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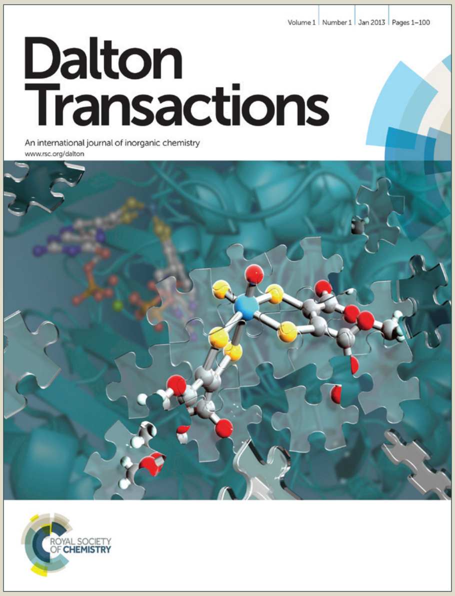

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Activation of A-H Bonds (A = B, C, N, O, Si) by Monovalent Phosphorus Complexes [RP→M]

Francois Mathey[a,b], Zheng Duan[a]

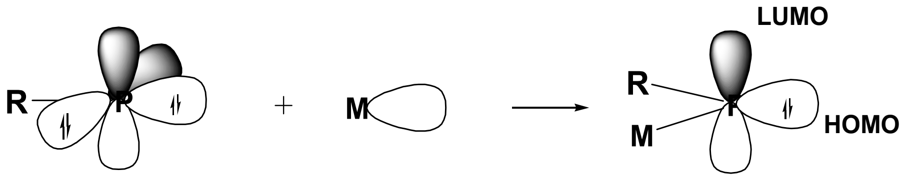
a) College of Chemistry and Molecular Engineering, International Phosphorus Laboratory, Joint Research Laboratory for Functional Organophosphorus Materials of Henan Province, Zhengzhou University, Zhengzhou 450001, P. R. China;

b) Division of Chemistry & Biological Chemistry, Nanyang Technological University, 21 Nanyang Link, Singapore 637371College of Chemistry and Molecular Engineering, International

Introduction

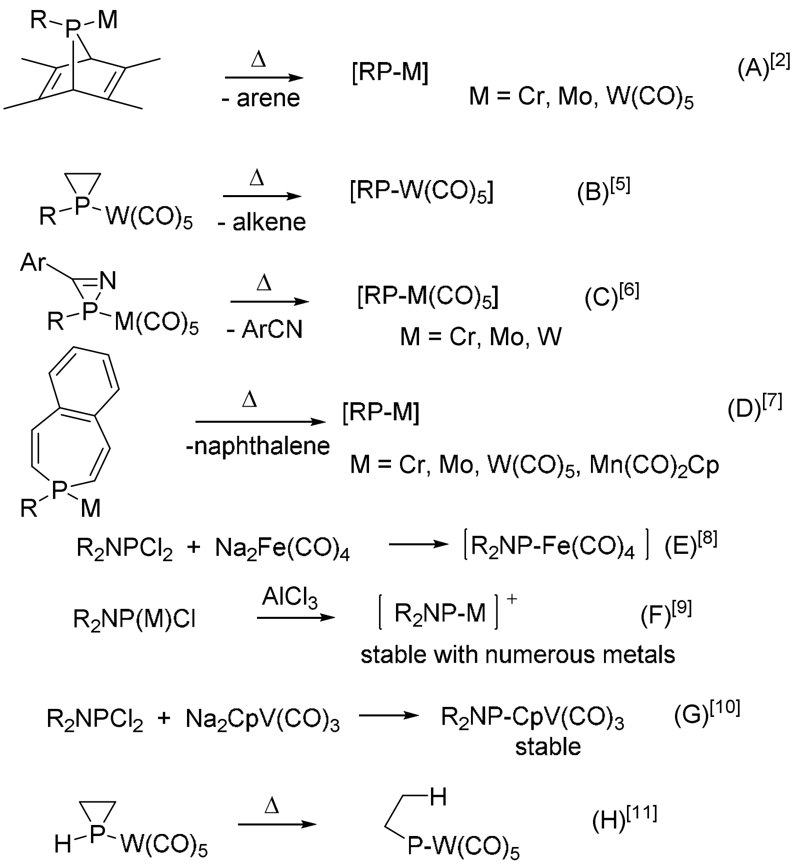
Recently, a few positive results have been reported concerning the generation and trapping of free phosphinidenes [RP].[1] However, this chemistry remains very limited in scope and has never led to any synthetic development. A key problem lies in the triplet ground state of phosphinidenes which prevents a satisfactory control of their reactivity. In 1982,[2] a first efficient precursor of terminal phosphinidene complexes [RP-M] (M = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$) was introduced. Contrary to free phosphinidenes, these complexes display a singlet ground state and a high electrophilicity. From then on, an extensive development of their chemistry took place that has been described in several reviews.[3] These complexes are formally built by combining a singlet phosphinidene with a singlet 16-electron transition metal moiety (Scheme 1). They display frontier orbitals very similar to those of singlet carbenes. As a result, their chemistry closely mimics carbene chemistry.

