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A role for free phosphinidenes in the reaction of magnesium and sterically encumbered $ArPCl_2$ in solution at room temperature

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Abstract

The reduction of $ArPCl_2$ (Ar = 2,6-$Trip_2C_6H_3$, 2,6-$Mes_2C_6H_3$, 2,6-$(2,6\text{-}Me_2C_6H_3)_2C_6H_3$, or 2,4,6-$^tBu_3C_6H_3$) by various forms of activated magnesium have been examined and compared with previously reported reductions using unactivated magnesium. The current reactions are more rapid and give rise to products that are reminiscent of products obtained by irradiation of phosphanylidene-σ^4-phosphoranes $ArP{=}PMe_3$ bearing the same Ar groups. The correlation in product distributions suggests the involvement of phosphinidenes in the reduction of aryldichlorophosphines by activated magnesium. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus; Phosphinidene; Cyclometallation; Diphosphene; Magnesium; *meta*-Terphenyl

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1. Introduction

A challenge for chemists interested in understanding the details of a process that converts starting materials to products is to deduce a reasonable series of events for a transformation. Intermediates are often unstable and undetectable species. In some cases intermediates can be detected by physical or kinetic methods, but often we are left to infer the nature of an intermediate by the identity of a stable final product(s). Such conclusions, despite being somewhat speculative, are commonly employed to discuss reaction mechanisms. In defense of this habit, however, it is also quite often the case that further evidence for an intermediate would come at great cost of time and effort.

One such class of substances that have been proposed as intermediates, often with little or no mechanistic data, are phosphinidenes [1]. Phosphinidenes are somewhat related to carbenes and nitrenes, in that these reactive fragments can be thought of as building blocks for constructing the homocoupled species olefins ($R_2C{=}CR_2$), azoalkanes (RN=NR), and diphosphenes (RP=PR), and the heterocoupled species imines ($RN{=}CR_2$), phosphaalkenes ($RP{=}CR_2$), and iminophosphines (RP=NR). Due to the similarity in the electronegativities of carbon and phosphorus, their bonding properties and chemical behavior of low-coordinate organophosphorus compounds are similar to the carbon analogues [2]. Considerable work has been devoted to methods for delivery of phosphinidenes in synthesis of new organophosporus species in a fashion similar to the way carbenes can be accessed via transition metal carbene complexes. Mathey has pioneered much of the work in this area [3], and has also been a voice of caution for those too quick to suggest the intermediacy of phosphinidenes in reactions [1]. As he correctly states, the formation of products that appear to be derived from phosphinidenes does not constitute proof of their involvement.

Regardless, a wide variety of reactions can be grouped together on the assumption of arising via the incorporation of phosphinidene intermediates. These reactions are far too numerous to be detailed here, but one subclass of these reactions is the reduction of dihaloorganophosphines by metals. Scheme 1 shows how some of these products may be realized by self termination of putative phosphinidenes. This subclass can be further divided into reactions that lead to (a)

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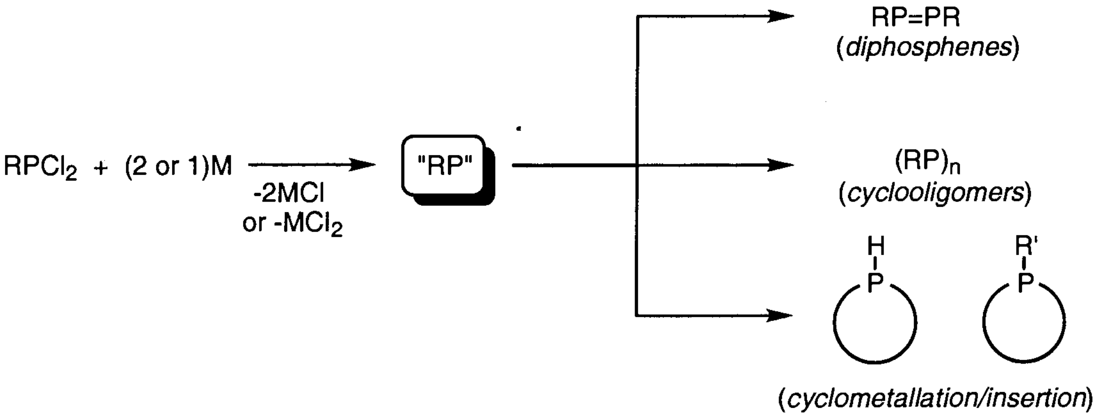
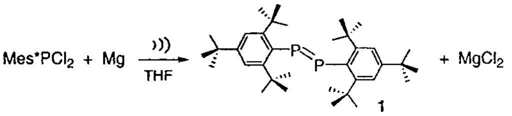


