Synthesis of Derivatives of (α-(Dimethylamino)ethyl)ferrocene via Lithiation Reactions and the Structure of 2-(α-(Dimethylamino)ethyl)-1,1′,3-tris(trimethylsilyl)ferrocene

Ian R. Butler, William R. Cullen,* and Steven J. Rettig[1]

Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

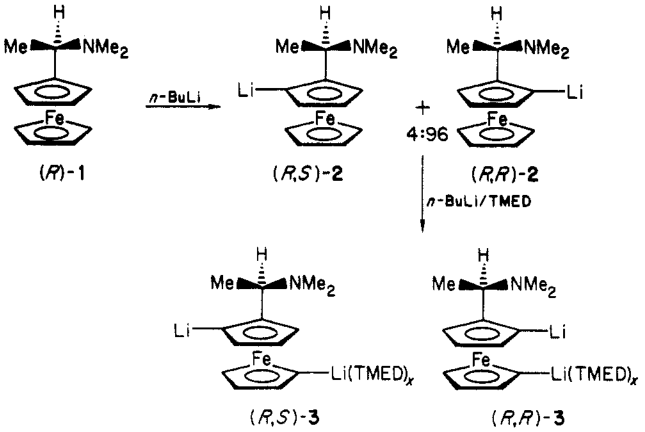
Received October 15, 1985

Dilithiation of $Fe(C_5H_4CHMeNMe_2)(C_5H_5)$ (1) with BuLi is predominantly homoannular but with BuLi/TMED is heteroannular. Heteroannular dilithiation predominates in the reaction of BuLi/TMED with $Fe(C_5H_3(CHMeNMe_2)SiMe_3\text{-}1,2)(C_5H_5)$, $Fe(C_5H_3(CHMeNMe_2)SiMe_3\text{-}1,2)(C_5H_4SiMe_3)$, and $Fe(C_5H_2(CHMeNMe_2)(SiMe_3)_2\text{-}1,2,3)(C_5H_4SiMe_3)$ (11). The lithioferrocenes react with $ClSiMe_3$ to afford isolable products although some mixtures of isomers are difficult to characterize. The [3]ferrocenophane $Fe(C_5H_3(CHMeNMe_2)\overline{S_3\text{-}1,2)(C}_5H_4)$ is obtained from 1 as are $[Fe(C_5H_5)(C_5H_3(CHMeNMe_2)\text{-}1,2)]_xQ$ (x = 2, Q = PPh; x = 1, Q = SMe; x = 1, Q = $PPhCMe_3$ (only one diastereomer because of strong chiral induction)) and $Fe(C_5H_4CHMeNMe_2)(C_5H_4AsPh_2)$. Crystals of 11 are monoclinic: a = 17.800 (2) Å, b = 11.760 (1) Å, c = 13.931 (2) Å, β = 107.142 (5)°, Z = 4, space group $P2_1/n$. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to R = 0.054 and R_w = 0.061 for 2745 reflections with $I \geq 3\sigma(I)$.

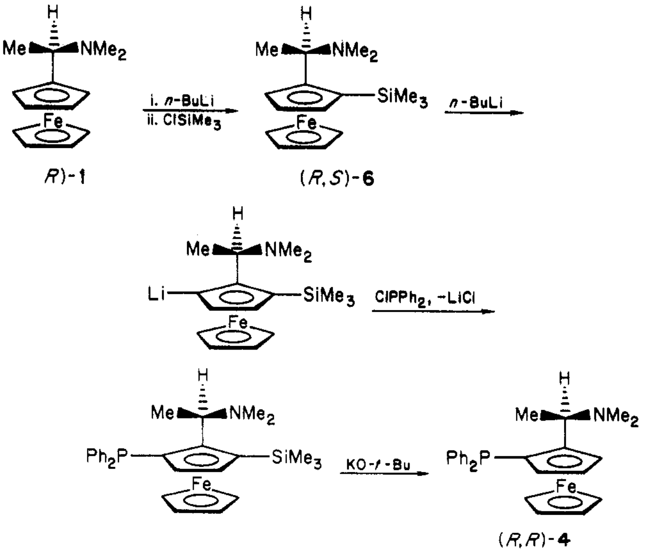
Introduction

(α-(Dimethylamino)ethyl)ferrocene (1) is easily resolved into its enantiomers which have been utilized as starting compounds in the preparation of a variety of useful chiral ferrocene ligands.[2-17] The lithiation of (*R*)- or (*S*)-*1* using 1 molar equiv of n-butyllithium in diethyl ether proceeds stereoselectively at the 2- and 5-positions (Scheme I).[2] Further treatment of solutions containing 2 with n-butyllithium/TMED leads to the formation of the diastereomeric dilithio derivatives 3. Subsequent reactions of 2 or 3 with a variety of XER_2 (X = halogen; E = P, As; R = alkyl or aryl) results in the formation of compounds such as (*R*,*S*)- or (*S*,*R*)-4, PPFA, and (*R*,*S*)- or (*S*,*R*)-5, BPPFA, which have served as useful chiral ligands in metal complex catalyzed asymmetric reactions. The *R*,*R* and *S*,*S*

Scheme I



Scheme II



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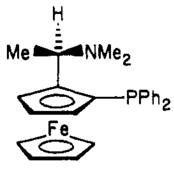
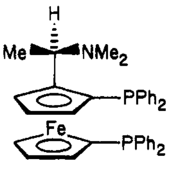


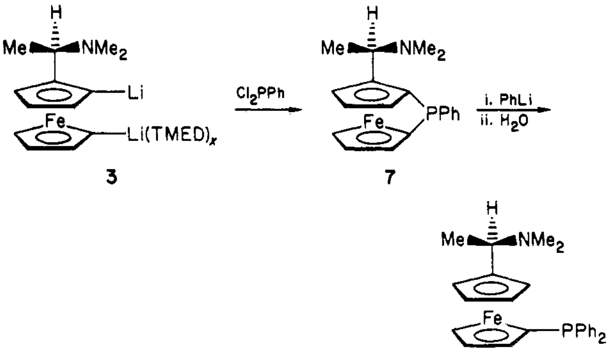
PPFA, **4**



BPPFA, **5**

diastereomers of **4** and **5** have been prepared by Kumada and co-workers[8] using a route which first involved blocking the more reactive 2-position on the substituted cyclopentadienyl ring with a trimethylsilyl group (Scheme II).

In the course of our own studies we have been interested in the structure of lithium compounds such as **2** and **3**[18,19] and their use as intermediates in the synthesis of novel ligands.[20-22] One such compound **8**, an isomer of **4**, was prepared from **3** as indicated in eq 1.[22]



(1)

In other studies directed toward the synthesis of **8** we have investigated the strategy of blocking both the 2- and 5-positions of **1** with trimethylsilyl groups with the objective of directing subsequent lithiation to the unsubstituted cyclopentadienyl ring. We now report the results of these studies which involve the stepwise reaction of **1** with *n*-butyllithium followed by chlorotrimethylsilane. The X-ray crystal structure of one product, the tris(trimethylsilyl) derivative **11**, is described. In addition, we also present the preparation of some other novel compounds derived from **1**.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen or argon. Workup of reaction products, however, was carried out in air unless otherwise stated. Microanalyses were performed by Mr. Peter Borda of the Chemistry Department, University of British Columbia. ^{1}H NMR spectra were recorded on either Bruker WP80, Varian XL-300, or Bruker WH 400 spectrometers. All solvents were predried and freshly distilled. Chlorotrimethylsilane (Aldrich) was used without further purification. **1** was prepared by the literature procedures.[2,22] Elemental analyses and selected spectroscopic data for new compounds are listed in Tables I–III.

Preparation of 6. **6** was prepared by a modification of the literature procedure.[8] To a solution of **1** (15.0 g, 58.4 mmol) in diethyl ether (150 mL) was added a solution of *n*-butyllithium in hexane (56 mL of a 1.55 M solution, 86 mmol). The reaction mixture was stirred for 6–8 h and then cooled to −70 °C before chlorotrimethylsilane (9.4 g, 87 mmol) was slowly added. The reaction mixture was warmed slowly to room temperature and was subsequently refluxed for 30 min before being recooled (0 °C). A saturated aqueous solution of sodium bicarbonate (100 mL) was then *carefully* added. The organic layer was separated and the resultant aqueous layer extracted with diethyl ether (50 mL). The combined organic fraction was then dried ($MgSO_4$) overnight and filtered and the ether removed under vacuum to give an orange oil which on chromatography (neutral alumina, hexanes/diethyl ether eluant) gave **6** (~90%) followed by **1** (~5%).

