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Mössbauer and NMR Spectroscopic Studies of Diphosphaferrocene in Trifluoromethanesulphonic (Triflic) Acid

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Abstract

A range of diphosphaferrocenes has been investigated in trifluoromethanesulphonic acid where iron protonated species result contrary to previous findings. 2,2′5,5′-Tetraphenyldiphosphaferrocene (TPDPF) has been shown to have an iron protonated structure rather than one arising from protonation of the phenyl side groups. Iron protonation has been demonstrated by ^{57}Fe Mössbauer spectroscopy and ^{31}P NMR. The iron bound proton is not always observed by ^{1}H NMR spectroscopy due to fast exchange which is evident by the loss of resolution of phosphorus–hydrogen coupling constants in the ^{31}P NMR. The structure of the protonated derivatives is discussed. An alternative synthetic route to alkyl diphosphaferrocenes has also been included.

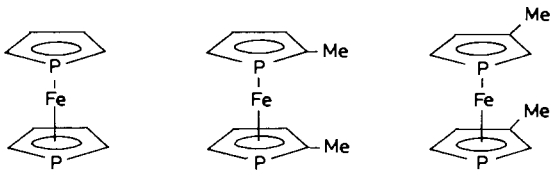
Introduction

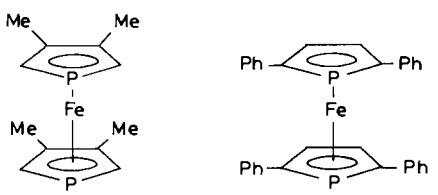
As a follow-up to our initial work on the study of diphosphaferrocenes in strong acids [1], we have recently undertaken a more detailed study of the behaviour of monophosphaferrocenes in trifluoromethanesulphonic acid (triflic acid) [2]. In view of the results obtained, we have re-examined the structure of diphosphaferrocenes in triflic acid, and with new data available we have had to revise the conclusions reached in ref. 1.

Some ^{31}P NMR chemical shifts have been incorrectly reported** and we now report the corrected results together with new data. All previous data on 2,2′5,5′-tetraphenyldiphosphaferrocene (TPDPF) and 3,3′4,4′-tetramethyldiphosphaferrocene (TMDPF) in triflic acid have been checked and expanded with the inclusion of new data for two dimethyl diphosphaferrocenes (DMDPF), the 2,2′-isomer (2DMDPF), the 3,3′ isomer (3DMDPF) and the parent diphosphaferrocene, DPF.

Results and Discussion

The following diphosphaferrocenes have been investigated†.





Monophosphaferrocenes are iron protonated in triflic acid [2] as are ferrocene [4] and alkylferrocenes [5]. Previous evidence for TPDPF and TMDPF indicated that iron protonation did not occur in these derivatives [1]. The major factor leading to this conclusion was the absence of a signal for the iron-bound proton in the ^{1}H NMR spectra of the diphosphaferrocenes in triflic acid and incorrect phosphorus chemical shift measurements.

All derivatives dissolved in triflic acid to give red-orange solutions stable for over four hours. The unchanged diphosphaferrocenes could be recovered on dilution with water.

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**We are grateful to M. F. Mathey for pointing out this error [3].

†2 and 3-DMDPF occur as inseparable structural isomers due to the asymmetry of the monosubstituted phosphorus ligand. The presence of such isomers is confirmed by ^{31}P and ^{13}C NMR.

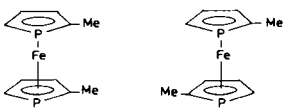

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TABLE I. ^{1}H NMR shifts[a]

Compound	Solvent	H_α	H_β	Fe–H	αMe	βMe	Others
DPF	$CDCl_3$	4.10(2d)	5.35(m)	–			
	CF_3SO_3H	3.80(d)	6.20(m)	2.20(s)			
TMDF	$CDCl_3$	3.75(d)[b]				2.10(s)	
	CF_3SO_3H	3.65(d)		−0.2(t)[c]	1.93(s)		
2DMDPF	$CDCl_3$	3.58(m)	5.51(m)		1.97(d)[e]		
	CF_3SO_3H	3.55(m)	6.27(m)	d	1.20(d)[e]		
3DMDPF	$CDCl_3$	3.7(d) 3.75(m)	5.18(m)			2.25(s)	
	CF_3SO_3H	3.90(m)	6.20(m)	d		2.20, 2.29	
TPDPF	$CDCl_3$		5.58(d)[f]				Ph7.0(s)
	CF_3SO_3H		~6.8	d			

