

[A0014]

# A NEW TUNGSTEN COMPLEX DERIVED FROM [(DIPHENYLPHOSPHINO)METHYL] DIPHENYLPHOSPHINE OXIDE

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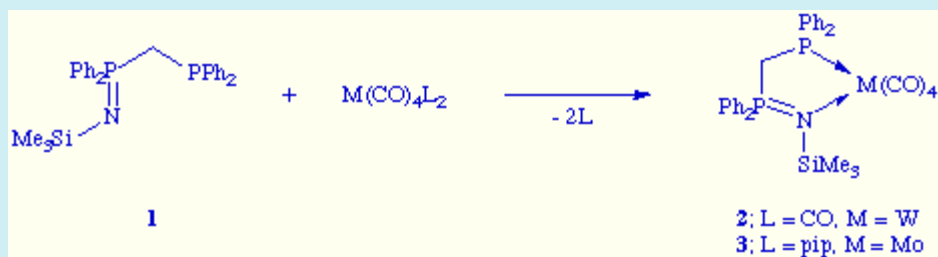
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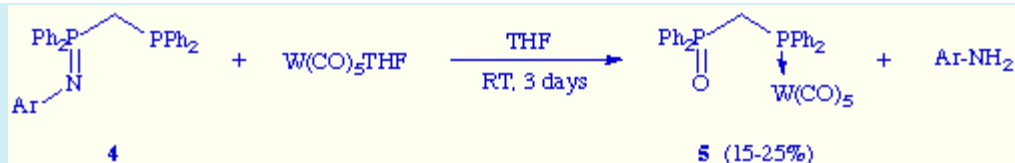
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• Compounds containing phosphine and phosphinimide units provide bifunctionality from a "soft" phosphorus(III) center (which is predisposed for combination with soft metals) and a "hard" nitrogen center (which is predisposed for combination with early transition metals) so that the complex formation process is favored in a variety of situations.

• Ten years ago it was reported [1] that tungsten and molybdenum carbonyls react with *N*-trimethylsilyl[(diphenylphosphino)methyl] diphenylphosphinimide **1** to give the cyclometallophosphinimide phosphanes **2** and **3**.

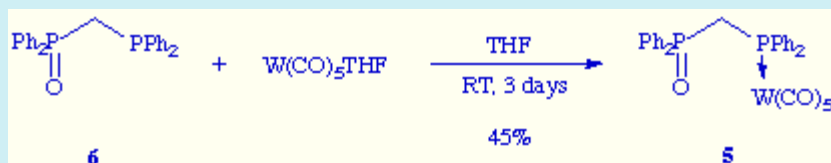


• In the course of our current research on the chemistry of [(diphenylphosphino)methyl]diphenyl phosphinimides we attempted a similar coordination of some *N*-aryl derivatives **4** under similar reaction conditions. In our hands, such small variation of the starting phosphinimides (*N*-aryl instead of *N*-trimethylsilyl) with respect to the scheme above resulted in notably different reaction products. Thus, the reaction of *N*-aryl[(diphenylphosphino)methyl]diphenylphosphinimides **4** [2] with  $W(CO)_5THF$  [3] gave rise to the previously unknown tungsten complexes **5** albeit in low yields. Compounds **5** precipitated out from the reaction medium as yellow solids and were isolated by filtration in virtually pure state.



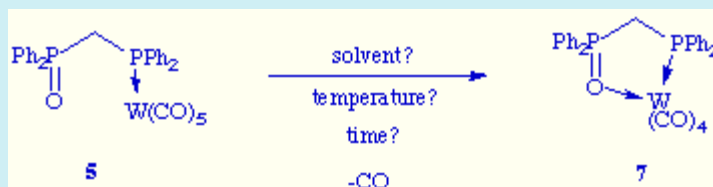
As shown in the scheme the coordination of the metal to the P(III) center was successfully accomplished but the phosphinimide function did not survive but hydrolyzed to the phosphine oxide and the corresponding aniline. At the present we can not say unequivocally if the nitrogen atom of the phosphinimide unit become or not coordinated to the metal previously to the hydrolytic process, but it seems quite clear that such coordination would enhance the susceptibility of the phosphinimide to the hydrolysis by making the P(V) atom more electrophilic. In the absence of the tungsten carbonyl  $W(CO)_5THF$  compounds **4** did not show such hydrolytic sensitivity[4].

We have established the structure of **5** by its analytical and spectroscopic data as well, as presumed, through its alternative preparation by reaction of [(diphenylphosphino)methyl]diphenylphosphine oxide **6** with  $W(CO)_5THF$ .



