For compound 4, oxygen atoms of the perchlorate ligand were found disordered. Two positions were introduced, the multiplicity of which converged toward 0.8 and 0.2; oxygen atoms of multiplicity 0.2 were isotropically refined. Almost all hydrogen atoms were found on difference maps but were geometrically located, except the bridging ones. We tried to refine the latter, but their positions did not converge; thus, we refined them with restraints on the metal–hydrogen bond lengths. In this way the isotropic thermal parameters kept reasonable values; we therefore could think they had been correctly located. Other hydrogen atoms were given an overall isotropic thermal parameter.

For compound 5 (toluene solvate), on account of the small number of significant reflections measured, the phenyl groups were isotropically refined. The toluene molecule was introduced as a rigid group, and PF_6^- was restrained to chemically reasonable dimensions. The maximum residual electron density was in the vicinity of PF_6^-. Hydrogen atoms did not appear in difference maps, and their positions were computed except for the bridging one, which was not introduced.

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Registry No. 1, 116405-31-3; **2**, 142237-62-5; **3**·BF_4^-, 142237-66-9; **3**·PF_6^-, 142292-98-6; **4**, 142237-67-0; **5**, 142237-64-7; **5**·C_7H_8, 142292-99-7; Ag(ClO_4)(PPh_3), 73165-02-3; AuMe(PPh_3), 23108-72-7; AuCl(PPh_3), 14243-64-2; Mn, 7439-96-5; Ag, 7440-22-4; Au, 7440-57-5.

Supplementary Material Available: Drawings of the molecular structures of compounds 4 and 5, showing all atoms, and tables of additional atomic coordinates and thermal parameters for compounds 4 and 5, and additional bond lengths and angles for compound 5 (11 pages). Ordering information is given on any current masthead page.

OM910385H

Notes

Ferrocene Derivatives. 27.[1] Ferrocenyldimethylphosphine

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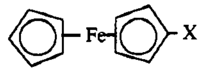
Summary: An improved synthesis of ferrocenyldimethylphosphine, $FcPMe_2$, is limited only by the unreliable literature procedure for preparing precursor dichloroferrocenylphosphine, $FcPCl_2$. The latter compound yields a crystalline copper(I) iodide complex on reaction with lithium dimethylcuprate. Methanolysis of $FcPCl_2$ yields unstable dimethyl ferrocenylphosphonite, $FcP(OMe)_2$, which is converted to methyl ferrocenylphosphinite, FcPH(O)OMe, on heating or chromatography.

The possibility of limitless variation in the identity of substituent groups has made trivalent phosphines and phosphites popular ligands in organometallic chemistry. Consequently, it has been possible to investigate both steric and electronic effects of these ligands and to influence the coordination number of the metal atom. Increasingly, interest is focusing on chiral phosphines and their complexes for use in asymmetric synthesis. Comprehensive reviews of different aspects of this chemistry have appeared.[2] Phosphorus derivatives of ferrocene were first investigated in 1962 by Sollott and co-workers[3] but most were poorly characterized or relatively inaccessible. Some synthetically useful intermediates have been reported,[4] but the most important derivatives are the chiral auxiliaries developed by Kumada and Hayashi.[5] The simple derivatives ferrocenyldimethylphosphine, $FcPMe_2$, and 1,1′-bis(dimethylphosphino)ferrocene, 1,1′-$Fc(PMe_2)_2$, have also been described,[6] but very surprisingly, the chemistry of these materials has not been developed, although each compound is expected to be a relatively strong σ-donor.[7] This paper describes a new synthesis of $FcPMe_2$, some aspects of its chemistry, and some related compounds.

