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RESEARCH ARTICLE

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A "masked" source for the phosphaalkene MesP=CH_2: Trapping, rearrangement, and oligomerization

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Abstract

We report the attempted synthesis of a "masked" phosphaalkene by treating MgA·3THF (A = anthracenide) with MesPCl(CH_2Cl). Although the desired "masked" phosphaalkene could not be isolated, indirect evidence for its formation was obtained. The product of trapping MesP=CH_2 with 1,3-cyclohexadiene was detected. In addition, the oxide MesPO(Me)A was isolated and crystallographically characterized from the MgA·3THF and MesPCl(CH_2Cl) experiment described above. Finally, the attempted isolation of "masked" phoshaalkene afforded P-containing oligomers with a trimodal molecular weight distribution [M_n = 640, 1.7×10^3 and 7.4×10^3 Da].

1 | INTRODUCTION

The elusive nature of low-coordinate and multiply bonded compounds of the heavier *p*-block elements inspired researchers to develop strategies to impart kinetic and thermodynamic stability to such species. Early strategies involved employing electron delocalizing substituents and permitted the isolation of phosphamethine cyanine cations and phosphinines, compounds with a delocalized P=C bond.[1–3] Subsequently, researchers realized that sterically bulky substituents may be employed to kinetically and thermodynamically stabilize E=E' bonds [E, E' = *p*-block element(s)]. Landmark developments include the isolation of compounds such as RP = C(OTMS)R' (R = Me, *t*-Bu, Cy, Ph; R' = *t*-Bu);[4] MesP=CPh_2;[5] *t*-Bu-C≡P,[6] Mes*P=PMes*,[7] $(TMS)_2$Si=C(OTMS)Ad,[8] and Mes_2Si=$SiMes_2$.[9]

Although these discoveries marked the beginning of a new and still growing field,[10,11] they often overshadow a distinctly different strategy to stabilize low-coordinate species, namely the concept of using a "mask" to stabilize unusual species in a ring system where their release is accompanied by a thermodynamically stable by-product such as an aromatic compound. In 1972, Roark and Peddle successfully synthesized and isolated a "masked" disilene (**A** in Figure 1) by treating dilithiated anthracene with $Me_2ClSiSiClMe_2$.[12] This species released the unstable disilene, $Me_2Si=SiMe_2$, accompanied by anthracene upon heating. The concept of a "mask" has been critical to the development of phosphinidene chemistry with examples including $7\lambda^3$-phosphanorbornadiene **B**,[13] oxide **C**,[14–16] and the metal complex **D**.[17,18] An alternative strategy to "mask" a phosphinidene is illustrated by azaphosphirine **E** in which the by-product is a nitrile.[19] Recently, a convenient route to "masked" phosphinidenes of type **F** was reported starting with the conveniently generated magnesium anthracenide, MgA·3THF.[20] This one-step methodology is also amenable to the preparation of "masked" digermene **G**.[21]

A tribute to Professor Naomichi Furukawa on the Occasion of his 82nd birthday - By Invitation only

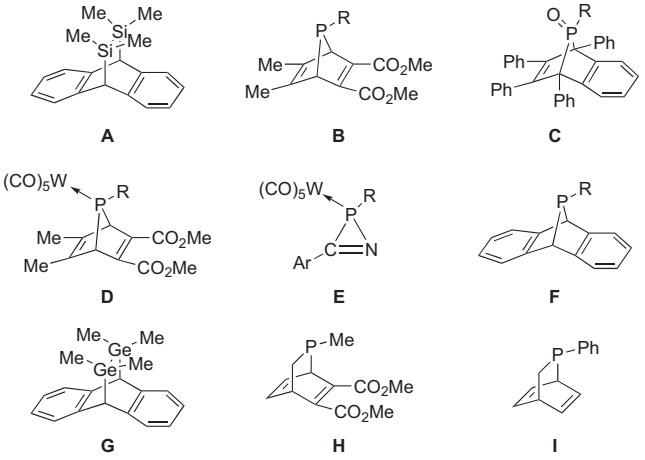
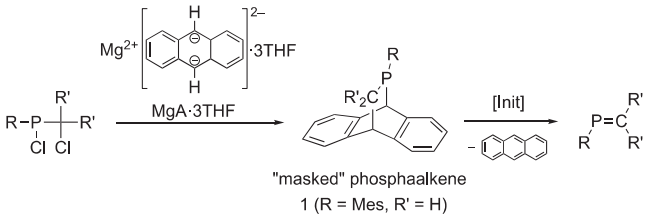


FIGURE 1 Selected examples of "masked" low-coordinated and/or multiply bonded compounds of the heavier *p*-block elements

We have been interested in the polymerization of multiply bonded main group element species, by analogy to the polymerization of olefins. In particular, the analogy between the P=C bond of a phosphaalkene and the C=C bond of an olefin has been exploited to generate an entirely new class of functional phosphine polymers.[22,23] The principle monomers for polymerization studies have employed bulky substituents at both carbon and phosphorus (ie, MesP=CAr_2).[24–31] The presence of sterically encumbering substituents greatly reduces the reactivity of the P=C bond toward polymerization. We have recently uncovered that polymerization of MesP=CAr_2 occurs through an unusual addition-isomerization mechanism involving the *o*-CH_3 of the *P*-Mes substituent. Therefore, smaller substituents to the P=C bond are desired for their potential polymerization. Ironically, such species cannot be isolated for deliberate studies of their initiation and polymerization due to their low stability toward self-oligomerization and side reactions.

We were intrigued by the pioneering work of Sakurai on the anionic polymerization of "masked" disilenes to generate numerous examples of achiral and chiral polysilanes.[32–38] Although "masked" phosphaalkenes **H** and **I** had been reported by Quin and co-workers, such compounds require multistep syntheses (10 steps for **I**), and only small quantities can be isolated.[39,40] To facilitate polymerization studies, we sought a method that could provide a "masked" phosphaalkene in fewer steps, higher yield, and in sufficient quantities for polymerization (>1 g). We hypothesized that the reaction of the conveniently accessible MgA·3THF, mentioned previously, with an appropriate chloromethyl-substituted chlorophosphine may provide access to "masked" phosphaalkenes in one step that could later be used in polymerization studies (Scheme 1).

Herein, we report the application of this proposed methodology to afford the "masked" MesP=CH_2, **1**. Although compound **1** could not be isolated in pure form, it was successfully trapped with 1,3-cyclohexadiene, a rearrangement product of **1** was isolated, and P-containing oligomers/polymers with appreciable molecular weight were isolated.



