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A Novel Synthesis of Vinylidene Diphosphine Complexes of Type $[M(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$, (M = W or Cr)

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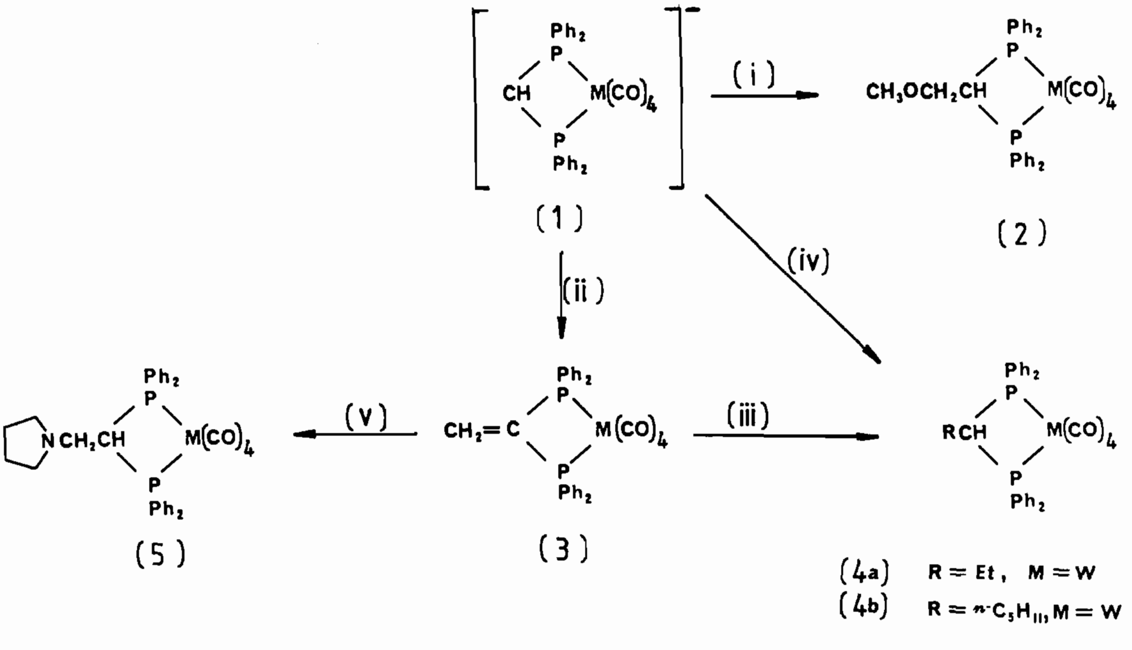
Introduction

There is great interest in the coordination/organometallic chemistry generated by $Ph_2PCH_2PPh_2$ (dppm), *e.g.* this ligand forms bimetallic complexes with or without metal–metal bonds, 'A-frames' and many other types of complex [1–3]. In contrast there has been very little done with substituted dppms of type $Ph_2PCHRPPh_2$ (R = alkyl, aryl or functional group) although one might anticipate interesting electronic and stereochemical effects due to the presence of the R group(s). We have shown that the benzoyl derivative $[\{W(CO)_4Ph_2PCH(COPh)PPh_2\}]$ undergoes a photochemically induced chelate ring expansion (4- to 6-membered) [4] and the corresponding hydrazone undergoes a thermal ring expansion, 4- to 7-membered [5]. We now report a simple synthesis of complexes of the new and reactive ligand tetraphenylvinylidene diphosphine, $Ph_2PC(=CH_2)PPh_2$.

Results and Discussion

Although the anion $[Ph_2PCHPPh_2]^-$ is ambident and usually reacts with electrophiles to give mixtures [6] we have shown that when complexed to a Group VI metal carbonyl $[M(CO)_4(Ph_2PCHPPh_2)]^-$ [7], or platinum(II) di-iodide $[PtI_2(Ph_2PCHPPh_2)]^-$ [8], it reacts as a carbanion. We now find that treatment



Scheme 1. Chemistry related to the formation and reactions of the vinylidine diphosphine complexes $[M(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$ (M = W or Cr).

The carbanions (1) were formed from $[M(CO)_4\{Ph_2PCH_2PPh_2\}]$ by treatment with $LiBu^n/Me_2NCH_2CH_2NMe_2$ in Et_2O for 2 hours as described previously [7].

(i) $MeOCH_2Cl/THF$/48 hours/20 °C, M = W or Cr.

(ii) $MeOCH_2Cl/C_6H_6$/4 hours (Cr) or 6 hours (W) at *ca.* 80 °C.

(iii) $MeLi/Et_2O$ for 24 hours at 20 °C, then MeOH added to give (4a): BuLi/n-hexane for 48 hours at 20 °C, then MeOH added to give (4b): similarly for the chromium complexes.

