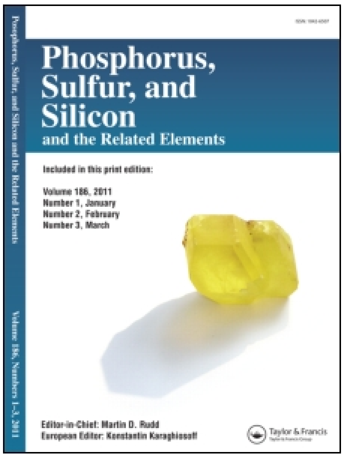


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Diphosphene and Phosphoranylidenephosphine Formation from a Terminal Phosphinidene Complex

Eugenijus Urnėžius; Shashin Shah; John D. Protasiewicz

To cite this Article Urnėžius, Eugenijus , Shah, Shashin and Protasiewicz, John D.(1999) 'Diphosphene and Phosphoranylidenephosphine Formation from a Terminal Phosphinidene Complex', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 137 — 139

To link to this Article: DOI: 10.1080/10426509908546201

URL: http://dx.doi.org/10.1080/10426509908546201

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 137-139
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Diphosphene and Phosphoranylidenephosphine Formation from a Terminal Phosphinidene Complex

EUGENIJUS URNĖŽIUS, SHASHIN SHAH and JOHN D. PROTASIEWICZ

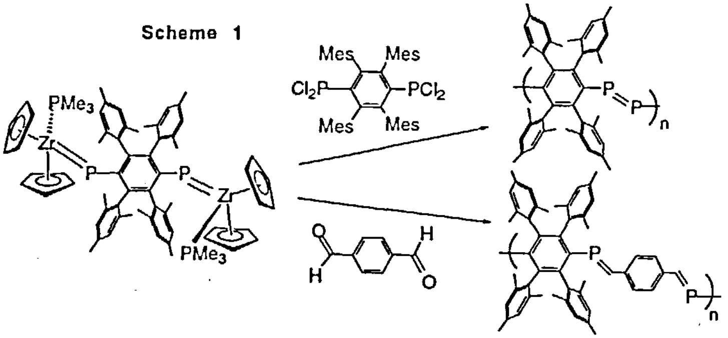
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078

The zirconium phosphinidene complexes [$Cp_2Zr{=}PDmp(PR_3)$] (Dmp = 2,6-$Mes_2C_6H_3$; R = Me: **1a**; R = Bu: **1b**) form the diphosphene DmpP=PDmp, [Cp_2ZrCl_2], and the phosphoranylidenephosphines $DmpP{=}PR_3$ (**3a**, **3b**) upon reaction with $DmpPCl_2$.

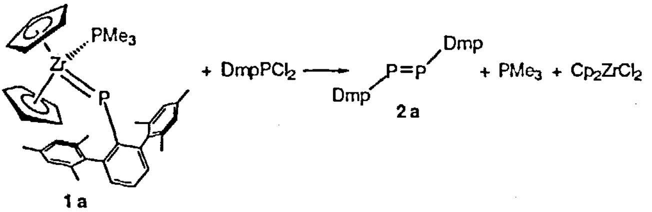
Keywords: phosphinidene complex; phosphoranylidenephosphine

Our research is directed to the synthesis of new materials having P=P and P=C multiple bonds (Scheme 1). Our particular approach features bis-phosphinidene complexes for synthesis of extended materials. Zirconium phosphinidene complexes, such as [$Cp_2Zr{=}PMes^*(PMe_3)$] (Mes^* = 2,4,6-$^tBu_3C_6H_2$) have been established as

