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1,2,3,4,6-Pentamethylfulvene: a convenient precursor to substituted tetramethylcyclopentadienyl transition metal complexes

Dennis M. Bensley, Jr. and Eric. A. Mintz *

Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045 (U.S.A.)

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Abstract

Reaction of 2,3,4,5-tetramethylcyclopent-2-enone with vinylmagnesium bromide in THF gave a 5/1 mixture of 1,2,3,4,6-pentamethylfulvene and vinyltetramethylcyclopentadienes. Treatment of this mixture with $LiAlH_4$ or LiR ($R = CH_3$, C_6H_5, $P(C_6H_5)_2$) gave the corresponding substituted tetramethylcyclopentadienide anions $\{[C_5(CH_3)_4]CH(CH_3)R\}^-$ ($R = H$, CH_3, C_6H_5, $P(C_6H_5)_2$) in high yields. Reaction of these substituted tetramethylcyclopentadienide anions with $FeCl_2$ in THF led to the formation of the corresponding substituted ferrocene complexes, $\{[C_5(CH_3)_4]CH(CH_3)R\}_2Fe$, in moderate yields.

Introduction

The electron-donating ability and steric bulk of the pentamethylcyclopentadienyl ligand has been found to typically impart to transition metal complexes an exceptional blend of stability and reactivity not found with other ligands. Pentamethylcyclopentadienyl substituted transition metal complexes have proven to be useful in the investigation of the reduction of both free and transition metal bound CO, and the activation of H_2 and C–H bonds [1–9]. In light of the chemistry that has been exhibited by transition metal complexes containing the pentamethylcyclopentadienyl ligand, it is surprising that functionalized tetramethylcyclopentadienyl ligands have not been widely prepared and utilized in organometallic chemistry. To date, the synthesis of only a small number of hydrocarbon substituted tetramethylcyclopentadienyl ligands have been reported, $[C_5(CH_3)_4H]R$ ($R = (CH_2)_nCH_3$ ($n = 1$–3) [10], $CH_2CH_2C{\equiv}CCH_2CH_3$ [11], $CH_2C_6H_5$ [12], C_6H_5 [10], $CH(CH_2CH_3)$-C_6H_5 [13]), however only one example of a heterosubstituted tetramethylcyclopentadienyl ligand has been published $[C_5(CH_3)_4H]P(C_6H_4\text{-}p\text{-}CH_3)_2$ [14]. A small number of bridged tetramethylcyclopentadienyl ligands have also been reported $[C_5(CH_3)_4H]_2X$ ($X = (CH_2)_n$ ($n = 1$–3) [12b,15], $Si(CH_3)_2$ [16], $[Si(CH_3)_2CH_2]_2$

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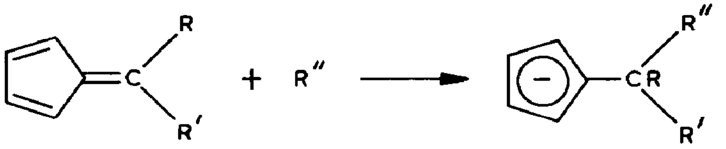
[16b], p-C_6H_4 [17], p-$C_6H_4C_6H_4$ [17]). The majority of these substituted tetramethylcyclopentadiene ligands are prepared by the dicondensation of the appropriately substituted ester with 2-butenyllithium followed by an acid catalysed dehydration and ring closure [10b,12a,13,15b,18].

The addition of nucleophiles to fulvenes has proven to be a successful route for the preparation of substituted cyclopentadienide ligands [19], as is illustrated below.



$R = CH_3 , C_6H_5$

$R' = H , CH_3 , C_6H_5$

$R'' = H , CH_3 , C_6H_5 , CH_2P(C_6H_5)_2$

We report here the use of 1,2,3,4,6-pentamethylfulvene, as a convenient starting material for the high yield synthesis of substituted tetramethylcyclopentadienyl ligands and their use in the preparation of substituted ferrocene complexes $\{[C_5(CH_3)_4]CH(CH_3)R\}_2Fe$ ($R = CH_3$, C_6H_5, $P(C_6H_5)_2$).

