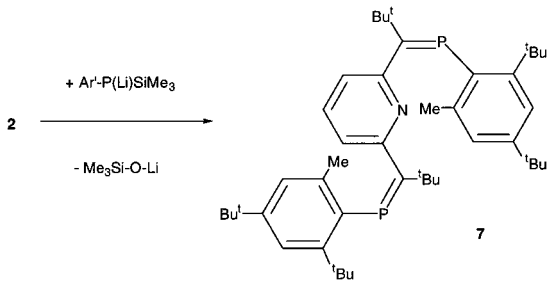


FIGURE 1 ORTEP drawing of 2-[6-(1′-hydroxo-1′-cyanomethyl-2′,2′-dimethylpropyl)pyridyl]*tert*-butylmethylene(2,4,6-tri-*tert*-butylphenyl)phosphine (**6**).

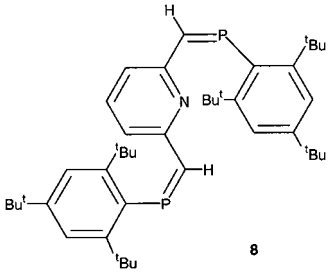
agreement with the assigned structure of compound **6**.

Because we were unable to obtain the bis-phosphaalkene through the use of the 2,4,6-tri-*tert*-butylphenyl group at phosphorus, we decided to apply the 2,4-di-*tert*-butyl-6-methylphenyl group for the protection of a two coordination status for the phosphorus atom. The 2,4-di-*tert*-butyl-6-methylphenyl group has been shown to allow the stabilization of diphosphenes [15,16], phosphaalkenes [17], dithiophosphoranes [18], and arsaalkenes [19].

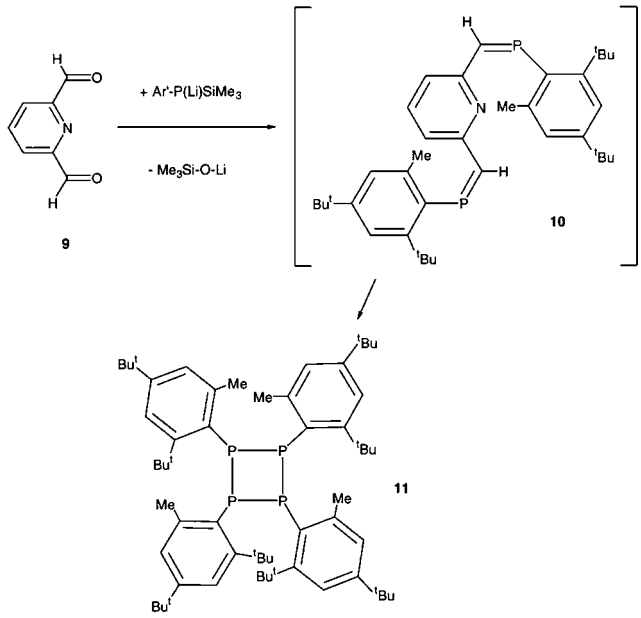
In contrast to the lithium trimethylsilyl (2,4,6-tri-*tert*-butylphenyl)phosphide, lithium trimethylsilyl(2,4-di-*tert*-butyl-6-methylphenyl)phosphide condensed with diketone **2** at room temperature with formation of the bisphosphaalkene **7**.



A crystal of compound **7** suitable for X-ray analysis was obtained from methylene chloride. The ORTEP drawing of **7** is shown in Fig. 2. ^{1}H, ^{13}C, and ^{31}P NMR spectra and elemental analysis data are in agreement with the assigned structure **7**. The 2,4,6-tri-*tert*-butylphenyl group has been reported [5] to allow the stabilization of bisphosphaalkene **8** without the presence of *tert*-butyl groups at the carbon atoms of the P=C π-bond.



Our attempt to synthesize an analogous bis-phosphalkene with the presence of the 2,4-di-*tert*-butyl-6-methylphenyl moiety led to isolation of tetrakis[2,4-di-*tert*-butyl-6-methylphenyl]tetraphosphetane (**11**).



The ORTEP drawing of **11** is presented in Fig. 3. The chemical shift δ ^{31}P of **11** is −45.5, practically identical to that published earlier [16]. The compound **11** has been prepared by the dehalogenation reaction of a 2,4-di-*tert*-butyl-6-methylphenyldihalophosphine with magnesium [16]. Presently, we do not know the role of the pyridine moiety in the reaction. The mechanism of the formation of **11** has not been investigated yet.