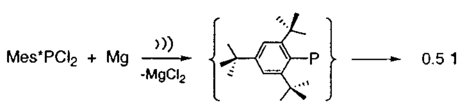
Scheme 1.

cyclooligomers of phosphinidenes $(RP)_n$ [4,5]; (b) diphosphenes RP=PR (actually a special case of $(RP)_n$, where $n = 2$) [6]; and (c) products derived by intramolecular reaction of a putative phosphinidene in some manner [1,7–9].

These particular reactions are of special interest for those interested in the chemistry of low coordinated phosphorus compounds, for it is this basic reaction that allowed Yoshifuji and coworkers to provide the chemical community with its first example of an isolable 'phosphobenzene' or diphosphene (Eq. (1)) [10]. This reaction is now 20 years old, and is one of the standard methods to prepare diphosphenes. A rather simplistic way of rationalizing the product of this reaction is to postulate its formation by the dimerization of two free phosphinindenes generated by the action of Mg upon Mes^*PCl_2 (Eq. (2)). Subsequent studies have postulated that formation of {Mes*P} leads to rapid subsequent attack of a proximal CH bond of an *ortho*-^{t}butyl group to form a phosphaindan. In particular, photochemical studies of {Mes*P} precursors consistently produce phosphaindan **2** (Eq. (3), X = PMes*, CO, $(N_3)_2$, CH_2CH_2, PMe_3) [11–15]. A more current view of the reaction of magnesium and Mes^*PCl_2 is that the reductant generates the phosphorus centered radical $Mes^*(Cl)P^\bullet$ (Eq. (4)). Electron rich olefins can reduce Mes^*PCl_2 to diphosphene **1** and also produce EPR observable $Mes^*(Cl)P^\bullet$ [16]. It should also be noted that the reaction of Mg and Mes^*PCl_2 can yield other products, such as Mes*P(H)P(H)Mes*, under certain conditions [17].



(1)



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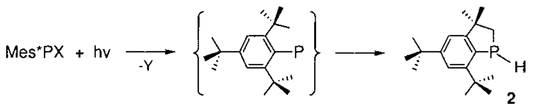

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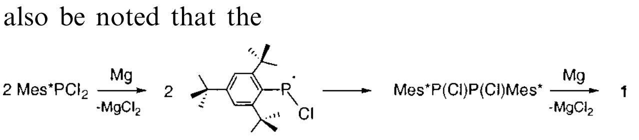


(4)

All of this work does not conclusively prove that the {Mes*P} phosphinidene cannot be generated from the reaction of Mg and Mes^*PCl_2. In fact, under relatively extreme conditions, flash vacuum pyrolysis of Mes^*PCl_2 over magnesium at 600 °C produces 2,4,6-tri-^{t}butylbenzene and the phosphaindan **2** in 20% yield [8]. In the current report we describe how modifying the nature of the magnesium metal and the reaction conditions for the reaction of magnesium and Mes^*PCl_2 can indeed yield the phosphaindan **2** in high yields at ambient conditions.