SCHEME 1. Building an Electrophilic Phosphinidene Complex



The initial researches have been focused on the duplication with monovalent phosphorus of the huge cycloaddition chemistry of carbenes with unsaturated hydrocarbons. They have been impressively successful. But there is another aspect of carbene chemistry that has been left almost untouched, the wide array of carbene insertion reactions into σ-bonds.[4] The purpose of this account is to summarize the few insertion reactions into A-H σ-bonds that have been described with electrophilic phosphinidene complexes so far, to try to understand why they have been successful and to establish the conditions that must be met to develop new insertion reactions with these monovalent phosphorus species. The various known methods for the generation of [RP-M] are summarized in Scheme (2).

SCHEME 2. Synthesis of Electrophilic Phosphinidene Complexes

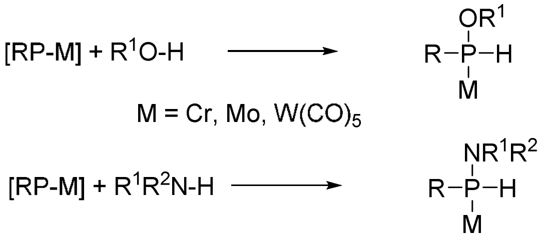


Except when otherwise noted, the thermal splitting of 7-phosphanorbornadiene complexes (method A) has been used in the various experiments described hereafter. Numerous nucleophilic terminal phosphinidene complexes [RP=M] have also been reported in the literature.[12] They are formally built by combining a triplet phosphinidene with a triplet metal moiety, they include a P=M double bond and derive from trivalent phosphorus. Their chemistry is entirely different from the chemistry of the electrophilic species and is not discussed here. The dichotomy between electrophilic and nucleophilic phosphinidene complexes parallels the well-known dichotomy between Fischer and Schrock carbene complexes.

Insertion into O-H and N-H bonds

From the very beginning, it has been known that [RP-M] easily inserts into the O-H bonds of water and alcohols and into the N-H bonds of primary and secondary amines[13] (Scheme 3).

SCHEME 3. Insertion of phosphinidene complexes into O-H and N-H bonds



Since it is known that, in some cases, electrophilic phosphinidene complexes can give stable adducts with amines[14] and phosphines[15], we suspected that these insertions proceeded via similar intermediate adducts. We decided to study the reaction of water with [MeP-W(CO)$_5$] by DFT in order to check this assumption. The computations were performed at the B3LYP/6-31G(d)-Lanl2dz(W) level.[16] We were, indeed, able to find a local minimum (no negative frequency) corresponding to the water adduct whose structure is shown in Figure (1).

