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Polymer-supported ferrocene derivatives. Some ^{13}C CP MAS NMR studies and use as hydrogenation catalysts

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Polystyrene derivatives react with the lithioferrocenes $Fe(\eta^5\text{-}C_5H_4Li)(\eta^5\text{-}C_5H_5)$, $Fe(\eta^5\text{-}C_5H_4Li)_2$, $Fe[\eta^5\text{-}C_5H_3(CHMeNMe_2)Li\text{-}1,2][\eta^5\text{-}C_5H_5]$, and with lithium ferrocenylphosphines, to yield iron-containing materials. The Mössbauer spectra confirm the loading of unstrained ferrocene fragments, some oxidized, in all cases. The ^{13}C CP MAS NMR spectra also show the loading but the resolution (structural information) is not as good as can be obtained on model solid samples. Palladium(II) derivatives of the amine- and phosphine- containing materials are active hydrogenation catalysts for olefins. Double-bond migration also occurs in the case of 1-hexene.

Keywords: Polymer-supported ferrocene derivatives, ^{13}C CP MAS spectra, polystyrene polymers, Mössbauer spectra, palladium derivatives, hydrogenation catalysts

Considerable effort has been expended on 'supporting' metal complexes on inert materials such as organic polymers, silica, alumina, and clays.[1–5] In the case of ferrocene derivatives, there have been few studies concerned with supporting them on these materials,[6–8] although a number of workers have studied polymers[3,9] prepared from substituted ferrocene monomers. There are advantages to be gained by supporting complexes such as ferrocenophanes, and ferrocene-derived polymers, on electrode surfaces.[10–14]

The present investigation is concerned with developing methods for the attachment of substituted ferrocene derivatives to polystyrene-type polymers. Particular emphasis is given to the characterization of the products by Mössbauer and ^{13}C (cross-polarization magic angle spinning) NMR spectroscopy. The ultimate objective of this work is to develop the use of the materials for heterogeneous reactions such as hydrogenation, hydrosilylation, and Grignard cross-couplings; these are known to be catalyzed homogeneously by metal derivatives of ligands based on ferrocene backbones.[15–24] In this paper some studies on olefin hydrogenation using palladium(II) derivatives of three of the polymers are described. Related polymers have been used as hydrosilylation catalysts.[8]

EXPERIMENTAL

General procedures

Unless otherwise stated, all air- or moisture-sensitive materials were manipulated under a nitrogen atmosphere by using standard Schlenk techniques. Chloromethylated cross-linked polystyrene $P—C_6H_4—CH_2Cl$ was obtained from Bio-Rad Laboratories as Bio-beads S × 1 200–400 mesh, 1.34 meq g^{-1}, polymer A, and 4.2 meq g^{-1}, polymer B. The beads were washed successively with 0.5 mol dm^{-3} sodium hydroxide, 0.5 mol dm^{-3} hydrochloric acid, water, methanol, and diethyl ether, and dried to constant weight under reduced pressure. The polymeric aldehyde $P—C_6H_4—CHO$ was prepared from Bio-beads B by dimethyl sulfoxide (DMSO) oxidation.[25] The final product contained no chlorine. All solvents were carefully dried,[26,27] and freshly distilled under nitrogen before use. Styrene, α-methylstyrene, 1-hexene, and cyclohexene were purchased from Aldrich, and passed through an alumina column prior to hydrogenation. Mössbauer spectra were recorded and processed as described previously.[28] Isomer shifts are listed relative to iron foil. Microanalyses were performed by Mr Peter Borda

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of this Department, the Canadian Microanalytical Service, Vancouver, and Mrs Ni of Wuhan University, China.

The high-resolution solid-state ^{13}C NMR experiments were carried out using a Bruker CXP 200 MHz NMR spectrometer, operating with resonance frequencies of 200 MHz for proton, and 50.3 MHz for carbon nuclei. Spin-locked cross-polarization was established through a matched Hartmann–Hahn condition,[29] by using external radiofrequency fields of 10G for proton, and 40G for carbon-13, in their respective rotating frames. The contact time between the proton and carbon reservoir was carefully determined to obtain a maximum signal-to-noise ratio. A side-band suppression pulse scheme together with a phase alternation pulse sequence was used throughout to eliminate base line and intensity artifacts.[30,31] The magic angle was set by using the ^{79}Br spectrum of KBr,[31] and the chemical shifts were measured relative to tetramethylsilane (TMS). Either Delrin or Kel-F rotors were used.

Preparation of materials

(For identification of polymer structures see Scheme 1.)

Polymers 1

To a dry Schlenk tube was added ferrocene (2.0 g, 10.8 mmol) followed by 30 cm^3 of diethyl ether. The well-stirred solution was treated with *n*-butyllithium in hexane (6.8 cm^3, 1.6 mol dm^{-3}, 10.8 mmol) and left for about 3 h before the addition of 50 cm^3 of tetrahydrofuran (THF) followed by Bio-beads B (1.34 g, 5.4 mmol). The reaction mixture was left stirring for four days at room temperature, and then hydrolyzed with deionized water. The beads were washed with ethanol, acetone, tetrahydrofuran, hexane, and ether, and dried under vacuum at room temperature. This procedure was repeated three times. Finally, the light yellow resin was extracted for 24 h with hot toluene (Soxhlet extractor) and dried to constant weight under vacuum. Mössbauer and analytical data are presented in Table 1, run 6. The results of other runs using Bio-beads B are summarized in Table 1. The procedure used for all runs was essentially as described above.

Polymer 2

Ferrocene (2 g, 10.8 mmol) was suspended in diethyl ether (30 cm^3) and *n*-BuLi (6.8 cm^3, 1.6 mol dm^{-3}, 10.8 mmol) in hexane was added. After 2 h, THF (30 cm^3) was added to the stirred reaction mixture followed by aldehydic resin (1.8 g, 5.4 mmol). The mixture was left stirring for four days at room temperature and then hydrolyzed with deionized water. The resin was collected and washed successively (× 3) with water, ethanol, acetone, THF, dichloromethane, hexane and diethyl ether. The orange–brown resin was dried at 100°C under vacuum. Mössbauer δ, 0.53 mm s^{-1}; Δ, 2.39 mm s^{-1}. Analysis: Fe, 1.3%.

