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THE INTERACTION OF METHYLENETRIPHENYLPHOSPHORANE WITH TRIS(METHYLVINYL KETONE)TUNGSTEN

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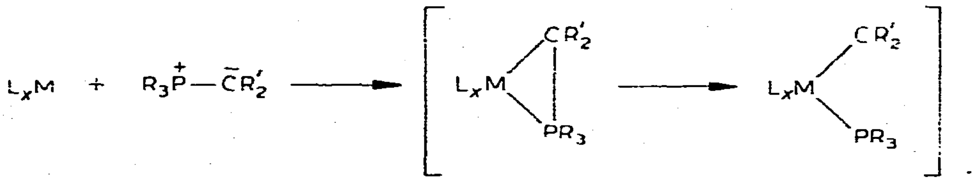
Summary

Tris(methylvinyl ketone)tungsten is treated with methylenetriphenylphosphorane to give a complex $W(\bar{C}H_2\overset{+}{P}Ph_3)_3$. No Wittig reaction products or rearranged ylide could be detected.

Introduction

Ylides represent a class of compounds that are polarized 1,2-dipoles, which have a heteroatom that can expand its coordination sphere by oxidative addition [1]. Ylides also have a wide range of chemical reactivities, which include complexation to a variety of transition metal compounds [2,3]. The possibility of oxidative addition to the transition metal atom with consequent "carbenation" of the complex is a matter of synthetic interest,



In this paper the results of treating phosphorus ylides with low-valent transition metal complexes with the aim of "carbenation" is presented.

Results and discussion

Tris(methylvinyl ketone)tungsten and methylenetriphenylphosphorane

Treatment of tris(methylvinyl ketone)tungsten (I) [4] with three equivalents

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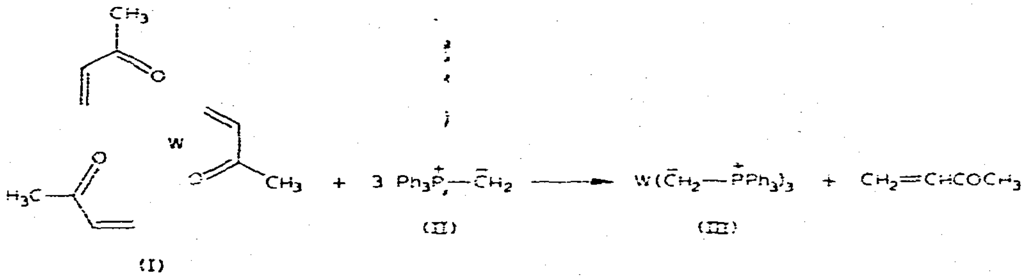
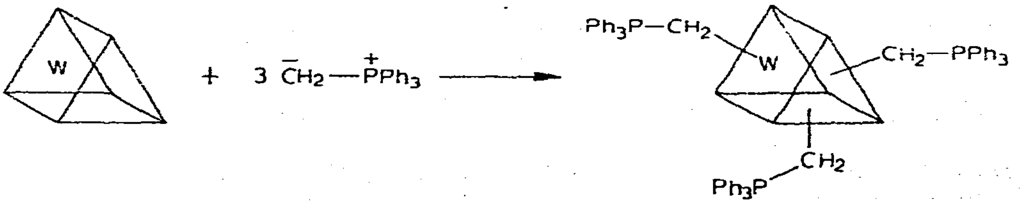
of methylenetriphenylphosphorane (II) in tetrahydrofuran (THF) at 20°C for 8 h gives a clear red-orange solution. Vacuum removal of the solvent at 0°C gives a bright red solution, and a bright red, air-sensitive solid, after complete removal of THF. The same product is obtained when benzene is used as the solvent. Quantitative gas chromatographic analysis of the volatile materials shows complete removal of the methylvinyl ketone, and no triphenylphosphine oxide or ylide reaction product, i.e., isoprene, can be detected.