Experimental

All operations were performed under an atmosphere of dry nitrogen. Solvents were purified by distillation from Na/K alloy under nitrogen. Vinylmagnesium bromide (Aldrich), methyllithium (Aldrich), n-butyllithium (Aldrich), phenyllithium (Aldrich), lithium wire (Aldrich), chlorodiphenylphosphine (Aldrich), $BH_3 \cdot THF$ (Aldrich), 1,5-cyclooctadiene (Aldrich), lithium aluminum hydride (Aldrich), and ferrous chloride (Strem) were used as purchased, and 2,3,4,5-tetramethylcyclopent-2-enone was prepared by a published procedure [20]. Column chromatography was carried out using Merck alumina under nitrogen.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 270, 67.8, and 109.25 MHz respectively on a JEOL GX 270 NMR spectrometer. Spectra were measured at ambient temperatures unless otherwise noted in C_6D_6 or $CDCl_3$, utilizing residual solvent peaks or tetramethylsilane as an internal standard for ^1H and ^{13}C spectra. The ^{31}P NMR spectra are reported relative to external 85% H_3PO_4. Melting points were determined on a Mel-Temp apparatus in sealed tubes under nitrogen and are uncorrected. Elemental analyses were performed by Microlytics, S. Deerfield, MA.

Treatment of 2,3,4,5-tetramethylcyclopent-2-enone, 1, with vinylmagnesium bromide

2,3,4,5-Tetramethylcyclopent-2-enone (**1**) (50.0 g, 362 mmol) in 100 ml of THF was added dropwise via an addition funnel to 398 ml (398 mmol) of 1.0 *M* vinylmagnesium bromide in THF with stirring at room temperature, in a 1000 ml, three-necked round-bottom flask equipped with a nitrogen inlet adapter, condenser, and a septum capped, pressure-equalizing dropping funnel. The resulting reaction mixture was stirred overnight, then quenched with approximately 50 ml of 20%

aqueous HCl. The organic layer was separated and washed with 50 ml portions of saturated aqueous sodium bicarbonate and then with 50 ml portions of water until neutral. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent removed under vacuum, to give 53.0 g (358 mmol, 99% yield) of a mixture of fulvene **2** and vinyltetramethylcyclopentadienes **3** as a thermally labile red oil which was stored at 0 ° C until used. Compounds **2** and **3** were determined to be present in an approximately 5/1 ratio by ^{1}H NMR.

IR (neat): 2990vs, 2940vs, 2880vs, 1705w, 1655w, 1635m, 1460s, 1390s, 1340m, 1305m, 1275w, 1230m, 1130w, 1110w, 1090w, 1050w, 990w, 970m, 930w, 890w, 870m, 845m cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ 1.17 (d, CH_3, 7.50 Hz), 1.28 (d, CH_3, 7.5 Hz), 1.89 (s, CH_3), 1.91 (s, CH_3), 1.96 (s, CH_3), 2.00 (s, CH_3), 2.04 (s, CH_3), 2.08 (s, CH_3), 2.26 (s, CH_3), 2.27 (d, CH_3, 7.1 Hz), 4.80 (d, CH_2, olefinic), 5.00–5.80 (m, CH and CH_2 olefinic), 6.31 (q, CH, 7.14 Hz), 6.60 (m, CH, olefinic), 6.70 (m, CH olefinic).^{13}C {^{1}H} (67.5 MHz, $CDCl_3$): δ [9.2, 10.2, 10.5, 10.6, 11.0, 11.3, 12.3, 13.7, 13.8, 14.1, 20.7] (CH_3), [14.6] (CH_3), [38.3, 51.9] (CH), [97.8, 114.7] (CH_2, olefinic), [110.6, 130.8] (CH, olefinic), [127.3] (CH, olefinic), [122.6, 124.7, 132.5, 135.1, 139.3, 140.4, 146.6, 150.1, 158.7] (olefinic).