Results and Discussion

We considered that dichloroferrocenylphosphine, $FcPCl_2$ (1), might be a convenient synthetic precursor. This compound was first prepared by a Friedel–Crafts method from ferrocene and phosphorus trichloride but was not isolated. An improved method using Me_2NPCl_2 was reported[3c] to give a cleaner product in higher (11%) yield. We have undertaken an extensive investigation of these literature[3c] processes and after 37 experiments find that the reactions are totally inconsistent and the yields are not reproducible. We have been unable to identify the reason



X = PCl_2 **1**, PH(O)OH **2**, PH(O)$OPCl_2$ **3**, $P(OMe)_2$ **4**,

PH(O)OMe **5**, PMe_2 **6**, $PMe_2.Fe(CO)_4$ **7**, $P(O)Me_2$ **9**.

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[3] (a) Sollott, G. P.; Howard, E., Jr. *J. Org. Chem.* **1962**, *27*, 4034. (b) Sollott, G. P.; Mertwoy, H. E.; Portnoy, S.; Snead, J. *J. Org. Chem.* **1963**, *28*, 1090. (c) Sollott, G. P.; Howard, E., Jr. *J. Org. Chem.* **1964**, *29*, 2451. (d) Sollott, G. P.; Peterson, W. R., Jr. *J. Organomet. Chem.* **1969**, *19*, 143.

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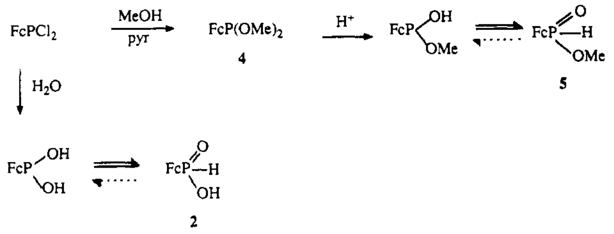
[6] Kiso, Y.; Kumada, M.; Tamao, K.; Umero, M. *J. Organomet. Chem.* **1973**, *50*, 297.

[7] Measurement of the Hammett σ–p function shows Fc to be a stronger electron donor than CH_3 (Nesmeyanov, A. N.; Perevalova, E. G.; Gubin, S. P.; Grandberg, K. I.; Kozlovsky, A. G. *Tetrahedron Lett.* **1966**, 2381).

for this behavior. We have investigated the influence of highly purified reagents, order of addition of reactants, reaction time and temperature, and possible participation of "additives" such as water, phosphorus trichloride, and dimethylamine as well as using several different batches of precursors obtained from different sources. The best experiment gave 25% yield; frequently the yield was zero. A procedure which was successful, but not always reproducible, is described in the Experimental Section.

We obtained 1 as an orange liquid which exhibited the expected molecular ion in the mass spectrum although microanalytical results were not within acceptable limits. The ^{1}H NMR spectrum gave the expected characteristic pattern of a monosubstituted ferrocene, but the ^{31}P NMR spectrum showed not only the expected strong singlet at δ 165.3 (lit. value δ 163.0)[8] but additional weak resonances at δ 28.6 (doublet) and 81.4 (singlet). After redistillation, the latter peaks were replaced by new, weak signals at δ 30.9 (s) and 38.0 (d), but the strong signal at δ 165.3 was retained. Clearly the literature procedure from Me_2NPCl_2, when it works, does not give a homogeneous product. Sollott had noted that his original Friedel–Crafts procedure using phosphorus trichloride gave a large number of products. We have not attempted to correlate the impurities giving the weaker ^{31}P NMR signals with any of Sollott's byproducts but instead hydrolyzed the redistilled product to ferrocenylphosphinic acid (2) in 64% yield. This material, a yellow crystalline solid mp 137 °C (lit. value mp 137–138 °C)[3d] exhibited the expected ^{31}P NMR doublet ($^1J_{PH}$ = 569.7 Hz) due to the directly bonded proton. A literature procedure[3c] was followed in an attempt to effect the reconversion of 2 to the ferrocenylphosphonous dichloride 1 by reaction with PCl_3; the product exhibited the same ^{1}H NMR spectrum as 1 but the ^{31}P NMR spectrum exhibited two broad[10] resonances, δ 81.65 (s), 83.5 (d, $^1J_{PH}$ = 570.1 Hz), probably a consequence of pyrophosphate, e.g., 3 formation.