[a]δ in ppm, external TMS. (H_α signals broad in CF_3SO_3H and absent in samples recovered from CF_3SO_3D). [b] $^2J_{P-H}$ 37 Hz. [c] $^2J_{P-Fe-H}$ 19 Hz. [d]not observed. [e] $^3J_{P-H}$ 10 Hz. [f] $^3J_{P-H}$ 5 Hz.

^{1}H NMR Spectra

The ^{1}H NMR results in CF_3SO_3H are given in Table I, together with those obtained in $CDCl_3$. The metal-bound proton could not always be unambiguously identified in TPDPF, TMDPF, 2-DMDPF, or 3-DMDPF. The signal was present at 2.20 ppm for DPF in triflic acid. This was confirmed as being due to an iron-bound proton since it integrated as a 1 H signal and disappeared when triflic acid-d_1 was used.

Encouraged by this result, we examined TMDPF in triflic acid using a higher resolution instrument and detected the metal-bound proton as a triplet ($2J$(PH) 19 Hz) at 20 ppm. Whilst the lack of such signals in the other derivatives would at first indicate dissimilar protonation sites, metal protonation occurs in all cases as shown using other probes. The variation in δFe–H is probably due to the change in the basicity of the iron atom. Comparison of absolute values of δ obtained in $CDCl_3$ and triflic acid is not valid due to unknown solvent shifts. However, the relative changes in δ for each diphosphaferrocene are significant.

The methyl resonance for 3-DMDPF in $CDCl_3$ is a sharp 6H singlet which is split into two (3H) singlets in triflic acid. Either the two methyl groups are magnetically non-equivalent in each structural isomer or they differ from one isomer to the other, the latter being more likely.

Such behaviour is not apparent in 2-DMDPF. The methyl resonance in $CDCl_3$ occurs as a doublet due to phosphorus–hydrogen coupling (confirmed by coupled and decoupled ^{31}P NMR spectra). In triflic acid, only one doublet is observed showing that the methyl groups of both isomers remain equivalent when the complex is protonated.

The separation of H_α and H_β in DPF, 3-DMDPF and 2-DMDPF is greater in triflic acid solution compared to $CDCl_3$. This effect appears to be due to deshielding of the β protons upon protonation and is confirmed by TPDPF in triflic acid where β-proton signal overlaps that of the arene. For diphosphaferrocene itself the difference (Δδ) in shift between the α and β protons is 1.2 in $CDCl_3$ and 2.4 ppm in CF_3SO_3H. Relevant to this analysis is the work of Bitterwolf and Ling [6] on protonated ferrocenophanes. By using specifically deuteriated derivatives it was shown that for [3]-ferrocenophane, where the incoming proton must enter in a direction opposite to the three-carbon bridge, the protons closest to the H^+ were deshielded by 0.3 ppm relative to those adjacent to the bridge. Thus for diphosphaferrocene, Δδ should decrease (to about 0.9 ppm) on protonation in contrast to the observed marked increase (2.4 ppm). It is instructive at this stage to consider the ^{31}P shifts which for DPF are −58 ppm ($CDCl_3$) and −122 ppm (CF_3SO_3H). Normally the phosphorus atoms lie in an almost *trans* disposition to one another [7]. Iron-protonation clearly causes a marked upfield shift. This, taken in conjunction with the ^{1}H NMR data, suggests a structure where both phosphorus atoms are *cis* with respect to one another but *trans* to the iron-bound proton (*vide infra*). Thus for the ^{1}H resonances, the shielding of the α protons is reinforced by the neighbouring ring (note H_α is at 4.1 in $CDCl_3$ but 3.8 ppm in CF_3SO_3H whereas H_β appears at 5.35 in $CDCl_3$ but at 6.2 ppm in CF_3SO_3H).