Anal. Found: C, 89.30; H, 10.91. $C_{11}H_{16}$ calc: C, 89.12; H, 10.88%.

Isolation of 1,2,3,4,6-pentamethylfulvene (2) by converting vinyltetramethylcyclopentadienes 3 to alcohols (4) via hydroboration with 9-BBN

A mixture of **2** and **3** (25.0 g, 169 mmol) was added to a 500 ml three-necked, round-bottom flask equipped as described above. A solution of 9-BBN, prepared from 65 ml (65 mmol) of 1 *M* $BH_3 \cdot THF$ and 8.0 ml (65 mmol) of 1,5-cyclooctadiene in 30 ml THF [21], was then added dropwise via an addition funnel at room temperature and the reaction mixture was stirred for 2 h. The addition of 4 ml H_2O, then 22 ml of 3 *M* NaOH followed by 22 ml of 30% H_2O_2 and the standard work-up [21], gave a mixture of **2** and alcohols **4** as a red oil. Compounds **2** and **4** were easily separated by chromatography on alumina (2 × 60 cm column). Elution of the column with hexane gave a red band, which after removal of the solvent under vacuum gave 12.0 g (80.9 mmol) of **2** as a red oil.

IR (neat): 2990vs, 2940vs, 2890vs, 1650w, 1460s, 1390s, 1350m, 1310w, 1220w, 1130w, 1120w, 1090w, 1005w, 965m, 840m cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ 2.00 (6H, s, CH_3), 2.04 (3H, s, CH_3), 2.26 (3H, s, CH_3), 2.27 (3H, d, CH_3, 7.14 Hz), 6.31 (1H, q, CH, 7.14 Hz). ^{13}C {^{1}H} (67.5 NHz, $CDCl_3$): δ [9.2, 10.5, 10.9, 13.6] (CH_3), [14.6] (CH_3, C_6), [122.5, 124.6, 135.1, 139.3, 146.5] (Cp), [127.2] (CH, olefinic).

Preparation of 1-ethyl-2,3,4,5-tetramethylcyclopentadienes, $[C_5(CH_3)_4H]CH_2CH_3$ (5)

A mixture of **2** and **3** (1.3 g, 8.8 mmol) was added to 0.77 g (20 mmol) of $LiAlH_4$ in 20 ml of ether at 0 ° C. The mixture was stirred for 15 min and then filtered, and the solvent was removed under vacuum to give a yellow oil. Hexane, 15 ml, was added to this yellow oil producing a white solid. This white solid was filtered and washed several times with 5 ml of hexane to remove unreacted **2** and **3**. Hexane was then added to the white solid and the mixture was carefully hydrolyzed with methanol and then with aqueous 50% HCl until all of the solid had dissolved. The yellow organic layer was separated and then washed several times with saturated aqueous sodium bicarbonate and then water. The organic layer was dried over magnesium sulfate, filtered, and the solvent removed under vacuum to give 0.82 g 95.5 mmol) of 1-ethyl-2,3,4,5-tetramethylcyclopentadienes (**5**) [10b], (75% yield based on **2**) as a yellow oil.

Preparation of bis(isopropyltetramethylcyclopentadienyl)iron(II), $\{[C_5(CH_3)_4]CH(CH_3)_2\}_2Fe$ *(**8**)*

Methyllithium, 5.6 ml of 1.5 *M* in ether (8.4 mmol), was added dropwise to 1.50 g (10.1 mmol) of the mixture of **2** and **3** in 10 ml of ether at room temperature in a 50 ml two-necked round-bottom flask equipped with a condenser, nitrogen inlet adapter and a septum. A white precipitate immediately formed and the mixture was allowed to stir for an additional hour. The mixture was then filtered and the white solid was washed several times with hexane. The solid was dried under vacuum to give 1.06 g (6.20 mmol) of lithium (1-isopropyl-2,3,4,5-tetramethylcyclopentadienide) (**6**) (74% yield based on methyllithium).

