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A New Versatile Route for the Conversion of Phospholes into Phosphinines

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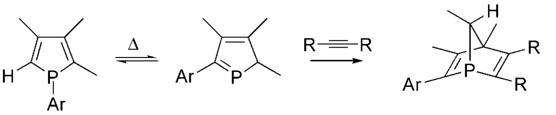
As a result of their aromaticity, phosphinines play a central role in phosphorus heterocyclic chemistry and, since the demonstration of their extraordinary efficiency as ligands in the rhodium-catalyzed hydroformylation of olefins,[1] the need for new versatile synthetic methods that allow the tuning of their electronic and steric properties becomes even more evident. We have, some time ago, demonstrated that the chemistry of the easily available phospholes was governed for a large part by the readily attained equilibrium between 1*H*- and 2*H*-phospholes.[2] From a synthetic standpoint, a major consequence of this equilibrium is that 1-phosphanorbornadienes become easily available through the reaction of 2*H*-phospholes with alkynes [Eq. (1)].



(1)

The versatility, the reaction conditions, and the efficiency of this cycloaddition chemistry heavily depend on the substitution scheme of the phosphole partner. By far the best phosphole in this respect is the readily made[3]1-phenyl-3,4-dimethylphosphole. From another standpoint, the ready availability of 1-phosphanorbornadienes designated them as natural starting points for the synthesis of phosphinines by extrusion of the carbene bridge. The strain of the bridge, the relative weakness of the P–C bonds, and the aromaticity of the phosphinine product suggested a rather easy transformation. Unfortunately, during a first series of attempts some time ago, we met a limited success in this direction. It appeared that only the 1-phosphanorbornadienes with a diphenylcarbene bridge made from 1,2,5-triphenylphosphole are susceptible to be transformed into phosphinines and, even in this case, the reaction conditions are drastic (230 °C) and the versatility is very limited.[4] Even worse, the 1-phosphanorbornadienes produced from 1-phenyl-3,4-dimethylphospholes proved to yield only decomposition products upon thermolysis. We reasoned that this extrusion is so difficult because the ground state of carbenes is a triplet,[5] thus implying that the extrusion is not a concerted but a stepwise process. On the basis of this working hypothesis, we decided to completely change our synthetic approach.

Our aim was to change the reaction pathway so that the extruded fragment would have a singlet ground state. Since there is no practical way to synthesize the 1-phosphanorbornadienes with aminocarbene bridges, we were led to investigate the oxidation of the strained P–C bridge bond as previously described in the literature.[6] This oxidation has two adverse effects for the kind of chemistry that we wanted to perform: it reduces the strain of the bridge and replaces a relatively weak P–C by a stronger P–O bond. Nevertheless, we were confident that the concerted extrusion of a carbonyl derivative would prove easier than the non-concerted extrusion of a carbene. This is indeed the case. Our preliminary experiments were carried out with compound **1a**, easily made from 1-phenyl-3,4-dimethylphosphole and diphenylacetylene. The oxidation was performed by hydrogen peroxide in xylene at 80 °C. The oxidized product **2a** was then converted into the corresponding P=S derivative **3a** by a stoichiometric amount of P_4S_{10} at 70 °C. In line with our expectations, it proved possible to perform the reduction-extrusion on **3 a** at only 180 °C using 1,2-bis(diphenylphosphino)ethane (dppe) as the reducing agent (Scheme 1).

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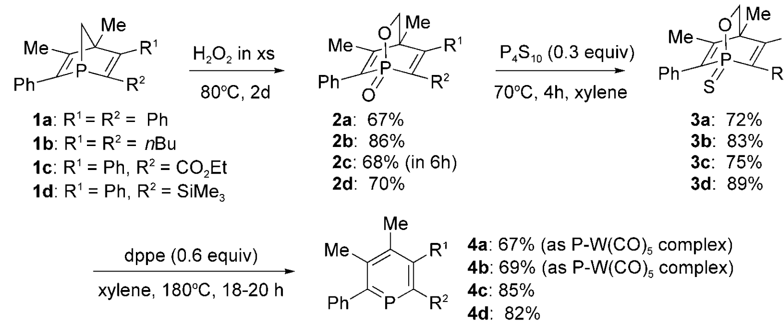
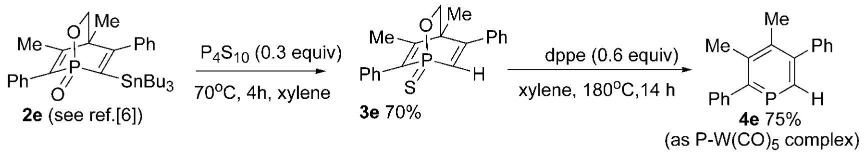


Scheme 1. Synthesis of phosphinines from 7-unsubstituted 1-phosphanorbornadienes.

