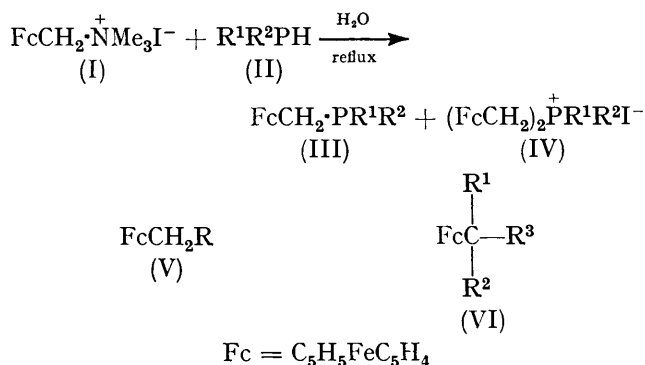


Organometallic Derivatives. Part VI.¹ Synthesis and Reactivity of Some (Ferrocenylmethyl)phosphines

By George Marr* and Trevor M. White, Department of Physical Sciences, The Polytechnic, Wolverhampton WV1 1LY

(Ferrocenylmethyl)phosphines have been prepared by the reactions of phenylphosphine, diphenylphosphine, and diphenylphosphine oxide with dimethylaminomethylferrocene methiodide. A series of α -substituted ferrocenylmethyl alcohols have been treated with phenylphosphine and diphenylphosphine. In these reactions the phosphine behaves both as a nucleophile, displacing the hydroxy-group to give a (ferrocenylmethyl)phosphine, and as a reducing agent, giving the corresponding ferrocenylalkane.

THE only previous reports of the preparation and reactivity of (ferrocenylmethyl)phosphines are those by Pauson and Watts² and Toma *et al.*³ Pauson and Watts treated dimethylaminomethylferrocene methiodide (I) with triphenylphosphine to give the methiodide (V; $R = \overset{+}{P}Ph_3I^-$), which was converted into the corresponding phosphorane (FcCH=PPh₃) with phenyl-lithium.



Reduction of this phosphorane with lithium aluminium hydride gave the (ferrocenylmethyl)phosphine (III; $R^1 = R^2 = Ph$). Toma *et al.* treated the methiodide

¹ Part V, G. Marr and J. Ronayne, *J. Organometallic Chem.*, 1973, **47**, 417.

² P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, 2990.

³ S. Toma and E. Kaluzayova, *Chem. Zvesti*, 1969, **23**, 540.

(I) with triethyl phosphite to give the (ferrocenylmethyl)phosphonate [V; $R = P(O)(OEt)_2$].

As part of a study of the chemistry of ferrocenyl phosphines⁴ we have investigated the reactions of primary and secondary phosphines with α -substituted ferrocenylmethanes. The reaction of diphenylphosphine with the methiodide (I) gave the (ferrocenylmethyl)phosphine (III; $R^1 = R^2 = Ph$) in good yield and the bis(ferrocenylmethyl)phosphonium salt (IV; $R^1 = R^2 = Ph$). The ready formation of the phosphine (III; $R^1 = R^2 = Ph$) was expected as phosphines are invariably stronger nucleophiles than the corresponding amines⁵ and diphenylamine will displace the trimethylammonium group in this system.⁶ The phosphine (III; $R^1 = R^2 = Ph$) readily formed the corresponding oxide on treatment with aqueous hydrogen peroxide. The phosphonium salt (IV; $R^1 = R^2 = Ph$) was presumably formed by nucleophilic attack of the phosphine (III; $R^1 = R^2 = Ph$) on the methiodide (I).

In a separate experiment the aminomethylferrocene methiodide (I) was treated with the phosphine (III; $R^1 = R^2 = Ph$) to give the phosphonium salt (IV; $R^1 = R^2 = Ph$) together with some ferrocenylmethanol.