SCHEME 1 Postulated synthetic route to "masked" phosphaalkenes in one step

2 | RESULTS AND DISCUSSION

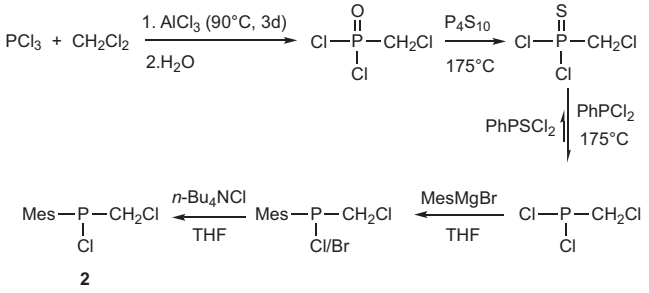
2.1 | ClH_2CPCl_2 and MesPCl(CH_2Cl)

The proposed route to "masked" version of the phosphaalkene MesP=CH_2 (**1**) first required the synthesis of the dichlorinated compound MesPCl(CH_2Cl) (**2**). We imagined that this compound would be readily accessible from the known $PCl_2(CH_2Cl)$.[41] The route to $PCl_2(CH_2Cl)$ from PCl_3 and CH_2Cl_2 is shown in Scheme 2. The first step involves their $AlCl_3$-mediated reaction followed by hydrolysis to afford known $P(O)Cl_2(CH_2Cl)$[42] which was isolated in 37% yield. Subsequent treatment of $P(O)Cl_2(CH_2Cl)$ with P_4S_{10} affords the phosphine sulfide $P(S)Cl_2(CH_2Cl)$ in 92% yield.[43]

The final step in the literature procedure involves reduction of $P(S)Cl_2(CH_2Cl)$ with PBu_3 (reported yield = 78%, our yield = 20%).[41] We obtained a higher yield when $PhPCl_2$ was employed as the reducing agent (yield = 47%). Since the reaction mixture consisted of an equilibrium mixture of reactants and products, distillation under reduced pressure was employed to remove the product, $PCl_2(CH_2Cl)$ (b.p. 30°C, 1 Torr), and to drive the reaction forward. A second distillation at atmospheric pressure under N_2 was required to separate the product from traces of PCl_3. The pure product (b.p. 125°C, 1 atm) was isolated in 47% yield.

The successful preparation of $PCl_2(CH_2Cl)$ was confirmed by analyzing the isolated liquid by ^{31}P NMR spectroscopy in $CDCl_3$ solution. The spectrum shows only a singlet resonance at 159.2 ppm. The ^1H NMR spectrum shows only a doublet resonance at 4.10 ppm with small coupling constant ($^2J_{PH}$ = 16 Hz) consistent with that expected for the CH_2 moiety. The $^{13}C\{^1H\}$ NMR spectrum displays a doublet at 48.2 ppm with a coupling constant consistent with that expected for the C–P bond ($^1J_{PC}$ = 55 Hz). These data are consistent with that reported previously in the literature for $PCl_2(CH_2Cl)$.[41]

With pure $PCl_2(CH_2Cl)$ in hand, the next task was to selectively substitute one of the chlorides of the PCl_2 moiety with Mes. Given our experience preparing $MesPCl_2$ from PCl_3 and the literature procedure,[44] we postulated that



SCHEME 2 Synthetic route to $MesPCl(CH_2Cl)$ (2)

careful addition of MesMgBr in a slight excess would result in complete substitution of the desired P–Cl with minimal double substitution. Thus, a THF solution of MesMgBr was slowly added to a solution of $PCl_2(CH_2Cl)$ in THF at −78°C over 4 hours. Subsequently, the reaction mixture was warmed to ambient temperature whereupon an aliquot was removed for ^{31}P NMR spectroscopic analysis. The spectrum is shown in Figure 2A and reveals two singlet resonances ($\delta = 74.9$, 60.3) that were assigned to $MesPCl(CH_2Cl)$ and $MesPBr(CH_2Cl)$, respectively. Similar mixed halogen species are often observed in reactions of chlorophosphines with Grignard reagents.

Following filtration to remove magnesium salts, a THF solution of the product was treated with excess *n*-Bu_4NCl. The progress of halide exchange was monitored by ^{31}P NMR spectroscopy and, within 10 minutes, the signal at 60.3 ppm was completely consumed, and the only signal present was at 74.9 ppm, assigned to $MesPCl(CH_2Cl)$ (**2**) [Figure 2B]. Although this compound has not previously been reported, the observed ^{31}P chemical shift is consistent with known $ArPCl(CH_2Cl)$ compounds ($Ar = C_6H_5$, $\delta = 71.5$; 2,4,6-*i*$Pr_3C_6H_2$, $\delta = 70.5$; 2,4,6-*t*$Bu_3C_6H_2$, $\delta = 67.5$).[45]

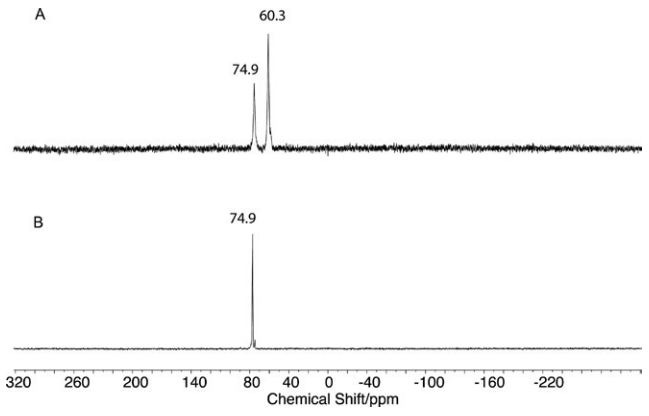


FIGURE 2 ^{31}P NMR spectra (THF, 161.9 MHz, 298 K) of: A) the reaction mixture obtained from treating $PCl_2(CH_2Cl)$ with MesMgBr (1 equiv); and B) crude $MesPCl(CH_2Cl)$ (**2**) obtained after treating the crude mixture isolated from (A) with *n*-Bu_4NCl (excess)

Following standard workup procedures compound **2** was isolated in 57% yield.