Phosphinine **4a** was characterized as its P−W(CO)$_5$ complex (made by reaction with [W(CO)$_5$(MeCN)] at 60 °C in THF). This chemistry was duplicated without any problem with 5-decyne to give the tetraalkylphosphinine **4b**. We were eager to check whether this route involving milder conditions than our older scheme (180 vs. 230 °C) was compatible with functionalities. The new scheme was easily transposed for the synthesis of the 2-ethoxycarbonylphosphinine **4c**. In this case, the phosphinine is more resistant toward oxidation and was characterized as such. The superiority of the new scheme was confirmed by our experiments with phenyl(trimetylsilyl)acetylene. Phosphanorbornadiene **1d** was converted into the 2-trimethylsilylphosphinine **4d** with an overall yield of 51 %, whereas the former route appeared to be incompatible with the silyl substituent. For the tin derivative **1e** (R^1 = Ph, R^2 = $SnBu_3$), the conversion followed a different path (Scheme 2). Indeed, the tin substituent was lost during the sulfurization step. Replacing P_4S_{10} by the milder Lawesson reagent did not prevent this loss. It must be noted, however, that the 2-unsubstituted phosphinine **4e** (R^2 = H) is difficult to make from phenylacetylene due to the poor yield of the synthesis of the starting phosphanorbornadiene.



Scheme 2. Synthesis of a 2-unsubstituted phosphinine from a tin 2-substituted 1-phosphanorbornadiene.

The P−W(CO)$_5$ complex of **4e** was characterized by X-ray crystal structure analysis (Figure 1). We note that the P−C bond lengths 1.703(4) versus 1.731(3) Å are significantly different. In another vein, we noticed that the $^1J_{PW}$ coupling constant is significantly lower when comparing the complex of **4e** (264.7 Hz) with the complex of **4a** (275.5 Hz). This coupling is known to be correlated with the nucleophilicity of the phosphorus lone pair: the higher the nucleophilicity, the lower the coupling.[7] As expected, both complexes are on the high side with respect to triphenylphosphine (245 Hz), but the influence of the substitution pattern appears to be higher than expected in phosphinines.

Changing the substituents on the side of the alkynes is the most evident way to get a range of different phosphinines by this method. Using the versatility of the 1,5-shifts in phosphole chemistry[2] is another possibility. We have chosen to illustrate this possibility by replacing the phenyl by the 9,9-dimethyl-2-fluorenyl substituent in the starting phosphole. The transposition works nicely as shown in Scheme 3.

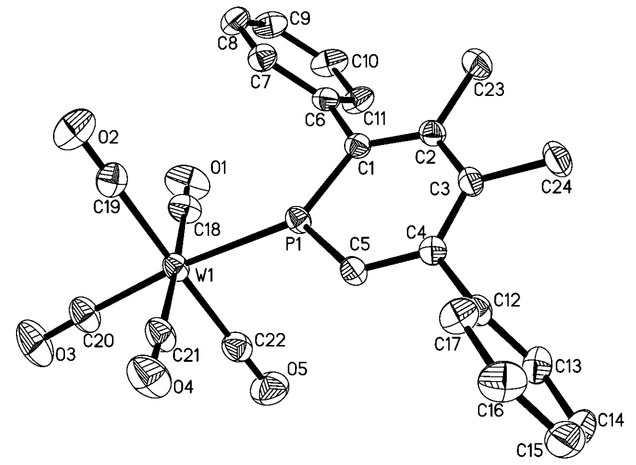
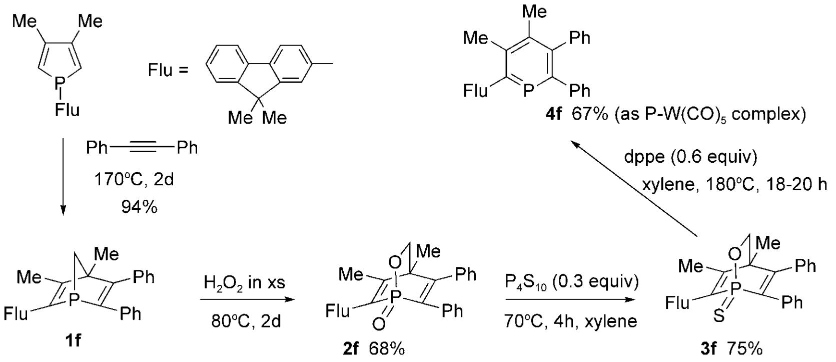


Figure 1. X-ray crystal structure of the pentacarbonyltungsten complex of phosphinine **4e**. Main bond lengths [Å] and angles [°]: P1−W1 2.4710(11), P1−C1 1.731(3), P1−C5 1.703(4), C1−C2 1.399(5), C2−C3 1.415(5), C3−C4 1.407(5), C4−C5 1.379(5); C1-P1-C5 103.65(17).

Finding an efficient route to convert 1-phosphanorbornadienes into phosphinines means that we can now use the broad and versatile phosphole chemistry as a starting point for an equally broad variety of phosphinines. Several methods have already been described in the literature for the conversion of phospholes into phosphinines,[8] but none of them has the same potential as this one. Among the most evident applications of this scheme, we can propose the conversion of 2,2′-bis-phosphanorbornadienes[9] into 2,2′-biphosphinines, the coordination chemistry of which has already proven its worth, and the use of phosphanorbornadienes



Scheme 3. Synthesis of a 2-(9,9-dimethyl-2-fluorenyl)-phosphinine (**4f**).

with enantiopure oxazoline substituents[10] to prepare optically active phosphinines. The results of these studies will be reported in due course.

Experimental Section

Full experimental details can be found in the Supporting Information. CCDC-777086 (**4e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: phosphinines · phosphorus · phospholes · synthetic methods

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