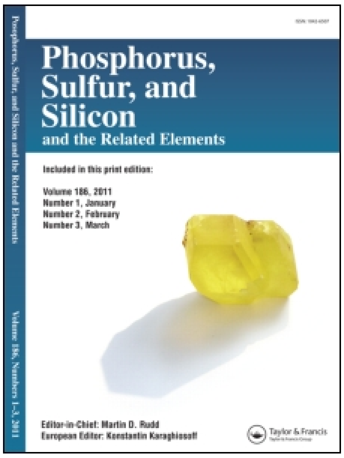

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Facile Phosphite to Phosphonate Rearrangement of a Trialkanolamine-derived Triphosphite Promoted by Triethylaluminum[1]

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Facile Phosphite to Phosphonate Rearrangement of a Trialkanolamine-derived Triphosphite Promoted by Triethylaluminum[1]

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A facile room temperature rearrangement of a trialkanolamine-derived triphosphite, ***1****, to the monophosphonate* ***5*** *promoted by three equivalents of triethylaluminum is described. The diphosphonate* ***6*** *was prepared by the addition of three equivalents of triethylaluminum to the monophosphonate* ***5****. A mechanism is suggested involving a transition state or intermediate with coordination of the trialkylaluminum to the migrating oxygen.*

Keywords Aluminum-phosphorus interaction; Michaelis-Arbusov reaction; P—C bond formation; phosphonate; Phosphite Rearrangement; trialkylaluminum; triethylaluminum

INTRODUCTION

The coordination of phosphites to late transition metals is well known in the literature. The use of both achiral and chiral phosphite ligands have been reported as viable alternatives to phosphine ligands in transition metal complexes.[2–9] Recently, we communicated the synthesis, solid-state conformation, and utility of a sterically congested achiral triethanolamine-derived trisphosphite **1** and the corresponding chiral tri-2-propanolamine phosphite ligand (*S*, *S*, *S*)-**2** (Figure 1) in the Rh(I)-catalyzed asymmetric hydrosilation of ketones.[10,11]

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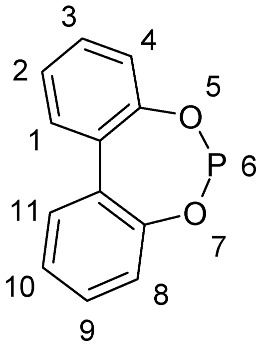


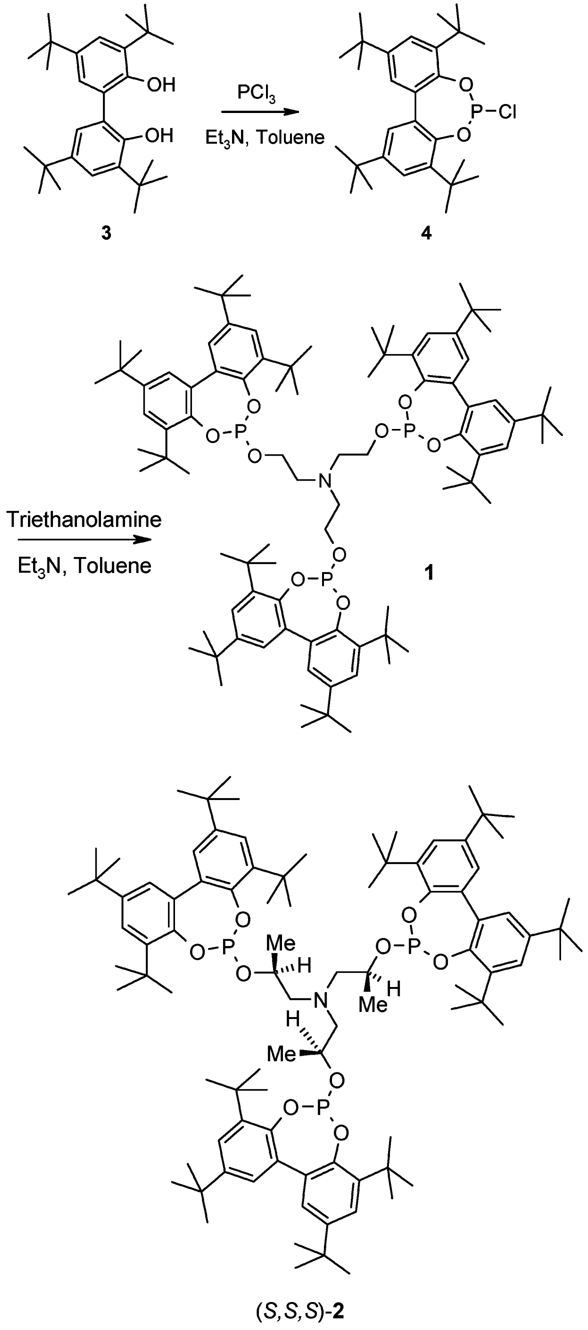
FIGURE 1 The *Chem. Abstr.* numbering system for the dibenzo[*d,f*][1,3,2] dioxaphosphepin ring system.