2. Results and discussion

We recently described the photochemical generation of phosphinidenes from phosphanylidene-σ^4-phosphoranes ($ArP{=}PMe_3$) and showed that they undergo various dimerization and insertion reactions [15]. During the course of this study an independently generated sample of phosphafluorene **3** was needed, which is the primary product of photolysis of $2,6\text{-}Trip_2C_6H_3P{=}PMe_3$. This phosphafluorene was first obtained by Power and coworkers by reduction of $2,6\text{-}Trip_2C_6H_3PCl_2$ with magnesium metal in 68% yield (Scheme 2) [9]. By contrast, reduction by potassium metal provides the diphosphene **4** as the main product. The formation of the phosphafluorene suggests the intermediacy of the phosphinidene $\{2,6\text{-}Trip_2C_6H_3P\}$.

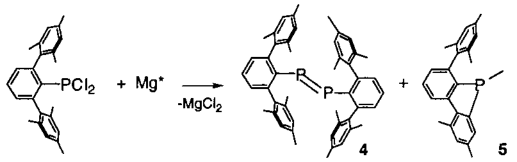
The mixtures obtained, however, may also reflect on the complexity of the reactions.

While seeking to maximize formation of the phosphafluorene relative to diphosphene, it was discovered that activation of the magnesium has profound impact on these reactions. One method that was facile and suitable for our needs was the activation of Mg turnings by stirring in THF overnight in the presence of small catalytic quantities of naphthalene. During this procedure the turnings lose their luster and become dull. The solution above the Mg turnings is decanted (minimizing contamination by naphthalene), and the Mg then weighed for *immediate* use. It is convenient to keep a batch of such activated turnings (Mg*) in the drybox for use as needed, stirring continuously in THF in the presence of small amounts of naphthalene.

Reduction of 2,6-$Trip_2C_6H_3PCl_2$ by one equivalent of Mg* turnings in THF produces phosphafluorene **3** as the sole product, as ascertained by ^{31}P-NMR spectroscopy of the reaction mixture. Furthermore, the reaction time is reduced from 24 h to 30 min. Such a result suggests that the phosphinidene {2,6-$Trip_2C_6H_3P$} is indeed formed by the action of the Mg* turnings on 2,6-$Trip_2C_6H_3PCl_2$.

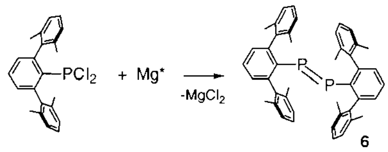
The use of this reductant on other sterically encumbered $ArPCl_2$ was then explored as a means to generate putative phosphinidenes {ArP}. The resulting products could be thus calibrated against the products obtained from the corresponding phosphinidenes {ArP} obtained by photolysis of the phosphanylidene-σ^4-phosphoranes $ArP{=}PMe_3$ bearing the same Ar groups [15].

The reaction of $DmpPCl_2$ (Dmp = 2,6-$Mes_2C_6H_3$) and one equivalent of Mg* turnings is rapid, and the ^{31}P-NMR spectrum of the reaction mixture after 45 min is shown in Fig. 1(b). For comparison, the ^{31}P-NMR spectrum of the products of photolysis of $DmpP{=}PMe_3$ is shown in Fig. 1(a). In both reactions, the diphosphene DmpP=PDmp (**4**) is the major product (90–95%). Clearly, these spectra are identical with the exception of the presence of PMe_3 in Fig. 1(a). It is noteworthy to mention that both spectra display the presence of a second species (5–10%) with a ^{31}P-NMR shift of δ −27 ppm. This phosphorus atom has no attached protons and has been tentatively assigned as the cyclometallated species **5** (Eq. (5)) by analogy to phosphafluorene **3**. This material has not yet been fully characterized, however, due to low yields and difficulty in separation from **4**.