Additional support for the formulation of the product as **2** was obtained from the ^1H NMR spectrum of the isolated product dissolved in $CDCl_3$. The spectrum is shown in Figure 3, and its analysis permitted assignment of signals that clearly elucidate the proposed formulation of Mes-containing **2**. Specifically, three signals were diagnostic of the Mes moiety [$\delta = 6.95$ (2H, *m*-H); 2.69 (6H, *o*-CH_3); 2.33 (3H, *p*-CH_3)]. The remaining two signals were assigned to the diastereotopic protons of the –CH_2Cl moiety [$\delta = 4.34$ (dd, $^2J_{HH} = 11$ Hz, $^2J_{HP} = 24$ Hz, 1H); 4.27 (dd, $^2J_{HH} = 11$ Hz, $^2J_{HP} = 28$ Hz, 1H)]. The assignments of the coupling constants were made with the aid of a $^1H\{^{31}P\}$ NMR spectroscopic experiment. These data were analogous to those of the aforementioned related compounds $ArPCl(CH_2Cl)$. Moreover, the ^1H-^{13}C HSQC NMR spectrum of compound **2**, shown in Figure 4, further corroborates the identity of **2**. In addition, the EI-MS spectrum of product revealed a major signal at $m/z = 234$ attributed to the molecular ion of **2**.

2.2 | $MesPPh(CH_2Ph)$ from $MesPCl(CH_2Cl)$

To ascertain whether or not it would be possible to perform nucleophilic substitution at both the P–Cl and C–Cl moieties, $MesPCl(CH_2Cl)$ was treated with PhMgBr in THF solution (Scheme 3). After the addition of PhMgBr (1 equiv), an aliquot was removed for ^{31}P NMR spectroscopic analysis. The spectrum revealed that the signal assigned to starting material **2** ($\delta = 74.9$) was replaced by a new singlet resonance at −16.7 ppm, tentatively assigned to $MesPPh(CH_2Cl)$ (**3**). This compared favorably to the ^{31}P NMR spectroscopic data for known Ph_2PCH_2Cl ($\delta = -11$).[46] In addition, an aliquot was removed from the reaction mixture, worked-up, and analyzed by ^1H NMR spectroscopy in $CDCl_3$. The spectrum was consistent with the assigned formulation of the product, displaying diagnostic signals assigned to the -C*H*$_2$Cl of **3.**

With intermediate **3** in hand, additional PhMgBr (1 equiv, 2 equiv total) was added to the reaction mixture. The progress of substitution was monitored by periodic ^{31}P NMR spectroscopic analysis of aliquots removed from the reaction mixture. After 30 minutes, two sharp resonances were observed at −16.7 and −18.8 ppm (Figure 5A). The latter signal was tentatively assigned to the desired product, $MesPPh(CH_2Ph)$ (**4**). Over 15 hours, the signal assigned to intermediate **3** was entirely consumed and was replaced by the signal assigned to the desired product **4** ($\delta = -18.8$ ppm, Figure 5B). Following work-up, compound **4** was isolated as a white solid. The ^{31}P, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopic data along with EI-MS data (m/z = 318) of the isolated product were consistent with that previously reported for compound **4** prepared following a different route.[47]

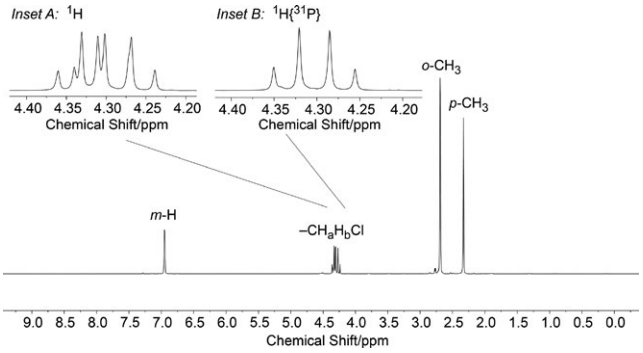


FIGURE 3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**. Inset A: expansion of the diastereotopic $–CH_2Cl$ region of the ^{1}H NMR spectrum; Inset B: ^{1}H{^{31}P} NMR spectrum of the same region

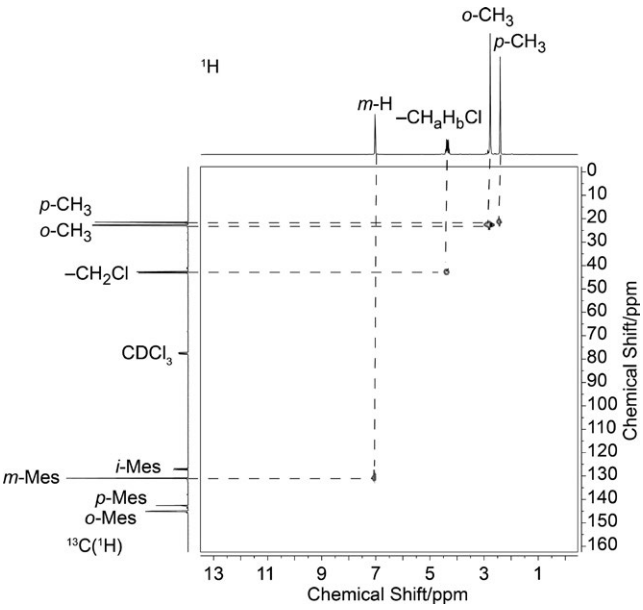
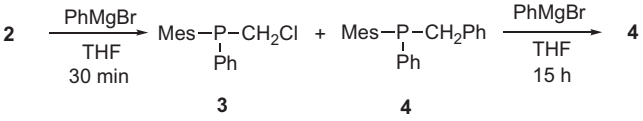


FIGURE 4 ^{1}H-^{13}C HSQC spectrum (400 MHz for ^{1}H, $CDCl_3$, 298K) of **2**. The ordinate shows the ^{13}C{^{1}H} NMR spectrum, and the abscissa shows the ^{1}H NMR spectrum



SCHEME 3 Nucleophilic substitution at both the P–Cl and C–Cl bonds of $MesPCl(CH_2Cl)$ (**2**) using PhMgBr

2.3 | "Masked" $MesP{=}CH_2$

In the previous section, we demonstrated that $MesPCl(CH_2Cl)$ (**2**) is amenable to nucleophilic substitution at both the P–Cl and C–Cl sites. Thus, the reaction of **2** with magnesium anthracene (MgA·3THF) was attempted as a route to "masked" phosphaalkene **1** (Scheme 4).