⁴ G. Marr and T. Hunt, *J. Chem. Soc. (C)*, 1969, 1070.

⁵ B. J. Walker, 'Organophosphorus Chemistry,' Penguin, England, 1972, p. 49.

⁶ M. Hadlington, B. W. Rockett, and A. Nelhans, *J. Chem. Soc.*, 1967, 1436.

This salt (IV; $R^1 = R^2 = \text{Ph}$) was degraded with boiling aqueous sodium hydroxide to give methylferrocene and the ferrocenylphosphine oxide [V; $R = \text{P}(\text{O})\text{Ph}_2$]. This reaction was repeated in the presence of an excess of phenol to generate the phenoxide ion, but the same products were obtained. These products were obtained by nucleophilic attack of the hydroxide ion on the phosphonium salt.⁷ No ferrocenylmethanol or ferrocenylmethyl phenyl ether was isolated; such products might have been expected because of the unusual

CH_2Fc , $R^2 = \text{Ph}$) was obtained presumably by nucleophilic attack of the first-formed phosphine (III; $R^1 = \text{H}$, $R^2 = \text{Ph}$) on the methiodide; further reaction of the former phosphine with the methiodide would give the salt (IV; $R^1 = \text{CH}_2\text{Fc}$, $R^2 = \text{Ph}$).

The current interest in the displacement of hydroxy- and similar groups from α -substituted ferrocenylmethanes prompted us to investigate the reactivity of phenylphosphines in these systems.^{9,10} Aniline will displace hydroxy-, dimethylamino-, phenoxy-, piperi-

TABLE 1

Yields (%) of (ferrocenylmethyl)phosphines from the reaction of ferrocenylmethyl quaternary salts with phenylphosphines

Reactants	Reaction time (h)	(Ferrocenylmethyl)phosphine	Yield (%) ^a
(I) + (III; $R^1 = R^2 = \text{Ph}$)	24	(IV; $R^1 = R^2 = \text{Ph}$)	66
(VI; $R^1 = R^2 = \text{Ph}$) + aq. NaOH	24	(V; $R = \text{OH}$)	23
(VI; $R^1 = R^2 = \text{Ph}$) + aq. NaOH-PhOH	24	[V; $R = \text{P}(\text{O})\text{Ph}_2$]	58
		FcMe	35
(I) + $\text{Ph}_2\text{P}(\text{O})\text{H}$	24	[V; $R = \text{P}(\text{O})\text{Ph}_2$]	35
		FcMe	49
(I) + PhPH_2	18	[V; $R = \text{P}(\text{O})\text{Ph}_2$]	27
		(FcCH_2) ₂ O	58
		(III; $R^1 = \text{H}$, $R^2 = \text{Ph}$)	12
		(III; $R^1 = \text{CH}_2\text{Fc}$, $R^2 = \text{Ph}$)	12
		(IV; $R^1 = \text{CH}_2\text{Fc}$, $R^2 = \text{Ph}$)	69
		(FcCH_2) ₂ O	4

^a Yields based on consumed starting material.

TABLE 2

Yields (%) of (ferrocenylmethyl)phosphines from the reaction of some ferrocenyl alcohols with phenyl- and diphenyl-phosphine