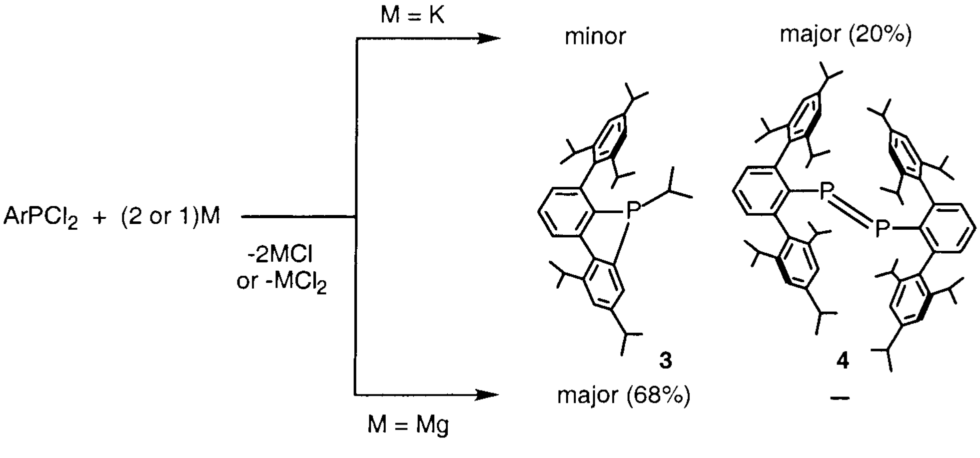
(5)

It is interesting to speculate why the two different *meta*-terphenyl ligated phosphinidenes behave differently. One reason may lie in the differences in the amount of electron density in the flanking aromatic rings in these systems. The Trip (Trip = 2,4,6-$^iPr_3C_6H_2$) rings are more electron-rich than the Mes rings, and hence, possibly more susceptible to attack by an electron deficient phosphorus center. The reaction of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3PCl_2$ [18] with Mg* turnings was thus examined with the anticipation that less cyclometallation might occur (and thus cleaner conversion to diphosphene) due to the less electron-rich xylyl rings that are susceptible to electrophilic attack. Indeed, this prediction is true (Eq. (6)) and the diphosphene **6** is quantitatively formed.



(6)

A parallel study of the photolysis of the new phosphanylidene-σ^4-phosphorane 2,6-(2,6-$Me_2C_6H_3)_2$-$C_6H_3P{=}PMe_3$ also revealed quantitative formation of diphosphene **6** and PMe_3. These results have prompted us to develop new *meta*-terphenyl ligands to examine the effect of other substituents (or lack of) on the outer



Scheme 2.