Reaction between the dichloride 1 and methanol gave only 2, but methanolysis in the presence of pyridine, following the method of Korpuin et al.,[9] gave predominantly unstable dimethyl ferrocenylphosphonite[11] (ferrocenyldimethoxyphosphine, 4). This material was identified by mass spectrometry and ^{1}H NMR spectroscopy; as expected, the methoxy doublet at δ 3.54 ($^3J_{PH}$ = 10.8 Hz) integrated to six protons relative to the unsubstituted cyclopentadienyl ring. Compound 4 was sensitive to chromatography, and passage through a silica gel column converted it totally into 5, methyl ferrocenylphosphinite.[11] This yellow liquid was characterized by microanalysis and spectroscopy and exhibited the expected ^{1}H NMR methoxy doublet at δ 3.80 ($^3J_{PH}$ = 14.4 Hz) (integral three hydrogens only) and the P*H* doublet at δ 7.70 ($^1J_{PH}$ = 561.6 Hz). This latter observation was confirmed by the ^{31}P NMR doublet of quartets centered on δ 32.75. Interestingly, the ^{13}C NMR spectrum of this compound showed five different signals for the substituted cyclopentadienyl ring, a consequence of the chiral phosphorus substituent, rendering the chemically equivalent carbon atoms magnetically nonequivalent. Compound 4 was also thermally sensitive, and after distillation, ^{1}H NMR spectroscopy showed the distillate contained a mixture of 4 and 5. A crystalline *tert*-butyl ester of 2 was also prepared in 76% yield from *tert*-butyl alcohol and 1 and characterized by spectroscopy and microanalysis.



Methylation of 1 with methyllithium gave ferrocenyldimethylphosphine (6) in 23% yield. This material was isolated as an orange-red oil and was identified by NMR and mass spectrometric analyses. The ^{1}H NMR spectrum differed from the literature values[6,12] but exhibited the expected clean doublet at δ 1.14 ($^2J_{PH}$ = 3.6 Hz), which shows good agreement with literature[13] values for similar compounds, e.g., Me_3P ($^2J_{PH}$ = 2.7 Hz) and Me_2PPh ($^2J_{PH}$ = 3.2 Hz). The ^{31}P NMR spectrum showed the expected septet (δ 35.62). Phosphine 6 was characterized additionally by conversion into the orange crystalline tetracarbonyliron complex 7.

Methylation of 1 with lithium dimethylcuprate gave an almost quantitative yield of a ferrocenyldimethylphosphine–copper(I) iodide complex, a petroleum-soluble orange crystalline solid, mp 140 °C. Solution molecular weight measurements indicated that this complex, $[FcPMe_2{\cdot}CuI]_3$ (8), possessed a trimeric structure, but this could not be detected mass spectrometrically, the fragment ion corresponding to 6 being the most abundant. Unfortunately, we were unable to obtain suitable crystals for X-ray investigation to elucidate the nature of the trimeric structure.[14] Although the ^{1}H and ^{13}C NMR spectra of this complex were unexceptional (see Table II), the ^{31}P NMR spectrum was more complicated than expected. Instead of the anticipated $^{31}P\{^1H\}$ sharp singlet, this was a broad peak with fine splitting, while the coupled spectrum showed a broad signal which approximated to an unsymmetrical septet with further fine splitting. We are unable to determine whether this complexity arises from extended *P–Cu–P* interactions or some other phenomenon, but the line broadening could arise from *Cu–P* spin–spin coupling [^{63}Cu, $I = {}^3/_2$, 69% natural abundance, and ^{65}Cu, $I = {}^3/_2$, 31% natural abundance; each has a large quadrupole moment].