In contrast to the numerous studies on the formation and use of transition-metal complexes of phosphites, the interaction of phosphites with aluminum has received scant attention in the literature.[12,13] In a recent monograph on ^{31}P NMR spectroscopy, a few reports of ^{27}Al – ^{31}P one-bond couplings (240–290 Hz) were cited.[14] The paucity of studies is surprising because phosphites are known to be processing stabilizers for polyolefins, where low levels of residual aluminum may be present from the polymerization catalysts.[15] Methylalumoxane , for example, is a well known co-catalyst in Ziegler-Nata type polymerizations of olefins. However, catalysts for both polymerization and oligomerization are often complex mixtures that may include triakylaluminum compounds in which the exact structure of the catalyst is unknown.[15e] The sterically congested triethanolamine phosphite **1** has been suggested to be a particularly effective processing stabilizer for polyolefins, in which peroxide decomposition was suggested to be the major stabilization mechanism.[16] The rearrangement of a phosphite to phosphonate by tributylaluminum reported by Sander[17] suggests that other mechanisms besides peroxide decomposition by phosphites may be involved in polymer stabilization. We report herein a study on the interaction of triethylaluminum with the triethanolamine phosphite **1**.

RESULTS AND DISCUSSION

Synthesis

The biphenyl-2,2′-diol **3** was prepared by the oxidative coupling of 2,4-di-*tert*-butylphenol with hydrogen peroxide under alkaline conditions as previously described by Shum et al.[18] The phosphorochloridite **4** was prepared in situ by the reaction of **3** with phosphorus(III) chloride in the presence of triethylamine as an acid acceptor (Scheme 1).[19,20] The


OH
OH
PCl3
Et3N, Toluene
O
P–Cl
O
3
4
Triethanolamine
Et3N, Toluene
O–P
N
1
Me
H
(S,S,S)-2