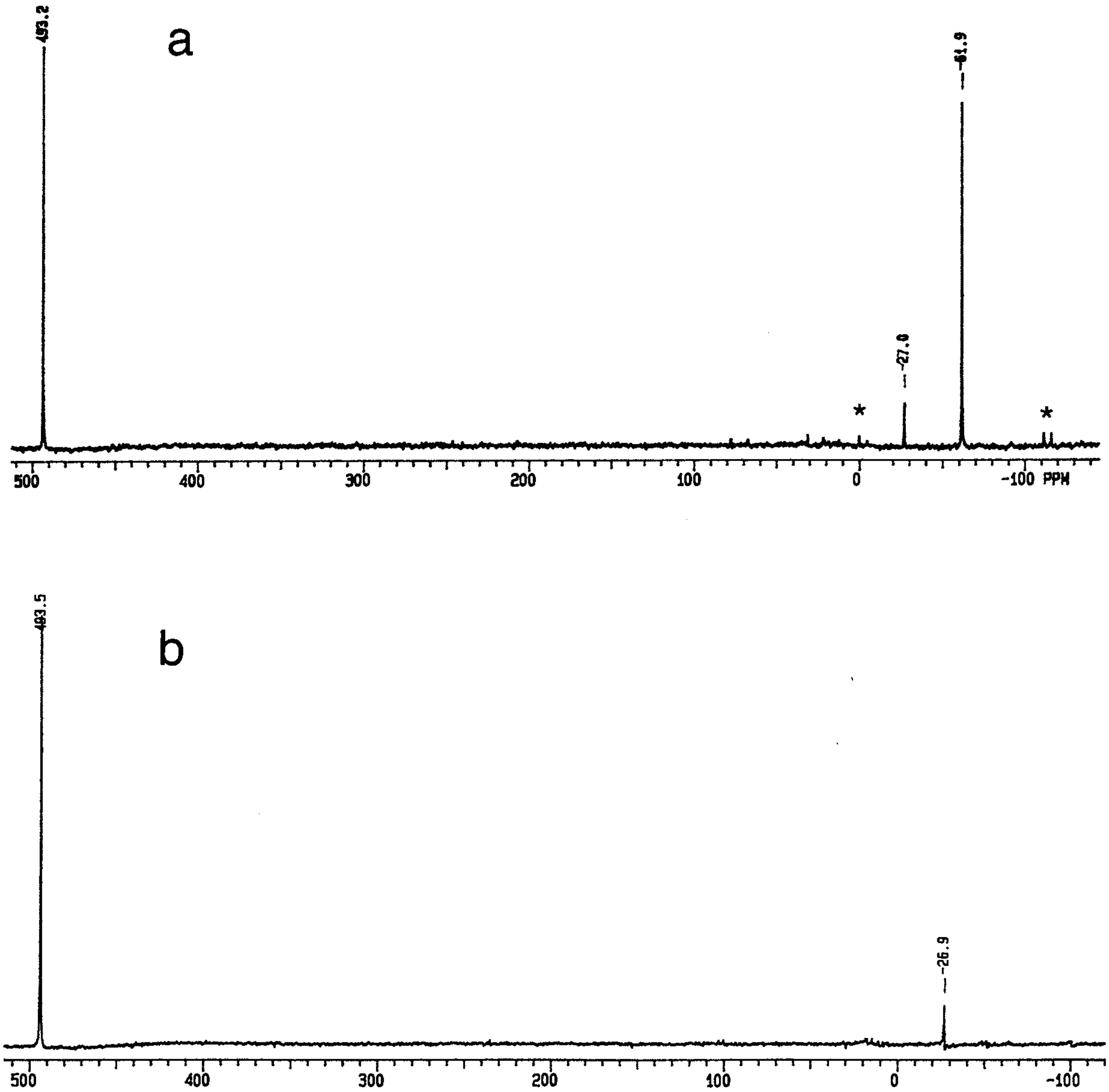


Fig. 1. (a) ^{31}P-NMR spectrum of photolysis of DmpP=PMe$_3$ in C_6D_6 after 1.5 h showing DmpP=PDmp, **5**, and PMe$_3$, from left to right (* indicates some remaining DmpP=PMe$_3$, quartz NMR tubes (Wilmad), 355 nm). (b) ^{31}P-NMR spectrum of reaction mixture of DmpPCl$_2$ and Mg* turnings showing DmpP=PDmp and **5**, from left to right.

aryl rings. Work is currently underway to test this concept.

The original synthesis and discovery of a phosphobenzene was then reexamined to determine if the reaction could be persuaded to proceed via phosphinidene intermediates, which would be indicated by formation of phosphaindan **2**. Reaction of Mes*PCl$_2$ with one equivalent of Mg* turnings in THF is rapid and complete in 30–45 min. ^{31}P-NMR spectroscopic analysis of a reaction aliquot was unfortunately disappointing. The major product was the diphosphene **1**. However, small amounts of phosphaindan **2** could be discerned in the spectrum. Operating under the assumption that lower concentrations of Mes*PCl$_2$ may promote unimolecular processes, it was found that slightly increased amounts of **2** could be obtained at lower concentrations. Reaction times were greatly increased, however.

It was then reasoned that it might be necessary to have a more activated form of magnesium. There are many methods reported for activation of Mg metal or for preparing reactive forms of Mg metal [19–22]. Closely related to our procedure is the use of catalytic amounts of anthracene to activate and 'solubilize' Mg metal [20]. Such systems utilize Mg(anthracene)(THF)$_3$ as a carrier for the reducing equivalents. Another closely related procedure uses sodium naphthalenide to reduce MgCl$_2$ to prepare reactive Mg* [19]. This form of highly activated magnesium powder was prepared and used in reactions with Mes*PCl$_2$. Reaction rates are very rapid (~ 10 min), but clean conversion of

Mes*PCl$_2$ to **2** proved challenging. Noted in the ^{31}P-NMR spectra of reaction aliquots were **1** and **2** as the major products, accompanied by Mes*(H)PP(H)Mes* ($\sim$10–20%). This material presumably arises from reduction of Mes*P=PMes* and subsequent protonation [17].

