Phosphorous Compounds

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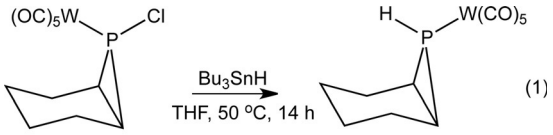
Isomerization of Secondary Phosphirane into Terminal Phosphinidene Complexes: An Analogy between Monovalent Phosphorus and Transition Metals

Jonathan Wong, Yongxin Li, Yanwei Hao, Rongqiang Tian, and François Mathey**

Abstract: *Secondary phosphirane complexes isomerize above 100°C to give the corresponding terminal phosphinidene complexes, which can be trapped by alkenes and alkynes. This reaction is a rare instance of the isomerization of a P^{III} derivative into a P^{I} derivative. It appears to mimic the reductive elimination of alkanes from transition-alkylmetal hydrides.*

Electrophilic terminal phosphinidene complexes [RP-M$(CO)_5$] (M = Cr, Mo, W) are now recognized as a powerful synthetic tool in organophosphorus chemistry.[1] They have been generated with a variety of substituents, but the parent species are still not accessible. We have recently shown that the phosphirane complexes derived from cyclohexene are good precursors for [RP-W$(CO)_5$] (R = Cl, Fc).[2,3] This observation led us to investigate the reduction of the chloro derivatives **1**[2] to obtain a potential precursor of [HP-W$(CO)_5$]. After several attempts (NaH, $LiAlH_4$), we found that Bu_3SnH was the reagent of choice, thus giving **2a,b** in 59% yield [Eq. (1)].



(1)

1a (major isomer shown)
1b (minor)

2a (minor)
2b (major isomer shown)

The structure of the major isomer (**2b**) was confirmed by X-ray crystal analysis (Figure 1).

Having in hand a potential precursor of [HP-W$(CO)_5$], we tested its reaction with alkenes and alkynes. The results were completely unexpected, as shown in Equation (2). It appeared that **2** isomerized to the terminal cyclohexylphosphinidene pentacarbonyltungsten complex **5** and gives the characteristic

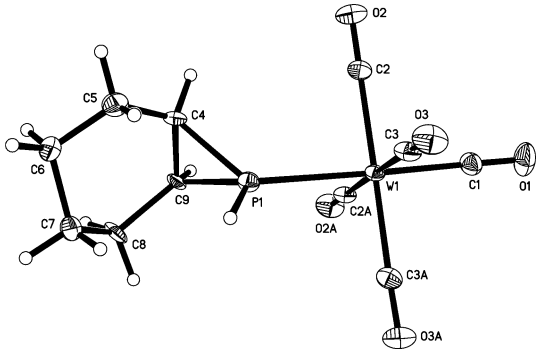


Figure 1. X-ray crystal structure of a secondary phosphirane (**2b**). Thermal ellipsoids shown at 50% probability. Main bond lengths [Å] and angles [deg.]: P1–W1 2.490(2), P1–C4 1.85(4), P1–C9 1.82(4), C4–C9 1.535(17); C4-P1-C9 49.5(5).

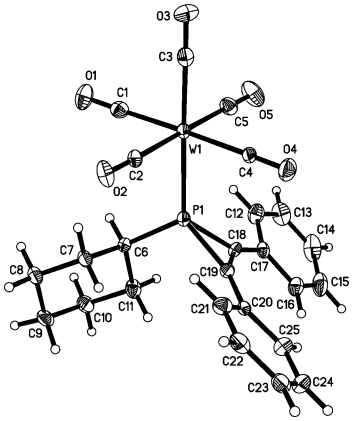


Figure 2. X-ray crystal structure of the phosphirene **3**. Thermal ellipsoids shown at 50% probability. Main bond lengths [Å] and angles [deg.]: P1–W1 2.5061(12), P1–C6 1.851(4), P1–C18 1.792(4), P1–C19 1.793(4); C18-C19 1.325(6); C6-P1-C18 108.6(2); C6-P1-C19 109.7(2); C18-P1-C19 43.40(19).

phosphirane and phosphirene [1+2] cycloaddition products. The formulation of **3** and **4b** was checked by X-ray crystal structure analysis (Figures 2 and 3). To check the feasibility of such an isomerization, we performed DFT calculations for **2b** and **5** at the B3LYP/6-31G(d)-lanl2dz(W) level of theory.[4]

The results indicate that the isomerization is feasible since **5** lies only 11.1 kcal mol^{-1} above **2b** in energy. The next step was to check the generality of this transformation. We prepared the parent phosphirane complex **6**,[5] from β-chloroethylphosphine as shown,[6] and reacted it with tolan [Eq. (3)].