Lithiation of 6. (i) A solution of **6** was lithiated according to the published experimental procedure.[8] The reaction solution was then treated with $ClSiMe_3$ (1.0 g) at −78 °C. The solution was warmed to room temperature and then refluxed for 30 min before being hydrolyzed with a saturated solution of sodium bicarbonate (50 mL). The product **9** was identified by TLC and isolated following chromatography on alumina as an orange oil following solvent removal. The maximum yield obtained with this procedure was ~20%; unreacted **1** may be recycled however.

(ii) A solution containing **6** (6.7 g, 20.4 mmol) in diethyl ether (50 mL) was treated with *n*-BuLi in hexane (13.2 mL of a 1.55 M solution) for a period of 60 h. The solution developed a red coloration. Excess $ClSiMe_3$ (3.0 g, 27.7 mmol) was then added to the cooled reaction solution (−78 °C). The mixture was stirred at 20 °C for 2 h and then gently refluxed for 2 h. The mixture was *carefully* hydrolyzed with a saturated sodium carbonate solution. The ether layer was separated and examined by TLC. Two principal bands were visible: the first orange band was identified as **9** (~25%) and the second as the starting material **6**. A similar reaction using 1.5 molar equiv of *n*-BuLi for 80 h gave **9** in 85% yield.

(iii) A solution of **6** (2.0 g, 6.1 mmol) in diethyl ether was treated with *n*-BuLi/TMED (1 molar equiv). The solution which reddened after ca. 1.5 h was stirred for 20 h before being cooled to −78 °C. Excess $ClSiMe_3$ (1.0 g) was then added. The stirred mixture was warmed (20 °C, 2 h) and then gently refluxed for 30 min. TLC indicated the presence of two compounds which have similar R_f values. The first to elute was an orange compound identified as **9** and the second a red-orange compound identified as **11** (see experiment iv below).

(iv) A solution of **6** (2.0 g, 6.1 mmol) in diethyl ether was treated with 2.1 molar equiv of *n*-BuLi/TMED. The reaction mixture was stirred overnight. Addition of $ClSiMe_3$ followed by the usual workup procedure gave **11** as the principal reaction product. **11** was crystallized from hexane by cooling following isolation by column chromatography (yield ~70%). Other byproducts included higher silylated products (identified by mass spectroscopy), compound **10**, and the isomers **12** which were isolated from the reaction mixture by using preparative plate TLC.

X-ray Crystallographic Analysis of 2-(α-(Dimethylamino)ethyl)-1,1′,3-tris(trimethylsilyl)ferrocene (11). A crystal bounded by the five faces (followed by their distances in millimeters from a common origin), ±(101), 0.100, (−1,1,0), 0.200, (4,−2,−3), 0.225, (−3,−2,2), 0.245, was mounted in a general orientation. Unit-cell parameters were refined by least squares on $(2 \sin \theta)/\lambda$ values for 25 reflections (2θ = 30–39°) measured on a diffractometer with Mo Kα radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å). Crystal data at 22 °C: $C_{23}H_{43}FeNSi_3$; monoclinic; a = 17.800 (2) Å, b = 11.760 (1) Å, c = 13.931 (2) Å; β = 107.142 (5)°; V = 2786.5 (5) Å^3; Z = 4; ρ_{calcd} = 1.599 Mg m^{-3}; $F(000)$ = 1024; μ(Mo Kα) = 6.75 cm^{-1}. Absent reflections, $h0l$, $h + l$ odd, and $0k0$, k odd, uniquely indicate the space group $P2_1/n$ [nonstandard setting of $P2_1/c$, C^5_{2h}, no. 14; equivalent positions $\pm(x, y, z;\ {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$].

Intensities were measured with graphite monochromated Mo Kα radiation on an Enraf-Nonius CAD4-F diffractometer. An ω–2θ scan at 1.34–10.06° min^{-1} over a range of $(0.85 + 0.35 \tan \theta)$° in ω (extended by 25% on both sides for background measurement) was employed. Data were measured to 2θ = 55°. The intensities of three check reflections, measured every 3600 s throughout the data collection, remained constant to within 2.5%. After data reduction,[23] an absorption correction was applied by using the Gaussian integration method.[24,25]

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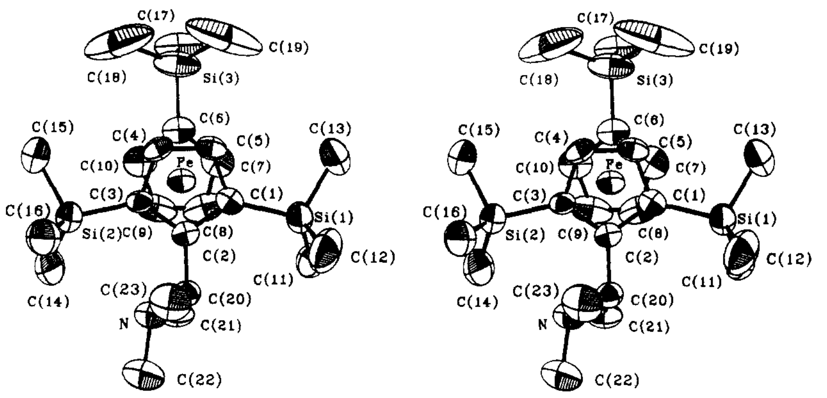

Figure 1. Stereoscopic view of the 2-(α-(dimethylamino)ethyl)-1,1′,3-tris(trimethylsilyl)ferrocene molecule (**11**) (50% probability thermal ellipsoids are shown).

Table I. Selected Elemental Analytical Data

compd	formula	anal. calcd (found) C	H	N
6	$C_{17}H_{27}FeNSi$	62.00 (61.59)	8.26 (8.55)	4.25 (4.51)
9	$C_{20}H_{35}FeNSi_2$	59.83 (59.84)	8.79 (9.06)	3.49 (3.46)
10	$C_{20}H_{35}FeNSi_2$	59.83 (60.16)	8.79 (9.04)	3.49 (3.45)
11	$C_{23}H_{43}FeNSi_3$	58.32 (58.43)	9.15 (9.40)	2.96 (3.00)
12	$C_{23}H_{43}FeNSi_3$	58.32 (58.62)	9.15 (9.10)	2.96 (2.77)
17	$C_{34}H_{41}Fe_2N_2P$	65.83 (65.84)	6.60 (6.65)	4.54 (4.45)
18	$C_{32}H_{45}Fe_2N_2P$	62.02 (62.21)	7.55 (7.53)	4.66 (4.53)
19	$C_{24}H_{32}FeNP$	68.42 (68.17)	7.66 (7.56)	3.32 (3.28)
21	$C_{14}H_{17}FeNS_3$	47.89 (47.76)	4.88 (4.79)	3.99 (4.00)
23	$C_{15}H_{21}FeNS$	59.41 (59.80)	6.98 (7.12)	4.62 (4.68)
25	$C_{26}H_{28}AsFeN$	64.35 (64.18)	5.82 (5.79)	2.89 (2.88)

Table II. ^1H and ^{29}Si NMR Data of (α-(Dimethylamino)ethyl)ferrocene Derivatives ($CDCl_3$)