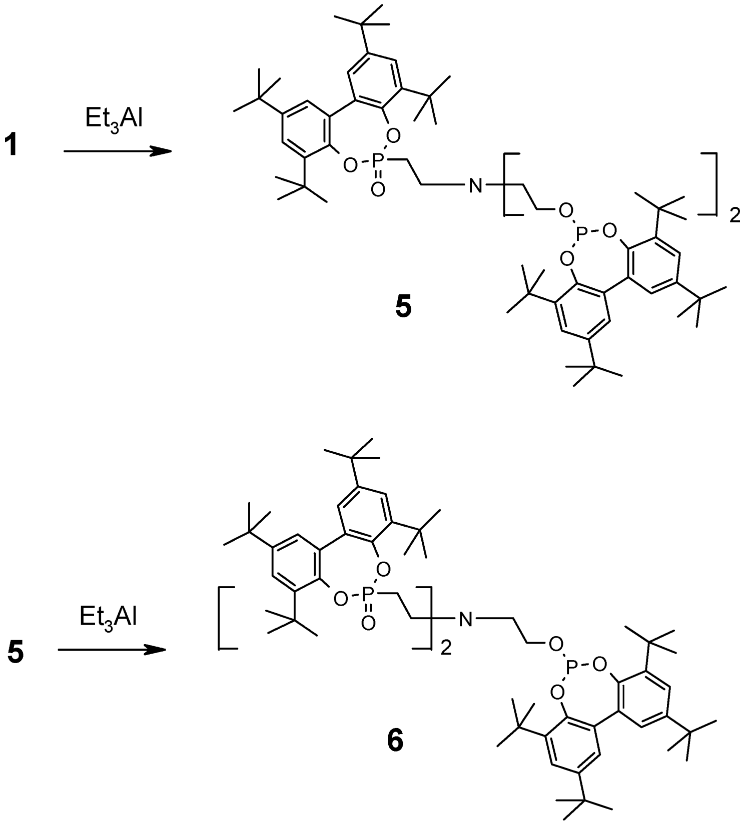
SCHEME 1

reaction of three equivalents of **4** with an equivalent of triethanolamine in the presence of triethylamine gave the tripodal phosphite **1** as described previously by Shum et al.[11] A cross peak is observed in the indirect detection $\{^{15}N/^{1}H\}$ gHMBC 2D NMR ($CDCl_3$)(50.59 MHz) experiment on **1** indicating a nitrogen chemical shift at $\delta - 356.8$, which is in the region expected for a tertiary amine nitrogen. The associated proton resonance evidences a three-bond correlation between the nitrogen atom and the methylene hydrogens of the carbon atom bonded to oxygen.

Interaction with Aluminum(III)

In the $^{31}P\{^{1}H\}$ NMR(CD_2Cl_2) spectrum of **1** at 26°C, a single signal is observed at δ 140.6 due to conformational averaging.[21] In the $^{31}P\{^{1}H\}$ NMR spectrum of the product formed by the reaction of **1** with three equivalents of triethylaluminum at ambient temperature (dichloromethane-*d*$_2$ with strict exclusion of oxygen and moisture), two singlets are observed at δ 138.4 and δ 35.4 in a 2:1 ratio by integration of their respective peak areas. No other signals due to phosphorus containing species were observed in the $^{31}P\{^{1}H\}$ NMR spectrum immediately after the addition of the trialkylaluminum (Scheme 2). Upon further addition of **1** to the reaction mixture, an additional singlet at δ 139.3 was observed that was assigned to **1**, which demonstrates that the singlet at δ 138.4 is due to the presence of a new compound. A early communication suggested that these observations were due to the complexation of Al(III) with the nitrogen and one phosphorus atom of **1**.[1] However, preliminary molecular orbital calculations on a number of conformations of a model six-membered chelate, in which both a nitrogen and phosphorus atom were coordinated to trimethylaluminum (used as a model), suggested that such a complex was not stable with respect to the dissociation of the phosphorus atom from aluminum.[22] Previously, Sander reported that tributylaluminum formed a coordination complex with tributyl phosphite that underwent a Michaelis-Arbusov-type reaction to the phosphonate when heated to 80°C.[17] The oxygen of the resultant phosphonate was strongly coordinated to Al(III), and the free phosphonate was obtained by hydrolysis or alcoholysis.[17,23] Nykerk[23] reported that the dissociation enthalpy of an adduct of $AlMe_3$ with trimethylphosphate is 25.6 kcal·mol^{-1}. The reaction of tributyl phosphite with trimethylaluminum was shown to be a stoichiometric rather than catalytic reaction.[17]

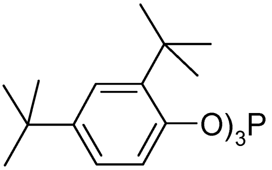
Indeed, scaling up the reaction of **1** with three equivalents of triethylaluminum led to the isolation of the monophosphonate **5**.[24] In the ^{1}H NMR spectrum of **5**, a doublet of triplets at δ 2.08($^{2}J_{HCP} = 18.7$ Hz;