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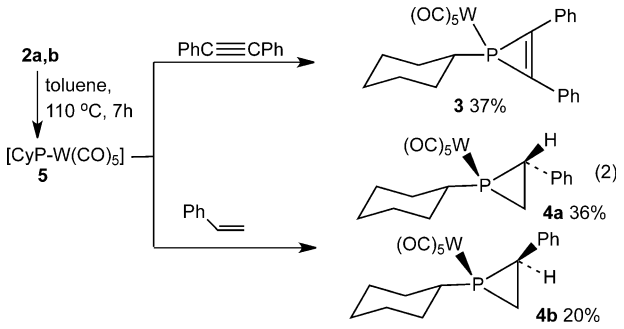


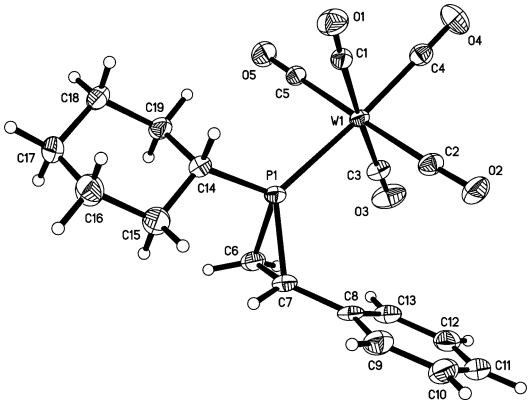
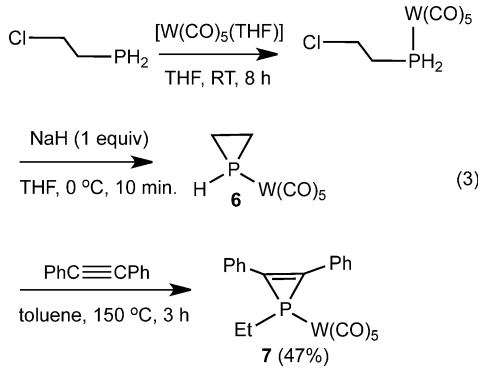
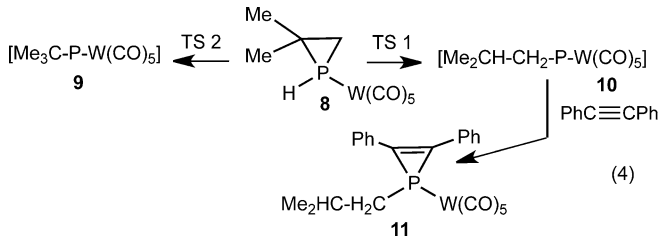


Figure 3. X-ray crystal structure of the phosphirane **4b**. Thermal ellipsoids shown at 50% probability. Main bond lengths [Å] and angles [deg.]: P1–W1 2.5079(17), P1–C6 1.824(7), P1–C7 1.858(7), P1–C14 1.856(6), C6–C7 1.529(10); C6-P1-C14 107.6(3); C7-P1-C14 108.3(3); C6-P1-C7 49.1(3).



The formation of the 1-ethylphosphirene complex **7**[7] suggested that this isomerization was general. To confirm this generality and to get useful data to identify a possible mechanism, we also studied the 2,2-dimethylphosphirane complex **8**, whose isomerization might give either the *tert*-butyl phosphinidene **9** or the isobutyl phosphinidene **10** [Eq. (4)]. The complex **8** was prepared from the corresponding chloro derivative $\mathbf{8}_{Cl}$ by reduction with Bu_3SnH [see Eq. (1)]. The trapping reaction with tolan exclusively produced the 1-isobutylphosphirene **11**.

We then performed a series of computations on a potential concerted H-shift mechanism, as well as on either an ionic or radical H-P dissociation/recombination mechanism. The only possibility was a concerted H-shift, which explained the exclusive formation of **10** from **8**. The computed structure of the corresponding transition-state TS 1 (one negative frequency) is shown in Figure 4. TS 1 lies 29 kcal mol^{-1} higher in energy [zero-point energy (ZPE) included] than the starting phosphirane **8**. The magnitude of this barrier is compatible with the experimental conditions (boiling toluene). TS 2 lies 34.9 kcal mol^{-1} higher in energy (ZPE included) than **8**, thus the formation of **9** is clearly disfavored.



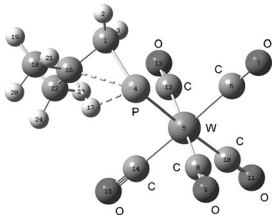


Figure 4. Computed transition state (TS 1) for the formation of **10** from **8**. Main distances [Å] and angles [deg.]: P–W 2.550, P–C1 1.929, P–C16 2.290, P–H17 1.523, C16–H17 1.540; P-H17-C16 96.75.

This isomerization of a trivalent P into a monovalent P derivative is a rare example. Most of the preceding examples concern the [2+1] cycloreversion of polycyclic phosphiranes into alkenes and phosphinidenes.[8] A single example concerns the rearrangement of an azaphosphiridine into a phosphinidene complex in which some stabilization is gained by interaction with a furan lone pair and a distant C=C bond.[9] The reported reaction provides a valuable route to terminal phosphinidene complexes without generating by-products, contrary to the known methods. From another standpoint, this isomerization is equivalent to the reductive elimination of an alkane from an alkylmetal hydride in transition-metal chemistry and is the reverse of the C–H activation by phosphinidene complexes, which have been described by several authors.[10]

Supporting Information: Complete experimental section. CCDC 1403838 (**2b**), 1403839 (**3**) and 1403840 (**4b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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