When I is treated with II in a 1 : 1 or 1 : 2 molar ratio, respectively, there is no detection of triphenylphosphine oxide or ylide reaction products. Vacuum removal of solvent and gas chromatographic analysis show only the removal of one and two equivalents of methylvinyl ketone, respectively, and the ^{1}H NMR spectrum of the isolated product shows the complex to have the corresponding ratio of methylvinyl ketone and methylenetriphenylphosphorane.

If the reaction product from the interaction of I and II in a 1 : 1 molar ratio is re-dissolved in THF and treated with fresh methylvinyl ketone, there is no triphenylphosphine oxide formed. This means that the ylide must be sufficiently well complexed to the tungsten to preclude formation of normal Wittig reaction products. However, if this same solution (with freshly added methylvinyl ketone) is treated with methylenetriphenylphosphorane, triphenylphosphine oxide is formed. These results show that II does not interact with complexed methylvinyl ketone to produce isoprene or tris(isoprenyl)tungsten. The methylvinylketone must remain complexed to the tungsten atom until the system is placed under vacuum because any free methylvinyl ketone would interact with II during the addition:



A view of the trigonal prismatic structure of tris(methylvinyl ketone)tungsten [5] is helpful in understanding the product of this reaction. The trigonal faces can conceivably act as acceptor sites for the nucleophilic methylenetriphenylphosphorane:



Although weak donors such as carbon monoxide or triphenylphosphine do not complex to I, the strongly nucleophilic methylenetriphenylphosphorane apparently can coordinate to the tungsten atom. This occurs without displacement of the methylvinyl ketone, since free methylvinyl ketone is not observed in the reaction mixture. The methylvinyl ketone is then weakly bound to the tungsten atom, and when the system is placed under vacuum, the methylvinyl ketone is easily removed physically. Treatment of the red complex III in THF with dry HCl gas gives a green solution and quantitative recovery of methyltriphenylphosphonium chloride:

$$\underset{\text{(III)}}{\mathrm{W}(\bar{\mathrm{C}}\mathrm{H}_2\text{—}\overset{+}{\mathrm{P}}\mathrm{Ph}_3)_3} + \mathrm{HCl} \rightarrow \mathrm{W(Cl)}_x + \mathrm{Ph_3PCH_3^+Cl^-}$$

which is identified by ^{1}H NMR, and IR comparison with an authentic sample. Complex III does not form a tricarbonyl adduct with carbon monoxide at 30°C in THF. No definite exchange products could be isolated when complex III was treated with tri-*p*-tolylphosphine.

Molecular weight measurements in benzene show that complex III is monomeric when freshly prepared. After 6 to 8 h, however, THF or benzene solutions of complex III slowly deposit an insoluble waxy solid, which could not be purified.

A ^{1}H NMR spectrum of complex III in benzene-d_6 shows δ 1.44 ppm, PCH$_2$, doublet, ^1J(PCH) 16 Hz, 2 H; δ 7.62 ppm, multiplet, *o*-C$_6$H$_5$, 12 H; δ 7.52 ppm, *m*, *p*-C$_6$H$_5$, multiplet, 18 H. By comparison, methylenetriphenylphosphorane has a ^{1}H chemical shift of 0.13 ppm with respect to Me$_4$Si [6]. The ^{31}P NMR spectrum shows a single peak of medium intensity at δ 5.87 ppm (H$_3$PO$_4$), small peaks at δ −20.0, and −23.7 ppm, an intense peak at δ −23.9 ppm and a small peak at δ −24.2 ppm. The peaks centered around −23.5 correspond to $\mathrm{Ph_3\overset{+}{P}\text{—}\bar{C}H_2}$ (chemical shift of $\mathrm{Ph_3\overset{+}{P}\text{—}CH_3X^-}$ δ −21.1 ppm) [7]. The peak at +5.87 above H$_3$PO$_4$ is free triphenylphosphine present in solution [8]. Evidently complexation of the methylenetriphenylphosphorane to the tungsten atom must induce cleavage of triphenylphosphine from the ylide carbon atom. There is no evidence in the ^{31}P NMR spectra for ^{183}W—^{31}P coupling which would suggest that some of the triphenylphosphine is coordinated to the tungsten atom. The ^{31}P chemical shifts do fall in the region where the phosphorus atom in Ph$_3$P—W(CO)$_5$ (δ (85% H$_3$PO$_4$) −20.6) has a signal, hence the result is not entirely conclusive [9].