The absence of a resonance for the metal-bound proton in some diphosphaferrocenes is due to faster exchange in the diphosphaferrocene system compared to monophosphaferrocenes [2]. This implies a weaker Fe–H bond in the diphosphaferrocenes commensurate with the decreased basicity of the central iron atom resulting from electron withdrawal by two phosphacyclopentadienyl ligands. Another possibility which cannot be excluded is that the signal is masked in alkyl derivatives, indicated by the similar values of δMe and δFe–H (for DPF).

The α protons of DPF, TMDPF, 3- and 2-DMDPF exchanged rapidly in triflic acid-d_1, whereas negligible

TABLE II. ^{31}P NMRdata

Compound	Solvent	$\delta\ ^{31}P$[a]	Coupling constants	$\Delta\ ^{31}P$[b]
$(C_6H_5)_3P$	$CDCl_3$	−4.24(s)		
$(C_6H_5)_3P$	CF_3SO_3H	+10.92(d)	$^1J_{P-H}$ 499 Hz	
$(C_6H_5)_3P$	CF_3SO_3D	+4.19(t)[c]	$^1J_{P-D}$ 76 Hz	
1,2,5-triphenylphosphole	$CDCl_3$	+4.00(s)		
1,2,5-triphenylphosphole	CF_3SO_3H	+7.06(d)	$^1J_{P-H}$ 505 Hz	
1,2,5-triphenylphosphole	CF_3SO_3D	+3.64[c]	$^1J_{P-D}$ 77 Hz	
DPF	$CDCl_3$	−58.00(s)	$^2J_{P-H}$ 36 Hz	
DPF	CF_3SO_3H	−122.75(s)		64.75
DPF	CF_3SO_3H/−30 °C	−123.13(s)		65.13
TMDPF	$CDCl_3$	−70.60(t)	$^2J_{P-H}$ 36 Hz	
TMDPF	CF_3SO_3H	−146.29(s)		75.69
TMDPF	CF_3SO_3H/−30 °C	−147.60(s)		77.00
TPDPF	$CDCl_3$	−60.95(s)		
TPDPF	CF_3SO_3H	−136.71(s)		75.76
TPDPF	CF_3SO_3H/−30 °C	−139.68(s)		78.73
2-DMDPF[d]	$CDCl_3$	−54.00, −54.86		
2-DMDPF[d]	CF_3SO_3H	−116.23, −119.26		62.23, 64.40
2-DMDPF[d]	CF_3SO_3H/−30 °C	−113.12, −116.66		59.12, 61.80
3-DMDPF[d]	$CDCl_3$	−58.30, −58.80		
3-DMDPF[d]	CF_3SO_3H	−127.61, −129.48		69.31, 70.68
3-DMDPF[d]	CF_3CO_2H	~−72 v/broad[e]		~12

[a]Reference 85% H_3PO_4/D_2O, δ +ve downfield shift. δ in PPM. s = singlet, d = doublet, t = triplet. [b]$\Delta\ ^{31}P$ = upfield shift of $\delta\ ^{31}P$ in triflic acid. Internal D_2O lock used for triflic acid spectra at ambient temperature, internal $CDCl_3$ lock for sub ambient temperatures. Spectra obtained at 32 °C unless otherwise stated. [c]Difference in $\delta\ ^{31}P$ between H and D acids due to different lock systems. [d]Results for 2 and 3 DMDPF obtained under broad band proton decoupling – see text. [e]Numerous minor signals at lower field due to decomposition. Results for DPF, TMDPF and TPDPF in $CDCl_3$ agree with results previously published (−59.00, −72.00, −63.63 respectively) [7].

exchange was found for β protons, where present, despite prolonged exposure to the deuteriated acid. These results are in accord with H/D exchange reactions previously reported for TPDPF [1] and monophosphaferrocenes [2]. A factor common to both systems is that the C_β sites are largely inert to electrophilic reactions compared to the C_α sites. This is in agreement with calculated residual electron densities at the α and β carbon atoms [8] and the electrophilic substitution patterns in monophosphaferrocenes [9].

^{31}P NMR Spectra

Initially the ^{31}P data and the lack of Fe–H signals led us to believe that quite different sites were protonated in TPDPF and TMDPF [1]. However the corrected data implies that very similar processes occur with both derivatives, and the new diphosphaferrocenes studied. We have completely checked all the previous data and the results are given in Table II together with the data for 2- and 3-DMDPF and DPF indicating a lack of phosphorus protonation in contrast to the behaviour of phosphines. [1,2,5-Triphenylphosphole (1,2,5-TPP) and triphenylphosphine have $^1J_{PH}$ of ~500 Hz in triflic acid and, as expected, a lower value of $^1J_{PD}$ of ~77 Hz in triflic acid-d_1.]