(A) Polymer 2 (1 g) was suspended in 30 cm^3 benzene. Gaseous hydrogen bromide was bubbled

Table 1 Reactions of P—CH_2Cl with FcLi

			Mössbauer (mm s^{-1})		Analysis (%)		
Run[a]	Initial solvent	THF added	δ	Δ	C	H	Cl[h]
1	Hexane	No	0.53	2.35[c,d]	—	—	13.3
			0.45	0.73			
2	Cyclohexane	No	None		—	—	13.1
3	THF	Yes	0.43	2.37[c]	—	—	6.16
4	THF	Yes	0.51	2.46	75.9	7.45	5.01[f]
			0.44	0.80			
5	Et_2O	No	0.40	2.36[c]	—	—	8.56
6	Et_2O	Yes	0.44	2.35	84.08	7.39	2.80[g]

[a] Apart from one exception, [b] the mole ratio of ferrocene to *n*-butyllithium was 2:1 and the appropriate amount of TMED was added. [b] The mole ratio of ferrocene to *n*-butyllithium was 1:1. [c] Weak signal. [d] Two doublets, intensity ratio ~ 1:10 with the Δ 2.35 signal being the smaller. [e] The washings from the beads after reaction contained only ferrocene. [f] Fe, 1.2%. [g] Fe, 3.39% (polymer 1). [h] Initial chlorine content of P—CH_2Cl was 14.3%.

through the well-stirred suspension until the color darkened, becoming dark brown. The mixture was filtered, washed, and dried as above to give polymer **2a**. Analysis: Br, 0.93%.

(B) Polymer **2a** (0.5 g) was suspended in benzene (30 cm^3). Excess aqueous dimethylamine ($HNMe_2$) was then added with stirring and the color of the polymer changed to orange–brown. The mixture was stirred for 10 min, after which H_2O (30 cm^3) was added. Following filtration, the resin was treated as above to give polymer **2b**. Analysis: N, 0.83%.

(C) Polymer **2** (0.5 g) was suspended in benzene (30 cm^3). Gaseous hydrogen bromide was bubbled through the well-stirred solution until the color of the polymer darkened. Excess aqueous $HNMe_2$ was then added with stirring; the color changed to orange–brown. The mixture was hydrolyzed and treated as in method A. Analysis: N, 0.87%.

Polymer 3

The solid dilithioferrocene/TMED adduct (3:2 stoichiometry[32]) (1.40 g, 4.46 mmol), prepared from ferrocene, *n*-butyllithium, and TMED in ether, was added to ether (20 cm^3) followed by 30 cm^3 of THF. Bio-beads A (6.66 g; 8.92 mmol) were added with constant stirring. After four days the tube contents were worked up as for polymer **1**. Mössbauer δ, 0.54 mm s^{-1}; Δ, 2.40 mm s^{-1}. Analysis (two preparations): C, 85.82, 87.9; H, 7.53, 7.60; Cl, 1.72, 1.60; Fe, 5.07, —%.

Polymer 4

The solid dilithioferrocene/TMED adduct (2.4 g, 7.5 mmol) was suspended in 50 cm^3 hexane and 50 cm^3 THF. Aldehydic resin (5 g, 15 mmol) was added and the mixture was left stirring for four days at room temperature. The orange–yellow resin was hydrolyzed with deionized water, collected, washed, and dried as above. Mössbauer δ, 0.54 mm s^{-1}; Δ, 2.39. Analysis: Fe, 4.30%.

Polymer 4a This was prepared as for **2a** from polymer **4**. Analysis: Br, 2.68; Fe, 1.47%.

Polymer 4b This was prepared as for **2b** from polymer **4a**. Analysis: Br, 1.38; N, 0.72%.

Polymer 5

A solution of lithio-*N*, *N*-dimethyl-α-ferrocenylethylamine[33] in hexane was prepared from *N*, *N*-dimethyl-α-ferrocenylethylamine (2.57 g, 10 mmol), and *n*-butyllithium (10 mmol) in 35 cm^3 of hexane/diethyl ether (6:1). THF (30 cm^3) was added followed by Bio-beads B (2.38 g, 10 mmol). The suspension was stirred for five days and worked up as above. Mössbauer δ, 0.53 mm s^{-1}; Δ; 2.45 mm s^{-1}. Analysis: C, 86.2; H, 7.31; N, 0.54; Cl, 3.11; Fe, 1.21%.

Polymer 6

In a similar manner a solution of lithio-*N*, *N*-dimethyl-α-ferrocenylethylamine (from 3.3 g, 12 mmol of amine) in ether/hexane was treated with aldehydic resin (1.13 g, 1.8 mmol) suspended in THF. The mixture was stirred for four days and worked up as above. Mössbauer δ, 0.53 mm s^{-1}; Δ, 2.42 mm s^{-1}. Analysis (two different damples): C, 84.20, 81.78; H, 7.78, 7.38; N, 0.75, 0.55; O, 3.08, 3.49; Cl, 0.0, 0.0; Fe, 2.83, 1.90%.

Polymer 7

1,1′-Bis(diphenylphosphino)ferrocene[24] (4.4 g, 8 mmol) was dissolved in 100 cm^3 of THF/hexane (1:1). To this solution, *n*-butyllithium (6 cm^3, 1.6 mol dm^{-3}, 9.6 mmol) was added, and the mixture was stirred for two days before aldehydic resin (2.7 g, 8 mmol) was added. The mixture was further stirred for four days and worked up as above. Mössbauer, not observed. Analysis: Fe, 0.30; P, 0.20%.

In a second experiment the ligand was dissolved in diethyl ether and the lithiation carried out with BuLi/tetramethylethylenediamine (TMED) as for polymer **8**. Mössbauer, not observed. Analysis: Fe, 0.38; P, 0.40%.

Polymer 8

(1-Diphenylphosphino-2-(1-*N*, *N*-dimethylaminoethyl)ferrocene[15] (1.76 g, 4 mmol) was dissolved in diethyl ether (50 cm^3). To this solution *n*-butyllithium in hexane (2.5 cm^3, 1.6 mol dm^{-3}, 4 mmol) was added, and the mixture was stirred for 2 h before the addition of a mixture of TMED (0.5 g, 4 mmol) and *n*-butyllithium in hexane (2.5 cm^3, 1.6 mol dm^3, 4 mmol). The reaction mixture was left stirring for two days, after which 50 cm^3 of THF was added, followed by aldehydic resin (1.35 g, 4 mmol). The mixture was further stirred for four days at 20°C. Following hydrolysis with deionized water, the resin was collected on a glass filter and worked up as above. Mössbauer δ, 0.53 mm s^{-1}; Δ, 2.37 mm s^{-1}. Analysis: N, 0.33; Fe, 1.50; P, 0.88%.

Palladium derivatives of polymers 6, 7, 8

Polymer **6** (1.9 g) was added to an acetone solution (30 cm^3) of $Na_2PdCl_4.4H_2O$ (220 mg, 0.6 mmol) with stirring. The mixture was stirred and refluxed for

2 h. The orange–brown palladium complex, polymer **6**-Pd, was then filtered off, and washed successively, three times, with water, ethanol, acetone, THF, CH_2Cl_2, hexanes and diethyl ether and dried at 100°C under vacuum. Mössbauer δ, 0.50 mm s^{-1}; Δ, 2.24 mm s^{-1}. Analysis: N. 0.75; Cl, 1.71; Pd, 2.44%.