In THF-d_8 the ^{31}P NMR spectrum is essentially the same as the one observed in benzene-d_6, except that a series of small peaks appear clustered around −24 ppm. The major peak at −24.3 ppm is only of moderate intensity with respect to the triphenylphosphine peak at δ +5.7 ppm. The latter is the most intense peak in the spectrum. Evidently the complex loses more triphenylphosphine when it is dissolved in THF rather than benzene.

The ^{1}H NMR spectrum in THF-d_8 shows a doublet at δ 1.7 ppm, J(PCH) 13 Hz and smaller but significant peaks in the range δ 4—7 ppm, cf. Fig. 1. These peaks also appear in the ^{1}H NMR spectrum of I in DMSO-d_6, but not in the NMR spectrum with benzene-d_6 as a solvent. The ^{1}H{^{31}P} NMR spectrum shows collapse of the peak at δ 1.7 ppm to a singlet, which means that the doublet must be the result of ^{31}P coupling to the methylene group. The smaller peak shown in Fig. 1 do not collapse under broad band ^{31}P decoupling. This means

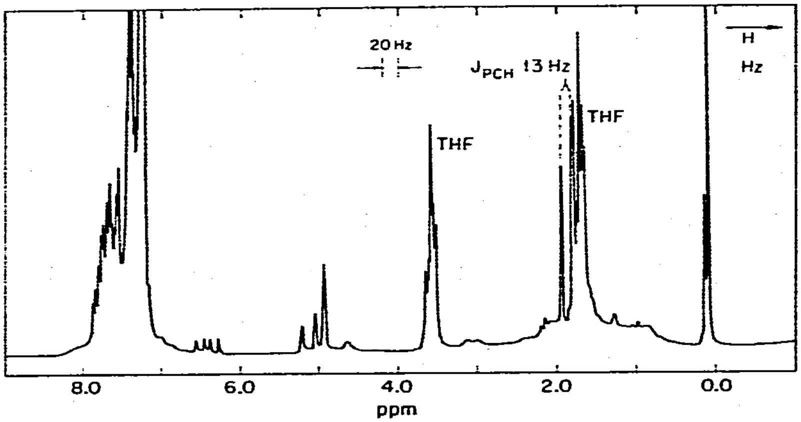


Fig. 1. The 100 MHz PFT ^1H NMR spectrum in THF-d_8 of the product obtained from the interaction of tris(methylvinyl ketone)tungsten and methylenetriphenylphosphorane.

that these protons belong either to π-complex benzene rings or to methylene groups bound to the tungsten atom. A ^1H NMR spectrum of the product obtained from I and $Ph_3\overset{+}{P}-\overset{-}{C}D_2$ shows complete absence of the δ 1.7 ppm peak. The peaks at δ 4.9 and 5.2 ppm are still present but the other peaks at δ 5.0 and 6.0—7.0 ppm completely disappear with the deuterated ylide. It is entirely possible that species such as $(Ph_3P-CH_2)_2W-CH_2 \cdot THF$, $Ph_3P-CH_2-W(CH_2 \cdot THF)_2$ and the like are present, but their relative concentration must be small. The disappearance of the bands at δ 5.0 and 6.0—7.0 ppm in the product with the deuterated ylide could be identified with such species. Such species with strongly coordinated THF have been observed by Marks in tungsten—germanium systems [14].