Many reagents were used in attempts to liberate the free phosphine 6 from complex 8. A successful method involved sonication with sodium in THF to produce a crystalline nonstoichiometric sodium iodide complex (vide infra) which on pyrolysis in a sublimer gave the desired phosphine 6 in 55% yield and a little of its less volatile oxide 9. Oxide 9 was obtained as a yellow crystalline solid, mp 132–134 °C, characterized by mass spectrometry and NMR spectra. In particular, the $^2J_{PH}$ coupling constant measured for the methyl doublet in the ^{1}H NMR spectrum (13.05 Hz) correlates well with literature values[13] for other phosphine oxides, e.g., $P(O)Me_3$, 13.4 Hz; $PhP(O)Me_2$, 13.3 Hz.

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(8) Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Inorg. Chem.* **1983**, *22*, 3475.

(9) Korpuin, O.; Lewis, R. A.; Chickos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842.

(10) Poor resolution of the broad ^{31}P NMR signals precluded the measurement of $^2J_{PP}$.

(11) The nomenclature used in this paper follows that of: Walker, B. J., Ed. *Organophosphorus Chemistry*; Penguin: London, 1972.

(12) Reference 6 describes the CH_3 signal as a deformed doublet, δ 1.23–1.45.

(13) Verstuyft, A. W.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 1495.

(14) A referee has suggested that the *apparent* trimeric structure of 8 could reflect an equilibrium between dimer and tetramer; this could also explain the observation of more than one ^{31}P NMR resonance and our inability to obtain good crystals of 8.

(15) Nesmeyanov, A. N.; Petrovskii, P. V.; Federov, L. A.; Robas, V. I.; Fedin, E. I. *Zh. Strukt. Khim.* **1973**, *141*, 49.

Table I. Chemical Shift of FcP*Me*$_2$ from Different Sources

	reaction/product	chem shift (δ, C_6D_6)
i	1 + MeLi	1.14 (d)
ii	8	1.48 (d)
iii	8 + $LiAlH_4$	1.50 (d)
iv	8 + Na	1.475 (d)
v	1 + MeMgBr	1.53 (d)
vi	FcLi + $ClPMe_2$	1.425 (d)
vii	after chromatography of vi on Al_2O_3	1.48 (d)
viii	lit. value[6]	1.23–1.45 (deformed doublet)

The formation of a nonstoichiometric complex, approximately $(FcPMe_2)_{2.4}NaI$, suggested an explanation for other initially confusing results, namely that reaction of $FcPCl_2$ with different nucleophilic methylating reagents gave different products, although each was obviously some form of complex with $FcPMe_2$. Similarly, different methods of removing copper(I) iodide from complex **8** also gave different $FcPMe_2$ products. Thus, while each product showed the expected PMe_2 ^{1}H NMR doublet, there were small but significant differences in the CH_3 chemical shifts in the same solvent (see Table I). In most cases, the solid products could be recrystallized to a constant melting point, but microanalyses indicated that the materials did not possess simple stoichiometry, although mass spectrometry always indicated the presence of the desired phosphine. We conclude that $FcPMe_2$ is such a strong σ-donor that it is capable of complexing to the group I–III metals used in the various methylation/reduction reactions.

Finally, the literature synthesis[6] of ferrocenyldimethylphosphine was reinvestigated. The two products isolated from this procedure had ^{1}H NMR spectra which corresponded neither to phosphine **6** nor to the literature molecule. These are probably complexes of the free phosphine with lithium and aluminum, the latter arising from our efforts to purify the material by column chromatography on neutral alumina.

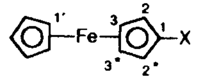
Conclusions

The literature procedure for synthesizing $FcPMe_2$ involves the reaction of poorly accessible $ClPMe_2$ with lithiated ferrocenes and yields a mixture of $FcPMe_2$ and 1,1′-$Fc(PMe_2)_2$ which can only be separated by pyrolysis/distillation and not by chromatography. The positive identification of **6** in this work suggests that Kiso et al.[6] probably isolated the phosphine in an unidentified complexed form. The methylation route described in this paper provides a superior method, but this is limited by an unrealiable method for obtaining $FcPCl_2$. Preliminary results suggest that **6** is an extremely powerful ligand (σ-donor) for a range of metals and merits further study.