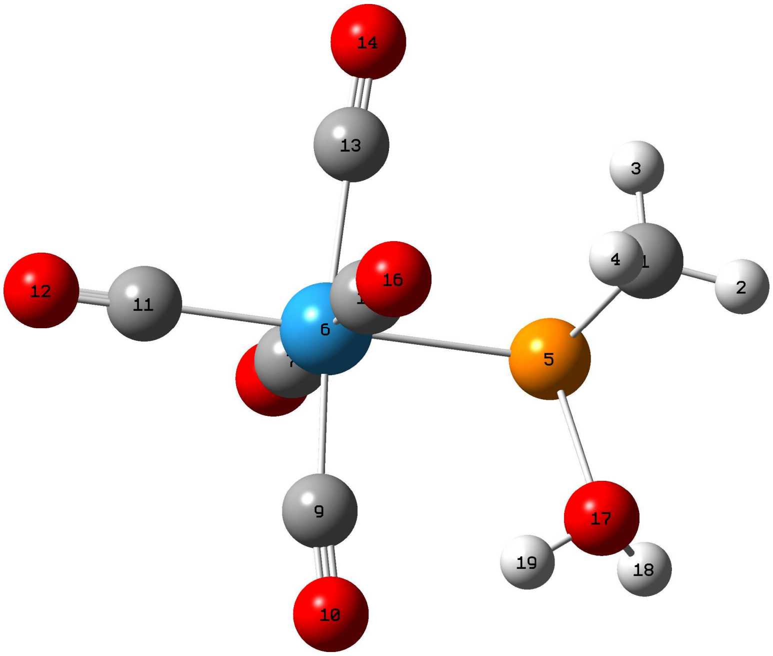


FIGURE 1. Computed structure of the adduct between water and [MeP-W(CO)$_5$]. Main bond lengths (Å) and angles (°): P5-W6 2.533, P5-O17 2.161, P5-C1 1.861,W6-P5-O17 104.08, C1-P5-O17 90.25, H18-O17-P5 104.10, H19-O17-P5 108.17.

The P-O bond is weak at 2.161 Å. The bond dissociation energy (BDE) is only 7.4 kcal mol^{-1} (ZPE included). The P-O bond is almost perpendicular to the water and phosphinidene planes, showing that the adduct results from the interaction of the phosphinidene LUMO with the π lone pair of water. The [1,2] shift of H from O to P gives the P(H)OH insertion product. The transition state (one negative frequency) (Figure 2) lies 11.4 kcal mol^{-1} above the water adduct (ZPE included). These data lead us to propose the mechanism depicted in Scheme (4) for the insertion of electrophilic phosphinidene complexes into the O-H bond of water.

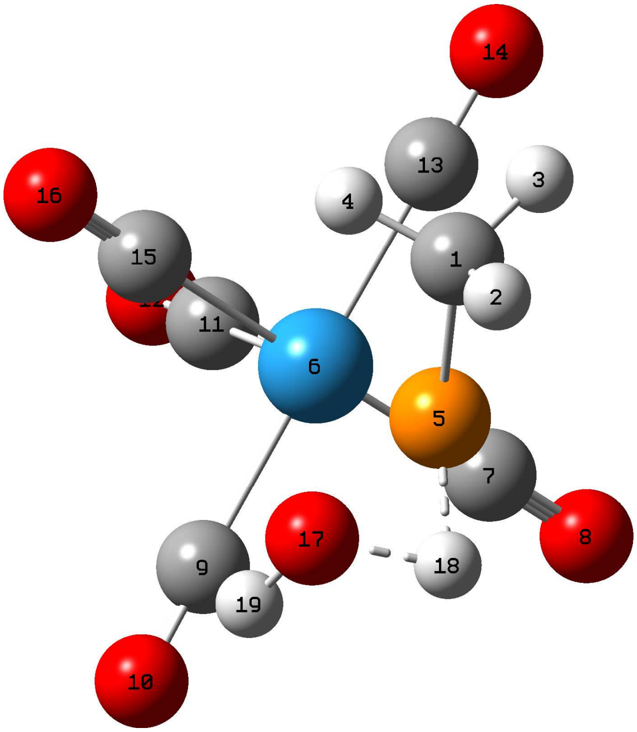
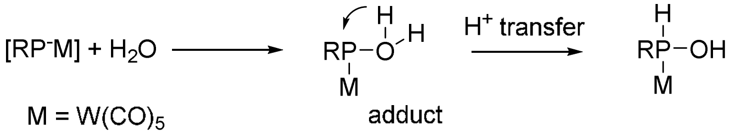


FIGURE 2. Computed structure of the transition state between the water adduct and [MeP(H)OH]W(CO)$_5$. Main bond lengths (Å) and angles (°): P5-W6 2.496, P5-O17 1.992, P5-C1 1.845, W6-P5-O17 113.31, C1-P5-O17 93.31, H18-O17-P5 52.64, H19-O17-P5 10649, H18-P5-O17 39.58.