The palladium complex of polymer **7**, **7**-Pd, was prepared analogously from polymer **7** (1 g) and $Na_2PdCl_4.4H_2O$ (50 mg, 0.14 mmol). The product **7**-Pd was orange–brown. Mössbauer, not observed. Analysis: Cl, 0.87; P, 0.20; Pd, 1.11%.

Similarly orange–brown **8**-Pd was prepared from polymer **8** (0.7 g) and $Na_2PdCl_4.4H_2O$ (73 mg, 0.2 mmol). Mössbauer, δ 0.53 mm s^{-1}; Δ, 2.39 mm s^{-1}. Analysis: N, 0.29; Cl, 1.20; P, 0.57; Pd, 1.36%.

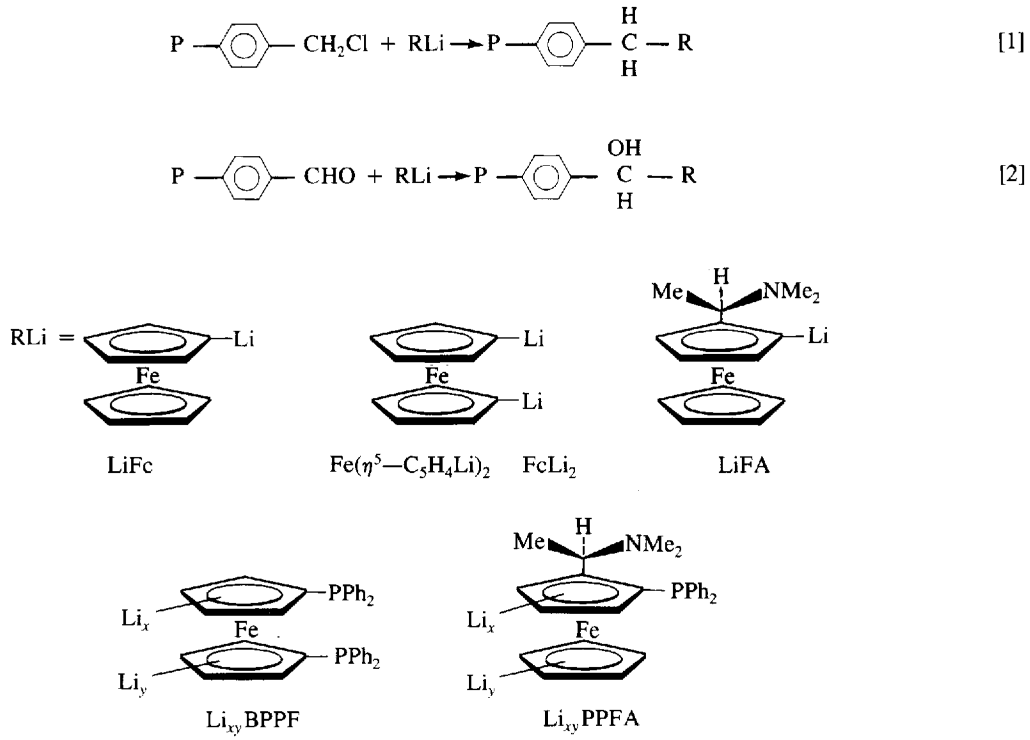
Hydrogenation of olefins

General procedure The appropriate amount of the palladium complex was suspended in the solvent in a Carius tube. The olefin was added, the system evacuated, and hydrogen was introduced at 1 atm. The tube was sealed with a Teflon valve and the stirred mixture was kept at the appropriate temperature for 2 h. The resin was removed by filtration in air and the reaction mixture was analyzed by gas chromatography.

RESULTS AND DISCUSSION

A principal objective of the present investigation was to develop methods for attaching ferrocene and its derivatives to inert supports. In view of the high reactivity and ease of preparation of lithioferrocenes,[33–36] these were the reagents of choice in experiments involving attachment to microreticular chloromethylated cross-linked polystyrene (P—C_6H_4—CH_2Cl) and to the derived aldehydic resin (P—C_6H_4—CHO). The reactions studied are shown in Scheme 1; reaction [1] was used for LiFc, $Fe(\eta^5\text{-}C_5H_4Li)_2$ and $Fe[\eta^5\text{-}C_5H_3(CHMeNMe_2)Li\text{-}1,2][\eta^5\text{-}C_5H_5]$ (LiFA).

Lithioferrocene, prepared from the reaction of a slight molar excess of ferrocene with *n*-butyllithium in ether/hexane solution,[35] reacts with chloromethylated polystyrene on the addition of THF to give an iron-containing product polymer **1**, Table 1, run 6. This maintains its yellow color after washing



Scheme 1

and extracting with boiling toluene. The Mössbauer spectrum of the product shows a quadrupole doublet whose isomer shift (δ) and quadrupole coupling (Δ) values, 0.44 and 2.33 mm s^{-1} respectively, are in the expected range for simple ferrocene derivatives,[37] e.g. compound [δ, (Δ)]: FcH [0.48, (2.40)].

Some data for other reactions involving FcLi and poly(chloromethylpolystyrene) are shown in Table 1. The chlorine content of the resin used in this series was 14.3%, so that runs 1 and 2 resulted in little attachment, presumably because of the absence of THF as swelling agent. The weak Mössbauer spectrum of the product from run 1 shows that some iron compounds are bound. The spectrum was difficult to fit, however. The outer doublet indicates the presence of a bound ferrocene group whilst the inner doublet, with its much smaller quadrupole splitting, indicates the presence of oxidized species, probably the ferricinium ion.[37] The pattern is very similar to that found for the mixed-valence compound $[Fc_2Se]^+I_5^-.\frac{1}{2}CH_2Cl_2$ [δ(Δ): Fe(II) 0.52(2.35), Fe(III) 0.53(0.50)].[38]

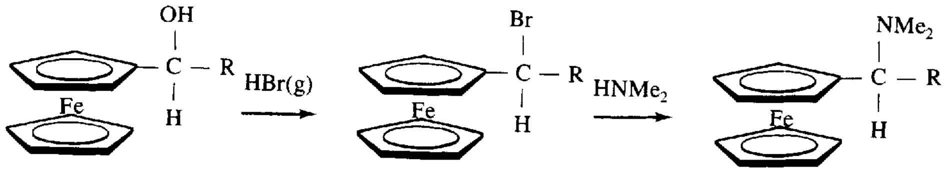
When diethyl ether or THF is used as the principal reaction solvent (butyllithium is added in hexane solution), runs 3–6, the chlorine content of the product indicates considerable reaction has taken place. However, the weak Mössbauer spectrum shows that few ferrocenyl groups are bound; possibly residual butyllithium has attacked the polymer. The absence of FcCl in the washings from runs 1 and 3 indicate that exchange reactions between P—CH_2Cl and FcLi are not important. Run 4 is included to show that sometimes oxidized products can be obtained even when least expected; the Mössbauer data of the product are very similar to those from run 1, Table 1.

