Exploring Diphosphene Synthesis with Trimethylsilylated and Imidazolidine Reductants

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Senior Honors Project Proposal
Katherine Miller
Exploring Diphosphene Synthesis with Trimethylsilylated and Imidazolidine Reductants
Abstract

Various reducing agents were tested to try and find a new way to synthesize the diphosphene DmpP=PDmp (Dmp = 2,6-dimesitylphenyl). The reducing agents tested were an organosilicon-based compound, 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD), 3,6-bis(trimethylsilyl)1,4-cyclohexadiene (BTCD), and 1,3,1′,3′-tetraethyl-bis(2,2′-imidazolidine). Through the use of dimesitylphenyl phosphorous dichloride (DmpPCl₂), it is thought that the chemistry exhibited by these reducing agents on similar compounds could be applied to compounds with PCl₂ groups, such as DmpPCl₂, in the hopes of creating the diphosphene DmpP=PDmp.

Introduction

Compounds with double bonds between phosphorous atoms (diphosphenes) are relatively new compounds that are of great interest in the organometallic field of chemistry as examples of compounds with multiple bonds between main group elements. Diphosphenes are unstable due to the small π-bond energy ca. 34 kcal mol⁻¹ compared to N-N π-bond energy of 94 kcal mol⁻¹.¹ Nitrogen and phosphorous are both Group 15 elements, but have drastically different π-bonding properties. As a result, the lower bond energy makes for a less stable molecule, compared to those with nitrogen double bonds. Despite the less stable π-bond, it has been shown that having a large protective bulky group can stabilize these low coordinated

organophosphorous compounds. The lower stability of the phosphorous π-bond is due to the less effective overlap of the orbitals compared to those seen in nitrogen. This overlap creates the stability seen in double and triple bonds between nitrogen atoms. However, the smaller overlap in the phosphorous electron cloud makes it more energetically favorable for phosphorous atoms to make single bonds, as opposed to double bonds. The bond length between diphosphenes of 1.985Å is shorter than the bond length between single P-P bonds of 2.22Å. This shorter bond length, due to π-bond formation as well as changes in the σ-hybridization, is commonly seen between single and double bonds. It is observed that this π-bond between phosphorous atoms is less stable than a single bond between phosphorous atoms.

Previous successful attempts at creating diphosphenes have been performed by reducing DmpPCl₂. Dimesitylphenyl, as seen in Figure 1 below, has been the most successful sterically bulky group to produce diphosphenes, such as DmpP=PDmp.

Figure 1: DmpPCl₂

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The diphosphene DmpP=PDmp, seen in Figure 2, was first successfully synthesized using activated magnesium as a way to reduce the DmpPCl$_2$ without creating phosphorous centered radicals in the process.

![Figure 2: DmpP=PDmp](image)

Creating phosphorous centered radicals is one way to obtain diphosphenes, however, other side products also include cyclooligomers of phosphinidenes in Figure 3. As the cyclooligomers are not of interest, a method to produce diphosphenes without them is being sought. When reducing DmpPCl$_2$ with activated magnesium, the reaction occurs very rapidly, and the DmpP=PDmp was successfully created. There were, however, other cyclometallated species, shown in Figure 4, that formed as well. Where a double bond should have occurred within the molecule, a ring structure was observed.  

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Finding other ways to create DmpP=PDmp, without the side products that have been previously observed using different reducing agents, has been the main topic of this research.

The organosilicon-based reductant, 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD) and 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCD) are shown in Figure 5.

Arteaga-Müller et al.\(^5\) found that both MBTCD and BTCD were successful in producing linear α-olefins through a catalytic system that involves the salt-free reduction of TaCl\(_5\) with these two compounds in the presence of ethylene. These two reducing agents are very similar, however MBTCD has a methyl group (CH\(_3\)) on the
designated R group where BTCD has a hydrogen. This catalytic system produces 2 equivalents of Me₃SiCl, C₆H₅R, (R=CH₃ or H) and Ta(III) species active for ethylene trimerization. This is important as it shows that MBTCD and BTCD are able to successfully reduce chloride compounds and abstract the chlorine atoms, as is the goal with the reduction of DmpPCl₂. These two reducing agents were also shown to generate low-valent niobium species, Nb(III). This was done by reduction of NbCl₅ with BTCD in the presence of 3-hexyne. This reduction led to the formation of a 3-hexyne complex of NbCl₃·(3-hexyne)(DME). ⁵

It was also shown by Tsurugi et al, that MBTCD could successfully reduce TaCl₅ in the presence of α-diimine ligands to lower valent tantalum complexes having redox-active α-diimine ligands. The following tantalum complexes that were created using MBTCD as a reductant show that MBTCD is a useful reductant to abstract chlorine atoms and create compounds which are stabilized by the sterically bulky groups.⁶