A 50 ml round-bottom flask, equipped with a condenser and a nitrogen inlet adapter was charged with 0.5 g (2.9 mmol) of anion **6**, 0.2 g (1.6 mmol) of anhydrous ferrous chloride and 20 ml of dry THF. This mixture was refluxed for 2 h, during which the solution turned dark red. The reaction mixture was then cooled to room temperature and the solvent was removed under vacuum to give a yellow oil. This oil was then taken up in ether and washed with saturated aqueous ammonium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered, and the solvent removed under vacuum. The resulting yellow oil was taken up in a minimum volume of hot methanol, and then the solution was allowed to slowly cool to room temperature, and then to 0 ° C to produce 0.27 g (0.7 mmol, 48% yield) of **8** as a yellow crystalline solid (m.p. 123–125 ° C).

Anal. Found: C, 75.32; H, 10.03. $C_{24}H_{38}Fe$ calc: C, 75.38; H, 10.02%.

Preparation of bis[1-phenyl-1-tetramethylcyclopentadienylethane]iron(II), $\{[C_5(CH_3)_4]CH(CH_3)C_6H_5\}_2Fe$ *(**9**)*

In a manner similar to that above 4.2 ml (10. mmol) of 2.4 *M* phenyllithium in 7/3 cyclohexane/ether was added dropwise to 2.00 g (13.5 mmol) of a mixture of **2** and **3** in 6 ml of ether. The solvent was removed under vacuum and 20 ml of hexane added, producing a white precipitate. The mixture was then filtered and the white solid was washed several times with hexane. The solid was dried under vacuum to give 2.34 g (10.1 mmol) of lithium[1-(1-phenylethyl)-2,3,4,5-tetramethylcyclopentadienide] (**7**) in quantitative yield (based on phenyllithium).

A 100 ml round-bottom flask, equipped with a condenser and a nitrogen inlet adapter was charged with 1.5 g (6.5 mmol) of anion **7**, 0.45 g (3.6 mmol) of anhydrous ferrous chloride, and 60 ml of THF. This mixture was refluxed for 3 h, during which time the solution turned dark red. The solution was allowed to cool to room temperature and worked-up in a manner similar to that described above for **8**. The resulting orange oil was taken up in a minimum volume of hot hexane and cooled to 0 ° C to produce 0.6 g (1.2 mmol, 37% yield) of **9** as a yellow crystalline solid (m.p. 162–165 ° C).

Anal. Found: C, 80.44; H, 8.50. $C_{34}H_{42}Fe$ calc: C, 80.62; H, 8.36%.

Preparation of 1-(tetramethylcyclopentadienyl)-1-diphenylphosphinoethanes, $[C_5(CH_3)_4H]CH(CH_3)P(C_6H_5)_2$ *(10)*

Lithium diphenylphosphide [22], prepared from 7.5 ml (42 mmol) of chlorodiphenylphosphine and 1.2 g (173 mmol) of lithium chips in 100 ml of THF, was added dropwise via an addition funnel to 7.7 g (52 mmol) of a mixture of **2** and **3** in 50 ml of THF at 0 ° C, in a 250 ml three-necked, round-bottom flask equipped with a nitrogen inlet adapter, condenser, and a septum capped, pressure-equalizing addition funnel. The resulting red reaction mixture was stirred overnight at room temperature, and then refluxed for 1 h. The mixture was then cooled to room temperature and the solvent removed under vacuum. The remaining yellow oil was taken up in benzene and the organic layer washed with deoxygenated water, aqueous ammonium chloride, and then deoxygenated water until neutral. The organic layer was dried over anhydrous calcium chloride, filtered, and the solvent removed under vacuum. The resulting yellow oil was taken up in dry hexane, filtered through two inches of celite and the solvent removed under vacuum. Diphenylphosphine formed during the work-up was removed by distillation at 80 ° C under high vacuum to give 10.5 g (31.4 mmol) of **10** (74% yield based on chlorodiphenylphosphine) as a viscous yellow oil.