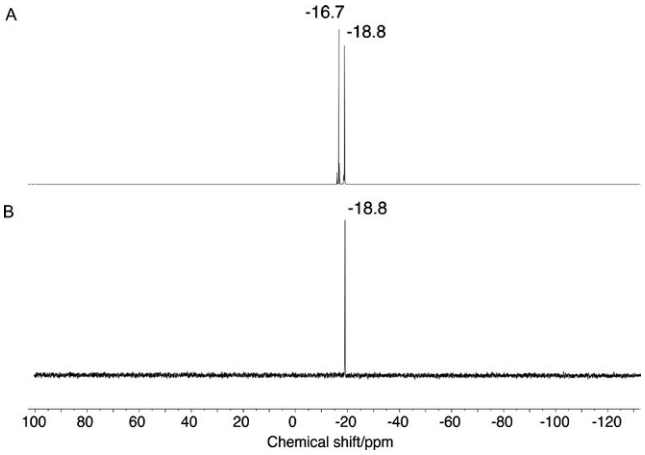
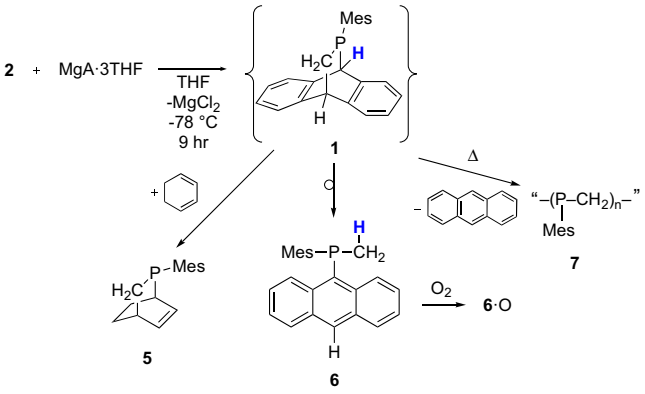


FIGURE 5 ^{31}P NMR spectra (161.9 MHz, THF, 298 K) of aliquots removed from the reaction mixture of $MesPCl(CH_2Cl)$ (**2**) and PhMgBr (2 equiv): A) after 30 min; B) after 15 h



SCHEME 4 Attempted synthesis of "masked" phosphaalkene **1** and the results of trapping, rearrangement, and oligomerization

MgA·3THF (1 equiv) was prepared according to the literature procedure.[48] This solid was added slowly over 3 hours to the solution of **2** (1 equiv) in THF at −78°C. Over 2 hours, the color of the reaction mixture changed from colorless to yellow. After 9 hours at −78°C, the reaction mixture was dark blue-green. A further color change to orange and finally to pale yellow was observed when the reaction mixture was slowly warmed to ambient temperature. Analysis of an aliquot removed from the reaction mixture using ^{31}P NMR spectroscopy revealed the presence of a sharp singlet resonance at −42.2 ppm [Figure 6A]. This signal is in the same region as that for "masked" phosphaalkenes **H** ($\delta = -47.0$) and **I** ($\delta = -29.3$)[39] and was tentatively assigned to "masked" phosphaalkene **1**. We also note the presence of several additional smaller broad signals between 60 to 30 and −20 to −50 ppm [Figure 6A]. These signals are consistent with those previously observed by Quin et al when working with phenylphosphaalkene, $Ph{-}P{=}CH_2$, obtained from **I**. Specifically, the broad signals

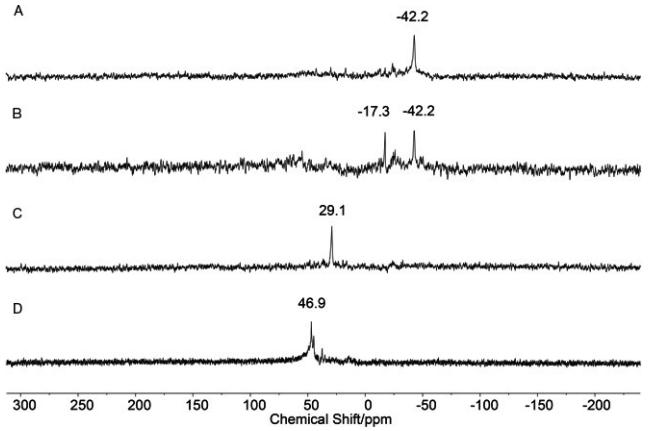


FIGURE 6 ^{31}P NMR spectra (161.9 MHz, THF, 298 K) of A) crude reaction mixture of products of MgA·3THF with 2, B) MgA·3THF and 2 from above was treated with 1,3-cyclohexadiene (after 9 hours), C) MgA·3THF and 2 from above after purification by column chromatography (fraction 2), D) MgA·3THF and 2 from above after column chromatography (fraction 3)

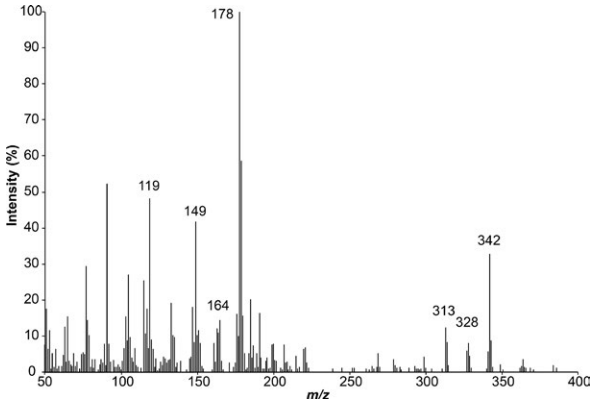


FIGURE 7 Mass Spectrum (EI, 70 eV) of the crude product isolated from the reaction of **2** with MgA·3THF showing evidence for "masked" phosphaalkene **1**

they observed between −40 to −50 ppm were attributed to head-to-head or head-to-tail oligomerization.[39] We speculate that a similar phenomena are occurring for **1** to afford oligomers of the general structure **7** (vide infra).

