

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

GARY R. COOPER, DAVID M. McEWAN and BERNARD L. SHAW*

School of Chemistry, The University, Leeds LS2 9JT, U.K.

Received October 30, 1982

Introduction

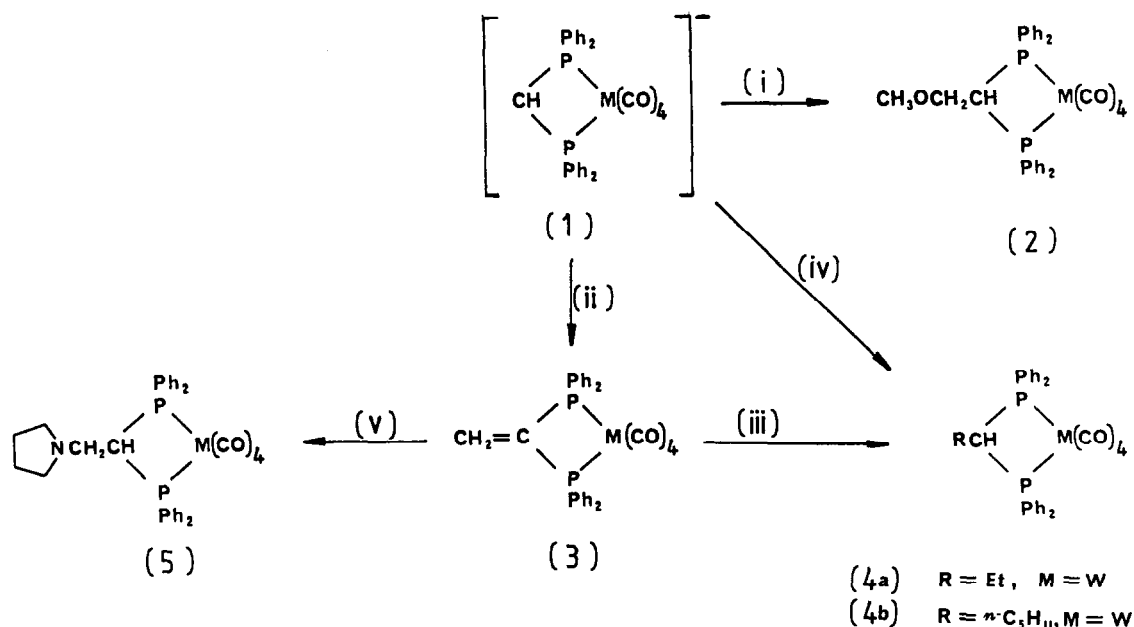
There is great interest in the coordination/organometallic chemistry generated by $Ph_2PCH_2PPh_2$ (dppm), e.g. this ligand forms bimetallic complexes with or without metal–metal bonds, ‘A-frames’ and many other types of complex [1–3]. In con-

trast 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

* Author to whom correspondence should be addressed.



Scheme 1. Chemistry related to the formation and reactions of the vinylidene 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 $LiBu^t/Me_2NCH_2CH_2NMe_2$ in Et_2O for 2 hours as described previously [7].

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

(ii) $MeOCH_2Cl/C_6H_6/4$ hours (Cr) or 6 hours (W) at ca. $80^\circ C$.

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

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

(v) 70 fold excess of pyrrolidine in $EtOH$ for 30 minutes at $20^\circ C$.

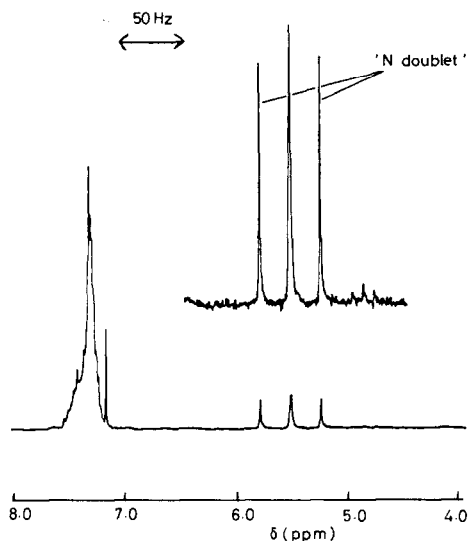


Fig. 1. ^1H NMR spectrum of $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_3\}]$ at 90 MHz over the range δ 4–8, in CDCl_3 solution showing the 'N-douplet' separation of 49.5 Hz in the virtual triplet $=\text{CH}_2$ pattern (see text).