compd	cyclopentadienyl	CH_3	$N(CH_3)_2$	CH	$Si(CH_3)_3$	others
6	4.10 (s, 5), 4.13–4.18 (m, 2), 4.27 (m, 1), 4.31 (m, 1)	1.25 (d, 3)	2.08 (s, 6)	3.87 (q, 1)	0.30 (s, 9)	^{29}Si, −10.70 ppm[a]
9	4.12 (s, 5), 4.19 (b m, 2)	1.61 (d, 3)	1.97 (s, 6)	2.79 (q, 1)	0.26 (b s, 18)	^{29}Si, −8.98, −11.07[a]
10	4.02 (m, 3), 4.07 (m, 1), 4.17 (m, 1), 4.24 (m, 2)	1.21 (d, 3)	2.03 (s, 6)	3.81 (q, 1)	0.22 (s, 9), 0.24 (s, 9)	...
11	4.03 (m, 1), 4.06 (m, 1), 4.17 (m, 2), 4.26 (m, 1), 4.37 (m, 1)	1.62 (d, 3)	1.98 (s, 6)	2.88 (q, 1)	0.23 (s, 9), 0.38 (s, 9), 0.37 (s, 9)	^{29}Si, −9.05, 11.07, −11.19[a]
12	3.83 (m, 1), 3.92 (m, 1), 4.06 (m, 2), 4.15 (m, 1), 4.31 (m, 1)	1.25 (d, 3)	2.04 (s, 6)	3.88 (q, 1)	0.21 (s, 9), 0.22 (s, 9), 0.26 (s, 9)	
17	3.60 (s, 5), 4.00 (s, 5), 4.22 (d, 2), 4.37 (d, 2), 4.47 (m, 1), 4.55 (m, 1)	1.27 (d, 3), 1.52 (d, 3)	1.70 (s, 6), 2.35 (s, 6)	4.01 (q, 1), 4.35 (q, 1)	...	7.55–7.80 (m, 2), 7.15–7.35 (m, 3), Ph
18	3.62 (s, 5), 4.17 (s, 5), 4.16 (m, 2), 4.45 (m, 2)	1.18 (d, 3), 1.46 (d, 3)	2.10 (s, 6), 2.32 (s, 6)	3.90 (q, 1), 3.96 (q, 1)	...	1.25 (d, 9), J_{P-H} = 12 Hz, $C(CH_3)_3$
19	4.15 (s, 5), 4.40 (m, 2), 4.72 (m, 1)	1.20 (d, 3)	1.60 (s, 5)	3.96 (q, 1)	...	0.65–2.30 (b m, 9 including bt 0.80 (3)), 7.10–7.60 (m, 5)
21	4.38 (m, 1), 4.35 (m, 1), 4.33 (m, 1),[b] 4.40 (m, 1), 3.59 (m, 1), 4.48 (m, 1), 4.59 (m, 1)	1.22 (d, 3)	2.16 (s, 9)	3.42 (q, 1)[b]	...	
	3.79 (m, 1), 3.83 (m, 1), 4.30 (m, 1), 4.33 (m, 1), 4.35 (m, 1),[c] 4.38 (m, 1), 4.44 (m, 1)	1.23 (d, 3)	2.17 (s, 6)	3.53 (q, 1)[c]		
23	4.32 (m, 1), 4.18 (m, 2), 4.10 (s, 5)	1.40 (d, 3)	2.12 (s, 6)	3.94 (q, 1)	...	2.31 (s, 3), SCH_3
24	3.67 (s, 5), 4.00–4.60 (m, 4)	1.27 (d, 3)	2.10 (s, 6)	4.00 (q, 1)		7.75–8.05 (m, 2), 7.25–7.50 (m, 3), 0.70 (d, 9), $C(CH_3)$
25	4.10 (b m, 4), 4.22 (m, 1), 4.33 (m, 2)	1.48 (d, 3)	2.20 (s, 6)	3.63 (q, 1)	...	7.25–7.32 (m, 10)

[a] Chemical shift related to $(CH_3)_3Si–O–Si(CH_3)_3$. [b] Major isomer present in solution. [c] Minor isomer present in solution.

Transmission factors ranged from 0.758 to 0.928 for 84 integration points. Of the 6369 independent reflections measured, 2745 (43.1%) had intensities greater than or equal to $3\sigma(I)$ above background where $\sigma^2(I) = S + 2B + (0.04(S - B))^2$ with S = scan count and B = normalized background count.

The structure was solved by conventional heavy-atom methods, the coordinates of the Fe and Si atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference map. Refinement of the non-hydrogen atoms with anisotropic thermal parameters gave $R = 0.079$. In the final stages of refinement the hydrogen atoms were included as fixed contributors in idealized positions (staggered methyl groups, C(sp^3)–H = 0.98 Å; C(sp^2)–H = 0.97 Å) recalculated after each cycle of refinement. The scattering factors

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Table III. Mass Spectroscopic Data (*m/e* (Relative Intensity)) of Selected Compounds

6	331 (3.98); 330 (16.85); 329, $M^{\bullet+}$ (54.41); 315 (10.55); 314 (33.77); 286 (25.06); 285 (100.00); 284 (20.87); 269 (15.56); 258 (14.59); 256 (15.51); 243 (12.98); 73 (31.39); 72 (30.59)
9	403 (9.72); 402 (27.30); 401, $M^{\bullet+}$ (71.87); 386 (16.70); 358 (36.23); 357 (100.00); 356 (50.15); 341 (16.23); 330 (13.95); 269 (13.31); 253 (14.50); 73 (99.30); 72 (92.32)
10	402 (14.61); 401, $M^{\bullet+}$ (39.90); 386 (15.49); 358 (30.21); 357 (74.66); 356 (54.42); 341 (8.55); 330 (8.60); 269 (18.48); 253 (13.55); 93 (12.08); 73 (100.00)
11	474 (14.41); 473, $M^{\bullet+}$ (33.42); 430 (24.77); 429 (51.63); 428 (51.92); 325 (11.51); 267 (3.78); 73 (100.00)
12	475 (6.59); 474 (15.62); 473, $M^{\bullet+}$ (40.78); 431 (11.03); 430 (28.0); 429 (41.99); 356 (6.67); 341 (7.97); 325 (7.95); 86 (27.05); 84 (40.74); 73 (100.00)
13	546 (4.99); 545 $M^{\bullet+}$ (10.08); 502 (10.47); 501 (12.80); 500 (15.76); 474 (6.83); 473 (11.90); 430 (9.15); 429 (16.20); 428 (18.49); 145 (12.17); 73 (100.00)
14	617 (2.57); 573 (4.30); 572 (7.01); 546 (8.55); 501 (7.21); 500 (12.65); 474 (22.49); 473 (42.48); 429 (39.87); 428 (50.01); 73 (100.00)
15	659 (14.1); 658 (22.1); 657, $M^{\bullet+}$ (29.7); 643 (29.5); 642 (27.8); 614 (25.9); 613 (28.5); 548 (25.5); 201 (100.00)
16	844 (11.29); 843 (32.32); 842 (68.29); 841, $M^{\bullet+}$ (100.00); 826 (2.45); 798 (8.58); 769 (2.82); 657 (6.12); 612 (3.61); 504 (9.25); 478 (23.05); 477 (58.72); 475 (20.09); 449 (11.28)
17	621 (7.25); 620, $M^{\bullet+}$ (18.08); 576 (12.77); 575 (32.07); 561 (38.20); 560 (100.00); 532 (14.71); 530 (13.66); 517 (2.65); 494 (2.42); 466 (4.49); 465 (5.81); 464 (4.98); 431 (3.65)
18	601 (13.58); 600, $M^{\bullet+}$ (34.11); 555 (9.40); 543 (20.97); 540 (14.53); 510 (2.78); 499 (20.01); 498 (61.29); 457 (11.67); 456 (10.18); 455 (29.84); 454 (23.79); 453 (69.26); 387 (11.51); 286 (11.30); 284 (40.98)
19	422 (4.35); 421, $M^{\bullet+}$ (8.93); 406 (5.29); 378 (3.00); 364 (32.28); 343 (6.80); 322 (12.31); 321 (54.16); 212 (22.91)
21	353 (15.9); 352 (21.2); 351, $M^{\bullet+}$ (100.00); 336 (29.5); 308 (14.6); 307 (46.4); 280 (15.1); 275 (12.3); 274 (15.0); 243 (14.5); 178 (29.1); 177 (11.2)
22	548 (16.76); 547 (36.21); 546, $M^{\bullet+}$ (84.37); 531 (32.55); 515 (13.81); 514 (21.16); 488 (17.74); 474 (24.52); 409 (51.34); 402 (14.60); 337 (21.64); 303 (20.95); 259 (36.69); 244 (81.98); 121 (100.00)

Table IV. Final Positional (Fractional, ×10⁴; Fe and Si, ×10⁵) and Isotropic Thermal Parameters ($U \times 10^3$ Å²) with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z	U_{eq}
Fe	38055 (4)	47840 (6)	17799 (5)	47
Si(1)	27299 (9)	52810 (15)	−7738 (12)	66
Si(2)	48983 (10)	21984 (14)	22170 (14)	69
Si(3)	48315 (13)	71469 (17)	31588 (17)	99
N	3397 (2)	1539 (4)	226 (3)	57
C(1)	3555 (3)	4614 (4)	236 (3)	45
C(2)	3614 (3)	3521 (4)	691 (3)	40
C(3)	4383 (3)	3393 (4)	1412 (3)	41
C(4)	4781 (3)	4433 (4)	1354 (4)	48
C(5)	4296 (3)	5169 (4)	667 (4)	48
C(6)	4041 (3)	6073 (5)	2846 (4)	60
C(7)	3268 (4)	6152 (5)	2179 (5)	73
C(8)	2833 (4)	5169 (7)	2216 (6)	88
C(9)	3325 (5)	4451 (6)	2916 (5)	90
C(10)	4043 (4)	4990 (6)	3293 (4)	73
C(11)	1754 (3)	5198 (5)	−539 (5)	88
C(12)	2666 (4)	4570 (7)	−1991 (4)	104
C(13)	2977 (4)	6802 (6)	−879 (6)	113
C(14)	4289 (4)	1418 (6)	2884 (5)	102
C(15)	5745 (4)	2843 (6)	3190 (5)	96
C(16)	5316 (4)	1174 (5)	1496 (6)	95
C(17)	4686 (4)	8100 (6)	4127 (6)	116
C(18)	5807 (5)	6409 (10)	3696 (11)	254
C(19)	4877 (9)	7913 (10)	2090 (8)	262
C(20)	2997 (3)	2587 (4)	363 (4)	50
C(21)	2487 (3)	2434 (5)	1072 (4)	71
C(22)	2889 (4)	535 (5)	34 (5)	91
C(23)	3726 (4)	1676 (5)	−611 (5)	82

[a] $U_{eq} = {}^1/_3$trace(diagonalized U).