A sample of the crude product mixture exhibiting a predominant signal at −42.2 ppm was taken directly from the glovebox freezer for mass spectrometric analysis. The EI-MS obtained is shown in Figure 7. Strikingly, a signal was observed at m/z = 342 which could be assigned to the molecular ion of "masked" phosphaalkene, $[\mathbf{1}]^+$ (formula: $C_{24}H_{23}P$). Moreover, the isotopic distribution for the ions at *m/z* = 342, 343, and 344 (1 : 0.267 : 0.043) is close to that expected for the molecular ion, $[\mathbf{1}]^+$ (1 : 0.263 : 0.033). Identifiable fragments include $[M\text{-}CH_2]^+$ (m/z = 328, 8%), anthracene (*m/z* = 178, 100%), $[MesP\text{-}1]^+$ (*m/z* = 149, 41.7%), and mesityl (m/z = 119, 48.2%). Importantly, ions at m/z = 164 and 165 could be assigned to phosphaalkene ions, $[MesP{=}CH_2]^+$ or $[MesP{=}CH_2{+}1]^+$, respectively. Although these data provide very convincing data for "masked" phosphaalkene **1**, unfortunately attempts to isolate this compound were unsuccessful.

In an effort to obtain indirect evidence for the presence of "masked" phosphaalkene **1** in the reaction mixture, an experiment was designed to trap $MesP{=}CH_2$. Specifically, 1,3-cyclohexadiene was added to the reaction mixture obtained when **2** was treated with MgA·3THF (ie, the aforementioned solution showing a dominant ^{31}P resonance at −42.2 ppm). Analysis of an aliquot removed from the reaction mixture by ^{31}P NMR spectroscopy revealed that a new signal was present at −17.3 ppm along with a less intense signal at −42.2 ppm [Figure 6B]. The new signal was tentatively assigned to "trapped" phosphaalkene **5** whilst the higher field signal was attributed to "masked" phosphaalkene **1**. Additional evidence for trapped product **5** was obtained from the EI-MS spectrum of this mixture which showed an ion at *m/z* = 244 (32.7%) and is consistent with the molecular ion $[M^+]$ expected for **5**.

Therefore, we turned our attention to the crude reaction mixture of **2** and MgA·3THF [ie, ^{31}P NMR spectrum in Figure 6A]. The solvent was removed *in vacuo* to afford a yellow residue. This crude residue was dissolved in diethyl ether, filtered to remove a white, insoluble solid (presumably $MgCl_2$). Unfortunately, attempts to isolate pure products by fractional recrystallization from a variety of solvents were unsuccessful as only mixtures were obtained. Thus, column chromatography was attempted using hexane:ethyl acetate (1:1) as eluent under aerobic conditions. Three fractions were collected. The first fraction was identified as anthracene ($R_f = 0.82$) from its ^{1}H NMR spectrum and ESI-MS. The second fraction ($R_f = 0.097$) was isolated as a solid residue by rotary evaporation. Fortuitously, single crystals were obtained from the second fraction by slow diffusion of hexanes into a MeOH solution of this solid.

Analysis of the crystals using ^{31}P NMR spectroscopy in THF showed a single resonance at 29.1 ppm in Figure 6C. The crystals were also analyzed by X-ray crystallography. The molecular structure is shown in Figure 8 and reveals the product to be phosphine oxide **6**·O. Although the metrical parameters are unremarkable, the structure confirms the desired P–anthracene connectivity. We postulate that compound **6** is formed from **1** following rearrangement and air-oxidation. Unfortunately, we were unable to isolate enough **6**·O to enable more detailed characterization.

The third fraction was washed off the column using pure ethyl acetate, and its ^{31}P NMR spectrum revealed broad resonances ranging from 30 to 70 ppm [Figure 6D]. We presume that these signals result from air-oxidation of the species that were previously assigned to oligomers and detected in Figure 6A (ie, **7** → **7**·O). These species may result from

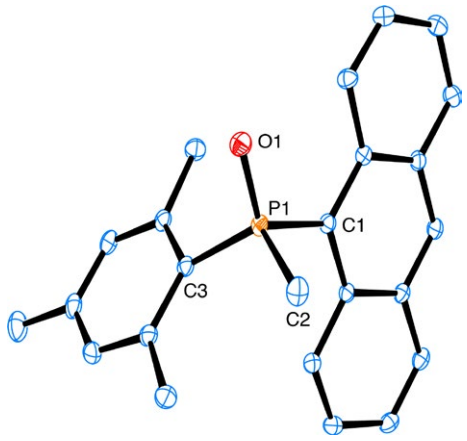


FIGURE 8 Molecular structure of 6·O by ORTEP 3. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.49760(8), P(1)–C(3) 1.83934(14), P(1)–C(1) 1.85179(16), P(1)–C(2) 1.80633(13), O(1)–P(1)–C(3) 71.769(6), O(1)–P(1)–C(1) 115.491(4), O(1)–P(1)–C(2) 108.799(5), C(3)–P(1)–C(2) 114.375(2), C(2)–P(1)–C(1) 100.973(3), C(1)–P(1)–C(3) 109.044(3). CCDC-

intermolecular reactions of mesitylphosphaalkene (Mes-P=CH_2) derived from **1**. Strong evidence for the presence of oligomeric material, such as **7**·O, was derived from a gel permeation chromatography multi-angle light scattering (GPC-MALS) experiment (Figure 9). A multimodal molecular weight distribution was observed with the main fraction having M_n = 630 Da (Đ = 1.89). Two smaller fractions were observed at higher molecular weight at 1700 and 7400 Da, respectively. Unfortunately, there was insufficient product available to unequivocally identify it as **7**·O. Nevertheless, it is clear that an oligomeric material has been generated and that this material contains phosphorus in an environment consistent with the postulated formulation as **7**·O.

3 | SUMMARY

We report a potentially convenient route to "masked" phosphaalkenes by treating MgA·3THF with MesPCl(CH_2Cl). Although the present study was not able to provide direct evidence for the "masked" phosphaalkene **1**, we have presented indirect evidence that strongly supports its intermediacy. For instance, trapping MesP=CH_2 with 1,3-cyclohexadiene afforded compound **5** which was characterized by NMR spectroscopy and MS. Compound **6**, a rearrangement product from **1**, was isolated and crystallographically characterized as its oxide. Finally, we have successfully shown that oligomeric material can be isolated from the attempted generation of **1**. Future work will aim to gain additional insight into the possible generation of "masked" phosphaalkenes using this methodology and to investigate their polymerization reactions.