(iv) EtI/24 hours/20 °C gives (4a), n-$C_5H_{11}I$/48 hours/20 °C gives (4b).

(v) 70 fold excess of pyrrolidine in EtOH for 30 minutes at 20 °C.

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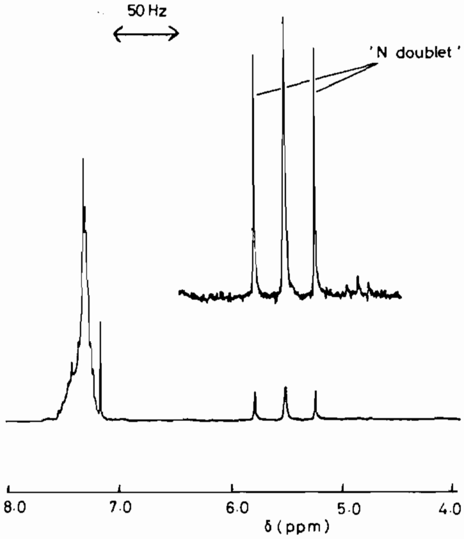

Fig. 1. ^1H NMR spectrum of $[W(CO)_4\{Ph_2PC(=CH_2)PPh_3\}]$ at 90 MHz over the range δ4–8, in $CDCl_3$ solution showing the 'N-doublet' separation of 49.5 Hz in the virtual triplet $=CH_2$ pattern (see text).

of the carbanions $[M(CO)_4(Ph_2PCHPPh_2)]^-$ (1) (M = Cr or W) with chloromethyl methyl ether at 20 °C gives the methoxymethyl derivatives $[M(CO)_4\{Ph_2PCH(CH_2OMe)PPh_2\}]$ (2) in good, ~60% yields, as orange crystalline solids: the corresponding reaction with molybdenum gave very dark products which could not be purified. However, similar treatment of these carbanions $[M(CO)_4(Ph_2PCHPPh_2)]^-$ with chloromethyl methyl ether at 80 °C for 4 hours (Cr), or 6 hours (W), gave the corresponding yellow, crystalline vinylidene complexes, $[M(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$ (3) in 68% (Cr) or 60% (W) yields (see Scheme 1). All these complexes were fully characterised by elemental analysis, mass spectrometry, IR spectroscopy and particularly by $^{31}P\text{-}\{^1H\}$, ^1H, and $^1H\text{-}\{^{31}P\}$ NMR spectroscopy. A remarkable feature of the ^1H NMR spectra is the presence of a 'virtual triplet' with the extremely large N-doublet separation of *ca.* 50 Hz (see Fig. 1). This separation is equal to $^3J(P\text{–}C\text{=}C\text{–}H)$ (*cis*) + $^3J(P\text{–}C\text{=}C\text{–}H)$ (*trans*) which are both probably large and positive in sign. Other alkenylphosphines have large values for $^3J(P\text{–}C\text{=}C\text{–}H)$ *cis* and *trans* and couplings are positive in sign [9, 10].

As might be expected the $CH_2\text{=}C$ double bond is activated by the $P_2M(CO)_4$ moiety: thus it readily undergoes Michael-type additions. Treatment of the vinylidene diphosphine tungsten complex, $[W(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$ with methyl-lithium followed by methanol gives the ethyl-derivative $[W(CO)_4\{Ph_2PCHEtPPh_2\}]$, which we have previously synthesised by treating the carbanion $[W(CO)_4\{Ph_2PCHPPh_2\}]^-$ with ethyl iodide [7]. Similarly, treatment of $[W(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$ with n-butyllithium, followed by methanol gives the n-pentyl derivative $[W(CO)_4\{Ph_2PCH(C_5H_{11})PPh_2\}]$ which we also synthesised by treating the anion, $[W(CO)_4\{Ph_2PCHPPh_2\}]^-$ with n-pentyl iodide (see Scheme). We also find that this vinylidene complex $[W(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$ readily reacts with pyrrolidine to give the adduct $[W(CO)_4\{Ph_2PCH(CH_2NC_4H_8)PPh_2\}]$ in 93% isolated yield. Similar results were obtained with the chromium analogues.

Thus far we have not been successful in trying to convert the methoxymethyl derivative $[W(CO)_4\{Ph_2PCH(CH_2OMe)PPh_2\}]$ (2) into the vinylidene derivative $[W(CO)_4\{Ph_2PC(=CH_2)PPh_2\}]$ either by heat (refluxing toluene solution) or by treatment with acidic (H_2SO_4/benzene) or basic $\{LiN(SiMe_3)_2\}$ reagents. In no case could any of the vinylidene complex be detected.

These vinylidene diphosphine derivatives contain an activated double C=C bond and are probably capable of many reactions in addition to those described above.

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