The reaction of FcLi with P—C_6H_4—CHO to produce polymer **2** was carried out under similar conditions to those used for polymer **1**. The loading of iron in the example given for polymer **2** is lower than found for polymer **1**. The Mössbauer spectrum of polymer **2** shows that bonding a ferrocenyl moiety via a CH(OH) group, rather than a CH_2 group as in polymer **1**, has little effect on the parameters.

Because the hydroxy group in polymer **2** is adjacent to the ferrocene moiety, it was of interest to see if the polymer would behave like its monomeric counterparts Fc—CH(OH)R in allowing easy displacement of —OH by other groups.[39–41] It is found that treating a suspension of polymer **2** in benzene with gaseous hydrogen bromide causes a darkening of color as in the homogeneous reactions, and simple filtration affords polymer **2a** (Scheme 2); the analytical data show that bromine is incorporated into **2a**. Although the reaction conditions have not been optimized for best yeilds, it is clearly facile, and should be useful for further elaboration. In the present work it has been established that **2a** readily reacts with dimethylamine affording **2b**. Alternatively **2** can be taken through to **2b** without isolating **2a**, as is done in the homogeneous reactions.[39,40]

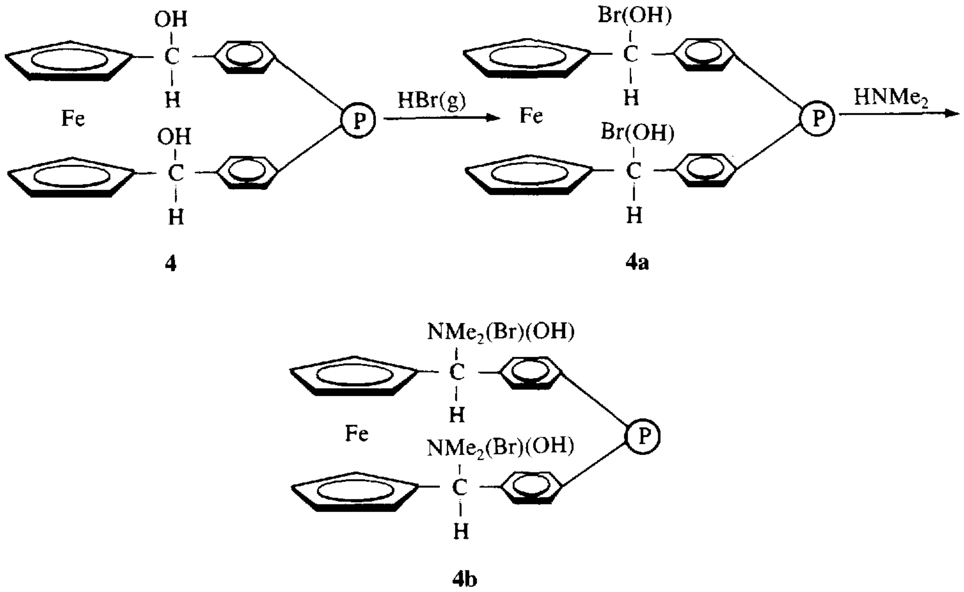
In order to bind dilithioferrocene, $Fe(\eta^5\text{-}C_5H_4Li)_2$, to the polymer the solid dilithioferrocene/TMED adduct was first isolated,[32] suspended in solvent, and allowed to react with the similarly suspended polymer beads. In the case of reaction [1], Scheme 1, a very good loading of an iron compound is achieved in the product polymer **3**. The Mössbauer spectrum shows only one doublet with a significantly greater isomer shift (0.54 mm s^{-1}) than that of polymer **1** (0.44 mm s^{-1}); this is good evidence that both rings are attached as anticipated. The quadrupole splitting is not diminished over normal values so there is no strain in the system resulting in ring tilt.[42] However, this particular criterion of tilt cannot be applied with complete confidence.[43]

The reaction of the dilithioferrocene, $Fe(\eta^5\text{-}C_5H_4Li)_2$, with aldehydic polymer also results in a polymer **4** (Scheme 3) with a high iron content (4.30%) and an almost identical Mössbauer spectrum to that of polymer **2**. Since **4** is like **2** in having —OH groups it was also treated with hydrogen bromide (Scheme 3). Polymer **4a** has a higher bromine content than **2a** reflecting the higher initial loading. Even so, the ratio Br:Fe is 1.3:1 rather than 2:1, the value which would be obtained if each original dilithioferrocene

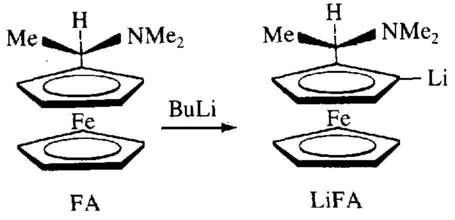


2 R = P — C_6H_4 — **2a** **2b**

Scheme 2



Scheme 3



Scheme 4

reacted to produce two —OH groups and ultimately two Br per Fe atom. A ratio of 1:1 or less would be obtained if only single-point attachment of $FcLi_2$ is achieved.

The amine FA (Schemes 1 and 4) is easily resolved into its enantiomers;[34] the initial lithiation to produce LiFA is essentially stereospecific (Scheme 4),[33] and introduces a new chiral center because of the presence of planar chirality. This, in principle, allows reactions [1] and [2] (Scheme 1) to be carried out to produce chiral polymers. Racemic FA was used in the present investigation and in order to encourage selective lithiation, TMED was not added with the n-BuLi. The microanalytical data indicate that the reaction proceeds as expected although, like run 3, Table 1, more chlorine has been lost than is accounted for by the gain in iron content. The Mössbauer spectra of polymers **5** and **6** are clean and show that attachment has taken place as anticipated. The reaction of Eqn [2] actually creates a chiral center; thus if R is chiral, diastereomers could be produced. Model studies[8] using Li_{x+y}PPFA (Scheme 1) indicate that highly asymmetric induction could be expected for reactions described by Eqn [2].

Because transition-metal complexes of ferrocenylphosphines such as PPFA and BPPF (Scheme 1) are useful catalysts for a number of reactions, including olefin hydrogenation and Grignard cross-coupling,[15–24] it was of interest to establish if these ligands could also be bound to polystyrene.