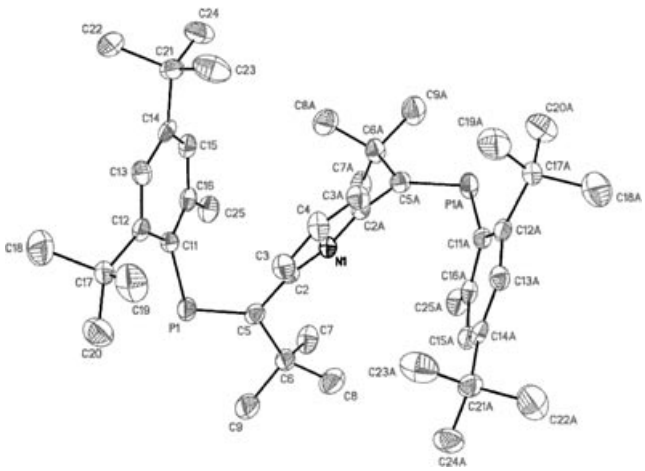


FIGURE 2 ORTEP drawing of 2,6-bis[1-(2′,4′-di-*tert*-butyl-6′-methylphenyl)phosphinidene-2″,2″-dimethylpropyl]-pyridine (**7**).

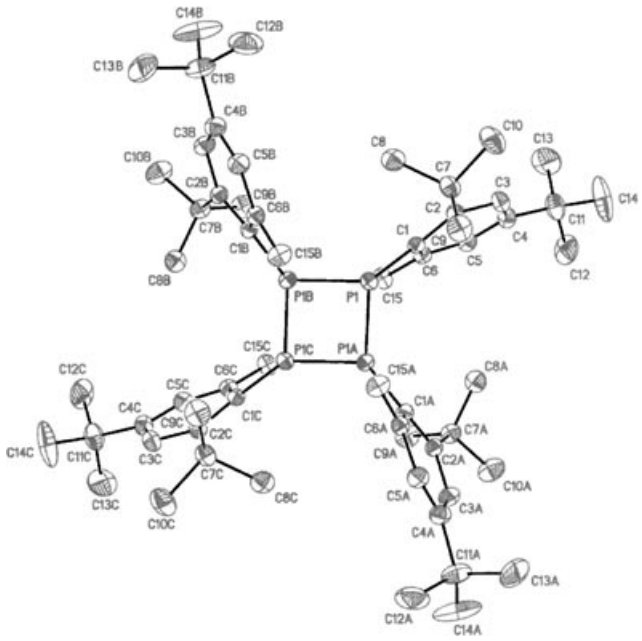


FIGURE 3 ORTEP drawing of tetrakis[2,4-di-*tert*-butyl-6-methylphenyl]tetraphosphetane (**11**).

By carefully tuning up the steric hindrance near the phosphorus and carbon atoms of the P=C π-bond, tridentate [P,N,P] ligands with preparative yields can be obtained for the catalysis applications.

EXPERIMENTAL

*Preparation of 2,6-Bis(2′,2′-dimethylpropionyl)pyridine (**2**)*

A 1.7 M solution of *tert*-butyllithium in pentane (60 ml) was added to a suspension of 18.66 g (0.098 mol) of CuI in 50 ml of THF at once at −78°C with vigorous stirring. The reaction mixture was kept for 1 h at this temperature and 10.0 g (0.049 mol) of 2,6-pyridinedicarbonyl dichloride in 40 ml of THF was added. The reaction mixture was allowed to warm to room temperature, treated with 10% NaOH in water, filtered, and extracted with pentane. Extracts were concentrated and the residue was subjected to chromatography on silica gel with hexane/ethyl acetate (10:1) as the eluent. The yield of **2** was 8.47 g (70%) as oil with $m/z = 247$, ^{1}H NMR: (CD_2Cl_2) $\delta = 7.82$ (broad, 3H, Py), 1.30 (s, 18 H, *t*-Bu); ^{13}C NMR: (CD_2Cl_2) $\delta =$ 206.92 (s, C=O), 154.39 (s, C=N), 138.60 (s, C=C), 126.57 (s, C=C), 44.45 (s, CMe_3), 28.05 (s, Me). The above data are close to the literature values [20].

*Preparation of 2-[6-(2′,2′-Dimethylpropionyl)pyridyl]*tert*-butylmethylene(2,4,6-tri-*tert*-butylphenyl) Phosphine (**4**) and 2-[6-(1′-Hydroxo-1′-cyanomethyl-2′,2′-dimethylpropyl)pyridyl]*tert*-butylmethylene(2,4,6-tri-*tert*-butylphenyl) Phosphine (**6**)*