SCHEME 4. Proposed mechanismn for the insertion of phosphinidene complexes into water

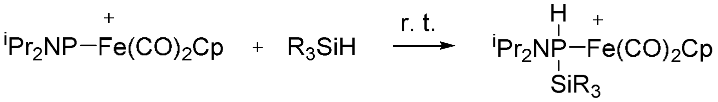


The reaction with alcohols and amines very probably follows the same pathway.

Insertion into Si-H and B-H bonds

The insertion of electrophilic phosphinidene complexes into the Si-H bonds of hydrogenosilanes has been described for the first time by Sterenberg.[17] (Scheme 5)

SCHEME 5. Insertion of phosphinidene complex into the Si-H bond



Similar results were obtained later with [PhP-W(CO)$_5$].[18] The reaction of the cationic complex proceeds at room temperature. DFT calculations indicated two triangular transition states lying 25 and 32 kcal mol^{-1} above the starting products. These data gave us the opportunity to compare the reactivity of these stable cationic species with that of the transient [RP-W(CO)$_5$] complexes. The barrier for the reaction of [MeP-W(CO)$_5$] with silane was computed at the same B3LYP/6-31G(d)-Lanl2dz(W) level. The triangular transition state is shown in Figure (3). The height of the barrier is computed to be only 5.6 kcal mol^{-1}(ZPE included). The insertion product lies 42.2 kcal mol $^{-1}$ lower in energy than the starting products. It is clear that the transient tungsten complexes are far more reactive than the stable aminophosphinidene iron complexes. In both cases, the reaction is driven by the initial interaction between the hydridic hydrogen and the electrophilic phosphinidene.

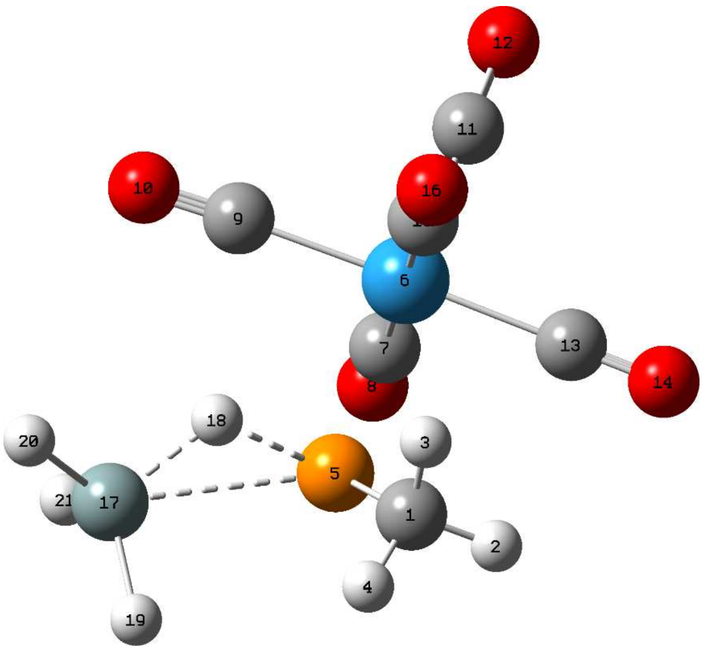
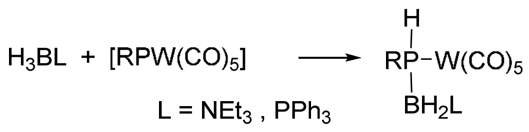


FIGURE 3. Computed structure of the transition state for the reaction between [MeP-]W(CO)$_5$] and silane. Main bond lengths (Å) and angles (°): P5-W6 2.514, P5-Si17 2.767, P5-C1 1.873, P5-H18 1.787, Si17-H18 1.563; W6-P5-Si17 121.05, C1-P5-Si17 98.85, H18-Si17-P5 37.00, H18-P5-Si17 31.77.