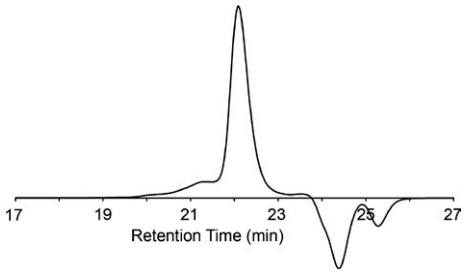


FIGURE 9 GPC chromatogram (refractive index traces) of oligomers derived from in situ generated **1**. Three modes are observed: M_n = 630 Da (major), 1700 Da (minor), and 7400 Da (minor)

4 | EXPERIMENTAL

4.1 | General procedures

All manipulation of air and/or water sensitive materials was conducted under nitrogen using Schlenk line techniques or in an Innovative Technology glovebox. Phosphorus trichloride (Sigma Aldrich), aluminum chloride (Acros Organics), phosphorus pentasulfide (Acros Organics), dichlorophenylphosphine (Sigma Aldrich), magnesium (Fisher Science Education), 2-bromomesitylene (Alfa Aesar), lithium (Sigma Aldrich), and cyclohexadiene (Sigma Aldrich) were used as received. Tetrabutylammonium chloride (Sigma Aldrich) was recrystallized from acetone by addition of diethyl ether and further dried *in vacuo*. Anthracene (Sigma Aldrich) was sublimed before use. THF was freshly distilled from sodium/benzophenone ketyl before use. Dichloromethane and hexanes were dried by passing through a column of activated alumina. $CDCl_3$ and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories Inc. MgA·3THF (A = anthracene) was prepared following literature procedures.[48] Compound $ClCH_2P(S)Cl_2$ was synthesized following known literature procedures.[41] ^{1}H, ^{31}P, ^{13}C NMR spectra were recorded on Bruker Avance 300 MHz or 400 MHz spectrometers. Chemical shifts are reported relative to residual $CHCl_3$ (δ = 7.26 for ^{1}H and δ = 77.23 for ^{13}C). 85% H_3PO_4 was used as external standard δ = 0.0 for ^{31}P. Mass spectra were acquired by Mr. Marshall Lappawa in the UBC Chemistry Mass Spectrometry Facility using a Kratos MS 50 in EI mode (70 eV). Polymer molecular weights (M_n) were determined by triple detection gel permeation chromatography (GPC-MALS) using an Agilent chromatograph equipped with an Agilent Technologies 1260 series standard autosampler, Phenomenex Phenogel 5 mm narrow bore columns 515 (4.6 × 300 mm) 10^4 Å (5000-500 000 Da), 500 Å (1000-15 000 Da), and 10^3 Å (1000-75 000 Da), Wyatt Optilab T-rEx differential refractometer (λ = 658 nm, 40°C), Wyatt miniDAWN TREOS laser light scattering detector (λ = 690 nm), and a Wyatt Viscostar-II viscometer. A flow-rate of 0.5 mL/min was

used, and samples were dissolved in THF (*ca*. 1 mg/mL). HPLC grade THF was used for GPC.

4.2 | Synthesis of $PCl_2(CH_2Cl)$

$PhPCl_2$ (8.99 g, 50.2 mmol) was added to $ClCH_2P(S)Cl_2$ (8.01 g, 43.7 mmol) at 175°C with vigorous stirring, and the color of solution changed from colorless to light yellow after 7 hours. Compound $ClCH_2PCl_2$, with PCl_3 as minor impurity, was isolated by reduced pressure distillation of the reaction mixture using water aspirator (1.0 Torr) and heating by oil bath (T = 40-80°C). The product was collected in a Schlenk flask immersed in liquid nitrogen. A second atmospheric pressure distillation heated with an oil bath (T = 140-145°C) to afford pure $ClCH_2PCl_2$ (b.p. 125°C)—the first drops contained PCl_3 and were discarded. Yield = 3.12 g (47%)

^{31}P NMR (161.9 MHz, $CDCl_3$, 298 K): δ 159.2 (s); ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ 4.10 (d, $^{2}J_{PH}$ = 16.0 Hz, 2H, -CH_2-); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 48.2 (d, $^{2}J_{PC}$ = 55.8 Hz, 2H, -CH_2-).

4.3 | Synthesis of $MesPCl(CH_2Cl)$ (2)

To a stirred suspension of activated Mg (0.98 g, 40.4 mmol) in THF (25 mL) was added bromomesitylene (5.06 mL, 33.1 mmol) dropwise. The reaction was monitored by ^{31}P NMR spectrometry. After refluxing for 2 hours, the Grignard reagent was formed as evidenced by the deep brown color. It was cannula-transferred into a THF solution of $ClCH_2PCl_2$ (4.17 g, 27.6 mmol) (25 mL) dropwise at −78°C. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo,* leaving a yellow oil. To the yellow oil was added hexanes (3 × 10 mL), and the suspension was filtered, and the solvent was removed *in vacuo* to obtain a light yellow oil containing **2** and $MesPBr(CH_2Cl)$.

To a stirred solution of the above mixture (0.50 g, 1.9 mmol) dissolved in THF (5 mL) was added dropwise tetrabutylammonium chloride (0.60 g, 2.2 mmol) in THF (5 mL). After vigorous stirring for 10 minutes, the solvent was removed *in vacuo,* leaving a pale yellow colored residue. To the residue was added hexanes (3 × 3 mL), the soluble portion was filtered, and the solvent removed *in vacuo* to afford **2**. Yield = 3.70 g (57%).

^{31}P NMR (161.9 MHz, $CDCl_3$, 298 K): δ 74.9 (s); ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ 6.95 (s, 2H, aryl H), 4.34 (dd, $^{2}J_{HH}$ = 11 Hz, $^{2}J_{HP}$ = 24 Hz, 1H, -CH_2-), 4.27 (dd, $^{2}J_{HH}$ = 11 Hz, $^{2}J_{HP}$ = 28 Hz, 1H, -CH_2-), 2.69 (d, $^{4}J_{HP}$ = 2 Hz, 6H, *o*-CH_3), 2.33 (s, 3H, *p*-CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): δ 144.1 (s, aryl C), 143.9 (s, aryl C),141.7 (s, aryl C), 130.3 (s, aryl C), 130.1 (s, aryl C), 127.0 (s, aryl C), 126.3 (s, aryl C), 42.4 (d, $^{1}J_{CP}$ = 42 Hz, -CH_2-), 22.4 (d, $^{2}J_{CP}$ = 22 Hz, *o*-CH_3), 21.5 (s, *p*-CH_3); MS (EI) : m/z = 236, 234 [60, 100, M^+].

