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$[Cp_2ZrHCl]_n$ A Useful Reducing Agent in Phosphorus Chemistry

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Abstract: Selective reductions of P=O, P=S, >C=C<, C=O bonds with $[Cp_2ZrHCl]_n$ are described, as well as halogen-hydride exchanges.

Reduction of phosphine oxides or sulfides can be achieved using a number of reagents[1] the choice being dictated by the sensitivity of the oxide or sulfide to reduction and by the presence of functional groups directly or not linked to phosphorus.

The most popular reductants are silanes which can be used generally in the presence of other functional groups in the molecule. However, the other reducing agents (lithium aluminium hydride, sodium borohydride, alanes, etc.) are not so selective and many more groups are sensitive to reduction by them.

We wish to report herein the remarkable behavior of the Schwartz reagent $[Cp_2ZrHCL]_n$ **1** as a versatile and selective efficient reducing agent towards a variety of functionalized phosphine oxides and sulfides.

In order to evaluate the reductant power of **1** towards tetracoordinated pentavalent phosphorus species, addition of **1** was first carried out on the phosphine oxides **2**-**4** (Scheme 1). Addition of 1 equiv. of **1** to a THF solution of compound **2** gives only half of the expected phosphine **5** and one additional equiv. of **1** is

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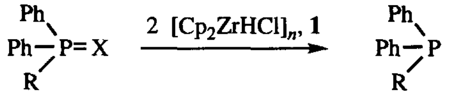
[1] Tél. : (33) (0)5 61 33 31 23 - Fax : 33 (0)5 61 55 30 03

necessary to go to completion with the quantitative formation of **5**. The presence of more bulky substituents on phosphorus dramatically reduces the yield of the resulting phosphanes **6** and **7** which can be however obtained in satisfactory yields (55 and 50% respectively) and in mild conditions when **3** and **4** are treated with **1** (2 equiv.).[3,4] Reduction of triphenylphosphine sulfide **8** into triphenylphosphine **9** easily occurs by heating **8** in the presence of **1** (2 equiv.) in THF at 60°C for 3 h (95 % yield).

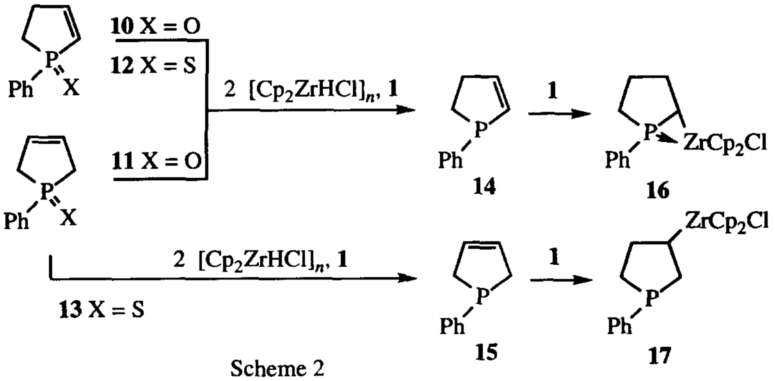


2 - 4 **5 - 7**

X = O **2, 5** R = Et
3, 6 R = Cy
4, 7 R = t-Bu
X = S **8, 9** R = Ph

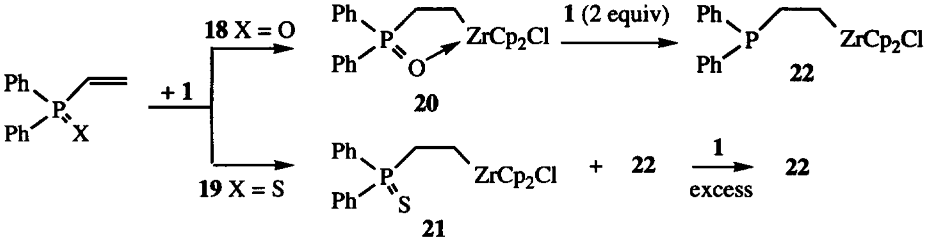
Scheme 1

Selective reduction on phosphorus also takes place when phospholene oxides **10** and **11** or sulfides **12** and **13** are treated with **1** (2 equiv.) with the formation of phospholenes **14** or **15**[4] (scheme 2). No reduction of the carbon-carbon double bond can be detected. This selective reduction is unexpectedly accompanied by the migration of the double bond in the case of **11**. Of course further addition of **1** (1 equiv.) to **14** or **15** affords the expected hydrozirconated phospholanes **16** and **17**.[5]