Table V. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

C(1)–Si(1)–C(11)	114.2 (2)	Si(1)–C(1)–C(2)	130.4 (4)
C(1)–Si(1)–C(12)	108.6 (3)	Si(1)–C(1)–C(5)	122.9 (4)
C(1)–Si(1)–C(13)	108.0 (3)	C(2)–C(1)–C(5)	106.7 (4)
C(11)–Si(1)–C(12)	109.0 (3)	C(1)–C(2)–C(3)	109.5 (4)
C(11)–Si(1)–C(13)	108.6 (3)	C(1)–C(2)–C(20)	124.5 (4)
C(12)–Si(1)–C(13)	108.2 (4)	C(3)–C(2)–C(20)	125.6 (4)
C(3)–Si(2)–C(14)	114.6 (3)	Si(2)–C(3)–C(2)	134.0 (4)
C(3)–Si(2)–C(15)	106.3 (3)	Si(2)–C(3)–C(4)	121.0 (3)
C(3)–Si(2)–C(16)	111.6 (3)	C(2)–C(3)–C(4)	104.8 (4)
C(14)–Si(2)–C(15)	107.6 (3)	C(3)–C(4)–C(5)	110.8 (4)
C(14)–Si(2)–C(16)	109.5 (3)	C(1)–C(5)–C(4)	108.2 (4)
C(15)–Si(2)–C(16)	106.9 (3)	Si(3)–C(6)–C(7)	129.4 (5)
C(6)–Si(3)–C(17)	109.2 (3)	Si(3)–C(6)–C(10)	127.4 (5)
C(6)–Si(3)–C(18)	109.1 (4)	C(7)–C(6)–C(10)	103.0 (5)
C(6)–Si(3)–C(19)	111.8 (4)	C(6)–C(7)–C(8)	111.1 (6)
C(17)–Si(3)–C(18)	107.6 (5)	C(7)–C(8)–C(9)	106.7 (6)
C(17)–Si(3)–C(19)	111.2 (5)	C(8)–C(9)–C(10)	107.9 (6)
C(18)–Si(3)–C(19)	107.7 (6)	C(6)–C(10)–C(9)	111.2 (6)
C(20)–N–C(22)	113.9 (4)	N–C(20)–C(2)	108.1 (4)
C(20)–N–C(23)	109.7 (4)	N–C(20)–C(21)	112.8 (4)
C(22)–N–C(23)	108.4 (4)	C(2)–C(20)–C(21)	113.7 (4)

of ref 26 were used for non-hydrogen atoms and those of ref 27 for hydrogen atoms. Anomalous scattering factors from ref 28 were used for the Fe and Si atoms. The weighting scheme $w = 1/\sigma^2(F)$, where $\sigma^2(F)$ is derived from the previously defined $\sigma^2(I)$, gave uniform average values of $w(|F_o| - |F_c|)^2$ over ranges of both $|F_o|$ and $(\sin\theta)/\lambda$ and was employed in the final stages of full-matrix refinement of 253 variables. Reflections with $I < 3\sigma(I)$ were not included in the refinement. Convergence was reached at $R = 0.054$ and $R_w = 0.061$ for 2745 reflections with $I \geq 3\sigma(I)$. For all 6369 reflections $R = 0.140$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

On the final cycle of refinement the mean and maximum parameter shifts corresponded to 0.03σ and 0.39σ, respectively. The mean error in an observation of unit weight was 2.167. A final difference map showed maximum fluctuations of −1.08 to +0.36 e Å^{-3} near Fe and was featureless elsewhere. The final positional and thermal parameters appear in Table IV. Bond lengths and angles appear in Tables V and VI, respectively. Tables of calculated hydrogen parameters, anisotropic thermal parameters, and a complete listing of torsion angles (Tables VII–IX) are included as supplementary material, as are measured and calculated structure factors.

Reaction of 3 with ClSiMe$_3$. A solid sample of **3** prepared according to the literature procedure[20] was suspended in diethyl ether and reacted with 2.2 molar equiv of ClSiMe$_3$. Workup using the standard procedure gave a solution containing principally **10** but small amounts of **12** were also present (identified by TLC comparison with an authentic sample prepared as above). **10** was isolated as a pale orange solid (~80% yield) following chromatography on neutral alumina.

Reaction of 10 and 11 with *n*-BuLi/TMED. A solution of **10** (or **11**) (1.0 g, 2.5 mmol, 2.1 mmol) in diethyl ether was stirred with 2.1 molar equiv of *n*-BuLi/TMED for 20 h. The reaction solutions were then treated with 2.1 molar equiv of ClSiMe$_3$ and also ClPPh$_2$ in the case of **11**. The product mixtures were worked up by using the procedures described above to give in each case an oily mixture. Further workup was carried out as follows:

(i) 10 with ClSiMe$_3$. TLC inspection showed the presence of several new products with high R_f values (hexane eluent). Isolation of the principal bands following preparative TLC indicated the major product fractions to be tetrasilylated products (mass spectroscopy and ^{1}H NMR). However, these products were composed of isomers. No further separations were undertaken.

(ii) 11 with ClSiMe$_3$. Similar treatment to (i) indicated the major reaction products to be the pentasilylated derivatives. The

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[26] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

[27] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[28] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table VI. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

Fe–C(1)	2.073 (5)	Si(3)–C(17)	1.829 (6)
Fe–C(2)	2.078 (4)	Si(3)–C(18)	1.888 (11)
Fe–C(3)	2.075 (5)	Si(3)–C(19)	1.763 (10)
Fe–C(4)	2.036 (4)	N–C(20)	1.463 (6)
Fe–C(5)	2.042 (4)	N–C(22)	1.463 (7)
Fe–C(6)	2.076 (5)	N–C(23)	1.459 (7)
Fe–C(7)	2.031 (5)	C(1)–C(2)	1.423 (6)
Fe–C(8)	2.048 (5)	C(1)–C(5)	1.435 (6)
Fe–C(9)	2.047 (5)	C(2)–C(3)	1.447 (6)
Fe–C(10)	2.039 (5)	C(2)–C(20)	1.525 (6)
Si(1)–C(1)	1.880 (5)	C(3)–C(4)	1.428 (6)
Si(1)–C(11)	1.862 (6)	C(4)–C(5)	1.387 (7)
Si(1)–C(12)	1.864 (7)	C(6)–C(7)	1.418 (8)
Si(1)–C(13)	1.858 (7)	C(6)–C(10)	1.416 (8)
Si(2)–C(3)	1.862 (5)	C(7)–C(8)	1.402 (8)
Si(2)–C(14)	1.865 (7)	C(8)–C(9)	1.388 (9)
Si(2)–C(15)	1.865 (6)	C(9)–C(10)	1.385 (9)
Si(2)–C(16)	1.858 (7)	C(20)–C(21)	1.535 (7)
Si(3)–C(6)	1.846 (6)		

information gained from the ^{1}H NMR spectrum was not helpful in establishing which positional isomers were present due to the large ratio of Si*Me*$_3$ to ferrocenyl proton signals. Mass spectral data are given in Table III.

(iii) 11 with ClPPh$_2$. The mixture in this case was column chromatographed initially by using the standard procedure. The major product bands were isolated and rechromatographed on a preparative TLC scale. Several product bands were isolated which included compounds containing one phosphine substituent (e.g., 15) identified by mass spectroscopy, compounds containing two phosphines (major products), e.g., 16, and compounds with three phosphines (M$^+$, *m/e* 1025). Repeated attempts to crystallize these fractions failed although a variety of solvents was used. Mass spectral data are given in Table III.

