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Communications

Metallacycle Transfer Reaction from Titanacyclopropenes: A New and Versatile Approach to Phosphirenes[†]

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Summary: Titanocene complexes of various electron-poor alkynes react with $PhPCl_2$ *and* PCl_3 *to afford the corresponding 1-phenyl and 1-chlorophosphirenes. A similar Ti to P transfer reaction occurs when dialkoxytitanium complexes of electron-rich alkynes are used.*

Metallacycle transfer from zirconium or titanium to group 13−16 elements is a convenient synthetic route to various heterocycles that are sometimes hardly available by classical methodologies.[1] Since the initial discovery by Fagan and Nugent, who reported in 1988 the successful preparation of a 1-phenyl-2,3,4,5-tetramethylphosphole from the corresponding zirconacyclopentadiene,[2] a number of transformations leading to four-, five-, or six-membered rings have been reported. Most of these transformations focused on phosphorus heterocycles, in view of their importance as synthons and ligands.[3] Four-membered rings such as 1,2-dihydrophosphetes were prepared independently by Doxsee and Tumas from titanacyclobutenes and dichlorophosphines.[4] In 1996, we described the first transfer to a six-membered ring through the synthesis of 1,3,2-diazaphosphinines.[5] Surprisingly, although a number of zircona- and some titanacyclopropenes are known, no metallacycle transfer reaction to heteroatom-containing three-membered rings has been reported so far (Scheme 1).[6,7]

The absence of such a method is of importance if one considers the powerful synthetic potential of phosphirenes in phosphorus chemistry.[8] Up to now, free phosphirenes are essentially accessible either by the direct condensation of dichlorophosphines with alkynes

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[†] This article is dedicated to Prof. Edgar Niecke on the occasion of his 60th birthday.

[1] For pertinent articles including leading references, see: (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889. (b) Doxsee, K. M.; Mouser, J. K. M.; Farahi, J. B. *Synlett* **1992**, 13−22.

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[3] (a) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365−369. (b) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Dupuis, L.; Meunier, P. *J. Chem. Soc., Chem. Commun.* **1997**, 279−280. (c) Zablocka, M.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Skowronska, A.; Meunier, P. *J. Chem. Soc., Chem. Commun.* **1997**, 1239−1240.

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[6] When this work was already completed, an independent study describing the synthesis of some phosphirenes and phosphiranes from dichlorophosphanes and intramolecularly P═O stabilized zirconacyclopropenes and zirconacyclopropanes was brought to our attention by J. P. Majoral. Zablocka, M.; Miguel, Y.; Igau, A.; Majoral, J.-P.; Skowronska, A. *Chem. Commun.*, in press.

[7] A zirconium-mediated route to phosphiranes relying on a phosphinidene transfer reaction has been reported: Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914−11921.

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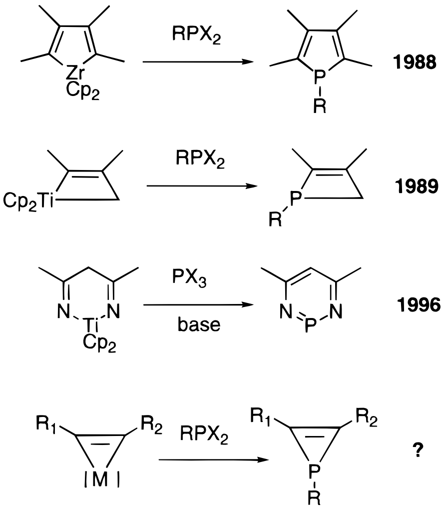
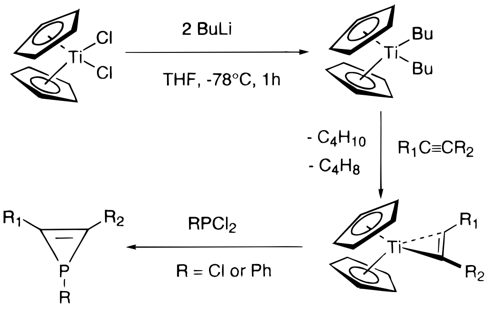
Scheme 1



followed by the reduction of the corresponding phosphirenium salts[9] or by decomplexation of the corresponding $W(CO)_5$ complexes.[10] Another interesting approach which gives access to a wide range of P-functionalized derivatives relies on the chemistry of *P*-chlorophosphirenes *via* nucleophilic substitution reactions.[11] Unfortunately, these latter compounds are not available using the classical condensation of phosphorustrichloride with alkynes and their preparation involves multistep processes requiring sophisticated starting materials.[10d,12] Therefore, a new and direct access to 1-chlorophosphirenes is desirable. The reaction of metallacyclopropenes with phosphorus trichloride should provide such an easy access to these P-chloro compounds.

With the intention of developing a very simple method, we focused our studies on titanacyclopropenes,[13] which are known to be stable as 16-electron complexes, unlike their zirconium counterparts.[14] In general, titanacyclopropenes are obtained in moderate yields from alkynes by condensation of titanocene, which is generated in situ by reduction of $TiCp_2Cl_2$ with magnesium.[14c,d] To achieve a more efficient access, excluding further purification, we investigated the direct condensation of alkynes with $TiCp_2Bu_2$, a convenient precursor for titanocene.[15] In a typical experiment,[16] a solution of $TiCp_2Cl_2$ in THF was reacted with 2 equiv of BuLi at −80 °C for 1 h. After addition of the alkyne at −78 °C and warming to room temperature, treatment of the resulting red-brown mixture with $RPCl_2$ or PCl_3 afforded the corresponding phenyl- or chlorophosphirenes with the concomitant release of the starting $TiCp_2Cl_2$. After a simple extraction with dry hexane, the phosphirenes were isolated in good to excellent yields (65−95% see Scheme 2).