Experimental Section

General Data. All experiments were conducted under an atmosphere of oxygen-free dry nitrogen. Neutral alumina was prepared by exposing active alumina to ethyl acetate for at least 10 days, washing (EtOH, H_2O), and reactivating at 150 °C for 18 h. Precoated "Polygram" silica gel (0.25-mm layer) and aluminum oxide (0.2-mm layer) TLC plates were obtained from Macherey-Nagel and Co. Solution molecular weight measurements were obtained with a Hitachi–Perkin-Elmer molecular weight apparatus, Model 115. NMR spectra were obtained with Bruker WM-250 and AMX-400 and Perkin-Elmer R32 (90 MHz) instruments and calibrated vs TMS (^{1}H), solvent (^{13}C), and external H_3PO_4 (^{31}P). Mass spectra were recorded in an AEI (Kratos) MS9 mass spectrometer. Melting points were determined in unsealed capillaries, unless otherwise stated, and are uncorrected. NMR values are recorded in Table II.

Table II. Summary of ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR Spectra[a]



	^{1}H NMR,[b] ppm					^{13}C[^{1}H] NMR,[c–e] ppm					
compd	X	H_1'	H_2	H_3	X	C_1'	C_1	C_2,C_2*	C_3,C_3*	X	^{31}P NMR,[b] ppm
1	PCl_2	3.94 (s)	4.31 (m)	4.09 (m)							165.3
2	PH(O)OH					69.64	69.86 (d, $^1J_{PC}$ = 157.2)	71.25 (d, $^2J_{PC}$ = 157.2)	71.83 (d, $^3J_{PC}$ = 13.2)		25.74 (d, $^1J_{PH}$ = 569.7)
4	$P(OMe)_2$	4.22 (s)	4.58 (m)	4.58 (m)	3.54 (d, O*Me*, $^3J_{PH}$ = 10.8)						
5	PH(O)OMe	4.30 (s)	4.40 (m)	4.40 (m)	3.80 (d, O*Me*, $^3J_{PH}$ = 14.4), 7.70 (d, P*H*, $^1J_{PH}$ = 561.6)	69.66	67.48 (d, $^1J_{PC}$ = 152.2)	72.14 (d, $^2J_{PC}$ = 19.5), *70.29 (d, $^2J_{PC}$ = 18.2)	71.98 (d, $^3J_{PC}$ = 13.2), *71.73 (d, $^3J_{PC}$ = 9.4)	52.14 (d, $^2J_{PC}$ = 6.6)	32.75 (dq, $^1J_{PH}$ = 552.7, $^3J_{PH}$ = 12.2)
6	PMe_2	4.07 (s)	4.07 (m)	4.16 (m)	1.14 (d, $^2J_{PH}$ = 3.6)	69.34 (dqt,[e] $^1J_{CH}$ = 175.4)	69.37 (d,[e] $^1J_{PC}$ = 150.9)	71.08 (dq,[e] $^2J_{PC}$ = 14.8, $^1J_{CH}$ = 174.05)	70.54 (dq,[e] $^3J_{PC}$ = 3.6, $^1J_{CH}$ = 174.5)	15.94 (dq,[e] $^1J_{PC}$ = 11.5, $^1J_{CH}$ = 127.8)	35.62 (spt, $^2J_{PH}$ = 12.9)
7	$PMe_2 \cdot Fe(CO_4)$	3.90 (s)	3.98 (m)	3.98 (m)	1.35 ($^2J_{PH}$ = 10.0)	69.92	69.98 (d,$^1J_{PC}$ = 31.3)	71.22 (d, $^2J_{PC}$ = 11.9)	71.46 (d, $^3J_{PC}$ = 8.2)	21.80 (d, $^1J_{PC}$ = 35.2, Me), 214.68 (d, $^2J_{PC}$ = 20.1, Fe(*CO*)$_4$)[f]	39.54 (spt, $^2J_{PH}$ = 10.0)
8	$PMe_2 \cdot CuI$	4.41 (s)	4.11 (m)	4.57 (m)	1.48 (d, $^2J_{PH}$ = 5.4)	69.53 (dqt,[e] $^1J_{CH}$ = 177.1)	68.94 (d,[e] $^1J_{PC}$ = 163.6)	71.70 (dm,[e] $^2J_{PC}$ = 12.8, $^1J_{CH}$ = 177.1)	70.63 (dm,[e] $^3J_{PC}$ = 6.4, $^1J_{CH}$ = 175.1)	15.60 (dq,[e] $^1J_{PC}$ = 21.2, $^1J_{CH}$ = 128.8)	54.83 (br spt)
9	$P(O)Me_2$	4.17 (s)	4.03 (m)	4.19 (m)	1.21 (d, $^2J_{PH}$ = 13.0)						