After a dozen trials or so, conditions were found that provided **2** in greater than 95% yield ($\sim$5% Mes*(H)PP(H)Mes*) from the reaction of Mg* powder and Mes*PCl$_2$. Several key factors were necessary for this accomplishment. The solvent THF must be rigorously dried. Even though the THF used in the initial studies was distilled from purple sodium benzophenone solutions and used in the drybox, this protocol was not sufficient. Further drying the THF by stirring with potassium metal for a 24 h period immediately prior to use gave best results. Furthermore, the activated magnesium powder used in the reaction must be used immediately after its generation. Use of Mg powder after some aging gave significant quantities of the diphosphene. Lower concentrations of Mes*PCl$_2$ also aided in clean conversion to **2**. Use of excess Mg* powder to expedite the reduction also leads to cleaner reactions. It also should be noted that one must be careful in these sorts of studies, for spectra showing **2** as the main product could also be obtained if an excess of Mg is used and if **1** is formed in significant amounts. Highly reactive Mg metal reduces **1** to a relatively stable radical anion, and this species is invisible by ^{31}P-NMR spectroscopy. Fortunately $\mathbf{1}^{\bullet-}$ is intensely purple in color and can be easily detected visually.

The parallels between the photochemistry of ArP=PMe$_3$ and the reductions of ArPCl$_2$ by Mg* are striking. For four different sterically encumbered ligands, a 1:1 correspondence in diphosphene and insertion products can be seen. It is easy to account for the CH or CC bond insertion products by attack of a phosphinidene into each corresponding type of bond (path D, Scheme 3). The mechanism of diphosphene formation is of interest. While it may be enticing to suggest that diphosphenes are formed by simple dimerization of two phosphinidenes (path A, Scheme 3), this hypothesis would require a buildup of a significant concentration of a highly reactive species for dimerization to be efficient. Alternative scenarios can be envisioned whereby the newly generated electrophilic phosphinidenes attack their immediate progenitor (which would be relatively nucleophilic by comparison), as shown in paths B and C, Scheme 3. We can indeed observe the diphosphine Dmp(Cl)PP(Cl)Dmp if one half equivalent of Mg* is used. However, as mentioned above, coupling of two Ar(Cl)P$^{\bullet}$ radical can also generate this species, as well as the reaction of a [ClMg{P(Cl)Dmp}] with DmpPCl$_2$. At this time a definitive answer is not available.

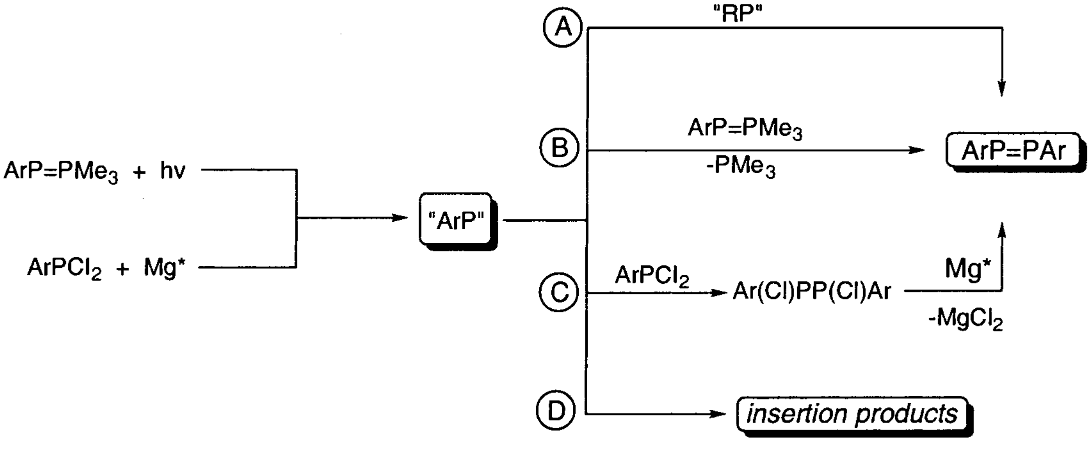
These results may have significant synthetic applications. Reduction of DmpPCl$_2$ with Mg* turnings in the presence of triphenylphosphine forms a mixture of the diphosphene and the corresponding phosphanylidene-σ^4-phosphorane DmpP=PPh$_3$ (^{31}P NMR(THF): δ 25.2, -138.8, $J_{PP} = 639$ Hz; Eq. (7)). This species could not be prepared by the methods used for