IR (neat): 3040s, 2940vs, 2900vs, 2840s, 1940w, 1870w, 1800w, 1630w, 1570m, 1465s, 1420vs, 1365s, 1315w, 1295w, 1255w, 1170w, 1080m, 1055m, 1015m, 990m, 900w, 880w, 835w, 790w, 730vs, 680vs cm^{-1}.

^1H NMR (270 MHz, C_6D_6): δ 0.70–1.00 (m, CH_3), 1.10–1.50 (m, CH_3), 1.50–1.90 (m, CH_3), 1.90–2.50 (m, CH), 2.95 (m, CH), 2.60 9m, CH), 6.90–8.00 (m, aromatic). ^{13}C $\{^1H\}$ NMR (67.8 MHz, C_6D_6): δ [11.1, 11.2, 11.4, 11.6, 11.8, 11.9, 12.3, 12.4, 12.6, 14.1, 15.1, 15.3, 15.4] (CH_3), [17.4, 17.6, 18.6, 18.7] (CH_3, $J(^{31}P-^{13}C)$ 19.5 Hz), [30.9, 31.6, 32.8] (CH, $J(^{31}P-^{13}C)$ 13.4 Hz), [50.9] (ring CH, $J(^{31}P-^{13}C)$ 7.4 Hz), [51.3] (ring CH), [52.0, 57.6] (ring CH, $J(^{31}P-^{13}C)$ 9.8 Hz), [127.6–142.4] (aromatic and olefinic carbons). ^{31}P $\{^1H\}$ NMR (109.25 MHz, C_6D_6): δ -10.6, -9.3, -8.4, -8.0, -6.0.

Anal. Found: C, 81.89; H, 8.64. $C_{23}H_{27}P$ calc: C, 82.60; H, 8.14%.

Preparation of bis[1-(tetramethylcyclopentadienyl)-1-diphenylphosphinoethane]iron(II), $\{[C_5(CH_3)_4]CH(CH_3)P(C_6H_5)_2\}_2Fe$ *(12)*

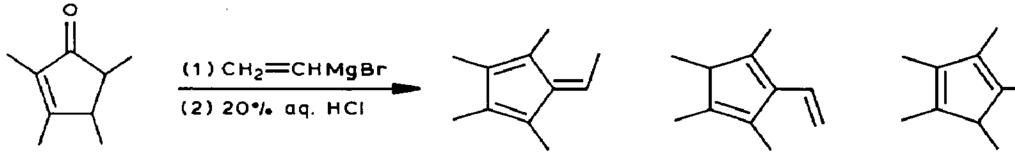
n-Butyllithium, 16.5 ml of a 1.6 *M* solution in hexane (26.0 mmol), was added to 8.0 g (24.0 mmol) of phosphine **10** in 40 ml of ether at 0 ° C. The resulting red solution was allowed to stir overnight and then the solvent was removed under vacuum to give a viscous red oil. This oil was washed several times with hexane and then dried under vacuum to give 7.0 g (21.0 mmol) of lithium[1-(1-diphenylphosphinoethyl)-2,3,4,5-tetramethylcyclopentadienide] (**11**) (86% yield based on **10**) as a yellow-orange powder.

A 250 ml round-bottom flask, equipped with a condenser and a nitrogen inlet adapter was charged with 5.4 g (15.9 mmol) of anion **11**, 1.50 g (11.8 mmol) of anhydrous ferrous chloride, and 120 ml of THF. The dark red mixture was refluxed for 24 h. The solution was then cooled to room temperature and the solvent removed under vacuum. The resulting dark purple-red residue was taken up in a minimum volume of hexanes and several grams of deactivated alumina was added. The solvent was removed under vacuum and the resulting coated alumina was placed on top of a column (2 × 60 cm) of deactivated alumina under nitrogen and was eluted with hexane, to remove unreacted phosphine **10**. An orange band was then eluted with ether, the solvent removed under vacuum to give 1.7 g (2.4 mmol, 30% yield) of **12** as a yellow solid (m.p. 149–150 °C). ^{31}P {^{1}H} NMR (109.25 MHz, C_6D_6): δ -4.6, −3.9.