SCHEME 2

${}^3J_{HCCH} = 8$ Hz) is observed, which was assigned to the methylene protons of the carbon atom bonded to the P(V) atom. The magnitude of the observed ${}^2J_{HCP}$ coupling as well as the chemical shift observed is consistent with a molecule containing a methylene carbon atom bonded to phosphorus.[25] A doublet of triplets was observed at δ 2.91 (${}^3J_{HCCP} = 6.2$ Hz; ${}^3J_{HCCH} = 8$ Hz), which was assigned to the methylene protons beta to the P(V) atom. In the ${}^1H$-${}^{31}P$ heteronuclear generalized HMBC (${}^1\underline{H}$-detected $\underline{m}$ultiple-$\underline{b}$ond heteronuclear multiple-quantum $\underline{c}$oherence)[26] spectrum of **5**, cross peaks between the P(V) singlet at δ 33.9 with the proton signals at δ 2.08 and δ 2.91 clearly established the connectivity. Consistent with this interpretation, cross peaks between the P(III) atom at δ 138.4 with the proton signal at δ 3.75 (${}^3J_{HCOP} = 8$ Hz; ${}^3J_{HCCH} = 6.5$ Hz) and δ 2.61 (${}^3J_{HCCH} = 6.5$ Hz) are observed. Small differences between the ${}^{31}P\{{}^1H\}$ chemical shifts in the NMR spectrum of the P phosphorus atoms in **5** in the reaction mixture and isolated product are suggested to be due to the complexation of the product phosphonate **5** oxygen atom as well as the nitrogen atom of **5** with aluminum in the crude reaction mixture, which alters the electronic environment about the phosphorus atoms. In the $^{13}C\{^1H\}$ NMR spectrum of **5**, a doublet is observed at δ 24.24 ($^1J_{PC}$ = 130.9 Hz) that was assigned to a methylene carbon atom bonded to phosphorus. The magnitude of the one-bond J coupling constant is completely consistent with a carbon atom bonded to phosphorus.[11] Cross peaks are observed in the indirect detection $\{^{15}N^1H\}$ gHMBC 2D NMR ($CDCl_3$) experiment on **5** indicating a nitrogen chemical shift at δ –351.2, as expected for a tertiary amine nitrogen. The cross peaks evidence three bond interactions between the nitrogen atom and the methylene protons on carbon alpha to phosphorus and the methylene protons on carbon alpha to oxygen.

The complexation of both the phosphonate oxygen and nitrogen in **5**, as well as the complexation of the nitrogen in **1**, with aluminum provides a possible explanation for the observation that three equivalents of triethylaluminum is required for facile rearrangement of **1** to the monophosphonate **5**, albiet, if this is the case, the stoichiometry of the reaction suggests that only two equivalents of triethylaluminum is required. However, the aggregation state of the aluminum in the reaction medium is unknown and may not be monomeric, which is a possible explanation of the observed stochiometry. No evidence for the formation of the diphosphonate **6** was observed in the crude reaction mixture, *vide infra*. If the mechanism of the observed rearrangement of the phosphite **1** to the phosphonate **5** is similar to that of a traditional Michaelis-Arbusov rearrangement[27] of a trialkylphosphite where Al(III) is acting as a Lewis acid (see Figure 2), a triaryl phosphite would not be expected to undergo a facile ambient-temperature rearrangement with triethylaluminum. Triphenyl phosphite, for example, only undergoes rearrangement with alkyl iodides at 200°C.[27b] The addition of triethylaluminum to a solution of the triaryl phosphite **7** (Scheme 3) showed no evidence



7

SCHEME 3

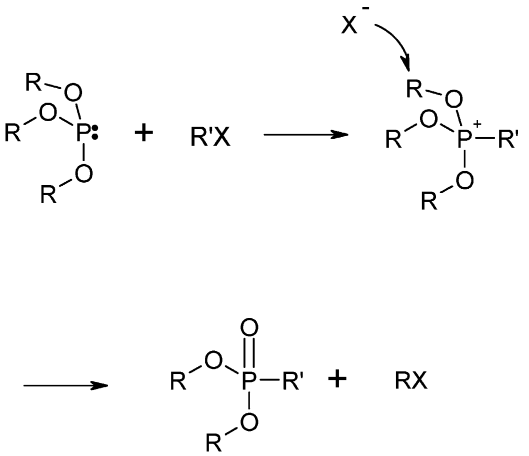


FIGURE 2 Mechanism of a typical Michaelis-Arbusov-type reaction involving a phosphite and a hydrogen halide.