Preparation of Solutions of 2. To a solution of 1 in diethyl ether (25 mL/mmol of 1) was added an equimolar solution of *n*-butyllithium. The reaction mixture was stirred for 4–10 h.

Reaction of 2 with Dichlorophosphines. A solution containing 2 (10 mmol) was cooled to –78 °C. Dichlorophenylphosphine (0.9 g, 5 mmol) was added dropwise to the well-stirred solution. The reaction mixture was allowed to warm to room temperature and was then stirred for a further 3 h. The solution was hydrolyzed and the organic layer separated and dried (MgSO$_4$). The residual aqueous layer and solid residue were extracted with diethyl ether (2 × 20 mL), and this was added to the bulk organic solution. A TLC examination of the reaction solution at this stage indicated the presence of three compounds later identified as 19, 17, and 1, in order of decreasing R_f values. After drying, the solution was filtered and concentrated to a few milliliters. The mixture was then chromatographed on neutral alumina eluting with mixtures of hexanes and diethyl ether of increasing polarity. Three fractions were thus obtained: the first, a pale yellow, on crystallization from hexane (–30 °C) afforded yellow platelets of 19 identified initially by mass spectroscopy (M$^+$, *m/e* 421). The second, 17, was also identified initially by mass spectroscopy (M$^+$, *m/e* 620). It was crystallized (hexane, –30 °C) to afford deep orange crystals. The third band which proved to be the starting material 1 was obtained as a yellow oil following solvent removal. The yields of the three fractions are variable when the experiment is repeated, the maximized values being approximately 10–15%, 60%, and 15% for 19, 17, and 1, respectively.

A similar reaction performed with Cl$_2$PCMe$_3$ instead of Cl$_2$PPh gave similar results, yielding 20, 18, and 1 respectively. 20 was obtained as a yellow oil (M$^+$, *m/e* 401), which readily oxidized in solution to give the corresponding phosphine oxide (M$^+$, *m/e* 417).

Reaction of 3 with S$_8$. Preparation of 21. An ether solution of 3[18,20] was treated with a fivefold excess of S$_8$. The reaction mixture was stirred overnight and then hydrolyzed with aqueous sodium bicarbonate solution. The ether layer was then separated and dried (MgSO$_4$), and after the solvent was removed the product was chromatographed on neutral alumina. The diffuse yellow band afforded an oil on isolation, and TLC investigation indicated the presence of several compounds. The oil was redissolved in the minimum volume of hexane and cooled (–30 °C), affording 21 as large orange-yellow crystals (yield ~40%). The mother liquor yielded more 21 following preparative plate TLC together with minor amounts of compounds such as 22 (mass spectrum, parent ion *m/e* 544).

Preparation of 23.[50] A solution of 2 was prepared according to the general procedure from 1 (3.0 g). Elemental sulfur (0.5 g) was added to the chilled reaction solution (–78 °C). After 5 min the solution was warmed slowly to room temperature and then to a gentle reflux (15 min) when a pale yellow precipitate appeared. The reaction mixture was again cooled to –78 °C, methyl iodide was added (3.0 g, dropwise), and the solution was allowed to warm slowly to room temperature. The solution was stirred at this temperature for 30 min before hydrolysis (H$_2$O). A deep red-orange aqueous layer and a pale orange organic layer resulted. Attempts to extract the aqueous layer with sodium carbonate and sodium hydroxide solutions were unsuccessful. The ether layer was filtered, reduced in volume, and cooled to –20 °C. Large yellow crystals of 23 were obtained (yield ~30%).

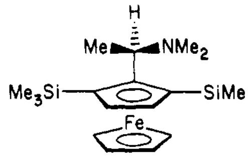
Preparation of 24. A solution of 1 (6.0 g, 23 mmol) in diethyl ether (100 mL) was treated with a 1.5 molar excess of *n*-butyllithium in hexane. The solution was stirred for 20 h and then cooled to –70 °C before *tert*-butylchlorophenylphosphine (7.5 g, 37 mmol) was added. After being warmed to room temperature, the solution was refluxed gently for 3 h before being hydrolyzed (H$_2$O, 50 mL). The separated ether layer was then dried (MgSO$_4$) and filtered and the volume reduced to a few milliliters. Column chromatography of the resultant oil gave initially P(Ph)(*n*-C$_4$H$_9$)(CMe$_3$) (isolated as white needles), and then an orange-yellow fraction which on crystallization from hexane (–30 °C) gave the product 24 as an yellow-orange crystalline solid. The yield of 24 varied from 45 to 85%.

Preparation of 25b. To a rapidly stirred solution of phenyllithium (10 mmol) in diethyl ether (35 mL) maintained at –78 °C was added a solution of **26b**[20] (2.0 g, ~5 mmol) in the minimum quantity of ether required for complete solution. On warming to room temperature, a clear orange solution resulted. The reaction mixture was recooled to ~–70 °C and chlorodiphenylarsine (2.65 g, 10 mmol) was added. The mixture was allowed to warm slowly to room temperature and was then stirred for a further 3 h. The reaction mixture was hydrolyzed (sodium bicarbonate solution) and the organic layer separated, dried, and then chromatographed on neutral alumina (hexane, ether, dichloromethane, increasing polarity) to give initially 27 (10–15%) and finally **25b** (50–70%). Crystallization of the second fraction from cold hexanes gave **25b** as an orange solid (M$^+$, *m/e* 485).

Results and Discussion

The known compound 6, prepared in good yield (~90%) by slight modification of an established procedure[8] (Schemes I and II), has the anticipated ^{1}H NMR spectrum (Figure 2). Because of the stereospecificity of this lithiation reaction[2] only one pair of enantiomers of 6 is obtained as is seen in the single sharp *Me*$_3$Si resonance in the ^{1}H NMR spectrum and the singlet in the ^{29}Si spectrum. The mass spectrum of 6 and other Me$_3$Si derivatives is discussed in a separate section below.

Lithiation of 6 with *n*-butyllithium (*n*-BuLi) in the absence of TMED, tetramethylethylenediamine, was first studied by Kumada and co-workers[8] in the synthesis of (*R*,*R*)-4 (Scheme II). They found that the reaction is slow (~50%, 2 h), presumably because the product is much less stabilized by the amine function, but did not observe lithiation at any site other than the 5-position. In our hands lithiation of 6 with 1 molar equiv of *n*-BuLi (under a variety of conditions, 2 h–2 days) followed by the addition of chlorotrimethylsilane affords the expected 2,5-disubstituted product 9 in variable yield. However, two byproducts identified as 10 and 11 are also produced in low yield. This result is similar to that obtained for the lithiation of ferrocene itself where monolithioferrocene is almost invariably accompanied by 1,1′-dilithioferrocene.[29,30]

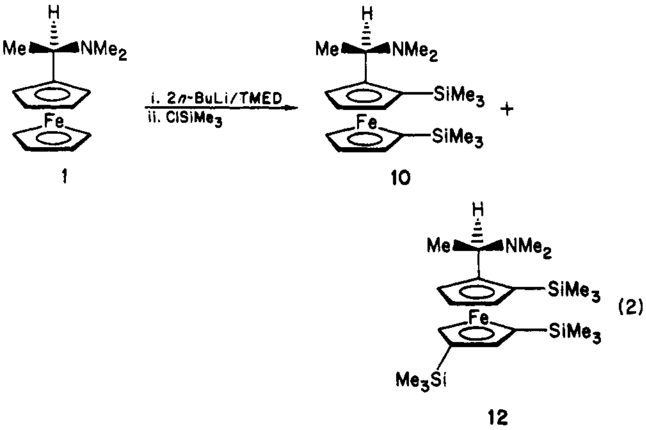


9

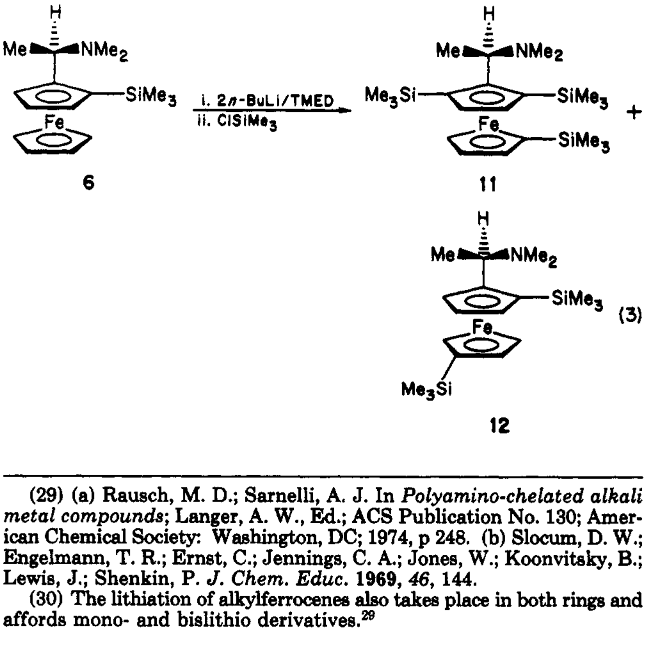
The isolation of **10** shows that even in the absence of TMED, lithiation of the unsubstituted cyclopentadienyl ring of **6** can take place.