We tried to obtain NMR spectra for methyl substituted 1-phenyl phospholes in triflic acid, but solutions gelled immediately indicating polymerisation. For the monophosphaferrocene system, iron protonation results in the appearance of a doublet due to P–Fe–H coupling which is further split by coupling to the H_α protons, when present [2]. The P–Fe–H coupling constants have values from 47.9 → 71.8 Hz as measured from ^{31}P NMR. Iron protonation causes an upfield shift of 139–185 ppm. The shift of $\delta\ ^{31}P$ for diphosphaferrocenes in triflic acid is in the same upfield direction but of smaller magnitude, 59–87 ppm, the signals appearing as broad singlets for DPF, TPDPF and TMDPF.

The differences in the ^{31}P spectra of mono and diphosphaferrocenes are due to faster exchange of the iron-bound proton in the latter causing a loss of resolution of both $^2J_{PCH}$ and $^2J_{PFeH}$. Rapid exchange would also explain why Fe–H resonances are difficult to observe in the ^1H NMR. Both 2- and 3-DMDPF give complex ^{31}P spectra when run with proton coupling, due to the presence of two structural isomers and complex proton coupling patterns. Broad multiplets result when these derivatives are run in triflic acid, but the linewidth precludes any large coupling such as would result from direct phos-

phorus protonation. When run under broad band proton decoupling two singlets are observed with very similar upfield shifts to DPF, TMDPF and TPDPF. The ^{31}P spectra of DPF, 2-DMDPF, TMDPF and TPDPF showed no temperature dependence down to −30 °C. TMDPF will not dissolve in the much weaker trifluoroacetic acid (TFA). 3-DMDPF dissolves to give a light purple solution in which fairly rapid decomposition occurs. The $\delta^{31}P$ shows a much smaller upfield shift, which shows that the magnitude of $\delta^{31}P$ in the diphosphaferrocene/acid system is dependent on the extent of metal protonation. Exchange of the α protons occurred in TFA-d_1.

We consider however that in the much stronger triflic acid both mono- and diphosphaferrocenes are fully protonated and the differences in the magnitude of the upfield shift of $\delta^{31}P$ between the two systems are due to geometric factors. In the non-protonated forms, phosphaferrocenes are slightly puckered about the C_α–$C_{\alpha'}$ axis due to steric repulsion between P and Fe [7]. In both protonated forms ^1H NMR indicate that the P atoms are *trans* to the Fe–H bond. This will tilt the rings so that the P atom will be forced closer to the Fe atom. Undoubtedly this results in an increase in the puckering about the C_α–$C_{\alpha'}$ axis and we believe that this is the cause of the upfield ^{31}P shifts of the protonated forms. In the case of disphosphaferrocenes, the tilting will be resisted by the presence of two P atoms *trans* to the Fe–H bond leading to a reduced distortion about C_α–$C_{\alpha'}$ and hence a smaller upfield shift.

Mössbauer Spectroscopy Results

The ^{57}Fe Mössbauer parameters for DPF, TMDPF, 2-DMDPF and 3-DMDPF are given in Table III. The reduced quadrupole splitting of DPF compared to ferrocene (QS = 2.40 mm s^{-1}) is in keeping with the inclusion of two phosphorus atoms in the cyclopentadienyl rings and is close to the value estimated (1.76 mm s^{-1}) [1, 2] from additivity considerations. The results for 3-DMDPF and TMDPF are in keeping with increasing methyl substitution, although 2-DMDPF has a QS value identical to the parent (within experimental error).