for reaction in the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture at ambient temperature. These observations are also consistent with the rearrangement of the alkyl-oxygen bond rather than the aryl-oxygen bond in phosphite **1**. The observed phosphite to phosphonate rearrangement of **1** to **5** with triethylaluminum does not involve the loss of any substituents and the mechanism would appear to be somewhat different that the typical mechanism proposed for the Michaelis-Arbusov reaction, although both organotin halides[28] and cyanogen iodide[29] are known to promote the reaction. Previous uncatalyzed thermal isomerizations of phosphites to phosphonates has been attributed to the presence of trace impurities, although the photochemical rearrangement of low molecular weight phosphites is well documented.[30] A transition state or intermediate involving coordination of aluminum to oxygen leading to either an ion pair or concerted rearrangement may be involved as illustrated in Figure 3. The possible involvement of the nitrogen atom beta to the migrating oxygen remains speculative. The involvement of the alkyl-oxygen bond in the suggested transition state or intermediate in the rearrangement of phosphite **1** to phosphonate **5** is consistent with the unreactive nature of the aryl-oxygen bonds present in **1** (higher bond strength of a C_{sp2}—O compared to a C_{sp3}—O bond).

The spectral data on the product of the reaction of **5** with three equivalents of triethylaluminum was fully consistent with the diphosphonate **6**. No evidence for the formation of the trisphosphonate was observed in the $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture. In the

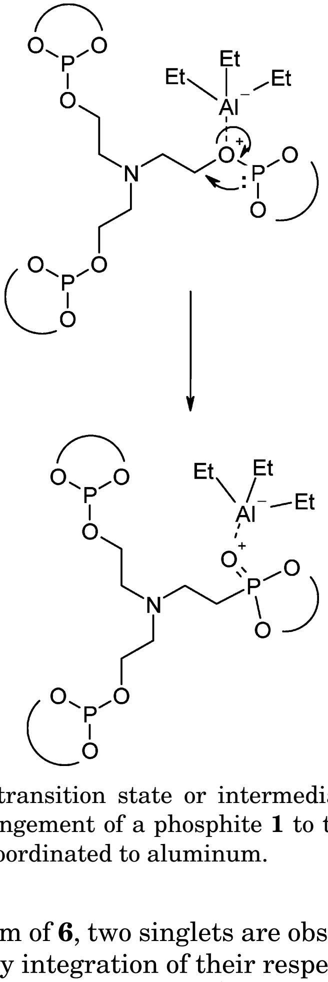


FIGURE 3 Suggested transition state or intermediate for the triethylaluminum promoted rearrangement of a phosphite **1** to the phosphonate **5** with the phosphoryl oxygen coordinated to aluminum.

$^{31}P\{^1H\}$ NMR spectrum of **6**, two singlets are observed at δ 135.93 and δ 33.84 in a 1:2 ratio by integration of their respective peak areas. The integration of the proton signals in the ^1H NMR spectrum of **6** is that expected for the diphosphonate structure illustrated.

