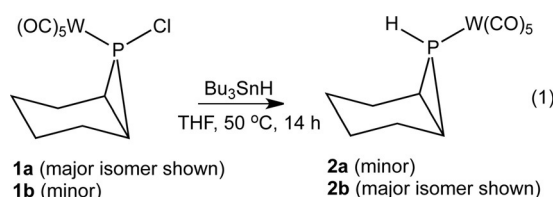


Isomerization of Secondary Phosphirane into Terminal Phosphinidene Complexes: An Analogy between Monovalent Phosphorus and Transition Metals

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)].



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

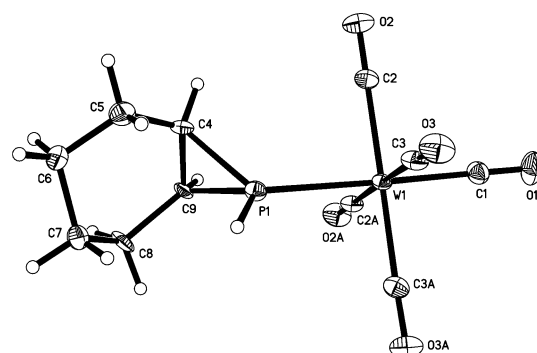


Figure 1. X-ray crystal structure of a secondary phosphirane (**2b**). Thermal ellipsoids shown at 50% probability. Main bond lengths [Å] and angles [deg.]: P1–W1 2.490(2), P1–C4 1.85(4), P1–C9 1.82(4), C4–C9 1.535(17); C4–P1–C9 49.5(5).

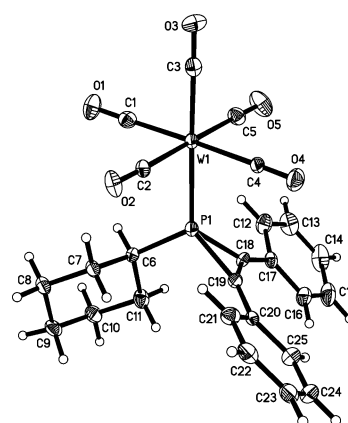


Figure 2. X-ray crystal structure of the phosphirene **3**. Thermal ellipsoids shown at 50% probability. Main bond lengths [Å] and angles [deg.]: P1–W1 2.5061(12), P1–C6 1.851(4), P1–C18 1.792(4), P1–C19 1.793(4); C18–C19 1.325(6); C6–P1–C18 108.6(2); C6–P1–C19 109.7(2); C18–P1–C19 43.40(19).

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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)].

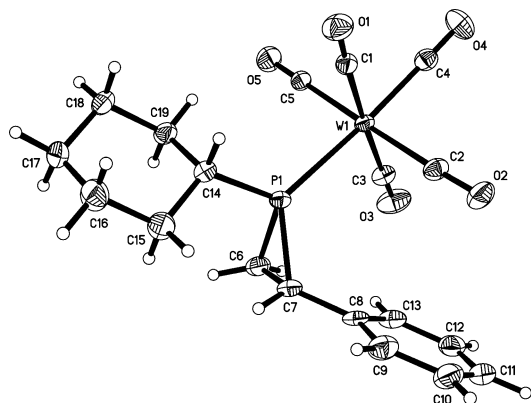
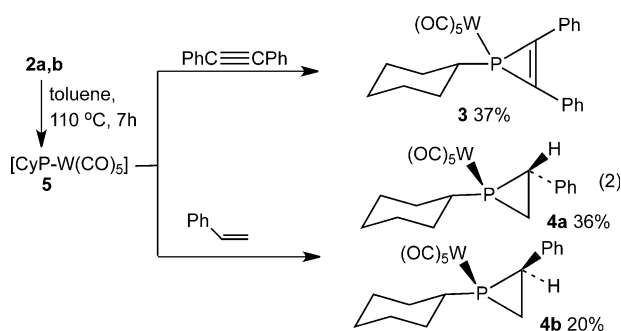
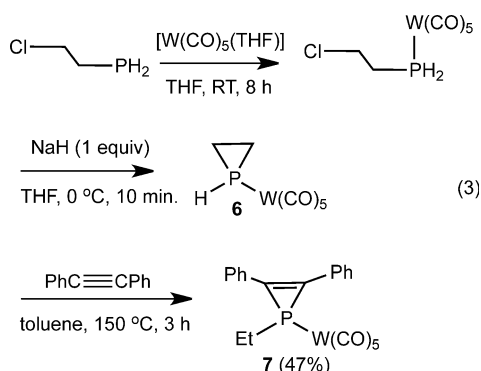
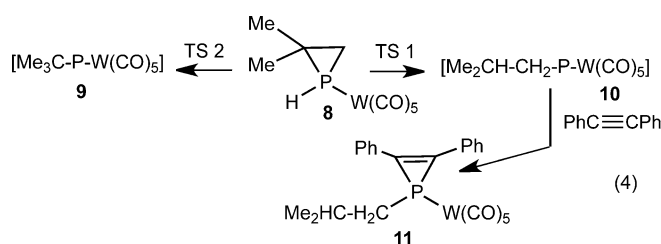


Figure 3. X-ray crystal structure of the phosphirane 4b. Thermal ellipsoids shown at 50% probability. Main bond lengths [Å] and angles [deg.]: P1–W1 2.5079(17), P1–C6 1.824(7), P1–C7 1.858(7), P1–C14 1.856(6), C6–C7 1.529(10); C6–P1–C14 107.6(3); C7–P1–C14 108.3(3); C6–P1–C7 49.1(3).



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 8_{Cl} by reduction with Bu₃SnH [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.

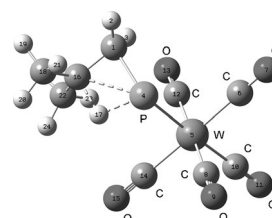


Figure 4. Computed transition state (TS 1) for the formation of 10 from 8. Main distances [Å] and angles [deg.]: P–W 2.550, P–C1 1.929, P–C16 2.290, P–H17 1.523, C16–H17 1.540; P–H17–C16 96.75.

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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