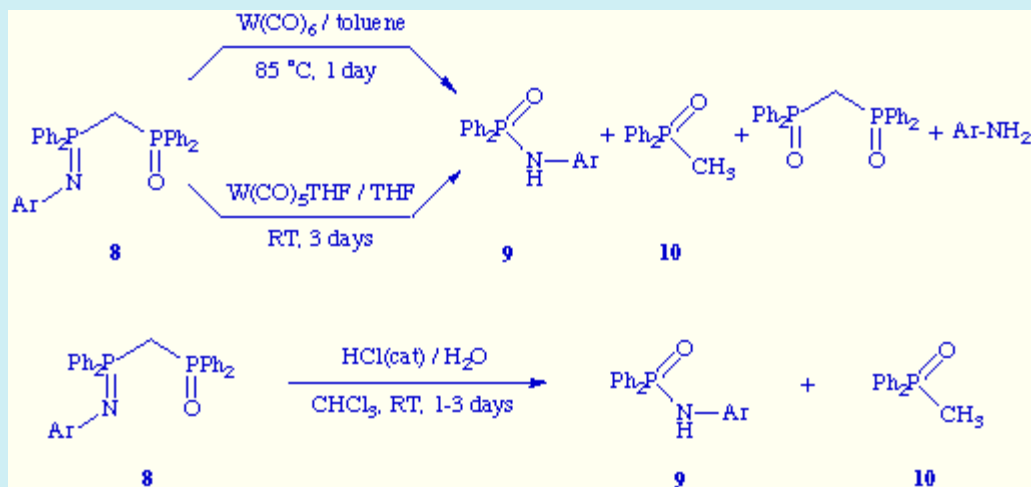
Relevant spectroscopic data of compound **5** (Ar = 4-Tolyl):

- The infrared spectrum shows absorption bands corresponding to overlapping  $E$  and  $A_1^{(1)}$  modes at  $1935\text{ cm}^{-1}$ ,  $A_1^{(2)}$  mode at  $2074\text{ cm}^{-1}$  and  $B_1$  mode at  $1983\text{ cm}^{-1}$ .
  - The methylene hydrogen atoms appear in the  $^1H$  NMR as a double doublet at  $\delta$  3.66 ppm with  $^2J_{H-P}$  coupling constants of 7.8 Hz and 11.6 Hz. By contrast, compounds **4** and **6** do not show coupling of their methylene protons with the P(III) atom, but only with the P(V) one (**4**:  $\delta$  3.22-3.24 ppm,  $^2J_{H-P} = 12.6-12.9$  Hz; **6**:  $\delta$  3.09 ppm,  $^2J_{H-P} = 12.9$  Hz).
  - The CO region of the  $^{13}C$  NMR spectrum consists of a set of downfield peaks assigned to the CO group *trans* to the coordinated phosphorus atom ( $\delta$  200.4 ppm,  $^2J_{C-P} = 22.2$  Hz) and a set of upfield signals arising from the *cis* CO groups ( $\delta$  198.0 ppm,  $^2J_{C-P} = 6.8$  Hz and  $^4J_{C-P} = 2.9$  Hz).
  - The  $^{31}P$  NMR spectrum shows two set of signals: one at  $\delta$  24.17 ppm a doublet for the P(V) atom with a coupling constant of  $^2J_{P-P'} = 3.7$  Hz, and another set centered at  $\delta$  3.87 ppm due to the phosphorus atom coordinated to the tungsten atom with the following coupling constants  $^2J_{P-P'} = 3.7$  Hz,  $^1J_{P-W} = 248.6$  Hz.
- As a continuation of this work we are now trying to achieve the formation of the new metallacycle **7** by intramolecular displacement of a carbonyl ligand on the tungsten by the phosphine oxide function:



We also have attempted to prepare other new tungsten complexes by using

[(diphenylphosphinoyl)methyl]diphenyl phosphinimides **8** but without success. Thus, the reaction of **8** with  $W(CO)_6$  or  $W(CO)_5THF$  did not give a tungsten complex by coordination of the metal to the oxygen or nitrogen atoms or both; instead of, these reactions gave rise mostly to the fragmentation of the putative ligands, yielding mainly phosphoranilides **9** and diphenylmethylphosphine oxide **10**, along with some minor amounts of the products resulting from the hydrolysis of the phosphoramidate unit of **8**. The fragmentation of compounds **8** to give **9** and **10** has been previously observed in our lab when those compounds were treated with catalytic amounts of HCl in  $CHCl_3$  solution, and an explanation for such P-C cleavage has been acquainted [4]. Taking this precedent into account, it seems that  $W(CO)_6$  and  $W(CO)_5THF$  play the role of simple Lewis acid catalysts in the here shown fragmentation processes.



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