CONCLUSIONS

The interaction of triethylaluminum with the trialkanolamine phosphite **1** was shown to lead to a facile phosphite to phosphonate rearrangement at room temperature. A mechanism is suggested that involves prior coordination of the aluminum alkyl to oxygen in the transition state or intermediate. A prior limited study on the trimethylaluminum promoted rearrangement of a trialkyl phosphite to a phosphonate reported that elevated temperatures are required for the reaction to proceed. The reason for the occurrence of a facile room temperature phosphite to phosphonate rearrangement of **1** to **5** with triethylaluminum suggests further mechanistic studies are warranted. Furthermore, the rearrangement of a phosphite to phosphonate by residual catalytic aluminum species in a polymer matrix during high-temperature processing may be an unrecognized mechanism of polymer stabilization.[32]

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (300.08 MHz and 499.84 MHz, respectively) spectra were obtained on a Varian Model Gemini-300, Unity-500, or Unity-INOVA 500 spectrometers. ^{13}C NMR (125.70 MHz) spectra and ^{15}N NMR (50.59 MHz) spectra were obtained on a Varian Model Unity-INOVA 500. ^{31}P NMR (202.33 and 121.47 MHz, respectively) spectra were obtained on a Varian Model Unity-500, Unity-INOVA 500, or Gemini-300 spectrometers. All ^{31}Pand ^{31}P{^{1}H} chemical shift values (proton coupled and decoupled, respectively) are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{15}N chemical shift values are reported in ppm relative to nitromethane, where a positive sign if downfield from the standard.[31] Significant ^{1}H NMR spectral data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddt, doublet of doublets of triplets), atom assignments, coupling constant in Hertz, and number of protons. IR spectra were obtained on a Bruker model Vector 22. Merck silica gel 60 (200–400 mesh) was used for column chromatography. MS spectra obtained on a Perspective Biosystems Voyager DE-STR matrix assisted laser desorption ionization mass spectrometer (MALDI TOF) equipped with a 337 nm N_2 laser and a time of flight analyzer. The instrument was operated in the positive ion reflector mode with an accelerating voltage of 24,900 volts. The samples were prepared by depositing a methylene chloride solution of the substrate onto a gold-metal coated sample plate. 2-Benzotriazol-2-yl-4-methyl-phenol was deposited as a matrix and silver trifluoroacetate (11 mg.mL^{-1} acetonitrile) was used as a cationization agent. Mass spectra were also obtained on a Fison VG Platform II mass spectrometer in APcI positive scanning mode. Merck pre-coated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Tris(2,4-di-*tert*-butylphenyl) phosphite, **7**, is commercially available from Ciba Specialty Chemicals Corporation. Toluene and triethanolamine were dried over 4 Angstrom molecular sieves prior to use. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen. Elemental analyses were performed by the Analytical Research Department, Ciba Specialty Chemicals.

Reaction Product of 1 with Triethylaluminum, (5)