Anal. Found: C, 77.07; H, 7.64. $C_{46}H_{52}P_2Fe$ calc: C, 76.45; H, 7.25%.

Results and discussion

Treatment of 2,3,4,5-tetramethylcyclopent-2-enone (**1**) [20] with vinylmagnesium bromide in THF at room temperature, followed by work-up with 20% aqueous HCl, and removal of solvent, produced a red oily mixture of 1,2,3,4,6-pentamethylfulvene (**2**), and vinyltetramethylcyclopentadienes (**3**) in quantitative yield, in an approximately 5/1 ratio as determined by ^{1}H NMR.



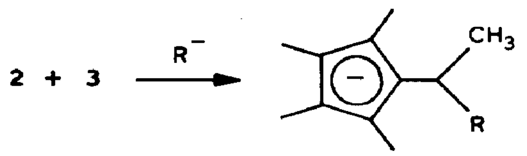
(1) (2) (3a) (3b)

Although **2** and **3** could not be easily separated, hydroboration of a mixture of **2** and **3** with 9-BBN [21] and subsequent work-up gave unreacted fulvene and the corresponding terminal alcohols (**4**). Fulvene **2** and the alcohols **4** were then easily separated by column chromatography on alumina. Based upon the reactivity differences of **2** and **3**, and the ease of separation of the substituted tetramethylcyclopentadienides from the unreacted **2** and **3**, it was unnecessary to "separate" **2** and **3** prior to use, *vide infra*.

Treatment of a mixture of **2** and **3** with $LiAlH_4$ in ether at 0 °C, led, upon work-up, to ethyltetramethylcyclopentadienes (**5**) [10b] in 75% yield as a pale yellow oil.

$$\mathbf{2}+\mathbf{3}\xrightarrow[2)\ H^{+}]{1)\ LiAlH_4}\underset{(\mathbf{5})}{[C_5(CH_3)_4H]CH_2CH_3}$$

Addition of methyllithium or phenyllithium to a mixture of **2** and **3** readily gave the corresponding substituted lithium tetramethylcyclopentadienides **6** and **7** in high yields. The hexane insoluble anions **6** and **7** were easily separated from unreacted **2** and **3**.

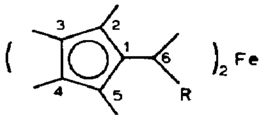


(**6**: R = CH₃;
7: R = C₆H₅)

Anions **6** and **7** were then treated with anhydrous ferrous chloride in refluxing THF

Table 1

^{1}H NMR data

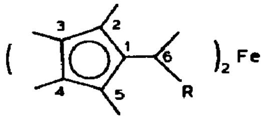


Compound [a]	Cp*-CH_3	C(6)	Me(6)	Phenyl
8	1.65(12H,s)	2.60(2H,m,7.0)	1.19(12H,d,7.0)	–
	1.69(12H,s)			
9	1.45(s)	3.87(m)	1.74(d,6.8)	7.00(m)
	1.55(s)			7.09(s)
	1.66(s)			
	1.70(s)			
	1.91(s)			
	1.95(s)			
12	0.85(s)	3.27(m)	1.70(d,6.9)	6.60–8.00(m)
	0.89(s)		1.75(d,7.3)	
	1.46(s)			
	1.48(s)			
	1.63(s)			
	1.65(s)			
	1.91(s)			
	1.99(s)			

[a] C_6D_6 solvent.

