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Insertion of phosphinidene complexes into the P–H bond of secondary phosphine oxides: a new version of the phospha-Wittig synthesis of P═C double bonds†

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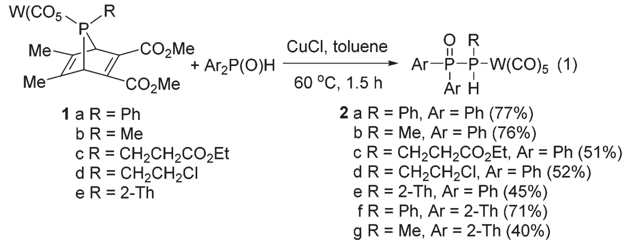
Terminal phosphinidene complexes [RP-W(CO)$_5$], as generated at 60 °C in the presence of copper chloride from the appropriate 7-phosphanorbornadiene complexes, react with secondary phosphine oxides Ar$_2$P(O)H to give the insertion products into the P–H bonds. After metalation with NaH, these products react with aldehydes to give the corresponding phosphaalkenes which are trapped by dimethylbutadiene.

For a long time, the development of the carbene-like chemistry of electrophilic terminal phosphinidene complexes [RP-M] (M = Cr, Mo, W(CO)$_5$, Fe(CO)$_4$ and cationic complexes) was centered on cycloaddition reactions.[1] The systematic development of insertion reactions into A–H σ bonds is more recent.[2] Noteworthy are the insertions into Si–H[3] and B–H[4] bonds. In both cases, the reaction is favored by the interaction of the electrophilic phosphinidene phosphorus with the hydridic hydrogen. The case of the P–H bond is more delicate. A secondary phosphine tends to displace the phosphinidene from its complex, thus leading to the failure of the insertion reaction. When replacing the secondary phosphine by its P-W(CO)$_5$ complex, no reaction is observed. Reactions using secondary phosphine oxides were more productive. These experiments are the subject of this report.

The copper chloride-catalyzed decomposition of 7-phosphanorbornadiene P-W(CO)$_5$ complexes **1** was used as a source of phosphinidene complexes.[5] The reaction was carried out at 60 °C in toluene or THF. Successful insertions of the phosphinidenes into the P–H bond were observed with secondary diphenyl and di-2-thienylphosphine oxides (Scheme 1).



Scheme 1 Insertion of [RP-W(CO)$_5$] into the P–H bond of secondary phosphine oxides.

The insertion products **2** were characterized by NMR and HRMS. The ^{31}P NMR data are collected in Table 1.

These data are very similar to those of the phosphonate analogues, the so-called phospha-Wittig reagents.[6] Compound **2a** was further characterized by X-ray crystal structure analysis (Fig. 1).

It is known that an easy tautomerism takes place between secondary phosphine oxides and phosphinous acids. The process is bimolecular and involves 6-membered transition states with activation barriers in the range 5–15 kcal mol^{-1}.[7] The key question concerning the mechanism of the insertion of phosphinidene complexes into the P–H bonds of secondary phosphine oxides is whether [RP-W(CO)$_5$] reacts with Ar$_2$P(O)H or Ar$_2$P-OH. We have studied the interaction of [MeP-W(CO)$_5$] with Ph$_2$P(O)H and Ph$_2$P-OH by DFT at the B3LYP/6-31G(d)-

Table 1 ^{31}P NMR for compounds **2**

Product	δ^{31}P	$^1J_{PP}$ (Hz)	$^1J_{PW}$ (Hz)	$^1J_{PH}$ (Hz)
2a	34.0, −33.2	72.0	226.4	327.8
2b	34.2, −68.3	62.7	223.6	320.4
2c	34.7, −53.7	65.8	223.9	330.1
2d	34.1, −61.5	64.3	226.7	323.2
2e	34.4, −53.7	66.1	231.6	336.3
2f	21.0, −19.9	46.9	228.3	330.6
2g	20.7, −54.2	38.2	226.0	322.9