![Tantalum complex formed from MBTCD]⁶

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⁶ Tsurugi, H., Carbon Radical Generation by d⁰ Tantalum Complexes with α-Diimine Ligands through Ligand-Centered Redox Processes. JACS. 2011, 133, 18673-18683.
Figures 6 and 7 show the five coordinate tantalum complexes that were formed with MBTCD. These complexes help show that MBTCD is a promising reagent to reduce phosphorous molecules containing sterically bulky groups with halides like DmpPCl$_2$. MBTCD was also shown to successfully reduce WCl$_6$ in a salt free environment. MBTCD was again used to create large complexes but instead with a tungsten center. It was hoped that this could be applied to DmpPCl$_2$ in creating diphosphenes in the following way:

![Scheme 1: Proposed reduction of DmpPCl$_2$ using trimethylsilylated cyclohexadienes](image)

**Scheme 1: Proposed reduction of DmpPCl$_2$ using trimethylsilylated cyclohexadienes**

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*7 Tsurugi, H, Tanahashi, H. Salt-Free Reducing Reagent of Bis(trimethylsilyl)cyclohexadiene mediates, Multielectron Reduction of Chloride Complexes of W (VI) and W(IV). 2013.*
Scheme 1 depicts the proposed reaction for either MBTCD or BTCD with DmpPCl₂. This compound was explored as another potential reducing agent due to the similar properties that it shares with MBTCD.

A second reducing agent, 1,3,1’3’-Tetraethyl-bis(2,2’-imidazolidene), which is a mild homogenous reducer of P-Cl bonds was also of interest to create DmpP=PDmp. This compound has been shown to successfully reduce P-Cl bonds in phosphonous or phosphinous chlorides to yield compounds that have phosphorous-phosphorous double bonds. It was shown to successfully reduce diarylphosphinous chlorides to tetra-aryldiphosphines faster than with metal reducing agents. The proposed reaction is as follows:

![Scheme 2: Proposed reduction of DmpPCl₂ via bis-imidazolidine](image)

**Experimental Section**

All reagents were obtained from Sigma-Aldrich unless otherwise stated. THF, pentane, benzene, and toluene were purified from Na-benzophenone solutions

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8 Goldwhite, H. Kaminski, J. et al. Phosphorous-phosphorous single of double bond formation from PCl₃₋₉ Rₙ (n=1 or 2) and a bis-imidazolidine reducing agent. 1986, 310, 21-25.
under N₂. ¹H and ³¹P NMR spectra were recorded using a 400 MHz Varian spectrometer. ¹H NMR spectra are referenced to CDCl₃ and ³¹P NMR spectra are referenced to H₃PO₄.

MBTCD was prepared as described by Laguerre et al.⁹ In a flame dried 250 mL round bottom flask, dry tetrahydrofuran (150 mL) was placed and sparged with argon. Dry toluene (100 mL, 950 mmol) was treated in the same way. Lithium metal (2.1g, 288.2 mmol, 50% excess) was added to a 500 mL round bottom flask. THF was added to the 500 mL flask via cannulation. Chlorotrimethylsilane (44 mL, 346 mmol) was added drop wise from a 50 mL graduated cylinder via cannulation. Toluene was added via cannulation. The reaction was put on ice and allowed to mix at 0°C for 24 hours. Pentane (100 mL) was added to stop reaction. A white precipitate, LiCl, formed and the solution was transferred to a new flask via cannulation. The solution was filtered and rotary evaporated to yield a clear liquid. Yield 16%. ¹H NMR (CDCl₃) 2s (9H and 9H) at 0.0 and 0.06 (2SiMe₃): 1m (3H) at 1.64 (Me-C=C-) 1m (2H) at 2.47(≡Si-CH-C=C-) 1m (1H) at 5.14 ppm (H ethlyenic). Spectra matched what was reported by Laguerre.⁹

BTCD was prepared in the same manner as MBTCD as mentioned above with modifications. Instead of using dry toluene, dry benzene was used as directed by Weyenberg et al.¹⁰ The product yielded a white crystalline solid, 15.8%. Melting point was determined to be 75-80°C. ¹H NMR (CDCl₃) 2s (9H and 9H) at -0.08 and

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¹⁰ Weyenberg, D. R. Toporcer, L, H. The Synthesis of 3-6-Disilyl-1,4-cyclohexadienes by the trapping of benzene aniion-radicals. 1962, 84, 2843-2844.
0.16 (2SiMe₃) 1s (2H) at 2.06 (Me-C) 1m (3H) at 5.33 and 7.42 (-C₆H₃-) ppm. Spectra matched what was reported by Weyenberg.¹⁰