$$\mathrm{DmpPCl_2 + Mg^* \xrightarrow[-\,MgCl_2]{PPh_3} DmpP{=}PPh_3} \qquad (7)$$

trimethylphosphine analogue (i.e. Zn dust, DmpPCl$_2$, and PMe$_3$). Unfortunately separation of the desired product from the diphosphene and PPh$_3$ has proved difficult. Efforts to further refine our reduction techniques to improve selectivity and to investigate trapping of putative phosphinidenes by other reagents are currently underway.

3. Conclusions

In conclusion, we have demonstrated an interesting 1:1 correlation between the photochemical generation of phosphinidenes from phosphanylidene-σ^4-phosphoranes ArP=PMe$_3$, and the generation of phosphinidenes



Scheme 3.

by reduction of $ArPCl_2$ and activated magnesium. Although these experiments do not constitute absolute proof for phosphinidenes, the simplest explanation for the diversity of products and the correlation seems to point in this direction. In particular, the reduction of Mes^*PCl_2 by the Mg* powder provides further evidence that phosphinidenes are probably not involved in the original synthesis of diphosphene **1**. The difficulty in generating these reaction products that mimic the chemistry of phosphinidenes also suggest that other reactions summarized by Scheme 1 may not involve phosphinidene intermediates.

4. Experimental

4.1. General procedures

All reactions, unless stated separately, were performed in a Vacuum Atmospheres dry-box under dry N_2. All solvents were distilled from purple sodium–benzophenone solutions. The THF used in the reduction of Mes^*PCl_2 by Mg* powder was further dried by stirring with potassium metal for 24 h prior to its use. Mes^*PCl_2, 2,6-$Trip_2C_6H_3PCl_2$ [9], $DmpPCl_2$ [23], 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3PCl_2$ [18] were prepared as reported. ^1H-NMR spectra were recorded on Varian Gemini 300 or 200 MHz instruments and referenced using residual solvent proton signals. ^{31}P-NMR spectra were recorded on the Varian Gemini 300 instrument operating at 121.47 MHz and referenced to external H_3PO_4 standard. Mass spectrometry was performed at the CWRU departmental facility.

4.2. Preparation of Mg* turnings

A batch of magnesium turnings is stirred with a crystal of naphthalene in 5–10 ml THF overnight. The surface of the activated magnesium turnings appears much darker and a suspension of black powder appears in the solution. The activated magnesium turnings may be stored in THF in the dry box in a capped vial or flask for extended periods of time. For use in reactions, the required amount of magnesium turnings is weighed out by removing them from the capped vial or flask with a spatula and THF wicked away by brief contact with Kimwipes®. The weighed amount is then quickly transferred to the reaction vessel.

4.3. Reaction of 2,6-$Trip_2C_6H_3PCl_2$ and Mg* turnings

A 20 ml vial was charged with 0.100 g (0.17 mmol) of 2,6-$Trip_2C_6H_3PCl_2$ and 4.2 mg of activated magnesium turnings (0.17 mmol), followed by addition of 5 ml of THF. The reaction solution progressively transforms from a clear to a brown–yellow to an eventual dark color. After 30 min, ^{31}P-NMR spectroscopy of a reaction aliquot indicates quantitative formation of **3**.

4.4. Reaction of $DmpPCl_2$ and Mg* turnings

A 20 ml vial was charged with 0.100 g (0.24 mmol) of $DmpPCl_2$ and 5.9 mg of activated magnesium turnings (0.24 mmol), followed by addition of 5 ml of THF. The mixture progressively transforms from a clear to a deep orange color. After 45 min, ^{31}P-NMR spectroscopy shows that DmpP=PDmp (90–95%) and the proposed cyclometallated species **5** (5–10%) are formed.