Reactants	Reaction time (h)	(Ferrocenylmethyl)phosphine	Yield (%) ^a
(V; $R = \text{OH}$) + PhPH_2	18	(III; $R^1 = \text{H}$, $R^2 = \text{Ph}$)	45
		(VI; $R^1 = \text{H}$, $R^2 = \text{CH}_2\text{Fc}$, $R^3 = \text{P}(\text{H})\text{Ph}$)	26
		(FcCH_2) ₂ O	5
(IV; $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{OH}$) + PhPH_2	20	(VI; $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{P}(\text{H})\text{Ph}$)	78
		[VI; $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{P}(\text{O})\text{HPh}$]	9
		(V; $R = \text{Me}$)	12
(IV; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{OH}$) + PhPH_2	20	(VI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{P}(\text{H})\text{Ph}$)	18
		[VI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{P}(\text{O})\text{HPh}$]	3
		(VI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{H}$)	68
		(VI; $R^1 = R^2 = \text{Me}$, $R^3 = \text{H}$)	76
(VI; $R^1 = R^2 = \text{Me}$, $R^3 = \text{OH}$) + PhPH_2	24	(VI; $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{P}(\text{H})\text{Ph}$)	51
		[VI; $R^1 = \text{H}$, $R^2 = \text{Me}$, $R^3 = \text{P}(\text{L})\text{Ph}_2$]	37
(VI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{OH}$) + Ph_2PH	20	(VI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{H}$)	52
		[VI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = \text{P}(\text{O})\text{Ph}_2$]	21
(VI; $R^1 = R^2 = \text{Me}$, $R^3 = \text{OH}$) + Ph_2PH	24	(VI; $R^1 = R^2 = \text{Me}$, $R^3 = \text{P}(\text{H})\text{Ph}$)	21
		[VI; $R^1 = R^2 = \text{Me}$, $R^3 = \text{P}(\text{O})\text{Ph}_2$]	22

^a Yields are based on consumed starting material.

stability of the α -ferrocenylcarbonium ion, which is all important in similar reactions with dimethylamino-methylferrocene methiodide.⁸ The reaction of diphenylphosphine oxide with the methiodide (I) gave the ferrocenylphosphine oxide [V; $R = \text{P}(\text{O})\text{Ph}_2$] and bis(ferrocenylmethyl) ether. Treatment of the methiodide (I) with phenylphosphine gave the salt (IV; $R^1 = \text{CH}_2\text{Fc}$, $R^2 = \text{Ph}$) as the major product together with the phosphines (III; $R^1 = \text{H}$, $R^2 = \text{Ph}$) and (III; $R^1 = \text{CH}_2\text{Fc}$, $R^2 = \text{Ph}$). The phosphine (III; $R^1 =$

dino-, and phenylsulphinyl¹¹ groups from the corresponding α -substituted ferrocenylmethanes and it has been shown that the nucleophilic character of the attacking group is important.¹⁰ From these earlier results it was thought that phenylphosphine could behave similarly. It was found that phenylphosphine would displace the hydroxy-group from ferrocenylmethanol to

⁷ A. J. Kirby and S. G. Warren, 'The Organic Chemistry of Phosphorus,' Elsevier, London, 1967, pp. 254-260.

⁸ J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, 1957, **22**, 355; M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

⁹ P. Dixneuf, *Compt. rend.*, 1969, **269** C, 424; P. Dixneuf and R. Dabard, *Bull. Soc. chim. France*, 1972, 2847; G. W. Gokel and I. K. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 191.

¹⁰ G. Marr, B. W. Rockett, and A. Rushworth, *J. Chem. Soc. (C)*, 1971, 4000; J. T. Pennie and T. I. Bieber, *Tetrahedron Letters*, 1972, 3535.

¹¹ J. B. Evans and G. Marr, *J.C.S. Perkin I*, 1972, 2502.

give ferrocenylmethyl(phenyl)phosphine and bis(ferrocenylmethyl)phenylphosphine. In this reaction the secondary and tertiary phosphines are formed directly from the reaction of an alcohol with a phosphine. Phenylphosphine behaves as a nucleophile in a similar manner to aniline. This is a new route to (ferrocenylmethyl)phosphines and the scope of the reaction has been investigated (see Table 2). In the case of the secondary alcohol (VI; $R^1 = H$, $R^2 = Me$, $R^3 = OH$) displacement of the hydroxy-group occurred to give the phosphine (VI; $R^1 = H$, $R^2 = Me$, $R^3 = P(H)Ph$) (85%)