TABLE III. ^{57}Fe Mossbauer Spectroscopy

Compound	IS[c]	QS[d]	Γ[e]	ΔQS
DPF[a]	0.50(1)	1.79(1)	0.18(1)	
DPF[b]	0.46(1)	1.92(2)	0.19(1)	0.13(3)
TMDPF[a]	0.47(1)	1.87(1)	0.19(1)	
TMDPF[b]	0.49(1)	1.86(2)	0.14(2)	
2-DMDPF[a]	0.51(1)	1.79(2)	0.14(2)	
2-DMDPF[b]	0.45(1)	1.97(1)	0.17(1)	0.18(3)
3-DMDPF[a]	0.50(1)	1.82(1)	0.17(1)	
3-DMDPF[b]	0.46(1)	1.92(1)	0.13(1)	0.10(2)

[a]Solid at 80 K. [b]Triflic acid frozen solution at 80 K. [c]IS = isomer shift. [d]QS = quadrupole splitting. [e]η half width at half height all mm s^{-1}. Results for TPDPF and TMDPF (solid only) have been previously reported in ref. 1.

In triflic acid frozen solution DPF and both dimethyl isomers showed increased QS values (ΔQS) and slightly decreased isomer shift values. These effects are indicative of iron protonated species, *cf.* ferrocenes [4] and monophosphaferrocenes [2]. TPDPF shows an increased QS value in triflic acid (0.25 mm s^{-1}) [1] which was reported to be caused by an α ferrocenyl carbonium ion type structure arising from protonation of the phenyl group. However in view of the increased QS values for the parent and dimethyl diphosphaferrocenes, where the formation of such carbonium ions is not possible, we now believe that in all cases the increased QS values of diphosphaferrocenes in triflic acid are caused by iron protonation. The similarity of all the ^{31}P NMR results in triflic acid also supports the hypothesis that an identical process occurs in all cases. The magnitude of ΔQS for TPDPF is larger than that found for other diphosphaferrocenes. However, this is found for 2,5-diphenylphosphaferrocene compared to other monophosphaferrocenes in which metal protonation is unambiguously confirmed by ^1H and ^{31}P NMR. TMDPF did not show a measurable increase in QS when protonated but the magnitude of such effects are dependent on the ring substitution [4] and other factors [2].

Synthesis of Diphosphaferrocenes

Diphosphaferrocenes are made by the reaction of phosphacyclopentadienyl metals (PCp^-M^+) with ferrous chloride [7, 10]. Whilst with phenyl substitution on PCp^- the standard synthesis is quite successful, alkyl substitution gives very poor yields [7, 10] for several reasons. Diphosphaferrocenes are destroyed by strong nucleophiles [11] such as phenyl metals produced as byproducts in the synthesis of PCp^-M^+ [12]. Alkyl substituted PCp^- also act as good reducing agents [12] and can reduce Fe^{II}. Several attempts have been made to improve the yields, by removing phenyl metals via the addition of t-butyl chloride [10] or by reducing the basicity of PCp^- by conversion to a Grignard type reagent [7]. The best method to date uses anhydrous aluminium chloride which removes phenyl metals, the resulting triphenyl aluminium acting as a catalyst in the formation of the diphosphaferrocene [3, 11, 13].

We have also investigated the synthesis of diphosphaferrocenes and have found that the addition of tributyl tin chloride to PCp^-M^+/ phenyl metal mixtures before the $FeCl_2$ considerably improves the yield of diphosphaferrocene in most cases The phenyl metal is removed as an inert organotin derivative.

The yields of 3,4-dimethyl DPF; 3-methyl DPF; 2-methyl DPF; 2,5-diphenyl DPF and DPF were respectively 40, 50, 50, 0 and 30%. The synthesis of TPDPF by this method failed, even with more vigorous conditions then employed for the alkyl derivatives. This indicates that the $FeCl_2$ is not able to cleave the phosphorous–tin bond, possibly due to the lower π donating power caused by phenyl substitution and/or steric factors.

Experimental

All preparations were carried out under dry argon. THF was dried over calcium hydride and distilled immediately prior to use. Triflic acid was purchased from 3 M chemicals and anhydrous ferrous chloride from Ventron GMBH.

Deuteriated acids were prepared from the corresponding anhydrides and D_2O. 1-Phenyl phospholes were prepared by literature methods. (1,2,5-Triphenylphosphole [1], 3- and 3,4-dimethyl-1-phenylphosphole [14], 1-phenylphosphole [14] and 2-methyl-1-phenylphosphole [2].