1,3,1’,3’-tetraethyl-bis(2,2’-imidazolidine) was prepared as described by Goldwhite et al.⁸ Dry benzene (50 mL) was added to a 250 mL flame dried round bottom flask via cannulation. N,N-dimethyl formamide dimethylacetal (10mL, 77 mmol) was added via 10 mL plastic syringe. N,N’diethylethylenediamine (9.3 mL, 66.5 mmol) was added via 10 mL plastic syringe. The solution was distilled at 240ºC for 3 hours. The solution was bright yellow. The remaining benzene was pulled off in vacuo and the solution was distilled under reduced pressure at 0.1mmHg using a Kuglerohr. The product is air sensitive.⁸ ¹H NMR (CDCl₃). 1m at 1.1 (CH₃), 1m at 2.63 (NCH₂) 1 m at 3.21 (CH₂CH₃) ppm. Spectra matched what was reported by Goldwhite.⁸

DmpPCl₂ was prepared by Alexandra Beckman.³¹P NMR (CDCl₃) 1s at 160 ppm. Spectra matched what was reported by Urnézius.¹¹

DmpP=PDmp synthesis was attempted with all three reducing agents that were discussed earlier. Three different catalysts were also incorporated during the synthesis attempts, these three catalysts are CuI, AgF₆P, and PdCl₂. All were performed in NMR tubes.

1. **MBTCD and DmpPCl₂**: A few crystals of DmpPCl₂ were placed in an NMR tube and dissolved in either dry toluene, dry CDCl₃, or dry THF. Two drops of

MBTCD were added via syringe and the reaction was let to react at room
temperature. $^{31}$P NMR spectra were taken after 2-3 hours and again after 24 hours. 
Results were inconclusive, as the $^{31}$P NMR spectrum did not contain the expected
peak at 500 ppm. $^{31}$P NMR (toluene) 1s at 25.33 and 1s at 161.66 ppm. $^{31}$P NMR
(CDCl$_3$) 1s at 26.49 and 1s at 160.63 and 1s at 335.06 ppm.

2. **BTCD and DmpPCl$_2$:** A few crystals of DmpPCl$_2$ were placed in an NMR tube
and dissolved in dry CDCl$_3$. A few crystals of BTCD were added and the NMR tube
was put under a nitrogen atmosphere and let react at room temperature. $^{31}$P NMR
spectra were taken after 2-3 hours and again after 24 hours. Results were
inconclusive. $^{31}$P NMR (CDCl$_3$) 1s at 26.89 and 1s at 159.92 ppm

3. **MBTCD and DmpPCl$_2$ with Cul:** A few crystals of DmpPCl$_2$ were placed in an
NMR tube and dissolved in either dry THF or dry toluene. A few drops of MBTCD
were added via plastic syringe and mixed. A small spatula of Cul was added and
mixed. The solution turned bright yellow after the addition of Cul. The tube was
mixed and let react at room temperature. $^{31}$P NMR spectra were taken after 2-3
hours and again after 24 hours. Results were inconclusive. $^{31}$P NMR (toluene) 1s at
160.07 ppm. $^{31}$P NMR (THF) 1s at 84.01 and 1s at 137.23 and 1s at 160.92 ppm.

4. **BTCD and DmpPCl$_2$ with Cul:** The NMR tube was prepared the same way
mentioned above (2) but a small spatula of Cul was added. The solution turned
bright yellow after the addition of Cul. The tube was mixed and let react at room
temperature. $^{31}$P NMR spectra were taken after 2-3 hours and again after 24 hours.
Results were inconclusive. $^{31}$P NMR (toluene) 1s at 160.37 ppm. $^{31}$P NMR (THF) 1s
at -62.27 1s at 84.01 and 1s at 135.01 and 1s at 160.04 ppm.
5. **MBTC and DmpPCl$_2$ with AgPF$_6$:** The NMR tube was prepared the same way mentioned above (1) but a small spatula of AgPF$_6$ was added. After mixing and letting react for a few hours at room temperature the solution turned purple and a grey precipitate formed. $^{31}$P NMR spectra were taken after 2-3 hours and again after 24 hours. Results were inconclusive. $^{31}$P NMR (toluene) 1s at 25.05 and 1s at 160.37 ppm. $^{31}$P NMR (THF) 1s at -7.81 1s at -2.1 1s at 3.49 and 1s at 23.43 ppm.