[a] Abbreviations: s, singlet; d, doublet; m, multiplet; spt, septet; dq, doublet of quartets; dm, double multiplet; qd, quartet of doublets; dqt, doublet of quintets. *J* values given in hertz. [b] C_6D_6 solution; δ value relative to TMS. [c] $CDCl_3$ solution except for compound **6** (C_6D_6). [d] The assignment of a particular chemical shift to C_2 or C_3 is not certain.[15] These assignments have been made assuming that $^1J_{PC} > {}^3J_{PC}$. [e] These multiplicities relate to the ^{13}C NMR spectrum. [f] Reference 17.

Dichloroferrocenylphosphine (1). (Dimethylamino)dichlorophosphine[16] was prepared by adding an ice-cooled solution of anhydrous dimethylamine (81.07 g, 1.8 mol) in anhydrous ether (120 mL) over 1.5 h to a cooled, stirred solution of phosphorus trichloride (141.09 g, 1.02 mol) in anhydrous ether (450 mL). During the addition, an abundant white precipitate formed. The reaction mixture was allowed to warm to room temperature and evaporated and the product (97.8 g, 66%) distilled (23 °C/1.5 Torr) as an air/moisture-sensitive colorless liquid (^{1}H NMR: δ 2.79 (s, 3 H); 2.92 (s, 3 H)). A solution of (dimethylamino)dichlorophosphine (14.6 g, 0.1 mol) in heptane (100 mL) was added dropwise over 20 min with stirring to a mixture of anhydrous aluminum chloride (13.4 g, 0.1 mol) and ferrocene (18.6 g, 0.1 mol) in heptane (250 mL). The mixture was heated at reflux for 3 h, the clear, orange, heptane phase was transferred while hot to a distillation flask, and the solvent, traces of ferrocene, and unreacted (dimethylamino)dichlorophosphine were removed in vacuo on a steam bath. The residual red oil was purified by adding heptane (100 mL), removing the insoluble white solids by filtration, evaporating the solvent and distilling the residue. Compound 1 was obtained as an orange oil (3.7 g, 13%) bp 90–96 °C/0.001 Torr. ^{31}P NMR showed that this material contained about 10% impurity. MS *m/z* 285.9171, and 289.9110 (M$^+$), 250.9493 and 252.9464 (M$^+$ – Cl). Anal. Calcd for $C_{10}H_9Cl_2FeP$ (M_r = 285.9168 ^{35}Cl; 289.9104, ^{37}Cl): C, 41.9; H, 3.2; Cl, 24.7. Found: C, 42.9; H, 3.0; Cl, 22.7.