Scheme 1

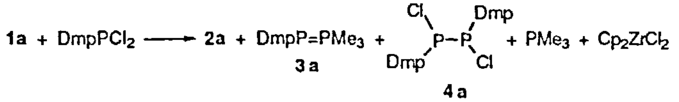


efficient phosphinidene precursors for synthesis of new materials.[1] Owing to the need to simultaneously provide steric shelter for two low coordinate phosphorus atoms, we must move from aromatics having protective *ortho-tert*-butyl groups (2,3,5,6-${}^{t}Bu_4C_6X_2$ aromatic systems would be very difficult or impossible to prepare) to 2,3,5,6-$Ar_4C_6X_2$ aromatic linking units. We have developed phosphorus systems containing the sterically encumbered group Dmp (Dmp = 2,6-$Mes_2C_6H_3$) which represents half of this linking group,[2,3] and prepared the analogous zirconium phosphinidene complex [Cp_2Zr=PDmp(PMe_3)] (**1a**) and tested its efficacy for diphosphene synthesis (eq. 1). Quite unexpectedly, the reaction actually produces a



(1)

mixture of three species (eq. 2), including the anticipated diphosphene DmpP=PDmp (**2a**). The two new species, the phosphoranylidenephosphine DmpP=PMe_3 (**3a**)[4] and the dichlorodiphosphine DmpP(Cl)P(Cl)Dmp (**4a**), have been independently



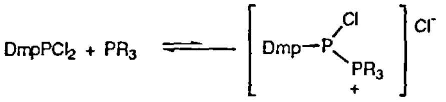
$$\mathbf{1a} + DmpPCl_2 \longrightarrow \mathbf{2a} + \underset{\mathbf{3a}}{DmpP{=}PMe_3} + \underset{\mathbf{4a}}{Dmp(Cl)P{-}P(Cl)Dmp} + PMe_3 + Cp_2ZrCl_2 \qquad (2)$$

prepared and characterized. The reaction of **1a** with Mes*PCl_2 (Mes* = 2,4,6-${}^{t}Bu_3C_6H_2$) reveals another level of complexity for these reactions, for not only is Mes*P=PMes*, Mes*P=PMe_3, and [Cp_2ZrCl_2], produced, but also **2a**, **3a**, and the mixed diphosphene Mes*P=PDmp.

The presence of the multiple PP bond forming reactions of **1** warranted further investigation prior to our successful use of Zr=P bonds as described in Scheme 1. Phosphoranylidenephosphine formation in these reactions beckoned for experiments to be performed in the presence of added PMe_3. Furthermore, previous work has suggested that the reactivity of **1a** may require initial PMe_3 dissociation.[1] Early studies, however, revealed that a slow direct reaction occurs between excess PMe_3 and $DmpPCl_2$ to yield DmpP=PMe_3 and Me_3PCl_2. Solutions of excess PBu_3 and $DmpPCl_2$ do not show any evidence for reaction. In order to probe the mechanism between **1a** and $DmpPCl_2$ in more detail and in the presence of excess PR_3, we have also prepared [$Cp_2Zr{=}PDmp(PBu_3)$] (**1b**).

Compound **1b** reacts analogously with $DmpPCl_2$ to produce **1a** and forms **2a**, $DmpP{=}PBu_3$ (**3b**), and **4a**. Upon addition of increasing amounts of PBu_3, the *reaction produces greater amounts of* **3b**. *Upon adding 10 equivalents of* PBu_3, **3b** is produced in ≥95% yield. Under these conditions the rate of reaction is promoted by at least tenfold.

No evidence for electrophilic behavior for **1** was found by ^{31}P NMR spectroscopic examination of solutions of **1** and PR_3. We thus propose that the mechanism for phosphoranylidenephosphine formation involves initial activation of the dichlorophosphine $DmpPCl_2$ by PR_3 (eq. 3).



(3)

Acknowledgments

The authors thank the Department of Chemistry at CWRU and the National Science Foundation (CHE-9733412) for support of this work.

References

[1] Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921.
[2] Umezius, E.; Protasiewicz, J. D. *Main Group Chemistry* **1996**, *1*, 369–372.
[3] Shah, S.; Burdette, S. C.; Swavey, S.; Urbach, F. L.; Protasiewicz, J. D. *Organometallics* **1997**, *16*, 3395–3400.
[4] Shah, S.; Protasiewicz, J. D. *J. Chem. Soc. Chem. Commun.* **1998**, in press.