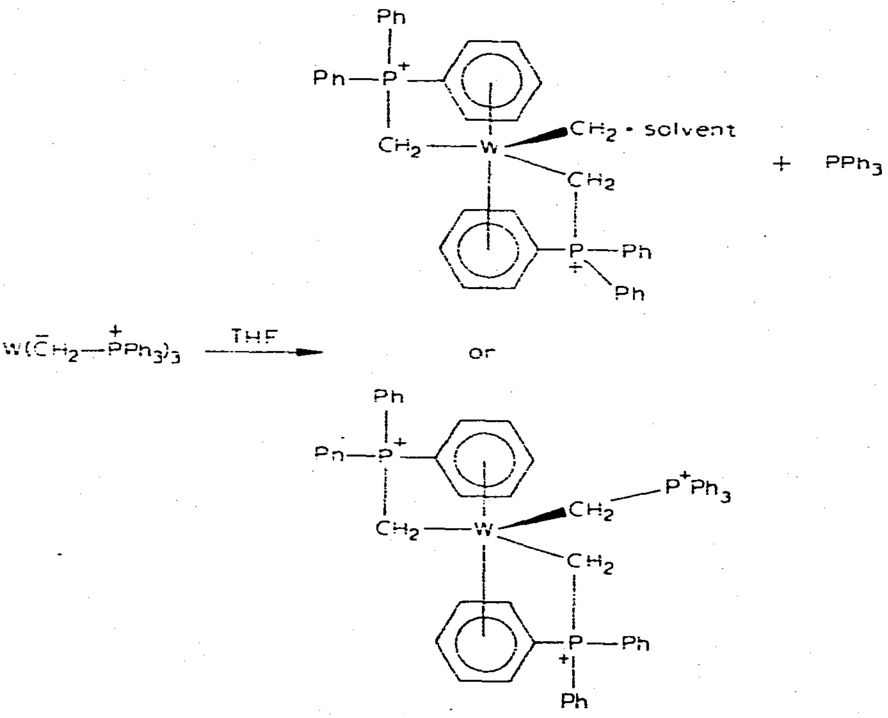
The $^{13}C\{^1H\}$ NMR spectrum shows a doublet at 16.9 ppm below TMS with a $J(^{31}P-^{13}C)$ of 79.4 Hz. By comparison, Kreissel and Held [10] observe that in $(CO)_5\overset{-}{W}-C(C_6H_5)_2\overset{+}{P}(CH_3)_3$, the chemical shift for the tungsten-carbon system is 40.6 ppm below TMS with $^1J(^{31}P-^{13}C)$ of 17.1 Hz. The $^{13}C\{^1H\}$ NMR of the $P-CH_3$ group shows a shift of 13.92 ppm below TMS with $^1J(^{31}P-^{13}C)$ of 58.6 Hz [10]. Furthermore, the $^{13}C\{^1H\}$ NMR of the complex $(CO)_5\overset{-}{W}-C(CH_3)(OCH_3)\overset{+}{P}(CH_3)_3$ shows δ(WC) of 72.87 ppm below TMS with $^1J(^{31}P-^{13}C)$ of 32.0 Hz [13]. There was no report of $^1J(^{183}W-^{13}C)$ coupling in either case. This coupling has not been observed in complex III. Moreover, there is no evidence for carbon-13 resonances at very low field which would be characteristic of "$W=CH_2$" species in III, in spite of the fact that in benzene and THF the ^{31}P NMR spectrum shows the presence of free triphenylphosphine.

A major comparison of these results can be made with the work of Wilke et al. on the interaction of bis(cyclooctadiene)nickel with phosphorus ylides [15]:

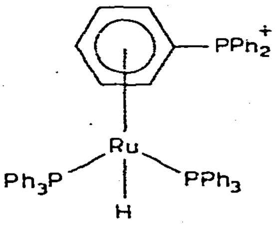
$$Ni(COD)_2 + \overset{-}{C}H_2-\overset{+}{P}(C_6H_5)_3 \rightarrow Ni[P(C_6H_5)_2CH_2C_6H_5]_4 + COD$$

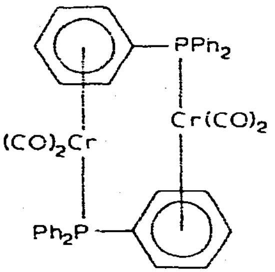
$$Ni(COD)_2 + \overset{-}{C}H_2-\overset{+}{P}Me_3 \rightarrow Ni(PMe_3)_4 + (CH_2)_x + COD$$