The lithiation of BPPF with two moles of *n*-butyllithium, with or without TMED, affords a mixture of metalated products which consist mainly of isomers of the hetero ring dilithiated species[44] (Scheme 1, $x = y = 1$ for Li_{x+y}BPPF). Isomers occur because, although most ferrocene substituents direct lithium mainly to the 3-position, the $—PPh_2$

group has an enhanced tendency to direct metalation to the 2-position,[44] making it more like the few exclusively 2-directing substituents (Scheme 4).[33] It should be noted that because of the presence of planar chirality in disubstituted metalocene rings, some of the isomers are actually mixtures of diastereomers. Because of these possibilities it seems unlikely that a well-defined polymer-bound BPPF ligand can be prepared via Li_{x+y}BPPF, and the results of the present study bear this out. Only low loadings of ligand are obtained from reaction with the aldehydic polymer, Eqn [2], either in the presence, or absence, of TMED. The Mössbauer spectrum of polymer **7** was too weak for processing.

The lithiation of PPFA with two moles of *n*-BuLi/TMED also results mainly in hetero ring dilithiation, although again other metalated products are present.[44,45] The dilithiated product Li_{x+y}PPFA, $x = y = 1$, Scheme 1, is also a mixture of isomers since lithiation can occur at any of the three remaining positions on the P···N-substituted ring, although the most likely position is '2' with respect to the amine function. This is the principal site of lithiation in the absence of TMED.[45]

In the present investigation, no polymer-bound product is obtained following reaction of monolithiated PPFA (no TMED added) with aldehydic resin, presumably because of steric hindrance. When two moles of *n*-BuLi/TMED are used, so that the η^5-C_5H_5 ring is metalated, the product, polymer **8**, from aldehydic resin shows a satisfactory loading. The Mössbauer spectrum is usually a clean doublet defined by δ 0.53; Δ 2.37 mm s^{-1}, although some preparations show a trace of an iron(III) impurity. The values for the free ligand are 0.44 and 2.34 mm s^{-1}. The increase in δ is probably an indication that substitution is, as anticipated, on the 'bottom' ring since the parameters for the di(tertiary phosphine) Fe(η^5-$C_5H_4PPh_2$)(η^5-$C_5H_3(PPh_2)(CHMeNMe_2$-1,2) are 0.52 and 2.35 mm s^{-1}.

The three polymers **6**, **7**, and **8** react with $PdCl_4^{2-}$ with incorporation of Pd and Cl as judged by the results of the microanalysis of the products **6**-Pd, **7**-Pd and **8**-Pd. The Cl:Pd ratio in each is *ca* 2:1. In polymer **6**-Pd the N:Pd ratio is 2.3:1 indicating that not all the nitrogen atoms are bound, as is likely if the complex is of the N_2PdCl_2 type. The Mössbauer parameters for **6**-Pd are little changed from those of the supported ligand **6**. Polymer **7**-Pd seems to have a considerable excess of Pd for a $PdCl_2$-type complex; the Pd:P ratio is 1:0.6 even though the Pd:Cl ratio is much as expected. It is difficult to account for these reproducible analytical results; perhaps in this case the side-chain has become involved. The data for **8**-Pd are reasonable for a (P—N)$PdCl_2$ complex with some unbound P—N groups. Certainly the Mössbauer spectrum of the polymer is essentially unchanged on complexation. The $PdCl_2$ complexes of free PPFA and BPPF are well characterized.[19,46]

Catalytic studies

The series of supported palladium(II) derivatives **6**-Pd, **7**-Pd, and **8**-Pd range from N-bound to P-bound probably (but see above) via the hard—soft combination of P—N binding in **8**-Pd. Although there are many examples of studies of the catalytic properties of P- and N-bound supported catalysts, little is known about mixed donor systems.[1] The results of a number of olefin hydrogenation reactions employing these catalysts are listed in Tables 2—5; all three polymers are effective hydrogenation catalysts.

Styrene and α-methylstyrene are readily hydrogenated by hydrogen (H_2) (1 atm) in benzene at 60°C in the presence of **8**-Pd, whereas cyclohexene is reduced at a slower rate (Table 2). Under the same conditions 1-hexene is both reduced and isomerized. *Trans*-2-Hexene is the major product. The catalyst can be recycled without loss of activity as is seen in runs 8—10.

The important effect of solvent on styrene hydrogenation catalyzed by **8**-Pd is shown in Table 3. The relative rate of reaction increases with solvent polarity even though benzene is a better solvent for

Table 2 Hydrogenation of olefins in benzene catalyzed by polymer **8**-Pd[a]

Run[b]	Olefin	Product	Yield (%)[c]
1	Styrene	Ethylbenzene	100
2	Styrene	Ethylbenzene	100
3	Styrene	Ethylbenzene	66
4	α-Methylstyrene	Isopropylbenzene	84
5	Cyclohexene	Cyclohexane	3
6	Cylohexene	Cylohexane	65[d]
7	1-Hexene	n-Hexane	10
		trans-2-Hexene	44
		cis-2-Hexene	19
8	Styrene	Ethylbenzene	100
9	Styrene	Ethylbenzene	100
10	Styrene	Ethylbenzene	100

[a] Olefin = 0.25 mol dm^{-3}, olefin:Pd = 100 unless otherwise stated. Benzene (1 cm^3), 60°C, 1 atm H_2, 2 h. [b] Run 1, olefin:Pd = 50; runs 8—10 re-used catalyst from run 1 for the 1st, 2nd and 3rd times respectively. Run 3, olefin:Pd = 200. [c] GLC yield based on starting olefin, Carbowax 20M or 20% tricresyl phosphate columns. [d] Time = 20 h.

Table 3 Hydrogenation of styrene catalyzed by polymer **8**-Pd[a]

Run	Solvent	Yield (%)[b]
1	Hexane	59
2	Benzene	66
3	THF	100
4	EtOH	100
5	MeOH	100
6	DMF	100
7	$CHCl_3$	20
8	CH_2Cl_2	20

[a] Olefin = 0.25 mol dm^{-3}, 1 cm^3 solvent, olefin:Pd = 200, 60°C, 1 atm H_2, 2 h. [b] GLC yield based on starting olefin.

swelling polystyrene than is ethanol. Low rates are obtained in halogenated solvents.

Table 4 shows the catalytic activities of all three polymers with respect to olefin hydrogenation at 30°C in methanol. The P—N-bound complex **8**-Pd is clearly less active than the other two. It is reported that palladium(II) derivatives of unidentate functionalized polymers are more active hydrogenation catalysts than derivatives of bidentate ones,[1] and this observation provides further indirect evidence for bidentate binding in **8**-Pd. It should be noted that homogeneous catalytic systems involving $[(P—N)PdS_2]^{2+}$ [(P—N) = PPFA, S = DMF] show higher activity for olefin hydrogenation than P—P-bound complexes.[19]

All the catalysts are active for 1-hexene hydrogenation and isomerization (Table 5). Again **8**-Pd seems less effective. Under the conditions shown, **8**-Pd affords more hexane than *trans*-2-hexene. The reverse is true in benzene at 60°C (Table 2). There also appears to be less selectivity with respect to *trans*-2-hexene formation when **6**-Pd and **7**-Pd are the catalysts.