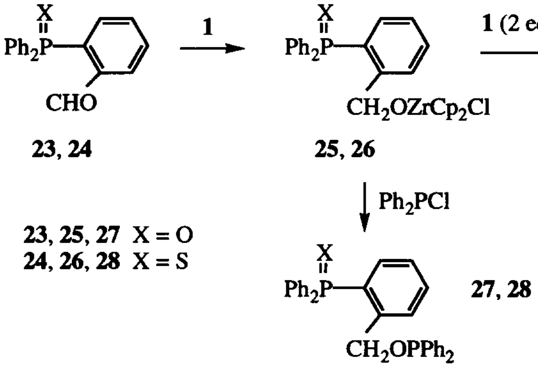
Scheme 2

Due to the highest reactivity of linear alkenes towards hydrozirconation, a reverse selectivity is observed when the vinylphosphine oxide **18** is reacted with **1**: hydrozirconation of the carbon-carbon double bond only takes place with the formation of the cyclic adduct **20**. Reduction of the phosphoryl group in **20** occurs when 2 equiv. of **1** is added (scheme 3) (80 % yield). A similar reaction performed with **1** and the vinyl phosphine sulfide **19** (room temperature, stirring for 20 h) allows to characterize the hydrozirconated phosphine sulfide **21** (60% yield) and the corresponding phosphine **22** (10% yield) (Scheme 3).[6] An excess of **1** is needed to allow the reaction to go to completion i.e. to transform **21** into **22** (74 % yield).



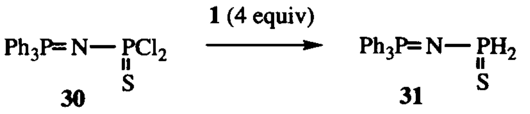
Scheme 3

Again a selective reaction is observed when **1** (1 equiv.) is added to a THF solution of the phosphine oxide **23** or sulfide **24**, bearing a carbonyl group. Hydrozirconation takes place quantitatively on the carbonyl group affording derivatives **25** or **26** which can be treated with diphenylchlorophosphine to give **27** (80 % yield) or **28** (82 % yield) (scheme 4).[4] It is noteworthy that addition of 3 equiv. of **1** to **23** or **24** leads to both hydrozirconation of the C=O group and reduction of the phosphoryl or thiophosphoryl group with quantitative formation of **29**.



Scheme 4

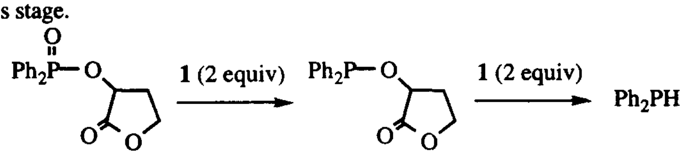
Another selective reaction involving **1** can be emphasized. Treatment of the N-substituted iminophosphorane **30** with **1** affords exclusively the thiophosphane **31**[4] arising from a clean halogen-hydride exchange reaction: no reduction of the P=S bond is detected. (**31** δ ^{31}P δ: -5.5 (dt $^{1}J_{PH}$ = 488.5 Hz, $^{2}J_{PP}$ = 9.9 Hz, P(S)H$_2$), 18.4 (d, $^{2}J_{PP}$ = 9.9 Hz, Ph$_3$P) (65 % yield from NMR) (scheme 5).



$$\mathrm{Ph_3P{=}N{-}\underset{\underset{S}{\|}}{P}Cl_2} \xrightarrow{1\ (4\ \mathrm{equiv})} \mathrm{Ph_3P{=}N{-}\underset{\underset{S}{\|}}{P}H_2}$$

Scheme 5

It was already demonstrated that the addition of **1** (2 equiv.) on β-, γ- or δ lactones takes place with ring opening and formation of dizirconated species.[7] Such a reaction does not occur when the phosphorylated lactone **32** is submitted to react with **1** (2 equiv.). Once again clean and selective reactions are observed. The first one is the reduction of the phosphinate group leading to the P_{III} species **33** (δ ^{31}P = +119 ppm) (90 % yield). Further addition of two additional equiv. of **1** to **33** provoks a phosphorus oxygen single bond cleavage and the formation of the secondary phosphane Ph_2PH (scheme 6). No ring opening reaction involving **32** or **33** is detected at this stage.



32 **33**

Scheme 6

In conclusion, the Schwartz reagent appears to be a remarkable agent acting selectively as a reducing agent towards P=S, P=O, C=C or C=O bonds, as a hydride transfer reagent towards halogenated phosphorus species; it even facilitates the cleavage of P-O bonds. Applications of these useful properties of **1** in organic phosphorus chemistry are in progress.

Acknowledgements

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References and notes

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3. Experimental conditions for the reduction of **2**-**4**: 4 h at 40°C then 48 h at 22°C in THF for **2**; 14 h at 55°C in THF (55% yield) for **3**; 20 h at 50°C in THF for **4**.
4. All the new compounds were isolated and fully characterized by ^{31}P, ^{1}H, ^{13}C NMR, mass spectrometry and elemental analysis.
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