4.4 | Synthesis of compound (4)

To a stirred suspension of magnesium (0.050 g, 2.1 mmol) in THF (10 mL) was added dropwise bromobenzene (0.30 g, 1.9 mmol). The reaction mixture was refluxed at 75°C for 2 hours. This freshly made Grignard reagent was added dropwise to the **2** (0.19 g, 0.80 mmol) dissolved in THF (5 mL) at −78°C. The reaction was monitored by ^{31}P NMR spectroscopy. Light yellow solution slowly turned to colorless after stirring for 15 hours. The solvent was removed *in vacuo*, leaving a white residue. The residue was dissolved in degassed EtOH (3 × 5 mL), and the suspension was filtered. The solvent was removed *in vacuo* leaving white solid product. Yield = 0.094 g (37%).

^{31}P NMR (161.9 MHz, $CDCl_3$): δ -18.8 (s); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.29-7.19 (m, 10H, aryl H), 6.88 (s, 2H, Mes), 3.65 (dd, $^{2}J_{HH}$ = −13.3 Hz, $^{2}J_{PH}$ = 33.1 Hz, 1H, -CH_2-), 3.55 (dd, $^{2}J_{HH}$ = −13.4 Hz, $^{2}J_{PH}$ = 33.4 Hz, 1H, -CH_2-), 2.28 (s, 3H, *p*-CH_3), 2.20 (s, 6H, *o*-CH_3);^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.0 (s, aryl C),141.5 (d, $^{2}J_{PC}$ = 16.9 Hz, aryl C), 137.1 (d, J = 10.8 Hz, aryl C), 129.5 (s, aryl C), 129.4 (s, aryl C), 129.1 (s, aryl C), 129.0 (s, aryl C),128.9 (s, aryl C), 128.3 (s, aryl C), 128.2 (s, aryl C), 126.5 (s, aryl C), 125.9 (s, aryl C), 33.8 (d, $^{1}J_{PC}$ = 18.4 Hz, -CH_2-), 23.2 (s, *o*-CH_3), 23.1 (s, *o*-CH_3), 21.0 (s, *p*-CH_3); MS (EI): *m/z* 319, 318 [39, 100, M^+].

4.5 | Trapping Product (5)

To a stirred solution of **2** (0.20 g, 0.85 mmol) in THF (10 mL) at −78°C was added in small portions MgA·3THF (0.36 g, 0.85 mmol) as an orange powder. The color of the solution gradually changed from colorless to yellow to dark blue-green after 9 hours. The reaction was monitored by ^{31}P NMR spectrometry with the major signal at −42.2 ppm. 1,3-Cyclohexadiene (0.10 mL, 1.0 mmol) was added dropwise into the dark blue-green reaction mixture. The reaction mixture was slowly warmed to ambient temperature and its color changed from dark blue-green to yellow. A ^{31}P NMR spectrum was recorded. The solution was filtered and the solvent was removed *in vacuo*, affording a small quantity of yellow solid, sufficient only for MS analysis.

^{31}P NMR (161.9 MHz, THF): δ = −17.3 (s), −42.2 (s). MS (EI): *m/z* = 244 [M^+].

4.6 | Reaction of 2 with MgA·3THF

To a stirred solution at −78°C of **2** (0.20 g, 0.85 mmol) dissolved in THF (10 mL) was added MgA·3THF (0.36 g, 0.85 mmol) orange powder in small portions. The color of the solution gradually changed from colorless to yellow to dark blue-green after 9 hours. The reaction was monitored by ^{31}P NMR spectrometry. After 9 hours, the reaction was

completed and slowly warmed back up to ambient temperature. The solution color went from dark blue-green to yellow. The reaction mixture was filtered to remove the black solid precipitate. The solvent was removed *in vacuo,* leaving a yellow solid. Diethyl ether (5 mL) was used to extract product mixture. The resulting yellow solution with white suspension was filtered, and the solvent was removed from filtrate *in vacuo*. The product mixture was dry-loaded onto a silica-gel column. A 1:1 mixture of hexanes-ethyl acetate was used as an eluent. The first fraction of colorless solution was dried *in vacuo*. Second collected fraction was a yellow solution with bright light blue fluorescence under UV light. The yellow third fraction only eluted when washed off the column with pure ethyl acetate.

4.6.1 | Fraction 1: Anthracene

Yield = 0.25 g (83%). $R_f = 0.82$. ^{1}H NMR (400.1 MHz, $CDCl_3$, 298K): δ 8.42 (s, 2H, aryl H), 8.05 (dd, 4H, aryl H) 7.50 (dd, 4H, aryl H). MS (ESI): 179, 178 [15, 100, M^+].

4.6.2 | Fraction 2: 6·O

Single crystals suitable for X-ray diffraction analysis of second fraction were obtained by slow diffusion of equal amount of hexane into product in MeOH solution. Yield = 0.028 g (9.3%). $R_f = 0.097$. ^{31}P NMR (161.9 MHz, $CDCl_3$, 298K): δ 29.1 (s); ^{1}H NMR (400.1 MHz, $CDCl_3$, 298K): δ 9.01 (dd, 2H, aryl H), 8.60 (s, 1H, aryl H), 8.05 (dt, 2H, aryl H), 7.41 (m, 4H, aryl H), 2.43 (d, 3H, $^2J_{PH} = 12.9$ Hz, -CH_3), 2.34(s, 6H, *o*-CH_3), 2.22(s, 3H, *p*-CH_3).

4.6.3 | Fraction 3: Oligomers/Polymer of Mes-P=CH_2

Yield = 0.011 g (8%). $R_f = 0$. ^{31}P NMR ($CDCl_3$, 161.9 MHz, 298K): δ 46.9 (br); GPC: Peak 1 (98.2%): $M_n = 630$, Đ = 1.89; peak 2 (1.6%): $M_n = 1700$, Đ = 1.04; peak 3 (0.2%): $M_n = 7400$, Đ = 1.12.

4.7 | X-ray crystallography

The single crystal was immersed in oil and mounted on a glass fiber. Data were collected at 90 ± 0.1 K on a Bruker X8 APEX 2 diffractomer with graphite monochromated Mo Kα radiation. Data were collected and integrated using the Bruker SAINT[49] software package and corrected for absorption effects with SADABS.[50] All data sets were corrected for Lorentz and polarization effects. The structure was solved by direct methods[51] and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXTL[52] crystallographic software package from Bruker-AXS. Crystallographic data were deposited with the Cambridge Database: CCDC-1871598.