Table 5 Hydrogenation of 1-hexene in methanol[a,b]

	Product, yield (%)		
Polymer catalyst	n-Hexane	*trans*-2-Hexene	*cis*-2-Hexene
8-Pd	28	8	4
7-Pd	46	23	11
6-Pd	61	31	8

[a] MeOH, 1 cm^3, 30°C, 1 atm H_2, 2 h. [b] See footnotes to Table 3.

At the completion of all reactions, the polymer-supported complexes can be easily separated from the reaction mixture by filtration. There are no obvious physical changes in the catalysts, especially in the color, which remains unchanged. Other PdX_2 complexes of polymer-supported N-donor ligands are good hydrogenation and isomerization catalysts and the oxidation state of the palladium is believed to be unchanged.[1] On the other hand, PdX_2 derivatives of supported unidentate phosphines seem to function as hydrogenation catalysts only after reduction to Pd(0).[1] The cause of this reduction has been ascribed to a lower P:Pd ratio in the polymer than that required, 2:1, in the unsupported system. As mentioned above, the overall lower activity of **8**-Pd may be due to the bidentate nature of the supported ligand.

CP MAS spectra

The high-resolution ^{13}C solid-state spectra of ferrocene and of a 1:1 mixture of ferrocene and the polymer chloromethylated polystyrene are shown in Fig. 1A and B. In Fig. 1A, the sharp resonance at 70.4 ppm is assigned to the ten equivalent carbon

Table 4 Hydrogenation of olefins in methanol[a,b]

Run	Polymer	Olefin	Product	Yield (%)
1	**8**-Pd	Styrene	Ethylbenzene	41
2	**7**-Pd	Styrene	Ethylbenzene	100
3	**6**-Pd	Styrene	Ethylbenzene	99
4	**8**-Pd	α-Methylstyrene	Isopropylbenzene	17
5	**7**-Pd	α-Methylstyrene	Isopropylbenzene	98
6	**6**-Pd	α-Methylstyrene	Isopropylbenzene	79
7	**8**-Pd	Cyclohexene	Cyclohexane	2
8	**7**-Pd	Cyclohexene	Cyclohexane	26
9	**6**-Pd	Cyclohexene	Cyclohexane	49

[a] MeOH (1 cm^3), 30°C, 1 atm H_2, 2 h. [b] See footnotes to Table 3.

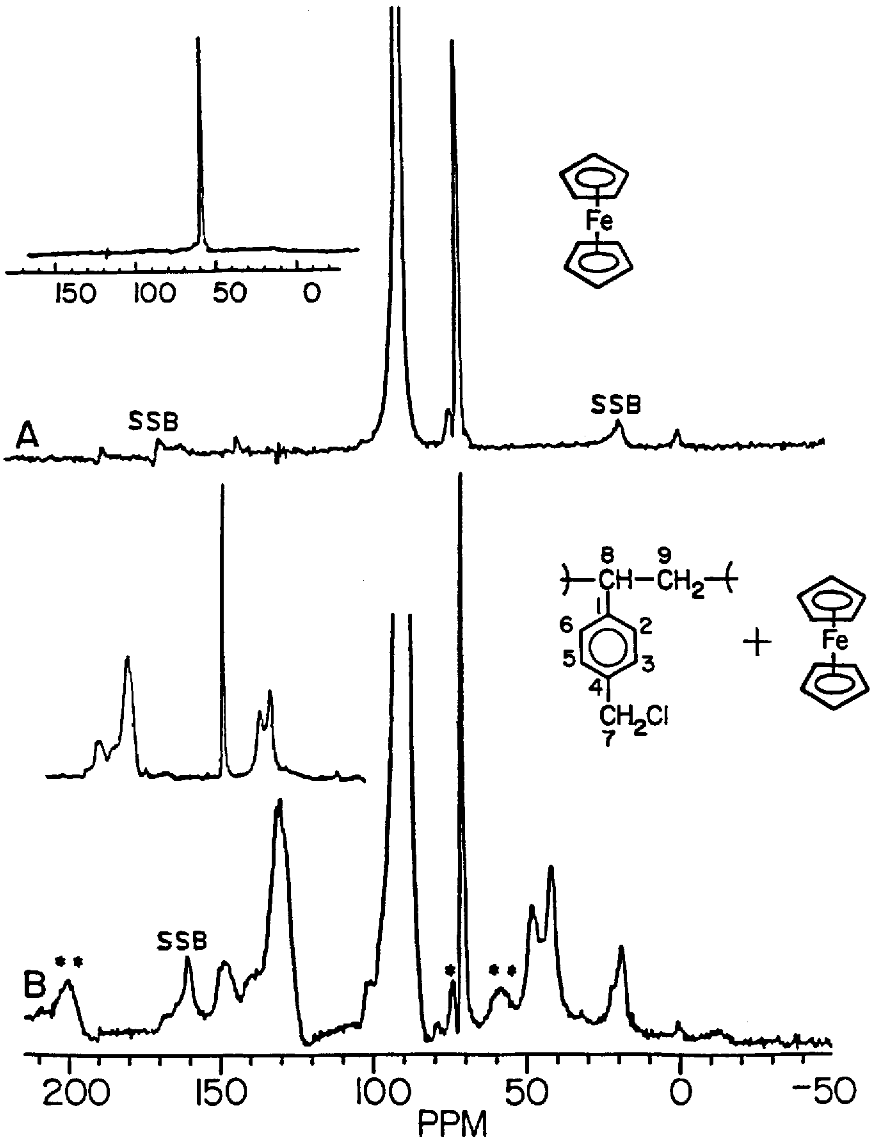


Figure 1 (A) ^{13}C CP MAS NMR spectrum of pure ferrocene, obtained with 1 ms contact time and 4 s delay between successive sampling pulses. About 1000 scans were accumulated to get a good S/N ratio. SSB indicates spinning side band from the Delrin spinner. The asterisks indicate side bands from the material. Insert: Kel-F spinner. (B) The ^{13}C CP MAS NMR spectrum of 1:1 mixture of ferrocene and the polymer, chloromethylated polystyrene. A single contact time of 1 ms was used and 5 s delay between pulses. The number of scans (NS) accumulated was around 15 000 before Fourier Transform to get a good signal. These experimental parameters are almost the same for most of the spectra reported here, unless otherwise stated. Insert: Kel-F spinner.