The reaction of the amine and phosphine-borane adducts with [RP-W(CO)$_5$] very probably follows the same pathway. The reaction appears to be quite general[19] (Scheme 6).

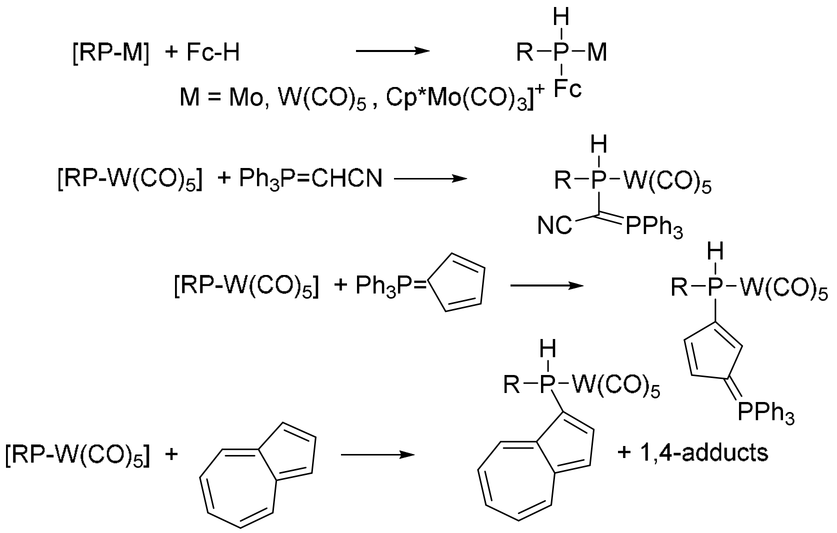
SCHEME 6. Insertion of phosphinidene complex into the B-H bond



Insertion into C-H bonds

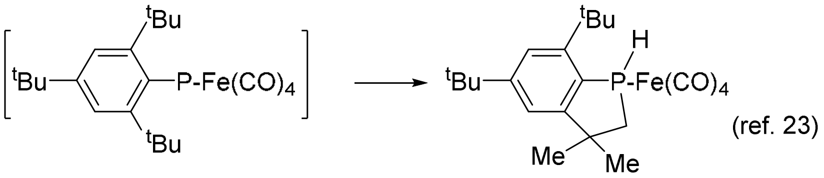
These insertion reactions are, by far, the most interesting ones from a synthetic standpoint. However, until recently, only a limited success was met in the attempts to activate C-H bonds by electrophilic phosphinidene complexes. Only a few intermolecular examples had been reported so far, with ferrocene[20], Wittig ylides[21] and azulene[22](Scheme 7). In these three cases, the insertion is obviously driven by the negative charge carried by the reactive C-H bond. In the ferrocene case, the insertion works with molybdenum and tungsten complexes but $Cr(CO)_5$ complexes are inactive.

SCHEME 7. Insertion of phosphinidene complexes into some C-H bonds



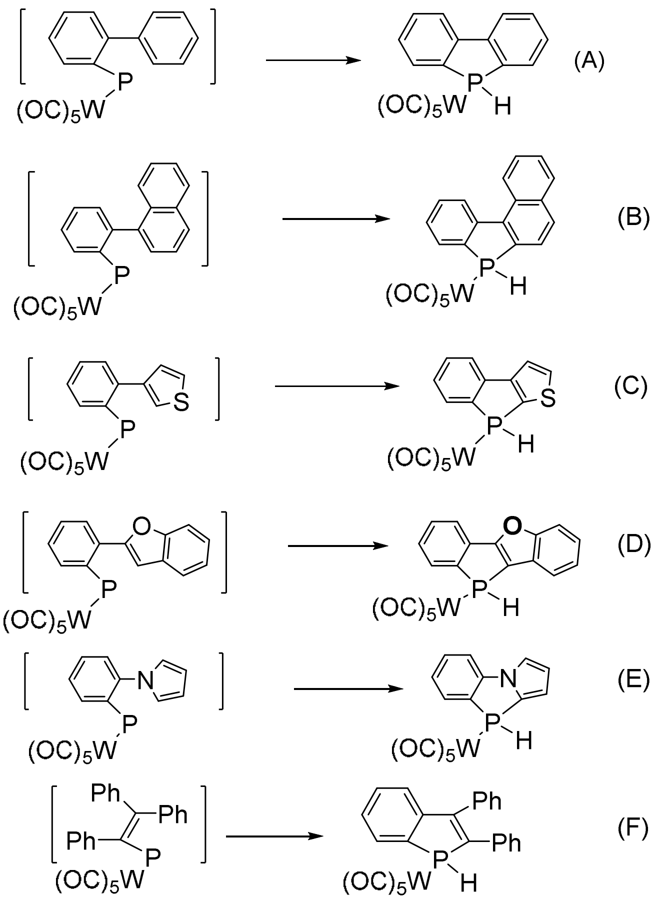
These results cannot be easily generalized. This is not the case with the intramolecular example described in Scheme (8).