Here the product is a Stevens rearrangement of the ylide to a phosphine. No such product was observed with tungsten. One possible reason is that the benzene rings interact with the tungsten atom, after all the methylvinyl ketone has been removed:



Similar species have been observed by Sanders [16], Schrock [17], Colton [18] and Elschenbroich [19],





A recent X-ray structural determination of [PhP(CH$_3$)$_2$]$_4$Mo [20] shows that the benzene rings can complex to the metal atom. This postulate can account for the observation of peaks at δ 4.9 and 5.2 ppm [19], which probably represent π-complexed benzene rings of triphenylphosphine groups, in the ^{1}H NMR spectrum of III cf. Fig. 1.

The aromatic region of the ^{13}C{^{1}H} NMR spectrum was very complex and did not correspond to typical Ph$_3\overset{+}{P}$—$\bar{C}$H$_2$ resonance patterns.

Experimental

Instrumentation

Proton magnetic resonance spectra were recorded with Varian T-60, XL-100 and Jeolco MH-100 instruments; chemical shifts are reported in δ (ppm) from tetramethylsilane (TMS). The carbon-13 Fourier Transform (FT NMR) spectra were recorded on Jeol PS-100 at 25 MHz and Varian CFT-20 instruments; chemical shifts were measured in δ (ppm) from TMS. The ^{31}P NMR spectra were recorded with a Bruker HFX-10 spectrometer in the FT mode with proton decoupling. An external reference of 85% H_3PO_4 in benzene-d_6 or THF-d_8 was used; positive values are upfield from H_3PO_4. Infrared spectra were recorded on a Perkin--Elmer 337 spectrophotometer; molecular weight measurements were made with a cryoscopy cell described by Shriver [21], and mass spectra were determined at 70 eV on an AEI MS-9 spectrometer.

Materials and methods

All operations with phosphorus ylides were performed under dry oxygen-free nitrogen or argon. Chemical analyses were performed by Chemanalytics, Inc., 2330 Industrial Park, Tempe, Arizona, 85287. Reagent grade solvents were freshly distilled from $LiAlH_4$ or solutions of benzophenone ketyl. Methylvinyl ketone was purchased from Aldrich Chemical Company and freshly distilled before use. Acetonitrile was dried and distilled from CaH_2. Triphenylphosphine was recrystallized from ethanol and stored under nitrogen. Tris(methylvinyl ketone)-tungsten was prepared according to King and Fronzaglia [4]. Methylenetriphenylphosphorane was prepared according to Schmidbaur et al. [22].

Tris(methylenetriphenylphosphorane)tungsten

Methylenetriphenylphosphorane (0.315 g, 1.145 mmol) dissolved in 15 ml of THF was added dropwise over 15 min to a stirred solution of tris(methylvinyl ketone)tungsten (0.150 g, 0.380 mmol) in 15 ml of THF. The solution became light orange and after 8 h at 25°C it became deep red. Vacuum removal of THF gave a deep red solid which could be precipitated from THF by addition of hexane, 0.3 g, 80% m.p. 78—79°C (Found: C, 67.5; H, 5.1; P, 9.2. $C_{57}H_{51}P_3W$ calcd.: C, 59.1; H, 5.6; P, 9.0%).

The carbon analysis for the product was consistently poor. Mol. wt. found: 1005. $W(CH_2PPh_3)_3$ calcd. 1012.

Tris(methylenetriphenylphosphorane)tungsten and HCl

A red solution of tris(methylenetriphenylphosphorane)tungsten (0.08 g, 0.079 mmol) was dissolved in 25 ml of THF. The red solution became yellow and cloudy with addition of gaseous HCl. The THF was removed and the green gummy solid was washed with ether. It was then dissolved in 10 ml of water, filtered and treated with an aqueous solution of sodium tetraphenylborate. The white precipitate (0.09 g, 0.076 mmol) m.p. 191—194°C was filtered, dried under vacuum and compared to an authentic sample made from methyltriphenylphosphonium bromide, m.p. 192—194°C.

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