atoms of ferrocene. The chemical shift is 67.9 ppm in solution.[47] In Fig. 1B, the aromatic carbons are all clustered to low field, and are seen as a broad peak at 129.5 ppm with only C_1 at 147.6 ppm distinct. The aliphatic carbon atoms are upfield; the peak at 41.5 ppm is assigned to C_8 and C_9, whilst the electronegative chlorine atom shifts the resonance of C_7 downfield to 47.6 ppm.[48,49]

The spectrum of polymer **1** is shown in Fig. 2A. The peaks associated with the polymer are broadened relative to those in Fig. 1B. This is due to the presence of both P—C_6H_4—CH_2R and P—C_6H_4—CH_2Cl in the

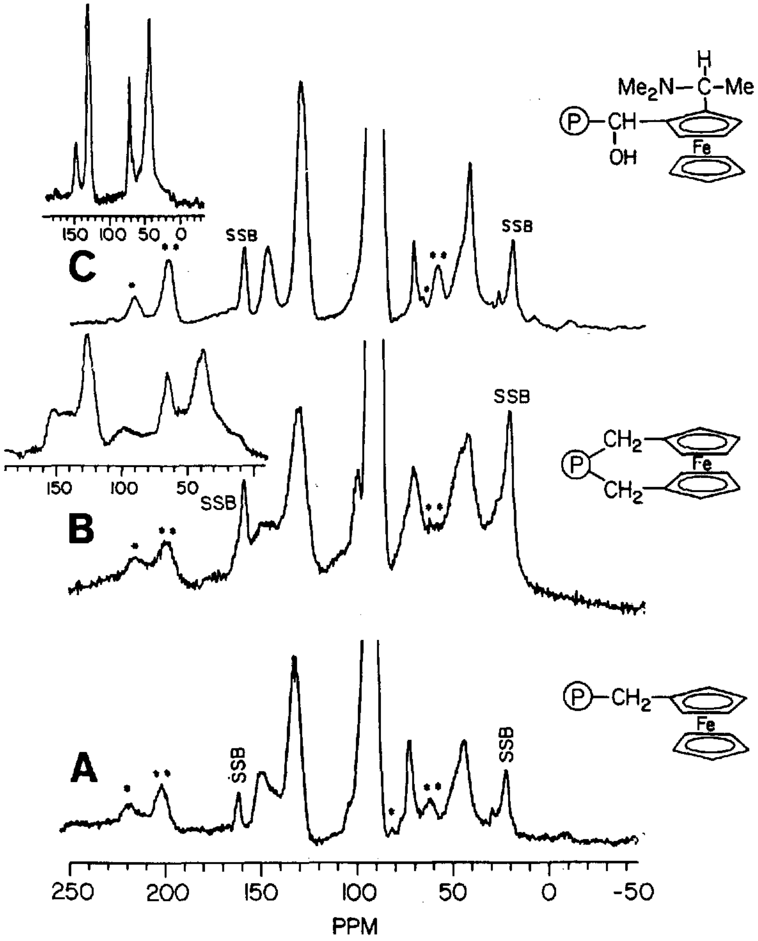


Figure 2 (A) ^{13}C CP MAS NMR spectrum of polymer **1** (see Table 1, run 6). (B) ^{13}CP MAS NMR spectrum of polymer **3**. Insert: Kel-F spinner. (C) ^{13}C CP MAS NMR spectrum of polymer **6**. Insert: spectrum of **6**-Pd, Kel-F spinner.

same polymer, an effect which would also be accompanied by a diminution of the intensity of the —CH_2—R (C_7) signal, as is seen. The cyclopentadienyl carbon atoms all appear as a single broad peak in Fig. 2A even though only one ring is substituted. In compounds of the type Fe(η^5-C_5H_5) (η^5-C_5H_4R), the solution ^{13}C NMR chemical shifts of the C_5H_5 rings are close to those of ferrocene itself, unless R is an electronegative group. The ^{13}C shifts for the substituted ring can vary greatly, with the greatest deviation being seen in the shift of the carbon atom bonded to R. In general the spread of shifts is not great if R is not electronegative and this is presumably the reason why the Fe(C_5H_5) (C_5H_4—) (Fc) peak in Fig. 2A is broadened.

The reaction of solid dilithioferrocene/TMED adduct with Bio-Beads A produces polymer **3** whose ^{13}C CP MAS spectrum is shown in Fig. 2B. The arguments presented above suggest that both rings are bound to the polymer and that a high loading of the ferrocendiyl group is present. The spectrum confirms the loading but the ring resonances are too broad to provide information about the binding mode. The spectrum obtained by using a Kel-F spinner confirms these general conclusions.

The ^{13}C CP MAS spectrum of polymer **4**, produced from the reaction of solid dilithioferrocene/TMED adduct with aldehydic resin, also shows similar intensity and broadness of the peak around 70 ppm, confirming the high binding of the ferrocene moiety. Reactions of polymer **4** with HBr(g) and $HNMe_2$ produces polymer **4b**. The corresponding CP MAS ^{13}C spectrum is broadened further in the ferrocene region.