To a solution of **1** (4.38 g, 3 mmol) in 50 mL of dichloromethane was added dropwise a 1M solution of triethylaluminum (9 mL, 9 mmol) in hexane. The reaction mixture was stirred for 2 h at ambient temperature until no starting material was observed by ^{31}P NMR. The reaction solvent and volatiles were removed in vacuo. The residue was purified by dry-column chromatography (95:5 heptane: ethyl acetate eluent) followed by trituration with acetonitrile to give 1.14 g (26%) of a white solid, mp 149–152°C. IR(neat sample-Attenuated Total Reflectance) v 1228 cm^{-1} (P=O); $^{15}N\{^1H\}$ NMR($CDCl_3$)(50.59 MHz) δ – 351.2; $^{31}P\{^1H\}$ NMR(CD_2Cl_2)(202.36 MHz) δ 138.4 (s, 2P), 35.4 (s, 1P); ^{1}H NMR(CD_2Cl_2)(499.85 MHz) δ 1.33 (s, 36 H), 1.34 (s, 18 H), 1.40 (s, 36 H), 1.41 (s, 18 H), 2.08 (dt, $CH_2P(=O)$,$^2J_{HCP} = 18.7$ Hz, $^3J_{HCCH} = 8.0$ Hz, 2 H), 2.61 (t, CH_2N, $3J_{HCCH} = 6.5$ Hz, 4 H), 2.91 (dt, CH_2N, $^3J_{HCCP} = 6.2$; $^3J_{HCCH} = 8.0$ Hz, 2 H), 3.75 (dt, CH_2OP, $^3J_{HCCH} = 6.5$ Hz, $^3J_{HCOP} = 8.0$ Hz, 4 H), 7.14 (d, $^4J_{HCCCH} = 2.4$ Hz, 4 H), 7.17 (d, $^4J_{HCCCH} = 2.4$ Hz, 2 H), 7.41 (d, $^4J_{HCCCH} = 2.4$ Hz, 4 H), 7.47 (unresolved dd, $^4J_{HCCCH} =2.4$ Hz, 2 H); $^{13}C\{^1H\}$ NMR (CD_2CL_2) (75.46 MHz) δ 24.2 (d, $\underline{C}P{=}O$, $^1J_{CP} = 130.9$ Hz), 31.0 (d, $C\underline{C}H_3$, $^5J_{CP} = 2.7$ Hz), 31.2 (s, $C\underline{C}H_3$), 31.3 (s, $C\underline{C}H_3$), 31.4 (s, $C\underline{C}H_3$), 34.7 (s, $\underline{C}CH_3$), 34.8 (s, $\underline{C}CH_3$), 35.4 (s, $\underline{C}CH_3$), 35.5 (s, $\underline{C}CH_3$), 48.8 (s, $\underline{C}CH_2P$), 54.5 (d, $\underline{C}CH_2OP$, $^3J_{CCOP} = 3.1$ Hz), 62.8 (d, $\underline{C}H_2OP$, $^2J_{COP} = 5.3$), 124.4 (s), 125.4 (s), 126.5 (s), 127.1 (s), 130.6 (s), 132.7 (d, $^3J_{PC} = 3.7$ Hz), 140.0 (d, $^3J_{PC} = 4.1$ Hz), 140.1 (s), 144.4 (d, $^2J_{PC} = 10.1$ Hz), 146.0 (d, $^3J_{PC} = 5.7$ Hz), 146.8 (s), 147.9 (s). MS(LC/APcI+) [M+1]1464; Anal. Calcd. for $C_{90}H_{132}NO_9P_3$: C, 73.79; H, 9.08; N, 0.96. Found: C, 73.73; H, 9.12; N, 0.82.

Reaction Product of 5 with Triethylaluminum, (6)

To a solution of **1** (0.6 g, 0.4 mmol) in 10 mL of dichloromethane was added dropwise a 1M solution of triethylaluminum (1.2 mL, 1.2 mmol) in hexane. The reaction mixture was stirred for 1 h at ambient temperature until no starting material was observed by ^{31}P NMR. The reaction solvent and volatiles were removed in vacuo. The residue was purified by dry-column chromatography (90:10, heptane: ethyl acetate eluent) followed by trituration with acetonitrile to give 0.14 g (24%) of a white solid, m.p. 181–185°C. $^{31}P\{^1H\}$ NMR($CDCl_3$)(121.48 MHz) δ 135.93 (s, 1P), 33.84 (s, 2P); ^{1}H NMR($CDCl_3$)(300.08 MHz) δ 1.28 (s, 18 H), 1.35 (s, 36 H), 1.41 (s, 18 H), 1.44 (s, 36 H), 2.14 (dt, C*H*$_2$P(=O),$^2J_{HCP}$ = 18.7 Hz, $^3J_{HCCH}$ = 8.0 Hz, 4 H), 2.56 (t, *CH*$_2$N, 3J_{HCCH} = 6.5 Hz, 2 H), 2.95 (dt, *CH*$_2$N, $^3J_{HCCP}$ = 6.2; $^3J_{HCCH}$ = 8.0 Hz, 4 H), 3.74 (dt, *CH*$_2$OP, $^3J_{HCCH}$ = 6.5 Hz, $^3J_{HCOP}$ = 8.0 Hz, 2 H), 7.16 (d, $^4J_{HCCCH}$ = 2.4 Hz, 4 H), 7.17 (d, $^4J_{HCCCH}$ = 2.4 Hz, 2 H), 7.40 (d, $^4J_{HCCCH}$ = 2.4 Hz, 2 H), 7.48 (unresolved dd, $^4J_{HCCCH}$ = 2.4 Hz, 4 H).

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