Ph) and Bis(ferrocenylmethyl)diphenylphosphonium Iodide (IV; $R^1 = R^2 = Ph$).—The quaternary salt (I) (11.5 g, 0.030 mol) and diphenylphosphine (11.2 g, 0.060 mol) were added to water (300 ml) and the mixture was heated under reflux for 18 h, cooled, and extracted with ether. The water layer and the ether extracts contained, in suspension, the phosphonium salt (IV; $R^1 = R^2 = Ph$) (2.45 g, 23%), which was filtered off and crystallized from methanol as needles, m.p. 251—253° (Found: C, 56.9; H, 4.7; P, 4.3. $C_{34}H_{32}Fe_2IP$ requires C, 57.5; H, 4.5; P, 4.3%), τ [(CD_3)₂CO] 2.20 (10H, m, 2 \times Ph), 5.22 and 5.42 (4H, d, 2 \times CH₂), and 5.70 and 5.87 (18H, 2 \times s, 2 \times ferrocene).

TABLE 3
Analytical data for some (ferrocenylmethyl)phosphines

Compound	M.p. (°C)	Found (%)			M^+	Formula	Calc. (%)			M
		C	H	Fe			C	H	Fe	
[VI; $R^1 = H$, $R^2 = Me$, $R^3 = P(O)Ph_2$]	200—202	69.6	5.6	13.5	414	$C_{24}H_{23}FeOP$	69.6	5.6	13.5	414
(VI; $R^1 = R^2 = Me$, $R^3 = PPh_2$)	96—98	72.8	6.2		412	$C_{25}H_{25}FeP$	72.8	6.1		412
[VI; $R^1 = R^2 = Me$, $R^3 = P(O)Ph_2$]	140—142	69.8	5.9		428	$C_{25}H_{25}FeOP$	70.1	5.9		428
(VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = H$)	43—44	74.4	6.3	18.9	290	$C_{18}H_{18}Fe$	74.5	6.2	19.2	290
[VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = P(O)Ph_2$]	192—193	73.4	5.7	11.5		$C_{30}H_{27}FeOP$	73.5	5.5	11.4	
(III; $R^1 = H$, $R^2 = Ph$)	32—34	66.2	5.6		308	$C_{17}H_{17}FeP$	66.3	5.6		308
(III; $R^1 = CH_2Fc$, $R^2 = Ph$)	123—124	66.4	5.4		506	$C_{28}H_{27}Fe_2P$	66.4	5.4		506
(IV; $R^1 = CH_2Fc$, $R^2 = Ph$)	<i>a</i>	55.9	4.7	19.6		$C_{39}H_{38}Fe_3IP$	56.2	4.6	20.1	
[VI; $R^1 = H$, $R^2 = Me$, $R^3 = P(O)HPh$]	197—199	63.8	5.7		338	$C_{18}H_{19}FeOP$	63.9	5.7		338
[VI; $R^1 = H$, $R^2 = Me$, $R^3 = P^+HPhMeI^-$]	147—149	49.2	5.0			$C_{19}H_{22}FeIP$	49.2	4.8		
(VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = P(H)Ph$)	74—76	72.3	6.0		398	$C_{24}H_{23}FeP$	72.4	5.8		398
[VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = P(O)HPh$]	85—89	69.2	5.9			$C_{21}H_{23}FeOP$	69.6	5.6		

a Slowly decomp. from 270°.

(identified as the methiodide), the corresponding phosphine oxide, and (unexpectedly) ethylferrocene (12%). In this reaction the phosphine behaves both as a nucleophile and as a reducing agent. In the case of the tertiary alcohol (VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = OH$) reduction was the principal reaction, giving ferrocenyl(methyl)phenylmethane together with some of the phosphine (VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = P(H)Ph$) and the corresponding phosphine oxide. In the case of the tertiary alcohol 2-ferrocenylpropan-2-ol only the reduction product 2-ferrocenylpropane was isolated.