of the carbanions $[\text{M}(\text{CO})_4(\text{Ph}_2\text{PCHPPh}_2)]^-$ (1) ($\text{M} = \text{Cr}$ or W) with chloromethyl methyl ether at 20°C gives the methoxymethyl derivatives $[\text{M}(\text{CO})_4\{\text{Ph}_2\text{PCH}(\text{CH}_2\text{OMe})\text{PPh}_2\}]$ (2) in good, $\sim 60\%$ 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 $[\text{M}(\text{CO})_4(\text{Ph}_2\text{PCHPPh}_2)]^-$ with chloromethyl methyl ether at 80°C for 4 hours (Cr), or 6 hours (W), gave the corresponding yellow, crystalline vinylidene complexes, $[\text{M}(\text{CO})_4\{\text{Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}]$ (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 $^{31}\text{P}\{^1\text{H}\}$, ^1H , and $^1\text{H}\{^{31}\text{P}\}$ NMR spectroscopy. A remarkable feature of the ^1H NMR spectra is the presence of a 'virtual triplet' with the extremely large N-douplet separation of ca. 50 Hz (see Fig. 1). This separation is equal to $^3\text{J}(\text{P}-\text{C}=\text{C}-\text{H})$ (*cis*) + $^3\text{J}(\text{P}-\text{C}=\text{C}-\text{H})$ (*trans*) which are both probably large and positive in sign. Other alkenylphosphines have large values for $^3\text{J}(\text{P}-\text{C}=\text{C}-\text{H})$ *cis* and *trans* and couplings are positive in sign [9, 10].

As might be expected the $\text{CH}_2=\text{C}$ double bond is activated by the $\text{P}_2\text{M}(\text{CO})_4$ moiety: thus it readily undergoes Michael-type additions. Treatment of the vinylidene diphosphine tungsten complex, $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}]$ with methyl-lithium followed

by methanol gives the ethyl-derivative $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCH}_2\text{EtPPh}_2\}]$, which we have previously synthesised by treating the carbanion $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCHPPh}_2\}]^-$ with ethyl iodide [7]. Similarly, treatment of $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}]$ with *n*-butyllithium, followed by methanol gives the *n*-pentyl derivative $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCH}(\text{C}_5\text{H}_{11})\text{PPh}_2\}]$ which we also synthesised by treating the anion, $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCHPPh}_2\}]^-$ with *n*-pentyl iodide (see Scheme). We also find that this vinylidene complex $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}]$ readily reacts with pyrrolidine to give the adduct $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCH}(\text{CH}_2\text{NC}_4\text{H}_8)\text{PPh}_2\}]$ 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 $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PCH}(\text{CH}_2\text{OMe})\text{PPh}_2\}]$ (2) into the vinylidene derivative $[\text{W}(\text{CO})_4\{\text{Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}]$ either by heat (refluxing toluene solution) or by treatment with acidic ($\text{H}_2\text{SO}_4/\text{benzene}$) or basic $\{\text{LiN}(\text{SiMe}_3)_2\}$ reagents. In no case could any of the vinylidene complex be detected.

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

Acknowledgement

We thank the Science and Engineering Research Council for support.

References

- 1 M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc. Dalton Trans.*, 1540 (1978).
- 2 L. S. Benner and A. L. Balch, *J. Am. Chem. Soc.*, **100**, 6099 (1978).
- 3 D. M. Hoffmann and R. Hoffmann, *Inorg. Chem.*, **20**, 3543 (1981) and references therein.
- 4 S. Al-Jibori, M. Hall, A. T. Hutton and B. L. Shaw, *J. Chem. Soc. Chem. Commun.*, 1069 (1982).
- 5 S. Al-Jibori, W. S. McDonald and B. L. Shaw, *J. Chem. Soc. Chem. Commun.*, 287 (1982).
- 6 K. Issleib and H. P. Abicht, *J. Prakt. Chem.*, **312**, 456 (1970).
- 7 S. Al-Jibori and B. L. Shaw, *J. Chem. Soc. Chem. Commun.*, 286 (1982).
- 8 S. Al-Jibori and B. L. Shaw, *Inorg. Chim. Acta Letters*, **65**, L123–124 (1982).
- 9 W. A. Anderson, R. Freeman and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963).
- 10 Y. Y. Samitov, E. A. Berdnikov, F. R. Tantasheva, B. Y. Margulis and E. G. Kataev, *Zhur. Obschei Khim.*, **45**, 2130 (1975).