Synthesis of Diphosphaferrocenes

TPDPF was prepared by a standard method [7]. DPF and TMDPF were prepared by the $AlCl_3$ modification [3, 13] of original methods [7, 10]. 2- and 3-DMDPF were prepared using the tributyl tin chloride modification in the following procedure.

3-Methyl-1-phenylphosphole (5 g, 0.029 mmol) was stirred in dry THF (~100 cm^3) with lithium (0.41 g, 0.058 g ats) for ~3 h. The solution was transferred via syringe to another flask containing Bu_3SnCl (19.05 g, 0.058 mmol) in dry THF (~30 cm^3). (The deep purple-brown colour of the solution is discharged when the reagents mix.) Anhydrous $FeCl_2$ (1.90 g, 0.015 mmol) was added and the reaction mixture stirred at room temperature for ~17 h. The mixture was quenched with water (~200 cm^3) and extracted with hexane (2 × 200 cm^3). The hexane was washed with HCl (200 cm^3, 2 N), then water.

The organic phase was dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The product was chromatographed on silica gel (70/230 mesh) or deactivated acidic alumina/5% H_2O with hexane/benzene (90.10 *v/v*). (The product may have to be chromatographed several times to remove all the organotin byproducts.) Yield 3-DMDPF 1.80 g (50%). A similar procedure starting with 2-methyl-1-phenylphosphole yielded 2-DMDPF (1.65 g, 46%). Both products were oils at room temperature and slightly less stable towards atmospheric oxidation than TMDPF and TPDPF.

Further structural data for the derivatives (molecular weight determination and ^{13}C NMR) appear below.

2-DMDPF

Molecular weight 250. ^{13}C NMR (CS_2) δ in ppm. J_{P-C} (Hz) in brackets if observed. C_α, 79.99 (63.70), 80.52, (63.59), C_α quat., 98.70 (62.22); C_β, ~82.79; ~84.43, complex multiplets. CH_3, 17.14 (23.8), 17 25 (23.36).

3-DMDPF

Molecular weight 250. ^{13}C NMR (CS_2): C_α, 80.27 (63.63), 80.68 (62.68); 81.07 (63.45); 81.47 (63.03); C_β, 84.85* (85.46); C_β quat., 98.54 (2.93), CH_3, 19.08.

^{13}C confirm the presence of two structural isomers for both 2- and 3-DMDPF.

^1H NMR spectra were obtained on a Varian EM 360 spectrometer at 28 °C and ^{31}P and ^{13}C NMR spectra on a Bruker spectrospin WP80. The spectrum of TMDPF in triflic acid was obtained on the WP80 FT instrument in CF_3SO_3H/D 90:10 *v/v* solvent. Molecular weight determination from mass spectra at 70 eV.

References

1 B. Lukas, R. M G. Roberts, J. Silver and A. S Wells, *J Organomet Chem., 256,* 103 (1983)
2 R. M. G Roberts, J Silver and A. S. Wells, *Inorg Chim. Acta,* in press.
3 F. Mathey, private communication
4 R. M. G Roberts, J Silver, R. Ranson and I E. G Morrison, *J Organomet. Chem , 219,* 233 (1981).
5 T. E. Bitterwolf and A. C. Ling, *J. Organomet. Chem , 40,* 197 (1972)
6 T. E. Bitterwolf and A. C Ling, *J. Organomet Chem., 215,*77 (1981) and refs. therein
7 G. D. Lauzon, B Deschamps, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem Soc., 102,* 994 (1980).
8 N. M. Kostic and R F. Fenske, *Organometallics, 2,* 1008 (1983)
9 F Mathey, *J. Organomet. Chem., 139,* 77 (1977)
10 G D. Lauzon, F. Mathey and M. Simalty, *J Organomet. Chem., 156,* C2 (1978).
11 F. Mathey, J Fischer and J. H. Nelson, *Struct. Bonding (Berlin), 55,* 154 (1983) and refs. therein.
12 E. H. Braye, I Caplier and R. Saussez, *Tetrahedron, 27,* 5523 (1971)
13 *Eur. Pat. 53 987* (1982) to B Deschamps and F. Mathey, *Chem. Abstr., 98,* 16858V (1982)
14 A. Breque, P Savignac and F Mathey, *Synthesis,* 983 (1981).

*Not sufficiently resolved for accurate measurement.