Confirmation of the structure of **9** comes from the NMR spectra (Table II). The ^{1}H spectrum shows a sharp singlet due to the unsubstituted C_5H_5 ring. Two ^{29}Si resonances are seen because the $SiMe_3$ groups are diastereotopic. The $(CH_3)_3$Si region is broadened at 80 MHz for the same reason but is resolved to two overlapping singlets at 400 MHz. Optimization of the preparation of **9** established that yields of ~85% can be obtained if 1.5 molar equiv of *n*-BuLi are employed and the reaction is allowed to proceed for a minimum of 60 h.

The independent synthesis of **10** and **11** is best carried out utilizing *n*-BuLi/TMED to facilitate lithiation of the unsubstituted cyclopentadiene rings of **1** and **6**, respectively. (It should be noted that the presence of TMED does not discourage lithiation at the substituted ring). Thus the reaction of **1** with 2 molar equiv of *n*-BuLi/TMED followed by chlorotrimethylsilane affords **10** in good yield as an orange solid. Under similar conditions **6** affords **11**. A common byproduct, **12**, was isolated in low yield from both reactions (eq 2 and 3).



(2)



(3)

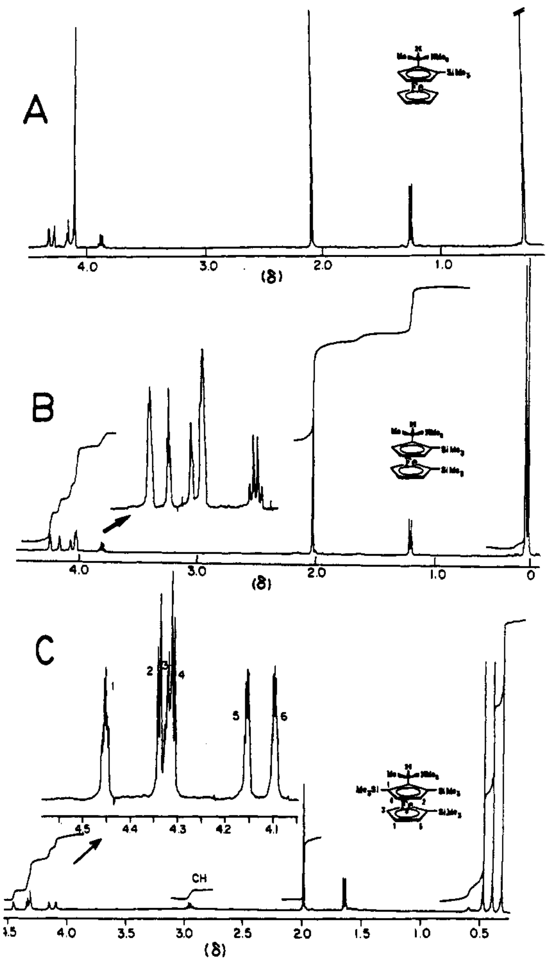


Figure 2. ^{1}H 400-MHz NMR spectrum of **6**, (A), **10** (B), and **11** (C).

Compound **11** is completely characterized by X-ray crystallography (Figure 1), and the spectroscopic properties are in accord. The ^{29}Si NMR shows the three Me_3Si groups as does the ^{1}H spectrum (Figure 2c). The assignment shown is based on those made for the $-S_3-$ bridged ferrocenophanes $Fe(C_5H_3P(S)Ph_2)(C_5H_4)S_3$ and $Fe(C_5H_4)(C_5H_3CHMeNMe_2)S_3$ where the rings are locked at ambient temperature.[31]

The structure of **11** (Figure 1) has some interesting features. The view down the ring–Fe–ring axis shows that the rings are symmetrically staggered (35.9 (7)°) with Si(3) trans to the bulk of the three substituents on the other ring. Staggered rings appear to be the rule in highly substitution ferrocenes,[7d,32,33] although some ferrocenophanes have eclipsed structure.[31b]

A model of the structure of **11** suggests that the rings could be locked; however, heating a solution of the compound to 100 °C does not result in a change in the ^{1}H NMR spectrum. On cooling the solution to −90 °C, broadening is observed, but at 300 MHz the resolution is not good enough to enable the calculation of rotation barriers. Thus the rings are not locked at 20 °C as is the case also for 1,1′,3,3′-tetra-*tert*-butylferrocene which has

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(29) (a) Rausch, M. D.; Sarnelli, A. J. In *Polyamino-chelated alkali metal compounds*; Langer, A. W., Ed.; ACS Publication No. 130; American Chemical Society: Washington, DC; 1974, p 248. (b) Slocum, D. W.; Engelmann, T. R.; Ernst, C.; Jennings, C. A.; Jones, W.; Koonvitsky, B.; Lewis, J.; Shenkin, P. *J. Chem. Educ.* **1969**, *46*, 144.

(30) The lithiation of alkylferrocenes also takes place in both rings and affords mono- and bislithio derivatives.[29]

(31) (a) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Herring, F. G.; Jaganathan, N. R.; Jones, R. H., unpublished results. (b) Butler, I. R.; Cullen, W. R.; Herring, F. G.; Jaganathan, N. R., unpublished results.

(32) (a) Kaluski, Z. L.; Gusev, A. I.; Kalinin, A. E.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1972**, *13*, 950. (b) Struchkov, Y. T.; Andrianov, V. G.; Sal'nikova, T. N.; Lyatifov, I. R.; Materikova, R. B. *J. Organomet. Chem.* **1978**, *145*, 213. (c) Skrzypczak-Jankun, E.; Kaluski, Z. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1976**, *24*, 719.

(33) Einstein, F. W. B.; Willis, A. C. *Acta Crystallogr., Sect. B:* **1980**, *B36*, 39.

a coalescence temperature of −27.5 °C and $\Delta G^{\ddagger}$ for ring rotation is 13.1 kcal mol^{-1}.[34a]

For further comparison, recent studies on 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene reveal a slightly lower barrier to ring rotation with $\Delta G^{\ddagger} = 11.3 \pm 0.8$ kcal mol^{-1}. The coalescence temperature is −52 °C.[34b]

The angles around Si(3) range from 107.6 (5) to 111.8 (4)°, around Si(1) the range is from 108.2 (4) to 114.2 (2)°, and around Si(2) the range is from 106.3 (3) to 114.6 (3)°. Thus Si(3) is essentially in a tetrahedral environment with Si(3) and Si(2) showing increasing distortion from this geometry probably because of steric interactions with the $-CHMeNMe_2$ group.

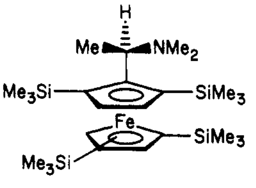
The orientation of the NMe_2 group is perhaps unexpected since the one adopted results in the methyl group of C(21) lying between the rings. The stereospecific lithiation sequences described above (Scheme I) indicates that C(1) would be the initial site of lithiation and thus **11** would be expected to reflect this by having the lone pair on the NMe_2 group directed toward C(1) and the methyl group of C(21) outside the rings. This is the situation found in the structure of **4**.[33] In the structure of (*S*,*R*,*S*)-$Fe(C_5H_5)(C_5H_3(CHMeNMe_2)(CHOHC_6H_4OMe)\text{-}1,2)$, obtained by reaction of **1** with anisaldehyde, this same feature is seen but is less pronounced.[2b] The NMe_2 group "points" toward the substituted carbon atom but is oriented in such a way through hydrogen bonding that both the CH_3 and H groups (*CHMe*NMe_2) lie between the rings. The NMe_2 group is observed as a singlet in the ^1H NMR spectrum, however; thus the barrier to rotation of the $CHMeNMe_2$ group must be low. This singlet resonance is also observed in the spectrum of **11** and (*R*,*R*)-$Fe[C_5H_3(P(CMe_3)_2)_2\text{-}1',3'][C_5H_3(CHMeNMe_2)P(CMe_3)_2\text{-}1,2]$. In the last example the solid-state structure reveals that the NMe_2 group lies between the rings and the 2-substituent arises via the minor isomer of Scheme I.[7d] Other examples of structures of ferrocene derivatives containing groups like $CHMeNMe_2$ are found in some [1]-ferrocenophanes. Thus in $Fe(C_5H_3(CHMeNMe_2)AsPh\text{-}1,2)(C_5H_4)$[20] the CH_3 group lies slightly between the rings and the NMe_2 group is adjacent to the substituent but the nitrogen lone pair is directed away from the substituent.[18] This same orientation of the NMe_2 group is found in $Fe(C_5H_3[CH(CHMe_2)NMe_2]PPh\text{-}1,2](C_5H_4)$, but the isopropyl group lies outside the rings.[20] In total these observations indicate that only small barriers exist for the rotation of all or part of the $CHMeNMe_2$ group attached to a substituted ferrocene ring so that the effects which give rise to the discrimination observed on lithiation (Scheme I) must be subtle.