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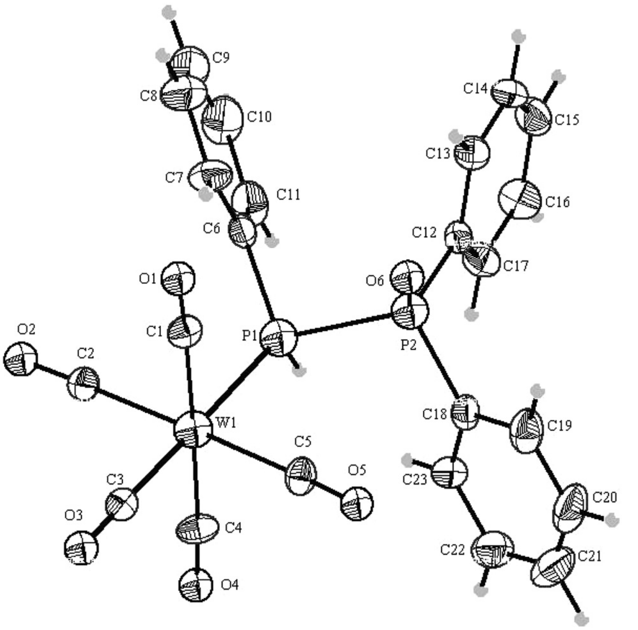


Fig. 1 X-ray crystal structure analysis of compound **2a**. Main bond lengths (Å) and angles (°): P1–P2 2.2081(18), P1–C6 1.824(5), P1–W1 2.5058(13), P2–O6 1.489(4), P2–C12 1.797(5), P2–C18 1.814(5); P2–P1–W1 113.54(6), C6–P1–W1 121.45(18), C6–P1–P2 100.97(16), C12–P2–C18 107.3(2), O6–P2–P1 109.97(17), O6–P2–C12 113.1(2), O6–P2–C18 113.8(3), C12–P2–P1 107.98(16), C18–P2–P1 104.14(18).

Lanl2dz (W) level.[8] We have not detected any interaction with the secondary phosphine oxide but a well defined P···O adduct is formed with the phosphinous acid (Fig. 2).

This adduct which corresponds to a local minimum (no negative frequency) is formed by the interaction of the phosphinidene LUMO with the in-plane lone pair of the hydroxyl oxygen. On this basis, we propose the mechanism depicted in Scheme 2 for the insertion of phosphinidenes into the P–H bonds.

The first two steps are very similar to those proposed for the insertion of phosphinidene complexes into water.[2] When the diaryl is replaced by a dialkylphosphine oxide, the phosphinous acid tautomer becomes such a strong ligand that it becomes able to displace tungsten from the phosphinidene complex or from its precursor and the insertion fails. For example, with secondary di-*n*-butylphosphine oxide, the main product is (^{n}Bu$_2$POH)W(CO)$_5$ (**3**) isolated in 41% yield.

It is possible to alkylate the PH bonds of the insertion products **2** as shown in Scheme 3.

But the most interesting aspect of the chemistry of these insertion products is their use as phospha-Wittig reagents[9] for the conversion of carbonyl derivatives into $P{=}C$ double bonds (Scheme 4).

The phosphaalkene intermediates were trapped as [2 + 4] cycloadducts with dimethylbutadiene. Adducts **6** and **9** were obtained as single diastereomers but their stereochemistry was not determined.

Finally, a few words on the thermal stability of compounds **2** are appropriate. The experiments were performed with **2a**.