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REFERENCES

[1] K. Dimroth, P. Hoffman. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 384.
[2] G. Märkl. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 846.
[3] A. J. Ashe. *J. Am. Chem. Soc.* **1971**, *93*, 3293.
[4] G. Becker. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242.
[5] C. Klebach, R. Lourens, F. Bickelhaupt. *J. Am. Chem. Soc.* **1978**, *100*, 4886.
[6] G. Becker, G. Gresser, W. Uhl. *Z. Naturforsch.* **1981**, *36b*, 16.
[7] M. Yoshifuji, I. Shima, N. Inamoto. *J. Am. Chem. Soc.* **1982**, *104*, 6167.
[8] A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury. *J. Chem. Soc., Chem. Commun.* **1981**, 191.
[9] R. West, M. J. Fink, J. Michl. *Science* **1981**, *214*, 1343.
[10] P. P. Power. *Chem. Rev.* **1999**, *99*, 3463.
[11] R. C. Fischer, P. P. Power. *Chem. Rev.* **2010**, *110*, 3877.
[12] D. N. Roark, G. J. D. Peddle. *J. Am. Chem. Soc.* **1972**, *94*, 5837.
[13] M. J. van Eis, H. Zappey, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt. *J. Am. Chem. Soc.* **2000**, *122*, 3386.
[14] K. Matsumoto, S. Hashimoto, S. Otani, T. Uchida. *Heterocycles* **1984**, *22*, 2713.
[15] J. K. Stille, J. L. Eichelberger, J. Higgins, M. E. Freeburger. *J. Am. Chem. Soc.* **1972**, *94*, 4761.
[16] Y. Kashman, I. Wagenstein, A. Rudi. *Tetrahedron* **1976**, *32*, 2427.
[17] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler. *J. Am. Chem. Soc.* **1982**, *104*, 4484.
[18] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler. *J. Chem. Soc., Chem. Commun.* **1982**, 667.
[19] R. Streubel, H. Wilkens, A. Ostrowski, C. Neumann, F. Ruthe, P. G. Jones. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1492.
[20] A. Velian, C. C. Cummins. *J. Am. Chem. Soc.* **2012**, *134*, 13978.
[21] A. Velian, W. J. Transue, C. C. Cummins. *Organometallics* **2015**, *34*, 4644.
[22] J. I. Bates, J. Dugal-Tessier, D. P. Gates. *Dalton Trans.* **2010**, *39*, 3151.
[23] A. M. Priegert, B. W. Rawe, S. C. Serin, D. P. Gates. *Chem. Soc. Rev.* **2016**, *45*, 922.
[24] C. W. Tsang, M. Yam, D. P. Gates. *J. Am. Chem. Soc.* **2003**, *125*, 1480.
[25] C. W. Tsang, B. Baharloo, D. Riendl, M. Yam, D. P. Gates. *Angew. Chem. Int. Ed.* **2004**, *43*, 5682.
[26] K. J. T. Noonan, D. P. Gates. *Angew. Chem. Int. Ed.* **2006**, *45*, 7271.

[27] P. W. Siu, S. C. Serin, I. Krummenacher, T. W. Hey, D. P. Gates. *Angew. Chem. Int. Ed.* **2013**, *52*, 6967.
[28] B. W. Rawe, C. P. Chun, D. P. Gates. *Chem. Sci.* **2014**, *5*, 4928.
[29] S. C. Serin, G. R. Dake, D. P. Gates. *Macromolecules* **2016**, *49*, 4067.
[30] S. C. Serin, G. R. Dake, D. P. Gates. *Dalton Trans.* **2016**, *45*, 5659.
[31] B. W. Rawe, C. M. Brown, M. R. MacKinnon, B. O. Patrick, G. J. Bodwell, D. P. Gates. *Organometallics* **2017**, *36*, 2520.
[32] K. Sakamoto, K. Obata, H. Hirata, M. Nakajima, H. Sakurai. *J. Am. Chem. Soc.* **1989**, *111*, 7641.
[33] K. Sakamoto, M. Yoshida, H. Sakurai. *Macromolecules* **1990**, *23*, 4494.
[34] K. Ebata, K. Furukawa, N. Matsumoto. *J. Am. Chem. Soc.* **1998**, *120*, 7367.
[35] T. Sanji, K. Kawabata, H. Sakurai. *J. Organomet. Chem.* **2000**, *611*, 32.
[36] T. Sanji, K. Takase, H. Sakurai. *J. Am. Chem. Soc.* **2001**, *123*, 12690.
[37] T. Sanji, S. Isozaki, M. Yoshida, K. Sakamoto, H. Sakurai. *J. Organomet. Chem.* **2003**, *685*, 65.
[38] H. Sakurai, R. Honbori, T. Sanji. *Organometallics* **2005**, *24*, 4119.
[39] L. D. Quin, A. N. Hughes, B. Pete. *Tetrahedron Lett.* **1987**, *28*, 5783.
[40] L. D. Quin, A. N. Hughes, J. C. Kisalus, B. Pete. *J. Org. Chem.* **1988**, *53*, 1722.
[41] K. Karaghiosoff, R. Mahnot, C. Cleve, N. Gandhi, R. K. Bansal, A. Schmidpeter. *Chem. Ber.* **1995**, *128*, 581.
[42] A. M. Kinnear, E. A. Perren. *J. Chem. Soc.* **1952**, 3437.
[43] R. Schmutzler. *Org. Synth.* **1966**, *46*, 21.
[44] S. T. Liddle, K. Izod. *Organometallics* **2004**, *23*, 5550.
[45] J. Fischer, P. Machnitzki, O. Stelzer. *Z. Naturforsch.* **1997**, *52b*, 883.
[46] S. O. Grim, R. C. Barth. *J. Organomet. Chem.* **1975**, *94*, 327.
[47] J. Albert, R. Bosque, J. M. Cadena, S. Delgado, J. Granell, G. Muller, J. I. Ordinas, M. F. Bardia, X. Solans. *Chem. - Eur. J.* **2002**, *8*, 2279.
[48] P. K. Freeman, L. L. Hutchinson. *J. Org. Chem.* **1983**, *48*, 879.
[49] Computer program: SAINT V. 7.03A ed, Bruker AXS Inc., Madison, Wisconsin, USA, **1997-2003**.
[50] Computer program: Bruker. SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.
[51] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Crystallogr.* **1999**, *32*, 115.
[52] *SHELXTL version 5.1*, Bruker, ZSX Inc., Madision, WI **1997**.

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