The Si–ring carbon distances show considerable variation being 1.846 (6) (Si(3)), 1.862 (5) (Si(2)), and 1.880 (5) Å (Si(1)) although they are within the usual range. Thus in $Fe(C_5H_4Si_2Me_5)_2$ this distance is 1.86 (3) Å (average),[35] in $Fe(C_5H_5)(C_5H_4SiPh_2H)$ this distance 1.856 (3) Å,[36] and in $C_5H_4SiMe_2Fe(CO)(\mu\text{-}CO)_2Fe(CO)(C_5H_4)$ this distance 1.876 (7) Å.[37] Even the ferrocenophanes $Fe(C_5H_4SiPh_2)(C_5H_4)$[38] and $Fe(C_5H_3(CHMeNMe_2)\text{-}SiCl_2)(C_5H_4)$[31b] have Si–C values at the lower end of the range, 1.847 (3) and 1.852 (3) Å, respectively, indicating a lack of strain in the bonds.

The distances from iron to ring CH carbon atoms are shorter than to others (substituted). This feature is commonly found in the structures of other ferrocene derivatives. Other bond angles and lengths are as expected.

The ^1H NMR spectrum of **10** (Figure 2) shows two *Me*$_3$Si groups. The ring proton resonances are not as disperse as those of **11**, and the spectrum in the cyclopentadienyl region is not readily assigned. An interesting feature seen in Table II is the difference in the chemical shift of the CH_3 resonance between **10** and its isomer **9**. This shift (~0.4 ppm) is observed whenever the 5-position is substituted, and similar shifts are seen in the resonances of N-CH_3 and C-*H* protons (~1 ppm).[40] The spectrum of **12** belongs to the unsubstituted 5-position class (along with **6** and **10**). Other data for **12** indicate that it contains three Me_3Si groups, and thus it is an isomer of **11**. The most likely structure is the one indicated, where the 1′,3′-disubstitution is seen. This pattern is found in the crystal structure of $Fe[C_5H_3CHNMe_2(P(CMe_3)_2)\text{-}1,2][C_5H_3(P(Me_3)_2)_2\text{-}1',3']$ although in this case an unexpected diastereomer was obtained.[7d]

The lithiation of **10** and **11** with *n*-BuLi/TMED was also studied. To characterize the products, they were reacted with chlorotrimethylsilane in both cases and in one case, **11**, with chlorodiphenylphosphine. Again heterodilithiation results. This is seen in the isolation of the tetrakis- and pentakis(trimethylsilyl) compounds **13** and **14** from **10** and **11**, respectively. These product mixtures have characteristic ^1H NMR and mass spectra. They both contain two principal isomers (TLC); however, large scale separation was not possible. In the case of **13** the isomers are probably diastereomers with 1′,3′-disubstituted rings.[41] In the case of **14** there are a number of possible structures.



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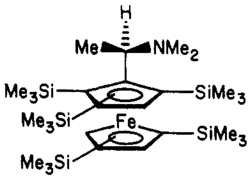
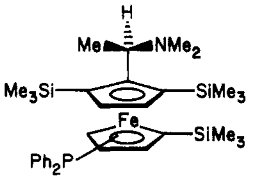


14

The mixture of phosphines obtained from **11** consists mainly of **16**, the result of dilithiation, with smaller amounts of **15**. These two can be separated from each other by preparative TLC although again isomers are present in each fraction as indicated by their complicated ^1H NMR spectra. Complexes with Pd(II) are being studied to obtain further structural information.[42]



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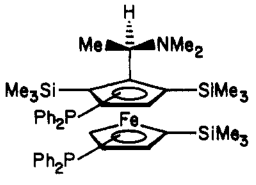

16

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(34) (a) Luke, W. D.; Streitwieser, A. *J. Am. Chem. Soc.* **1981**, *103*, 3241. (b) Brumback, D. S.; Nile, T. A.; Chance, J. M.; Sottery, J. P., unpublished results.

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(39) The shift of the CH_2 group in the spectra of the compounds $Fe(C_5H_5)(C_5H_3(CH_2NMe_2)X\text{-}1,2)$ is very sensitive to the nature of X.[40]

(40) Slocum, D. W.; Engelmann, T. R. *J. Organomet. Chem.* **1970**, *24*, 753.

(41) In the alkylferrocenes metalation at the 3-position over the 2-position is favored by factors of 8 (Me) to 98 (CMe_3).[29]

(42) Butler, I. R.; Cullen, W. R., unpublished results.

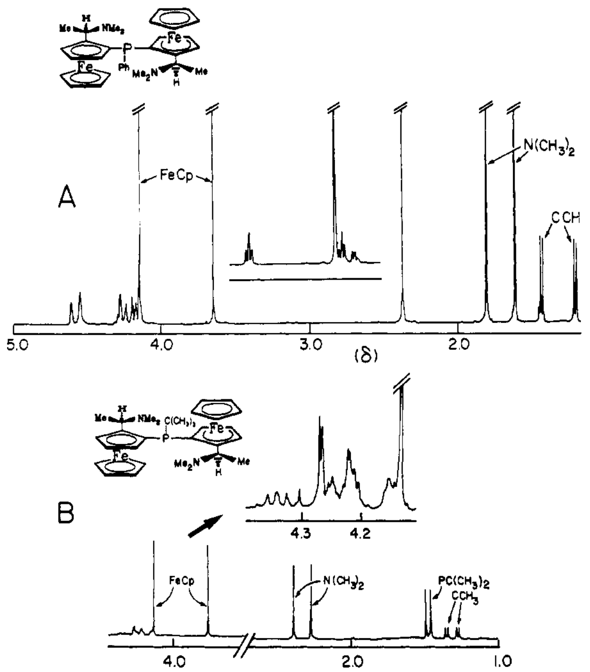


Figure 3. ^{1}H 400-MHz NMR spectra of **17** (A) and **18** (B).

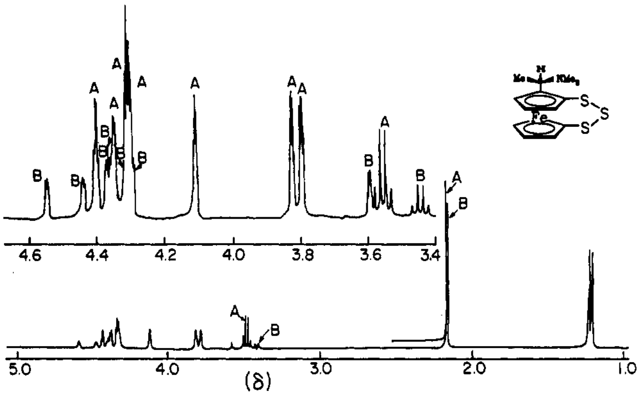
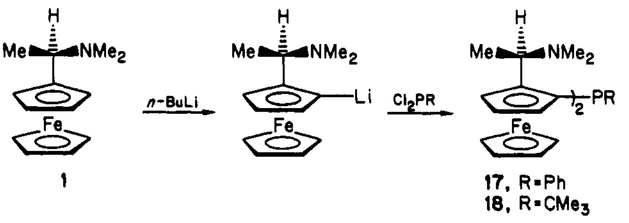


Figure 4. ^{1}H 400-MHz NMR spectrum of **21**: A, proton resonances from major isomer; B, proton resonances from minor isomer.