When FA (Scheme 1) is reacted with an aldehydic

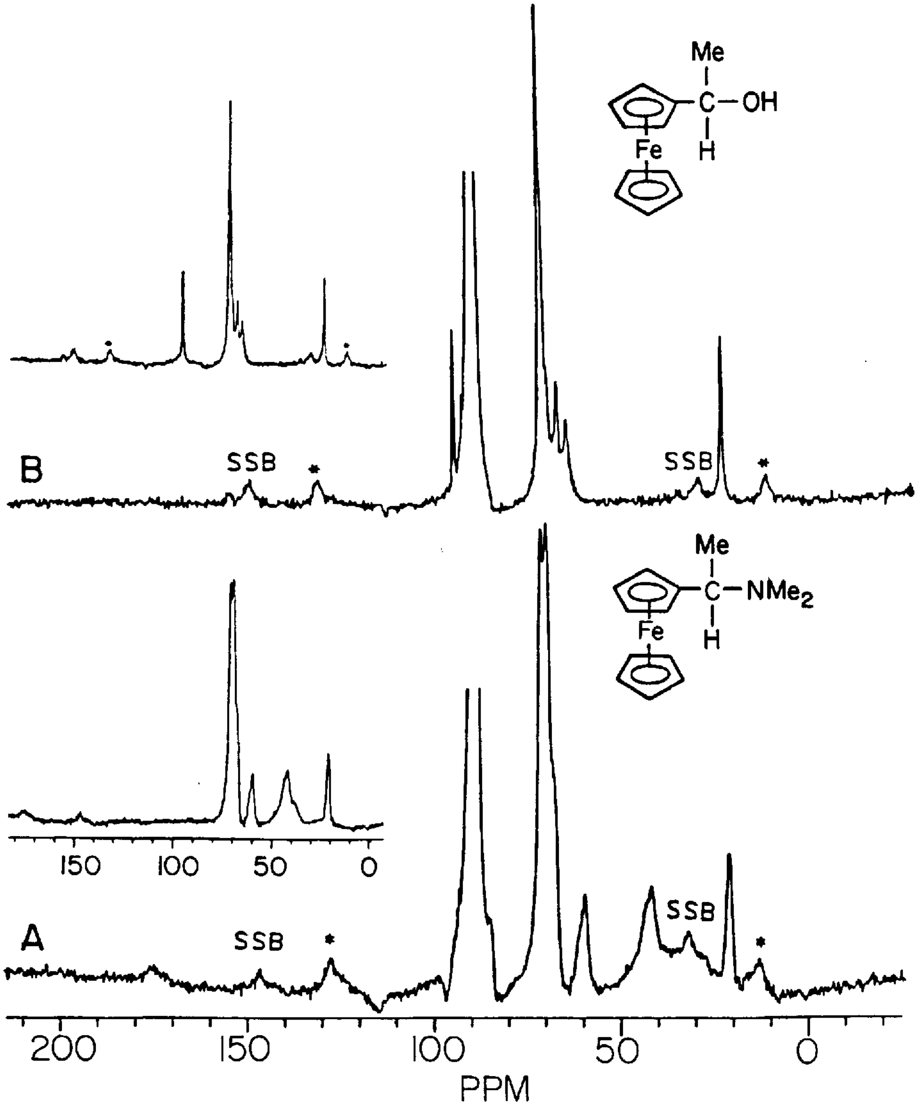


Figure 3 (A) ^{13}C CP MAS NMR spectrum of FA: 1 ms contact time with NS = 500. (B) Spectrum of compound indicated, NS = 2000. Insert: Kel-F spinner.

resin, polymer **6** results. The analytical and Mössbauer data indicate a high loading (2.8% Fe) and this is reflected in the broad peak at ~70 ppm for the ferrocene signal in the ^{13}C CP MAS spectrum shown for this compound (Fig. 2C). The sharper resonance in the 41 ppm region is no doubt due to the NMe_2 group, which, in addition to the polystyrene, resonates in this region (see below). The $PdCl_2$ derivative of this polymer, polymer **6**-Pd, has essentially the same ^{13}C spectrum. This is shown as an insert in Fig. 2C.

Given the right conditions, namely pure compounds, ^{13}C CP MAS NMR spectra are capable of resolving chemical shift differences for cyclopentadienyl carbon atoms. This is evident in the spectrum of FA (Scheme 4; Fig. 3A). Here two peaks are seen at 71.4 and 70.0 ppm in the ring region and the remaining carbon atoms are readily assigned as indicated. ($-\underline{C}HCH_3$, 59.7; $CH\underline{C}H_3$, 21.2; $N(\underline{C}H_3)_2$, 41.8 ppm). [The ^{13}C NMR spectrum of FA is as follows ($CDCl_3$): δ 16.2($C-\underline{C}H_3$); 40.5($N(\underline{C}H_3)_2$); 58.4($\underline{C}HCH_3$); 66.5, 66.9, 67.0, 68.5, 69.1($\underline{C}_5H_4-$); 68.3($\underline{C}_5H_5$).] The broadness of the $N(CH_3)_2$ resonance in the solid-state spectrum is likely due to quadrupolar interaction with the nitrogen atom.[50] When the $-NMe_2$ group in FA

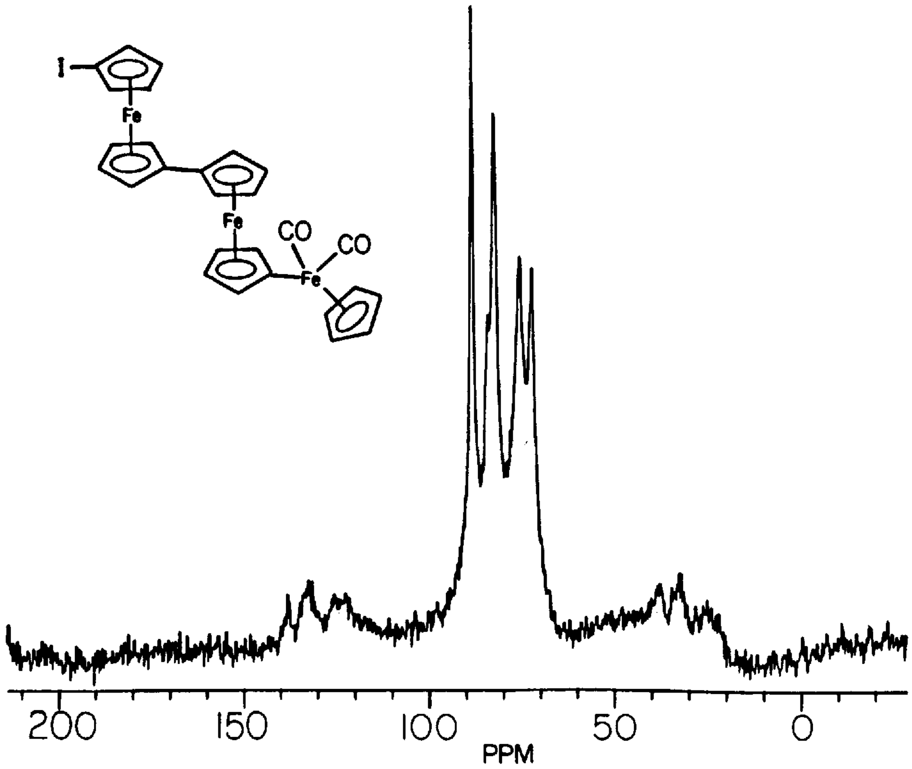


Figure 4 ^{13}C CP MAS NMR spectrum of the compound indicated. A Kel-F spinner was used.

in replaced by —OH, the spectrum, Fig. 3B, is further resolved, illustrating the effect of the more electronegative group [$-\underline{C}HMe-$, 94.2; $Fe(\underline{C}_5H_5)(\underline{C}_5H_4-)$ 71.6, 69.6, 66.7; $\underline{C}H_3$, 22.6]. Even more detail is seen in the spectrum of the derivative shown in Fig. 4.

In summary, ferrocene and its derivatives can be easily supported on polystyrene polymers. Mössbauer and ^{13}C CP MAS NMR studies confirm this and give useful structural information. The palladium(II) derivatives of the ferrocenyl-amine- and phosphine-containing polymers are active hydrogenation catalysts for styrene, α-methylstyrene, cyclohexene and 1-hexene; double-bond migration also occurs in the latter case. The catalysts can be easily separated from the reaction mixture by filtration and can be recycled without any loss of activity.

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