Dimethyl Ferrocenylphosphonite (4) and Methyl Ferrocenylphosphinite (5). Dichloroferrocenylphosphine (0.4 g, 1.39 mmol) in hexane (10 mL) was stirred and cooled to 0 °C while methanol (0.112 g, 3.50 mmol) and pyridine (0.23 g, 2.93 mmol) were added. Stirring was continued for 2 h at 0 °C and a further 1 h at room temperature. The precipitated pyridine hydrochloride was removed by filtration and the filtrate concentrated to yield an orange oil (0.34 g). The ^{1}H NMR spectrum of this product, **4**, showed a methoxy doublet at δ 3.54 ($^3J_{PH}$ = 10.8 Hz, 6 H). This oil was chromatographed through a short column of silica gel and the eluate evaporated to leave an orange oil, **5**, having a ^{1}H NMR methoxy doublet at δ 3.80 ($^3J_{PH}$ = 14.4 Hz, 3 H).

The above reaction was repeated and the product purified by distillation (bp 100 °C/0.15 Torr) instead of chromatography. This product showed two ^{1}H NMR methoxy doublets (δ 3.54 and 3.80) corresponding to a mixture of **4** and **5**. The orange oil was redistilled to give a single substance, **5**, having a ^{1}H NMR methoxy doublet at δ 3.80. MS *m/z* 265.0044 (M$^+$ + 1), 263.9975 (M$^+$), 248.9773 (M$^+$ – CH$_3$), 247.9698 (M$^+$ – CH$_3$, H). Anal. Calcd for $C_{11}H_{13}FeO_2P$ (M_r = 264.0002): C, 50.0; H, 5.0. Found: C, 50.0; H, 5.2. Osmometric molecular weight 257 (toluene, 312.7 K).

A similar procedure was used to prepare *tert*-butyl ferrocenylphosphinite from 1 (0.2 g, 0.695 mmol), *tert*-butyl alcohol (0.13 g, 1.75 mmol), and pyridine (0.12 g, 1.46 mmol). The product (0.16 g, 76%) was obtained as orange crystals, mp 97 °C (ether–petroleum). ^{1}H NMR (C_6D_6) δ 1.58 (s, 9 H), 4.34 (s, 5 H), 4.40–4.62 (m, 4 H), 4.68, 10.88 (d, 1 H, P*H*, $^1J_{PH}$ = 558.0). MS *m/z* 307.0499 (M$^+$ + 1), 306.0485 (M$^+$), 249.9843 [(M$^+$ + 1) – *t*-Bu]. Anal. Calcd for $C_{14}H_{19}FeO_2P$ (M_r = 306.0472): C, 54.9; H, 6.3. Found: C, 54.6; H, 6.0.

Ferrocenyldimethylphosphine (6). Methyllithium (4.46 mL, 6.69 mmol, 1.5 M in hexanes) was syringed into a flask fitted with a septum, a pressure-equalized dropping funnel, and a nitrogen supply, and magnetic stirring commenced. Ferrocenyldichlorophosphine[3c] (0.48 g, 1.67 mmol) in dry ether (20 mL) was added dropwise with ice-cooling. A precipitate began to appear almost immediately, and stirring was continued for 3 h until the mixture reached room temperature. The reaction was quenched with water (20 mL) and the ether layer separated, washed, dried (MgSO$_4$), filtered and evaporated in vacuo. Ferrocenyldimethylphosphine (0.096 g, 23%) was obtained as an orange oil after distillation, bp 120 °C (0.01 Torr). MS *m/z* 247.0261 (M$^+$ + 1), 246.0262 (M$^+$), 231.0039 (M$^+$ – CH$_3$), 215.9788 [M$^+$ – (2 × CH$_3$)]. Anal. Calcd for $C_{12}H_{15}FeP$ (M_r = 246.0261): C, 58.6; H, 6.2. Found: C, 58.85; H, 6.1.