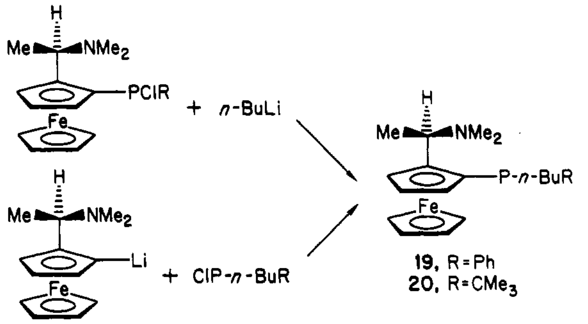
There is considerable interest in the use of metal complexes of chiral alkyl- and arylphosphines as catalysts[4,5,43] so it could be of value to prepare compounds such as **17** and **18** since these could be obtained as pure enantiomers. Kumada and co-workers found that the lithio derivatives of **1** did not react easily with dichlorophenylphosphine to give **17** (eq 4) and developed a low yield synthesis via a trimethylstannyl derivative.[8] In our hands both **17** and **18** can be obtained as crystalline solids in good yield (~60%) by this previously abandoned route. Use of (*S*)-**1** for the initial lithiation reaction ensures that diastereomers are not produced.



(4)

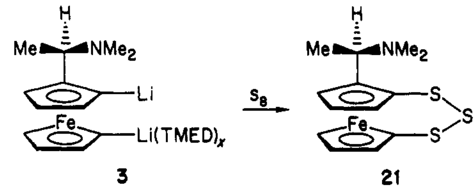
The ^{1}H NMR of (*SR*;*SR*)-**18** shows one *tert*-butyl resonance (J_{P-H} = 12 Hz), but all other resonances are doubled with respect to their normal pattern as found for a derivative such as **1** (Figure 3). This indicates that the two ferrocenyl fragments are in different environments possibly one "up" and the other "down" with respect to the phosphorus lone pair. This phenomenon is also seen in the spectrum of **17** although Kumada and co-workers made no comment following their initial synthesis.[8] Both **17** and **18** are potentially tridentate ligands, but preliminary investigations indicate that ligand decomposition may occur on complexation.[42] Certainly if the structure is as suggested above, the phosphorus atoms could be inaccessible to Lewis acids.

Byproducts such as **19** and **20** are also obtained in low yield. These result from reaction of *n*-BuLi with the chlorophosphine (eq 5). Compound **19** can be obtained as yellow platelets, and the analytical and spectroscopic data are as expected. Compound **20** was isolated as an oil and microanalytical data were not obtained; the mass spectrum (M$^+$, *m*/*e* 401) and ^{1}H NMR spectrum provide good substantiation for the formulation.

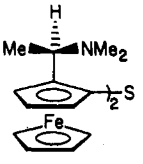


(5)

Other Derivatives of 1. As mentioned in the introduction, the final section of this paper is devoted to the description and characterization of some important compounds which have been preparated as part of some earlier studies. Such a compound is **21** prepared from **3** by reaction with elemental sulfur (eq 6). The analytical and spectroscopic data (Figure 4) are in accord with its formulation.[44] Several byproducts such as **22**, identified by mass spectroscopy, are obtained from this reaction mixture. The reaction of **2** with 1 molar equivalent of sulfur followed by treatment with MeI gives **23** as the major reaction product.[50] Again, the analytical data are in accord.



(6)



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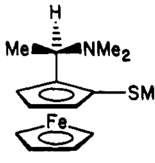

23

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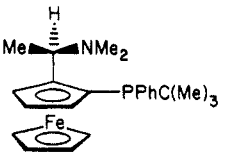
[43] Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon: Oxford, 1982; Vol. 3, Chapter 53.

[44] A complete treatment of the NMR spectra of the diastereomers of **21** will be presented elsewhere.[42] The isomers arise because of the combination of the disubstituted cyclopentadienyl ring with the $-S_3-$ bridge. This topic is also covered in ref 31.

[45] The low yield in the preparation of **23** is attributable to the formation of many byproducts including deaminated compounds probably resulting from reactions of quaternary ammonium salts formed as a result of reaction of methyl iodide and the amine.

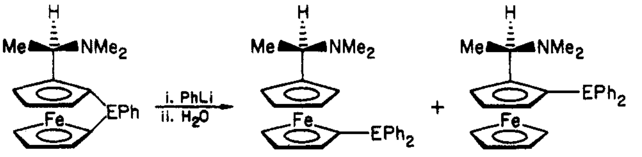
A similar reaction of 2 with *tert*-butylchlorophenylphosphine gives the expected 2-substituted derivative 24.



24

This reaction introduces a second asymmetric center into the molecule because of the asymmetric phosphorus atom. Crystallization of the reaction mixture obtained from racemic 1 resulted in the isolation of a product which, as judged by its ^{1}H NMR spectrum, consists of only one isomer, suggesting that the metathesis reaction is stereoselective. When the reaction was repeated starting with (*R*)-1, one isomer with an identical ^{1}H NMR spectrum was obtained. Thus the asymmetric induction at the incipient chiral center on phosphorus is essentially 100%. Ugi and co-workers[2b] found little induction in the case of the reaction of 2 with anisaldehyde. The crystal structure of the [(P–N)RhNBD]ClO_4 complex, P–N = 24, shows that the CMe_3 group lies outside the ferrocene rings minimizing steric repulsions.[46]

Finally the reaction shown in eq 7 was used to prepare the compound **25b**. The same sequence had previously been employed to prepare **25a**.[47] Compounds 25 and 27 are isomers, and it is of interest to prepare 25 because of the well-established utility of metal complexes of 27 in catalyzed asymmetric reactions.[4,5] The catalytic activity of complexes of **25a** and **25b** is being studied.[42]



26a, E = P
b, E = As

25a, E = P
b, E = As

27a, E = P
b, E = As

(7)

Mass Spectra of Silyl Compounds. The mass spectra of trimethylsilyl derivatives are useful only when the sample contains no trace impurities since very small quantities of the more volatile higher substituted derivatives are easily detected and can lead to erroneous conclusions regarding degree of substitution.[48] The best procedure to obtain reliable mass spectroscopic data is to employ GC/mass spectroscopy even when samples are analytically pure or a time-delayed sampling technique in which case the more volatile components are ionized initially and the "true" spectra may be obtained subsequently. Most spectra reported in Table III were obtained by the latter technique on highly purified samples.

In conclusion the directed lithiation of 1 with BuLi at the 2-position continues to be a useful step in the synthesis of a range of potentially chiral homoannular disubstituted ferrocenes. Blocking the 2-position results in lithiation at the 5-position predominantly although this is accompanied by some heteroannular metalation. This latter reaction predominates when BuLi/TMED is used. Dilithiation of 1, 2-substituted 1, and 2,5-disubstituted 1 is predominantly heteroannular, like ferrocene itself, allowing the synthesis of ferrocenophanes. Thus exclusive metalation of the "bottom" ring of a derivative of 1, an objective mentioned in the Introduction, probably is not possible to achieve with use of BuLi or BuLi/TMED.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council Canada for financial support to W.R.C., Professor James Trotter (Academic Supervisor, University of British Columbia Crystallographic Service) for the use of laboratory facilities, and the University of British Columbia Computing Centre for assistance. Dr. T. Nile kindly provided a copy of his poster no. 159 from the 1985 National Meeting of the American Chemical Society, Miami, FL.

Registry No. 1, 31904-34-4; **2**, 102043-87-8; **3**, 98777-05-0; **6**, 102043-88-9; **9**, 101953-06-4; **10**, 101932-77-8; **11**, 101932-78-9; **12**, 101932-79-0; **13**, 101953-08-6; **14**, 101953-09-7; **1k**, 101953-10-0; **16**, 101953-11-1; **17**, 101932-80-3; **18**, 101932-81-4; **19**, 101953-07-5; **20**, 101932-82-5; **21**, 101932-83-6; **22**, 101932-84-7; **23**, 102043-89-0; **24**, 101932-85-8; **25b**, 101932-86-9; **26b**, 83547-87-9; **27b**, 102043-90-3.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic thermal parameters, torsion angles, and observed and calculated structure amplitudes (Tables VII–X) (32 pages). Ordering information is given on any current masthead page.

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(47) Butler, I. R.; Cullen, W. R. *Can. J. Chem.* **1983**, *61*, 147.

(48) Similar observations have been made previously.[49]

(49) Halaska, A. F.; Tate, D. P. *J. Organomet. Chem.* **1970**, *24*, 769.

(50) **Note Added in Proof.** An alternate synthesis[51] of 23 has appeared in the recent literature.

(51) Honeychuck, R. V.; Okoroafor, M. O.; Shen, L.-H.; Brubaker, C. H., Jr. *Organometallics* **1986**, *5*, 482.