6. **BTCD and DmpPCl$_2$ with AgPF$_6$:** The NMR tube was prepared the same way mentioned above (2) but a small spatula of AgPF$_6$ was added. After mixing and letting react for a few hours at room temperature the solution turned purple and a grey precipitate formed. $^{31}$P NMR spectra were taken after 2-3 hours and again after 24 hours. Results were inconclusive. $^{31}$P NMR (toluene) 1s at 25.91 and 1s at 161.48 ppm. $^{31}$P NMR (THF) 1s at -7.76 1s at -2.07 1s at 3.42 1s at 23.40 and 1s at 288.71 ppm.

7. **MBTC and DmpPCl$_2$ with PdCl$_2$:** The NMR tube was prepared the same way mentioned above (1) but a small spatula of PdCl$_2$ was added. The solution turned dark brown after mixing. $^{31}$P NMR spectra were taken after 2-3 hours and again after 24 hours. Results were inconclusive. $^{31}$P NMR (toluene) 1s at 20.19 1s at 161.23 and 1s at 302.29 ppm. $^{31}$P NMR (THF) 1s at 25.99 1s at 161.50 and 1s at 280.82 ppm.

8. **Bis-imidazolidine and DmpPCl$_2$:** In an NMR tube DmpPCl$_2$ (.027g) was placed and dissolved in a few drops of toluene. Bis-imidazolidine (0.0288g) was obtained and mixed with toluene. The bis-imidazolidine was added drop wise to the DmpPCl$_2$ and mixed. The solution turned yellow and a white precipitate formed. $^{31}$P
NMR spectra were taken after 2-3 hours and again after 24 hours. Results were inconclusive. $^{31}$P NMR (toluene) 1s at 17.76 1s at 116.40 1s at 160.56 and 1s at 174.73 ppm.

**Results and Discussion**

From the results it appears as if the DmpP=PDmp compound was not synthesized from MBTCD, BTCD, or bis-imidazolidine with DmpPCI$_2$. The identifying peak of DmpP=PDmp at $\delta$ 493 ppm would have been observed in the $^{31}$P NMR spectrum if it were successfully synthesized. Although there were no observed peaks in the various $^{31}$P NMR spectra taken that indicated DmpP=PDmp was made, there were a few peaks that repeatedly occurred. The proposed reduction of DmpPCI$_2$ with a trimethylsilylated cyclohexadiene to form DmpP=PDmp produces ClSiMe$_3$ and toluene as the other products of the reaction, as shown above in Scheme 1. It was proposed in Scheme 1 that the coordination number of phosphorous changes from three to two after the reduction of DmpPCI$_2$. When the trimethylsilylated cyclohexadienes were used to reduce early transition metal halides to form sterically bulky tantalum complexes, these complexes did not change in coordination number. Tantalum complexes were formed from TaCl$_5$ and MBTCD as shown above in Figures 7 and 8.

These tantalum complexes show that the coordination number on tantalum does not change after it is reduced. In both complexes the coordination number remains five after TaCl$_5$ is reduced by MBTCD. When the MBTCD and BTCD were used with DmpPCI$_2$ to create the diphosphene in question, the coordination number
on the phosphorous atoms differ from DmpPCl₂ to DmpP=Pdmp. The coordination number on the phosphorous atom must change from three to two in order for the diphosphene to form. The trimethylsilylated cyclohexadiene might not be a strong enough reducing agent to reduce DmpPCl₂ and change the coordination number of phosphorous. Given that phosphorous is more stable with a coordination number of three with three single bonds and a valence number of three, as opposed to a coordination number of two with a valence number of three, this could attribute to the failure of this reaction. It was previously shown that with activated Mg turnings, DmpPCl₂ could easily be reduced into DmpP=Pdmp. As magnesium is a very strong reducing agent, perhaps MBTCD and BCTD are not strong enough to reduce DmpPCl₂, as Mg has been shown to do. From the experimental section it can be observed that CuI and AgF₆P and PdCl₂ were also used in some of the reactions carried out in an attempt to create DmpP=Pdmp. These compounds were used as catalysts to try and force the reactions to completion.

The second method to create DmpP=Pdmp was with the use of bis-imidazolidine. Goldwhite et al. was able to demonstrate that bis-imidazolidine can reduce diarylphosphinous chlorides to the tetra-aryldiphosphines. It was proposed that bis-imidazolidine would act in a similar way to reduce DmpPCl₂ to DmpP=Pdmp as seen above in Scheme 2.