4.5. Reaction of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3PCl_2$ and Mg* turnings

The reaction of 0.100 g 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3PCl_2$ (0.26 mmol) and 6.3 mg Mg* (0.26 mmol) turnings in 10 ml THF at room temperature is complete in 30 min, ^{31}P-NMR spectroscopy shows the diphosphene **6** as the sole product.

4.6. Synthesis of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3P{=}PMe_3$

To a solution of 0.300 g of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3PCl_2$ (0.77 mmol) in 5 ml of THF was added 0.100 g Zn dust (1.53 mmol)) and 0.35 g dry PMe_3 (2.55 mmol). After 4.5 h of stirring, and ^{31}P-NMR spectroscopy indicated clean formation of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3$-$P{=}PMe_3$ (^{31}P-NMR: δ −1.54 (d, $J_{PP} = 572$ Hz) and −113.2 (d, $J_{PP} = 572$ Hz)). Filtration and removal of solvent and excess PMe_3 in vacuo gave a 92% yield of essentially pure 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3P{=}PMe_3$. Further purification by recrystallization from hexanes at −35 °C affords yellow crystalline 2,6-(2,6-$Me_2C_6H_3)_2$-$C_6H_3P{=}PMe_3$ in 70% yield. ^1H-NMR (300 MHz, C_6D_6) δ 0.55 (dd, 9H, $^2J_{HP} = 12$, $^3J_{HPP} = 3$ Hz), 2.36 (s, 12H), 6.89 (d, 2H, $J_{HH} = 7$ Hz), 7.02–7.14 (m, 7H).

4.7. Photolysis of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3P{=}PMe_3$

A 0.4 M solution of 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3P{=}PMe_3$ was prepared by dissolving 0.157 g (0.400 mmol) 2,6-(2,6-$Me_2C_6H_3)_2C_6H_3P{=}PMe_3$ in 1 ml C_6D_6. A 0.4 ml aliquot of this solution was placed in a quartz NMR tube and was irradiated under conditions identical to photolysis of $DmpP{=}PMe_3$. [15]. After 1 h, ^{31}P-NMR spectroscopy indicated exclusive formation of the diphosphene **6** and PMe_3.

4.8. Reaction of Mes^*PCl_2 and Mg* powder

The following procedure was adapted from the literature [19]. A solution of sodium napthalenide was generated by stirring 1.00 g naphthalene (7.80 mmol) and

0.170 g Na (7.39 mmol) in 8 ml THF for 2 h. To this solution was added 0.400 g $MgCl_2$ (4.20 mmol). After addition of the $MgCl_2$ the deep green sodium naphthalide solution turns brown and eventually darkens to a nearly black slurry over a 2 h period. This resulting slurry was diluted to 100 ml with THF and transferred to a 250 ml round bottom flask. A 0.040 g sample of Mes^*PCl_2 (0.12 mmol) was added all at once with vigorous stirring. After about 5 min, the reaction mixture is filtered through a medium porosity frit to remove excess Mg* powder and the solvent is removed in vacuo. The result is almost exclusive formation of **2**, with ~5% of Mes*P(H)P(H)Mes*, as ascertained by ^{31}P-NMR spectroscopy.

4.9. Reaction of $DmpPCl_2$ and Mg turnings and PPh_3*

A 20 ml vial was charged with 0.100 g (0.24 mmol) of $DmpPCl_2$, 5.9 mg of activated magnesium turnings (0.24 mmol), 0.063 g of PPh_3 (0.24 mmol) and 5 ml of THF. The solution progressively transforms from a clear to a yellow to an eventual light orange color. After 45 min, the reaction is complete and ^{31}P-NMR spectroscopy indicates formation of DmpP=PDmp and $DmpP{=}PPh_3$ in about a 2:3 ratio. ^{31}P-NMR(THF): δ 25.2, -138.8, $J_{PP} = 639$ Hz.

Acknowledgements

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