A 1.6 M solution of butyllithium in hexane (14 ml) was added to a solution of 2,4,6-tri-*tert*-butylphenylphosphine (5.59 g, 0.02 mol) in 250 ml of THF at 0°C. After that, 2.39 g of chlorotrimethylsilane was added dropwise and warmed to room temperature. Butyllithium (14 ml) was added again at 0°C into the solution that had been cooled to −78°C and 2.48 g (0.01 mol) of 2,6-bis(2′,2′-dimethylpropionyl)pyridine **2** in 20 ml of THF was added dropwise. After the addition, the solution was warmed to room temperature and 40 ml of dry acetonitrile was added. The solvents were evaporated under reduced pressure. The residue was purified by silica-gel chromatography with hexane/methylene chloride (1:1) as the eluent to give 0.710 g (7% yield) of phosphaalkene **4**, as a white solid (from acetonitrile) with mp 212.95°C. ^{1}H NMR: (CD_2Cl_2) $\delta = 1.15$ (s, 9H, *p*-*t*-Bu), 1.31 (s, 9H, *t*-Bu—CO), 1.42 (s, 9H, *t*-Bu—C=P), 1.43 (s, 9H, *o*-*t*-Bu), 6.4–7.5 (multiplets, 5H, Py and Ph-protons); ^{31}P NMR: (CD_2Cl_2) $\delta = 256.0$. Chemical ionization m/z calculated for $C_{33}H_{51}NOP$: 508.3708; found 508.3719. Anal calcd for $C_{33}H_{50}NOP$: C, 78.11%; H, 9.86%; P, 6.11%. Found: C, 78.06%, H, 10.02%, P, 6.56%. Phosphaalkene **6** was isolated with 16% yield (1.75 g), as a white solid with with mp 154.02°C. ^{1}H NMR: (CD_2Cl_2) $\delta = 0.80$ (s, 9H, *p*-*t*-Bu), 1.10 (s, 9H, *t*-Bu—COH), 1.31 (s, 9H, *t*-Bu—C=P), 1.39 (s, 9H, *o*-*t*-Bu), 1.53 (s, 9H, *o*-*t*-Bu), 2.98 (m, 2H, CH_2), 6.0–9.5 (multiplets, 5H, Py and Ph-protons); ^{31}P NMR: (CD_2Cl_2) $\delta = 251.0$. Chemical ionization m/z calculated for $C_{34}H_{54}N_2OP$: 549.3974; found 549.3995. Anal calcd for $C_{35}H_{53}N_2OP$: C, 76.64%; H, 9.67%; N, 5.11%. Found: C, 76.40%, H, 9.71%, N, 4.99%.

*Preparation of 2,6-Bis[1-(2′,4′-di-*tert*-butyl-6′-methylphenyl)phosphinidene-2″,2″-dimethylpropyl]-pyridine (**7**)*

A 1.6 M solution of butyllithium in hexane (36 ml) was added to a solution of 2,4,6-di-*tert*-butyl-6-methylphenylphosphine (12.42 g, 0.0526 mol) in 100 ml of THF at 0°C. After that, 6.3 g of chlorotrimethylsilane was added dropwise and the mixture was warmed to room temperature. Butyllithium (36 ml) was added again at 0°C to the solution that had been cooled to −78°C and 6.5 g (0.0263 mol)

of 2,6-bis(2′,2′-dimethylpropionyl)pyridine **2** in 20 ml of THF was then added dropwise. After the addition, the solution was warmed to room temperature. The solvents were evaporated under reduced pressure. The residue was extracted and recrystallized from pentane. The yield of **7** was 14.56 g (81%) as a white solid with 215.63°C. ^{1}H NMR: (CD_2Cl_2) $\delta = 0.95$ (s, 9H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu), 2.15 (s, 9H, *o-t*-Bu), 2.18 (s, 9H, *t*-Bu), 2.15 (s, 6H, Me), 6.0–7.5 (multiplets, 5H, Py and Ph-protons); ^{31}P NMR: (CD_2Cl_2) $\delta = 239.0$. Anal calcd for $C_{45}H_{67}NP_2$: C, 77.47%; H, 9.61%; N, 2.01%; P, 8.90%. Found: C, 77.14%, H, 9.91%, N, 1.99%; P, 8.43%.

*Preparation of Tetrakis[2,4-di-*tert*-butyl-6-methylphenyl]tetraphosphetane (***11***)*

A 1.6 M solution of butyllithium in hexane (11 ml) was added to a solution of 2,4,6-di-*tert*-butyl-6-methylphenylphosphine (3.67 g, 0.0155 mol) in 100 ml of THF at 0°C. After that, 1.86 g of chlorotrimethylsilane was added dropwise, and the mixture was warmed to room temperature. Butyllithium (11 ml) was added again at 0°C to the solution that had been cooled to −78°C, and 1.0 g (0.0074 mol) of 2,6-pyridinedicarboxaldehyde **9** in 20 ml of THF was added dropwise. After the addition, the solution was warmed to room temperature. The solvents were evaporated under reduced pressure. The residue was extracted and recrystallized from benzene. The yield of **11** was 2.47 g (68%), orange crystals ^{31}P NMR: (CD_2Cl_2) $\delta = -45.5.0$ [16]. The X-ray structure is shown in Fig. 3.

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