Tetracarbonyl(ferrocenyldimethylphosphine)iron (7). Compound **6** (65 mg, 0.264 mmol), enneacarbonyldiiron (100 mg, 0.290 mmol), and benzene (10 mL) were stirred together in the dark for 1.5 h. The reaction mixture was then filtered through kieselguhr and the solvent removed in vacuo to leave an orange oil (87 mg). This oil solidified in the freezer and was recrystallized (ether–petroleum) to give orange-red crystals (71 mg, 65%), mp 122–123 °C. IR (petroleum) ν(CO) 2040 (s), 1961 (s), 1920 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{15}Fe_2O_4P$: C, 46.4; H, 3.65. Found: C, 46.7; H, 3.7.

Reaction of Dichloroferrocenylphosphine (1) with Lithium Dimethylcuprate. Methyllithium (50 mL, 75.2 mmol, 1.5 M solution in hexane) was added dropwise, with stirring, over a period of 1 h to a suspension of copper(I) iodide (7.16 g, 37.6 mmol) in dry ether (50 mL) cooled to –15 °C. The reaction mixture was stirred for a further 0.5 h, and then 1 (2.16 g, 7.52 mmol) in dry ether (50 mL) was added dropwise, maintaining the reaction temperature near 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. Water (25 mL) was added dropwise, and the layers were separated. The organic layer was dried (MgSO$_4$), filtered, and evaporated in vacuo to leave an orange gum. After chromatography [silica gel; ether/petroleum (3:7)], an orange crystalline substance was obtained (3.18 g, 97%), mp 140 °C. MS (M$^+$ not observed) *m/z* 246.0246 (M$^+$ – CuI). Osmometric molecular weight found 1308 (toluene, 312.7 K). Anal. Calcd for $C_{36}H_{45}Cu_3Fe_3I_3P_3$ (M_r = 1309.5; M$^+$ – CuI/3 *m/z* 246.0261): C, 33.0; H, 3.5; I, 29.1. Found: C, 33.3; H, 3.2; I, 29.1.

A solution of the copper complex (0.1 g) in ether (2 mL) was passed through a short column (15 cm) of air-deactivated alumina using chloroform as the eluant. A yellow-orange solid (0.04 g) was recovered. The ^{1}H NMR spectrum (C_6D_6) of the recovered material showed a methyl doublet at δ 1.21 ($^2J_{PH}$ = 13.0 Hz) corresponding to the phosphine oxide **9**.

Preparation of Phosphine 6 from the Copper(I) Iodide Complex 8 by Ultrasonication with Sodium. A solution of the copper complex **8** (2 g, 4.58 mmol) in dry THF (10 mL) was added to a sodium dispersion (0.3 g, excess) in dry THF (30 mL) and the mixture sonicated for 3 h. The reaction mixture was filtered and the filtrate evaporated in vacuo to leave a red-brown solid (1.3 g) which gave an amorphous red-brown solid, mp 139 °C, after recrystallization (bp 60–80 °C petroleum). Anal. Calcd for $C_{24}H_{30}Fe_2INaP_2$: C, 44.9; H, 4.7. Anal. Calcd for $C_{36}H_{45}Fe_3INaP_3$: C, 48.7; H, 5.1. Found: C, 46.6; H, 4.9. A sample of this solid was placed in a sublimer and heated in vacuo. Phosphine **6** was distilled as a red oil (bp 80 °C/0.001 Torr) and removed. Raising the temperature caused the sublimation of a small quantity of a yellow-orange solid, mp 132–134 °C, identified as the phosphine oxide **9**. MS *m/z* 263.0240 (M$^+$ + 1), 262.0197 (M$^+$), 246.0269 (M$^+$ – *O*). Anal. Calcd for $C_{12}H_{15}FeOP$ (M_r = 262.0210).

Registry No. 1, 1291-31-2; 2, 93786-14-2; 4, 142068-48-2; 5, 142068-49-3; 6, 41684-66-6; 7, 142068-50-6; 8, 142244-53-9; 9, 142068-51-7; (dimethylamino)dichlorophosphine, 683-85-2; ferrocene, 102-54-5.

OM910687J

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