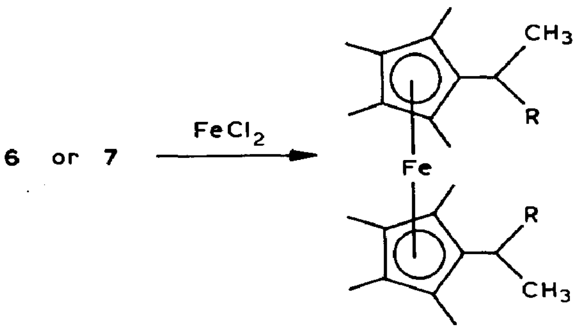
Table 2

^{13}C {^{1}H} NMR data



Compound [a]	C(1)	C(2,5)/ C(3,4)	Me(2,5)/ Me(3,4)	C(6)	Me(6)	Phenyl
8	89.6	77.1	9.7	26.3	23.1	–
		78.9	10.6			
9	86.6	77.7	10.0	39.1	23.8	125.7
	86.9	78.1	10.1	39.9	24.0	127.4
		79.2	10.4			128.3
		79.4	10.7			148.7
		79.8	12.0			149.1
		79.9	12.5			
12 [b]	86.7(d, 15.8)	77.5(d, 3.6)	9.7(d, 7.4)	30.9(d, 15.7)	19.6(d, 22.0)	127.1–138.9(m)
	87.5(d, 15.9)	78.5(d, 2.4)	9.9(s)	31.1(d, 14.6)	20.1(d, 23.2)	
		78.7(s)	10.0(d, 8.5)			
		79.2(d, 15.9)	11.5(d, 8.6)			
		79.5(s)	12.9(d, 7.3)			
		79.8(d, 15.9)				

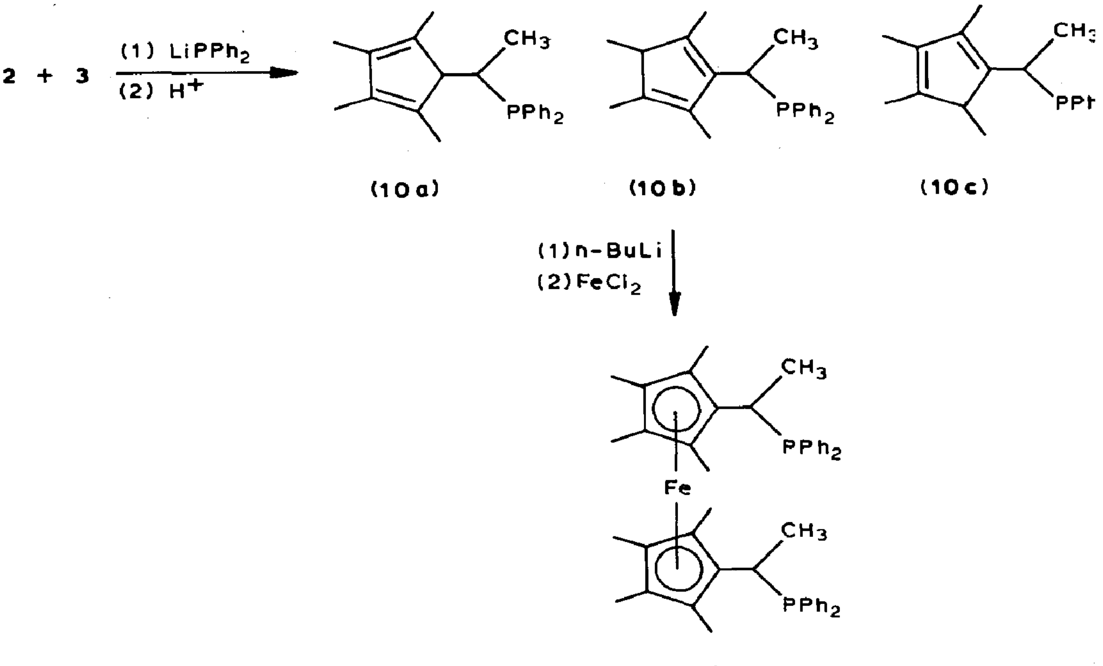
[a] C_6D_6 solvent. [b] δ(m, $J(^{31}P-^{13}C)$ (Hz)).