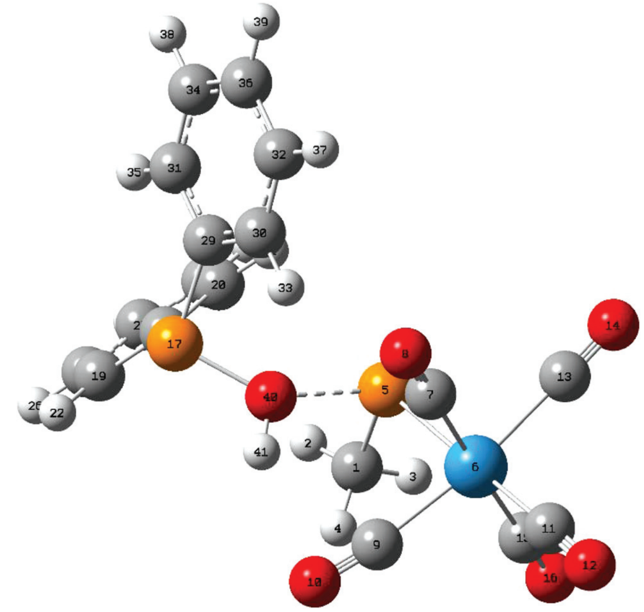
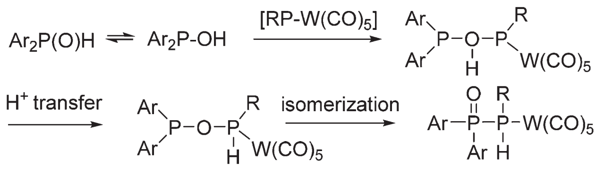
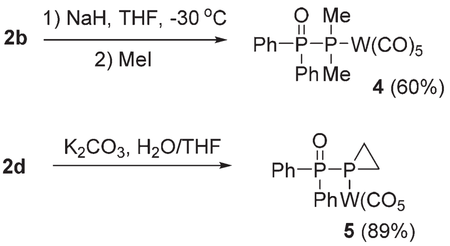


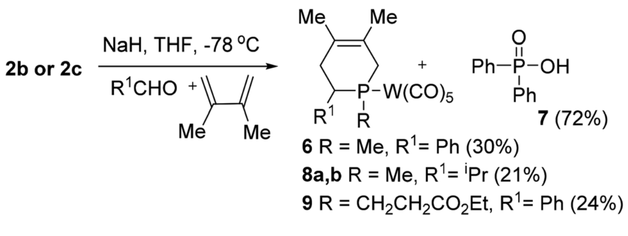
Fig. 2 Computed structure of the adduct [MeP-W(CO)$_5$]-HOPPh$_2$. Main bond lengths (Å) and angles (°): P5–O40 2.042, P17–O40 1.770, P5–C1 1.870, O40–H41 0.977; P5–O40–P17 136.06, P5–O40–H41 111.06, P17–O40–H41 109.89, C1–P5–O40–H41 66.96.



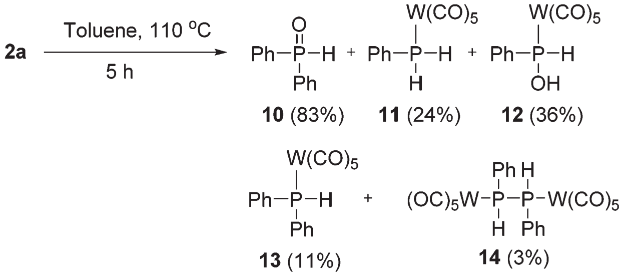
Scheme 2 Insertion mechanism of [RP-W(CO)$_5$] into the P–H bond of Ar$_2$P(O)H.



Scheme 3 Alkylation of insertion products **2**.



Scheme 4 Compound **2** as phospha-Wittig reagents.



Scheme 5 Thermal decomposition of **2a**.

Compound **2a** decomposes in boiling toluene to give a plethora of products (Scheme 5).

The initial step of the decomposition seems to be the de-insertion of the phosphinidene from the P–H bond giving back the secondary phosphine oxide **10** in high yield. The suspected phosphinidene complex gives a variety of products **11**, **12** and **14**. **11** and **14** apparently come from the reaction of the phosphinidene with hydrogen[10] whose source is unknown. **12** and **13** probably arise from a H to OH exchange between the tautomers of **10** and **11**. Alternatively, the decomposition of **2a** could also occur *via* a bimolecular mechanism.

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