SCHEME 8. Intramolecular insertion of a phosphinidene complex into C-H bonds



Here the insertion is driven by the proximity between the phosphinidene centre and the activated C-H bond. This approach can be easily generalized. Very recently, we have been able to take advantage of this proximity effect to devise a new synthesis of annelated phospholes[24] (Scheme 9).

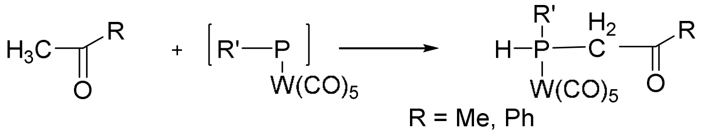
SCHEME 9. Synthesis of annelated phospholes by C-H activation



As can be seen, this synthesis is quite general and works with a lot of arenes and heteroarenes. In the case of thiophene, when both α and β C-H are accessible, the insertion exclusively takes place at the α position whose carbon is more negative. The activation barrier has been computed for case (A) and is extremely low at 2.0 kcal mol^{-1} (ZPE included).

Using an oxygen or nitrogen lone pair to localize a phosphinidene complex close to an activable C-H bond is an obvious idea that has already been exploited in two cases. With methylketones, an insertion product into one of the methyl C-H bonds is formed[25] (Scheme 10).

SCHEME 10. Insertion of phosphinidene complexes into methylketones



The reaction conditions are relatively drastic and the yields are modest. In order to clarify the mechanism of these insertions, we investigated the reaction of [MePW(CO)$_5$] with acetone by DFT at the B3LYP/6-31G(d)-Lanl2dz(W) level. We detected a P-O adduct whose structure is shown in Figure (4).