Although the NMR tube reactions that were carried out displayed similar visual results that Goldwhite reported, the ³¹P NMR did not show the desired results. The reaction of bis-imidazolidine and DmpPCl₂ produced a yellow solution with a
white precipitate. The reactions performed also demonstrated consistent chemical shifts. $^{31}\text{P NMR (toluene)}$ at $\delta-17.76\text{ppm}$, $\delta-116.40\text{ppm}$, $\delta-160.56\text{ppm}$ and $\delta-174.73\text{ppm}$. The desired chemical shift for $\text{DmpP=PDmp}$ appears at $\delta-493\text{ppm}$. The diphosphanes reported, were created with 2,4,6-tri-t-butylphenylphosphonous dichloride as opposed to $\text{DmpPCl}_2$. The three butyl groups are less bulky than the two mesityl groups, which could be a potential reason why the diphosphene was not made with $\text{DmpPCl}_2$.

For the reactions between MBTCD or BTCD and $\text{DmpPCl}_2$ a peak around $\delta-26\text{ppm}$ appeared multiple times when these reactions were performed in toluene and CDCl$_3$. The shift around $\delta-26\text{ppm}$ also appeared when these reactants were used with the AgF$_6\text{P}$ catalyst in toluene and THF.

When MBTCD and $\text{DmpPCl}_2$ and BTCD and $\text{DmpPCl}_2$ were used with CuI as the catalyst there was no reaction with toluene as the solvent for either reaction. With THF as the solvent, peaks were observed at around $\delta-135\text{ppm}$ and $\delta-84\text{ppm}$ for both reactions.

The reaction of MBTCD and $\text{DmpPCl}_2$ with PdCl$_2$ as a catalyst was tested with both toluene and THF as the solvents. In both reactions it was observed that after a few hours there were peaks appearing at around $\delta-280\text{ppm}$. After 24 hours the shifts changed to around $\delta-300\text{ppm}$.

From the NMR tube reactions with MBTCD and $\text{DmpPCl}_2$ and BTCD and $\text{DmpPCl}_2$ there is evidence that they react differently with each of the catalysts used. For all three catalysts used there were distinctly different chemical peaks in the $^{31}\text{P}$
NMR spectra that were taken. However, it appears that between each of the catalysts, AgPF$_6$ was the only one that truly acted as a catalyst. It is also possible that it did not react at all and was simply a bystander in the reaction. From the spectra obtained the NMR tube reactions with MBTCD and DmpPCl$_2$ and BTCD and DmpPCl$_2$ without any catalysts had peaks around δ -26 ppm. When AgF$_6$P was added the chemical peaks did not change and appeared at δ -26 ppm again.

**Conclusion**

From these findings it is concluded that MBTCD, BTCD and bis-imidazolidine are not successful reducing agents to form DmpP=PDmp from DmpPCl$_2$. It was observed that none of these reducing agents successfully yielded DmpP=PDmp from the $^{31}$P NMR spectra taken. These reactions were also unsuccessful with the addition of various catalysts.
Supporting Information

MBTCD $^1$H NMR Spectra
MBTCD and DmpPCL₂ in toluene $^{31}$P NMR Spectra

MBTCD and DmpPCL₂ in CDCl₃ $^{31}$P NMR Spectra
BTCD and DmpPCl₂ in toluene $^{31}$P NMR Spectra

BTCD and DmpPCl₂ in CDCl₃ $^{31}$P NMR Spectra
MBTCD and DmpPCl$_2$ and Cul in toluene $^{31}$P NMR Spectra

MBTCD and DmpPCl$_2$ in THF with Cul $^{31}$P NMR Spectra
BTCD and DmpPCl₂ with CuI in Toluene \(^{31}\text{P}\) NMR Spectra

BTCD and DmpPCl₂ with CuI in THF \(^{31}\text{P}\) NMR Spectra
MBTCD and DmpPCI₂ with AgF₆P in toluene $^{31}$P NMR Spectra

MBTCD and DmpPCI₂ with AgF₆P in THF $^{31}$P NMR Spectra
BTCD and DmpPCl$_2$ with AgF$_6$P in toluene $^{31}$P NMR Spectra

BTCD and DmpPCl$_2$ with AgF$_6$P in THF $^{31}$P NMR Spectra
MBTCD and DmpPCI₂ with PdCl₂ in toluene $^{31}$P NMR Spectra

MBTCD and DmpPCI₂ with PdCl₂ in THF $^{31}$P NMR Spectra
Bis-imidazolidine and DmpPCl2 in toluene $^{31}$P NMR Spectra
Bibliography


Tsurugi, H, Tanahashi, H. Salt-Free Reducing Reagent of Bis(trimethylsilyl)cyclohexadiene mediates, Multielectron Reduction of Chloride Complexes of W (VI) and W(IV). 2013.