($\mathbf{8}$: R = CH_3;
$\mathbf{9}$: R = C_6H_5)

to give the corresponding ferrocene derivatives **8** and **9** in good yields. Complex **9** was formed as an approximately 2/1 mixture of diastereomers. The ^1H and ^{13}C NMR spectra of the mixture of diastereomer **9** are complex (Tables 1 and 2), because each of the diastereomers exhibits diastereotopic resonances for the protons and carbons at the 2 and 5 ring positions.

Treatment of a mixture of **2** and **3** with lithium diphenylphosphide in THF upon hydrolysis and work-up gave 1-(tetramethylcyclopentadienyl)-1-diphenylphosphinoethanes (**10**) as an orange oil in good yield. Phosphine **10** exists as a mixture of three tautomers, two of which (**10b** and **10c**) contain two chiral centers giving rise to two sets of diastereomers. This mixture gives rise to extremely complex ^1H (Fig. 1) and ^{13}C NMR spectra. The ^{31}P NMR of **10** exhibits five resonances, one for **10a**,



(10a) (10b) (10c)

(12)

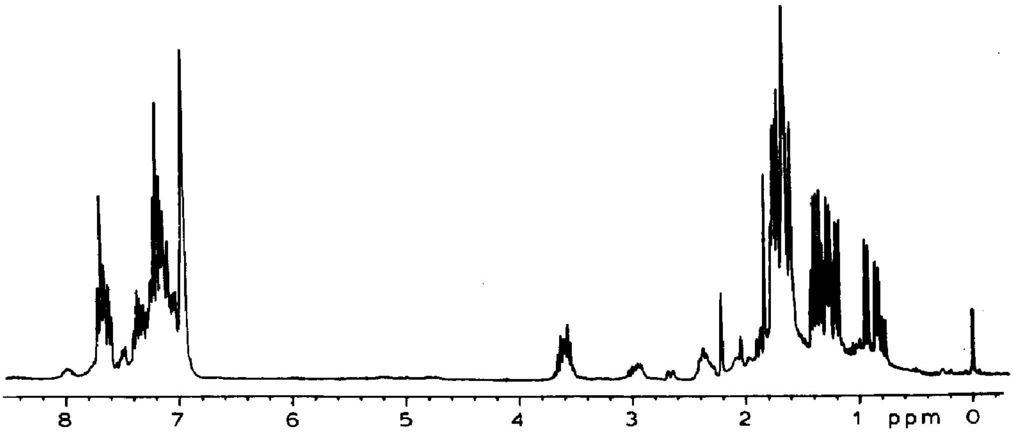


Fig. 1. 270-MHz ^{1}H NMR spectrum of $\{[C_5(CH_3)_4]CH(CH_3)P(C_6H_5)_2\}_2Fe$ in C_6D_6.

and one for each of the diastereomers of **10b** and **10c**. Treatment of phosphine **10** with n-butyllithium followed by anhydrous ferrous chloride in refluxing THF gave **12** in 30% yield.

Complex **12** is formed as an approximately 1/1 mixture of diastereomers, giving rise to two ^{31}P NMR resonances, one for each diastereomer. The ^{1}H and ^{13}C NMR resonances (Tables 1 and 2) of the protons and carbons at the 2 and 5 ring positions in each of the diastereomers exhibits diastereotopic resonances as well coupling to the ^{31}P.

1,2,3,4,6-Pentamethylfulvene has proven to be a convenient starting material for the high yield preparation of substituted tetramethylcyclopentadienyl ligands. Further work is in progress to explore the utility of **2** as a starting material for the preparation of other heteroatom substituted tetramethylcyclopentadienyl ligands and transitional metal complexes, and to utilize **10** and **12** to prepare new bimetallic complexes.

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