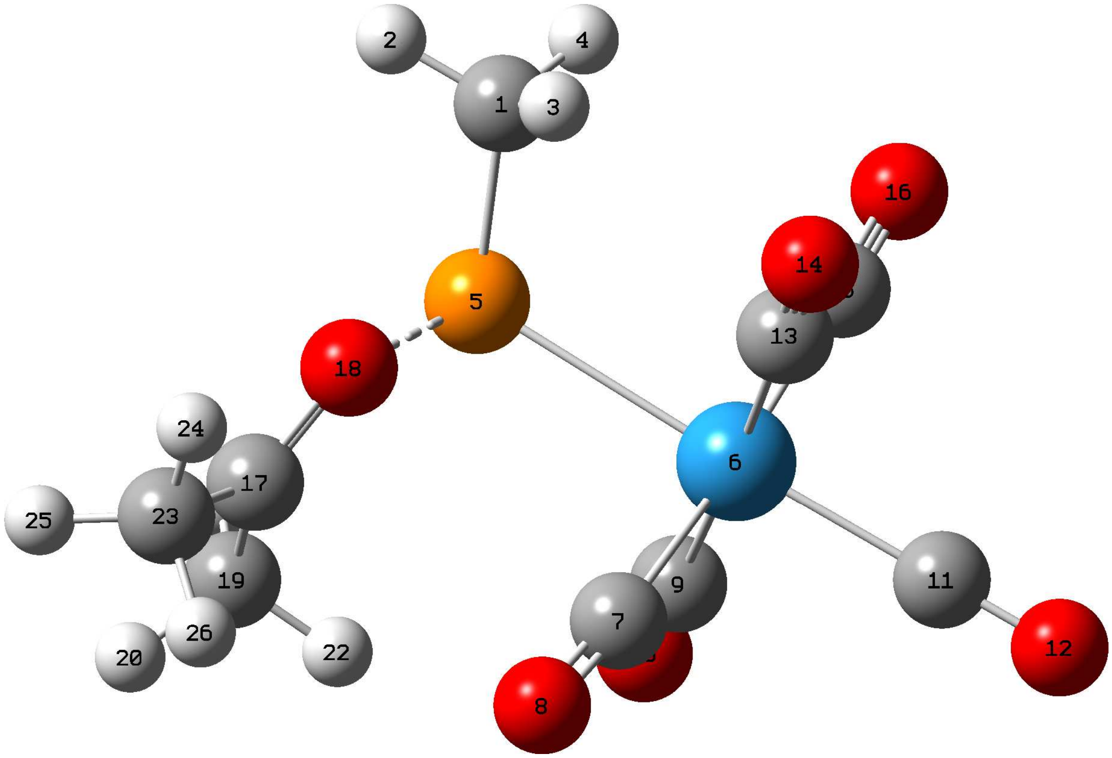


FIGURE 4. Computed structure of the adduct between acetone and [MeP-W(CO)$_5$]. Main bond lengths (Å) and angles (°): P5-W6 2.609, P5-O18 1.881, P5-C1 1.862; W6-P5-O18 103.70, C1-P5-O18 91.51, C17-O18-P5 126.29.

A similar adduct, formed by P-C bond cleavage of an oxaphosphirane, has been studied by Streubel and Espinosa.[26] The dissociation energy of this adduct is relatively high at 10.9 kcal mol^{-1} (ZPE included). The insertion proceeds via a transition state (one negative frequency) that is depicted in Figure (5).