The treatment of ferrocenylmethanol with a secondary phosphine, diphenylphosphine, gave (ferrocenylmethyl)diphenylphosphine in 84% yield. In similar reactions the secondary alcohol (VI; $R^1 = Me$, $R^2 = H$, $R^3 = OH$) and the tertiary alcohol, 2-ferrocenylpropan-2-ol, gave the phosphines (VI; $R^1 = Me$, $R^2 = H$, $R^3 = PPh_2$) and (VI; $R^1 = Me$, $R^2 = Me$, $R^3 = PPh_2$), respectively; the corresponding phosphine oxides were also isolated. However in the case of the tertiary alcohol (VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = OH$) reduction was the principal process, giving 1-ferrocenyl-1-phenylethane (see Table 2).

EXPERIMENTAL

Light petroleum used had b.p. 40—60° unless otherwise stated; diethyl ether was washed with aqueous iron(II) sulphate and dried over sodium wire prior to use. All reactions were carried out under oxygen-free nitrogen. The phenylphosphine and diphenylphosphine were used as supplied by Strem Chemicals.

(Ferrocenylmethyl)diphenylphosphine (III; $R^1 = R^2 =$

The dried ($MgSO_4$) ether extracts were evaporated to leave a red oil, which was chromatographed on alumina. Ether-light petroleum eluted the phosphine (III; $R^1 = R^2 = Ph$) (8.80 g, 76%), which crystallised from ether-light petroleum as brown-orange crystals, m.p. 84—86° (lit.,² 85—87°) (Found: C, 71.7; H, 5.6%; M^+ , 384. Calc. for $C_{23}H_{21}FeP$: C, 71.9; H, 5.5%; M , 384), τ (CCl_4) 2.82 (10H, s, 2 \times Ph), 6.07 and 6.20 (9H, s and m, ferrocene), and 7.00 (2H, s, CH₂).

The oxide [V; $R = P(O)Ph_2$] was obtained by treatment of the phosphine (III; $R^1 = R^2 = Ph$) in acetone with 20% hydrogen peroxide as yellow needles, m.p. 207—209° (from methanol) (Found: C, 69.2; H, 5.4; P, 8.0%; M^+ , 400. $C_{23}H_{21}FeOP$ requires C, 69.0; H, 5.3; P, 7.7%; M , 400).

Reaction of Ferrocenylmethyl Quaternary Salts with Phenylphosphine.—The reactions of the quaternary salt (I) with phenylphosphine, diphenylphosphine oxide, and (ferrocenylmethyl)diphenylphosphine and the reactions of the phosphonium salt (IV; $R^1 = R^2 = Ph$) with aqueous 2M-sodium hydroxide and aqueous sodium hydroxide in the presence of a 50% excess of phenol were carried out similarly. The reaction times, products, and yields are given in Table 1 and analyses and m.p.s in Table 3.

Reaction of Ferrocenylmethanol with Diphenylphosphine.—Ferrocenylmethanol (2.0 g, 0.0093 mol) and diphenylphosphine (3.5 g, 0.019 mol) were added to water. The mixture was heated under reflux for 24 h, cooled, and extracted with benzene. The dried ($MgSO_4$) extracts were evaporated to leave a red oil which was chromatographed on alumina. Ether-light petroleum mixture eluted the (ferrocenylmethyl)phosphine (III; $R^1 = R^2 = Ph$) (1.50 g, 84%).

Reactions of the Hydroxymethylferrocenes (VI; $R^1 = Me$, $R^2 = H$, $R^3 = OH$), (VI; $R^1 = Me$, $R^2 = Ph$, $R^3 = OH$),

and (VI; $R^1 = R^2 = \text{Me}$, $R^3 = \text{OH}$) with *Phenylphosphine* and *Diphenylphosphine*.—These reactions were carried out similarly. The reaction times, products, and yields are given in Table 2 and the analyses and the m.p.s of the products in Table 3.

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