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Preliminary communication

THE CHEMISTRY OF VINYLPHOSPHINE CHALCIDES

I. THE PREPARATION OF DIPHENYLVINYLPHOSPHINE OXIDE TETRACARBONYLIRON(0)

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Summary

Reaction of diphenylvinylphosphine oxide with dodecacarbonyltriiron(0) gives $Ph_2P(O)CH{=}CH_2 \cdot Fe(CO)_4$, in which coordination of the iron-containing moiety to the phosphine oxide is considered to take place through the carbon—carbon double bond of the latter.

Vinylphosphine oxides are known to be reactive, in a Michael-type sense, towards nucleophiles [1, 2], but will react only with powerful electrophiles, under forcing conditions [2]. It was of interest to us to see whether isolable complexes of vinylphosphine oxides with metals in low oxidation states might be preparable. Complexes of inter alia diphenylvinylphosphine oxide (I) with metals in normal oxidation states are well characterised, and coordination of the phosphine oxide occurs through phosphoryl oxygen [3]. Further stimulus for our research was provided by the report that an intermediate tetracarbonyliron(0) derivative of 2,5-dihydrothiophene 1-oxide had been isolated (and the iron moiety coordinated through the sulphoxide oxygen) in the preparation of the more stable tricarbonyliron(0) derivative [4].

Treatment of phosphine oxide I with a slight molar excess of dodecacarbonyltriiron(0) in tetrahydrofuran at ambient temperature led to the isolation of the tetracarbonyliron(0) complex II as lemon-yellow needles (ether; decomp. > 85°C) in 16% yield*** (Scheme 1).

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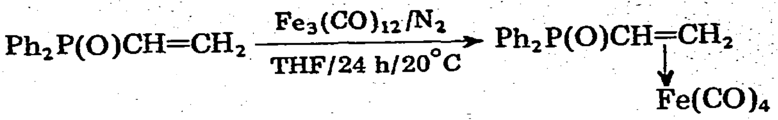
***Satisfactory analytical and mass spectroscopic data were obtained for this compound.



$$Ph_2P(O)CH{=}CH_2 \xrightarrow[\text{THF/24 h/20°C}]{Fe_3(CO)_{12}/N_2} \underset{\begin{array}{c}\downarrow\\ Fe(CO)_4\end{array}}{Ph_2P(O)CH{=}CH_2}$$

(I) (II)

SCHEME 1

Increasing the reaction time led to the isolation of increasing amounts of brown polymeric material, as did carrying out the reaction at higher temperatures. None of complex II was isolated in reactions employing benzene as solvent.

On the basis of its infrared spectrum (similar in pattern to other tetracarbonyliron(0) complexes of olefins [5]) and NMR data, complex II was assigned the structure shown in Scheme 1, with bonding to the iron moiety via the olefinic centre. Tables 1—3 include spectroscopic data for this compound and for the parent phosphine oxide I.

TABLE 1

INFRARED DATA FOR PHOSPHINE OXIDE I AND COMPLEX II[a]

	$Ph_2P(O)CH{=}CH_2$	$Ph_2P(O)CH{=}CH_2 \cdot Fe(CO)_4$
ν(P=O)	1173	1215
ν(C=C)	1608	absent
ν(C=O)		2097, 2033, 2018, 1992

[a] Values given in cm^{-1}; recorded in $CHCl_3$ solution.

TABLE 2

^{1}H NMR DATA FOR PHOSPHINE OXIDE I AND COMPLEX II[a]

$Ph_2P(O)CH{=}CH_2$	2.15—2.80 (11H), 2.90—4.00 (2H)
$Ph_2P(O)CH{=}CH_2 \cdot Fe(CO)_4$	2.00—2.25 (4H), 2.40—2.55 (6H), 6.90—7.35 (3H)

[a] Values given in τ (ppm); recorded in $^2HCCl_3$ solution.

TABLE 3

^{13}C NMR DATA FOR PHOSPHINE OXIDE I AND COMPLEX II[a]

	$Ph_2P(O)CH{=}CH_2$	$Ph_2P(O)CH{=}CH_2 \cdot Fe(CO)_4$
δ (C(1))	131.5	120.8
J(P—C(1))	96.4	86.9
δ (C(2))	134.4	117.0
J(P—C(2))	11.8	0

[a] Recorded in $^2HCCl_3$ solution; chemical shifts (δ) given in ppm downfield from TMS; coupling constants (J) given in Hertz. C(1) and C(2)[b] were distinguished by selective off-resonance decoupling experiments. [b] C(1) is the vinyl carbon α to phosphorus; C(2) is β to phosphorus.

Efforts to obtain a tricarbonyliron(0) derivative of phosphine oxide I from complex II were not successful. Pyrolysis of II gave black polymeric material. Photolysis of II in benzene at 15°C gave only brown polymeric material, and a methanol-soluble grey solid of approximate composition $(Ph_2POCH{=}CH_2)_5$-$Fe(CO)_4$. The latter had an infrared spectrum similar to that of complex II, but with much weaker carbonyl absorbances. Attempts to prepare other metal complexes of phosphine oxide I have not yet met with success; no reaction was observed between I and 1,5-cyclooctadieneplatinum(II) chloride or bis(acetonitrile)-

platinum(II) chloride, and treatment of I with bis(ethylene)rhodium(I) chloride dimer, and subsequent reaction with cyclopentadienylthallium(I), gave only trace amounts of a light-sensitive red solid.

Acknowledgement

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