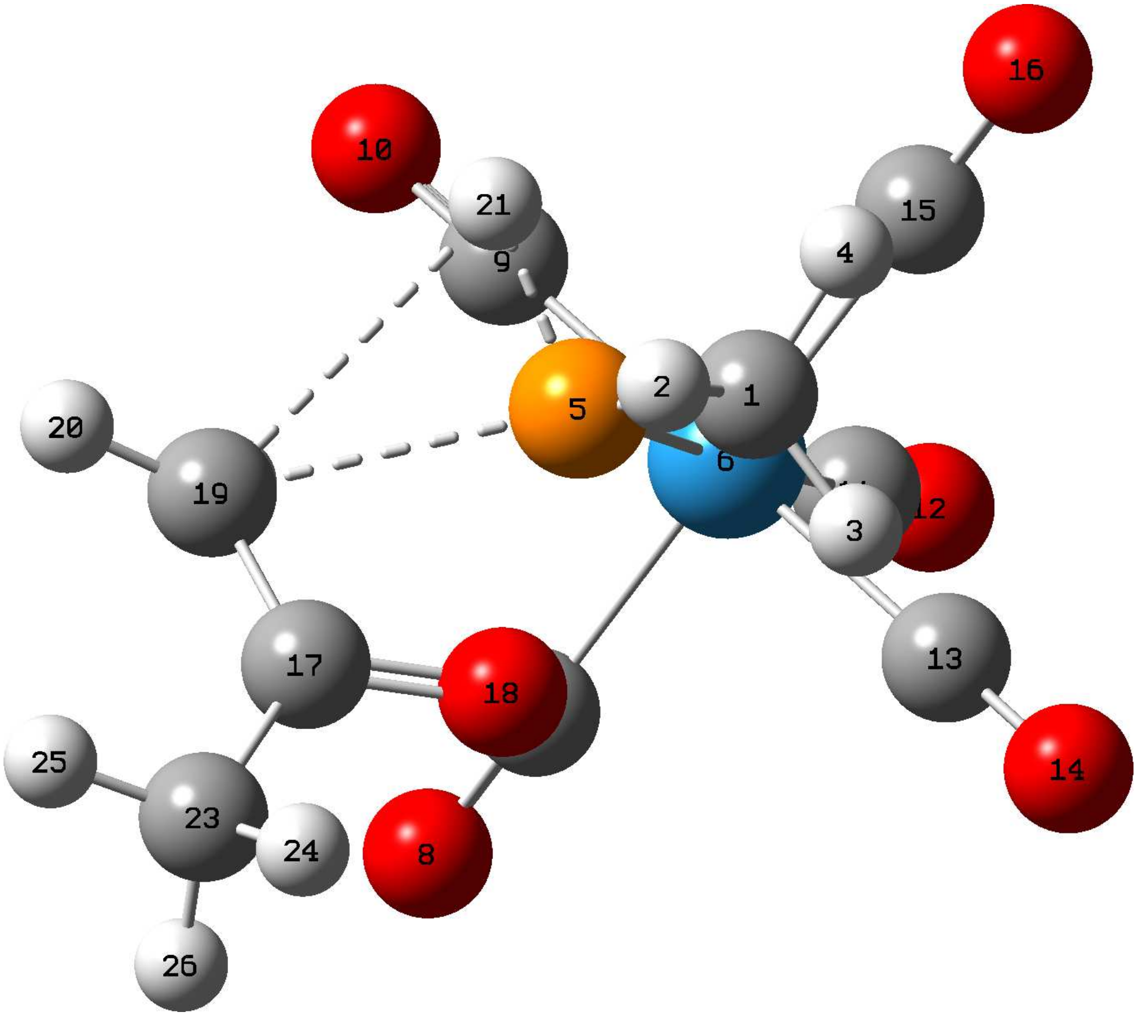
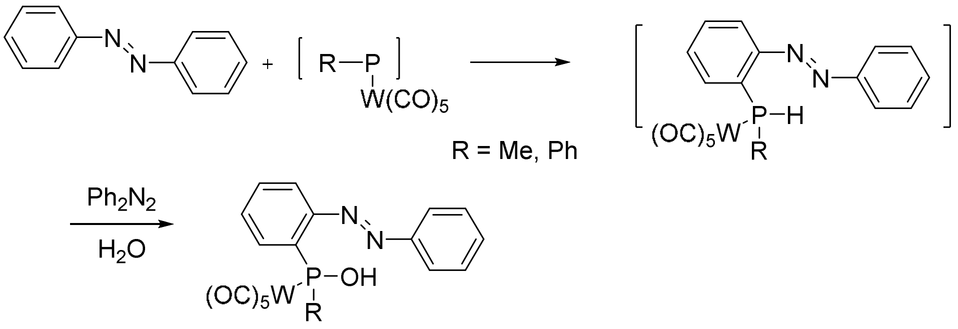


FIGURE 5. Computed structure of the transition state for the reaction between [MeP-]W(CO)$_5$] and acetone. Main bond lengths (Å) and angles (^{o}): P5-W6 2.528, P5-C19 2.433, P5-O18 2.000, P5-C1 1.842, P5-H21 1.426; W6-P5-C19 117.17, C1-P5-C19 119.25, H21-C19-P5 32.72, H21-P5-C19 80.03.

The activation barrier of the methyl C-H bond is rather high at 29.8 kcal mol-1 and this explains why the experimental conditions are relatively drastic.

A similar directing effect has been found with azobenzene[27] (Scheme 11).

SCHEME 11. Insertion of phosphinidene complexes into azobenzene



The P-H bond of the insertion product is oxidized by the excess of azobenzene.

Conclusion

Electrophilic terminal phosphinidene complexes [RP-M] (M mainly $W(CO)_5$) can efficiently activate A-H bonds provided that an initial interaction forces the phosphinidene to stay close to the potentially activated bond. This interaction can be the formation of a Lewis adduct with a lone pair on A (O-H, N-H) or close to A (acetone, azobenzene), some hydride character for H (Si-H, B-H), some negative charge on carbon (ferrocene, Wittig ylids, azulene) or a simple proximity effect for intramolecular insertions. It is quite clear that it will be possible to extend the synthetic applications of phosphinidene complexes by following these easily met conditions.

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Table of contents entry:

The insertion of electrophilic terminal phosphinidene complexes [RP-M] into A-H bonds (A = B, C, N, O, Si) have been reviewed and some new mechanistic proposals have been made.