Scheme 2



1: $R_1 = R_2 = R = Ph$ (80%)
2: $R_1 = R_2 = SiMe_3$, $R = Ph$ (80%)
3: $R_1 = Ph$, $R_2 = SiMe_3$, $R = Ph$ (65%)
4: $R_1 = Ph$, $R_2 = Ph$, $R = Cl$ (80%)
5: $R_1 = Ph$, $R_2 = SiMe_3$, $R = Cl$ (88%)
6: R_1 = *n*-Bu, $R_2 = SiMe_3$, $R = Cl$ (90%)
7: $R_1 = R_2 = SiMe_3$, $R = Cl$ (85%)
8: $R_1 = Ph$, R_2 = *t*-Bu, $R = Cl$ (95%)
9: $R_1 = Fc$, $R_2 = SiMe_3$, $R = Cl$ (75%)

Apparently this type of transformation cannot be transposed to electron-rich alkynes. Indeed, the reaction of $[TiCp_2]$ with 3-hexyne or *tert*-butylmethylacetylene, followed by quenching with $PhPCl_2$ or PCl_3, exclusively led in each case to the recovery of the starting chlorophosphine and the alkyne. This is no doubt due to the instability of the corresponding titanacyclopropenes. Such complexes are only stable when one of the ligands at least is a pentamethylcyclopentadienyl group.[14b] To circumvent this limitation, we then investigated the reactivity of a titanocene equivalent,[17] the easily available transient complex $[Ti(O\text{-}i\text{-}Pr)_2]$, which has recently found numerous applications in

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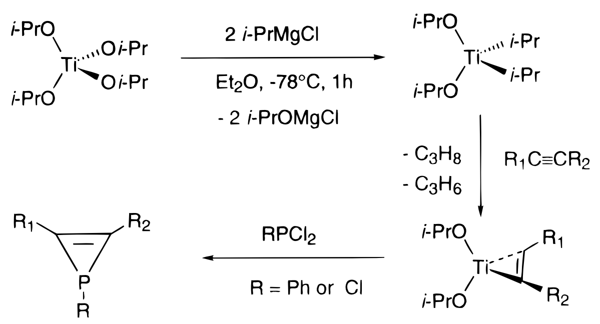
(16) A representative experiment is as follows: Cp_2TiCl_2 (10^{-3} mol, 0.25 g) is dissolved in 10 mL of THF and cooled to −78 °C. Two equivalents of BuLi (2.1 10^{-3} mol, 1.33 mL, 1.5 mol/L) is slowly syringed in, and the temperature is kept at −78 °C for 1 h. The alkyne (10^{-3} mol) is then added, and the mixture is warmed to room temperature. After it is stirred for 15 min, the solution is cooled to −50 °C and 1 equiv of $RPCl_2$ is syringed in. The mixture is warmed back to room temperature and stirred for an additional 1 h. The mixture is taken to dryness and the phosphirene extracted with hexanes.

Scheme 3



10: R$_1$ = R$_2$ = Et, R = Ph (65%)
11: R$_1$ = *t*-Bu, R$_2$ = Me, R = Ph (72%)
12: R$_1$ = R$_2$ = Et, R =O*i*-Pr (60%)

organic synthesis.[18] Worthy of note is the transient formation of diisopropoxytitanacyclopropenes from Ti(O-*i*-Pr)$_4$ and *i*-PrMgCl, evidenced by trapping reactions.[18b] We thus investigated the reactivity of these dialkoxytitanacyclopropenes toward PhPCl$_2$ and PCl$_3$.[19] As illustrated in Scheme 3, the synthesis of *P*-phenyl derivatives can be carried out without any difficulties. On the other hand, the procedure described here does not allow the isolation of the corresponding *P*-chlorophosphirenes, since *i*-PrOMgCl, released during the formation of [Ti(O-*i*-Pr)$_2$], reacts at the P−Cl bond to afford the corresponding isopropoxyphosphirenes.

In conclusion, we have developed a highly efficient and simple method for the synthesis of a wide range of phosphirenes. The ready availability of *P*-chloro derivatives is an important result which paves the way for a systematic study of P-functionalized phosphirenes. Further developments in phosphorus chemistry, as well as the extension of this type of metallacycle transfer to elements of other groups, are currently under investigation and will be reported in due course.

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Supporting Information Available: Text giving full experimental details and analytical data for compounds **1**−**12** (2 pages). Ordering information is given on any current masthead page.

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(19) A mixture of Ti(O-*i*-Pr)$_4$ (10^{-3} mol, 297 μL) and alkyne (10^{-3} mol) in 9 mL of Et$_2$O is cooled to −78 °C. Two equivalents of *i*-PrMgCl (2.0 10^{-3} mol, 1 mL, 2.0 mol/L) is then slowly syringed in, and the temperature is raised and kept for 1 h at −50 °C. One equivalent of RPCl$_2$ (10^{-3} mol) is then added and the mixture brought back to room temperature. After 1 h, the mixture is filtered and the solution reduced to dryness *in vacuo*. 1-Phenylphosphirenes are purified by fast column chromatography using hexane as eluant. 1-isopropoxyphosphirene (**12**) was distilled under vacuum using a bulb-to-bulb apparatus.