

oxide < PCl₃ < pyridine < arsines < phosphines ≈ phosphites ≈ isocyanides ≈ carbon monoxide.

Comparison to Other Thermodynamic Data. Several zerovalent group VI complexes similar or identical with those in Table III have been studied by other groups. Differential scanning calorimetry has been used to investigate reactions of the complexes AmMo(CO)₅ (Am = pyridine, piperidine, etc.).^{42,43} High-temperature thermal decomposition and iodination studies have appeared for some of the complexes we have examined.^{2,27,44,45} Our solution thermochemical results are qualitatively in agreement with these gas-phase values. Quantitative disagreements may be attributed to differences between the gas and solution phases. The absolute value for the Mo-mesitylene²⁷ bond strength in the gas phase is taken as a benchmark for our solution results. A second gas-phase value for Mo-CO in Mo(CO)₆²⁸ determined by laser pyrolysis also seems to be in accord with our solution bond strength estimates.

Since the primary use of bond strength data is to calculate heats of reaction in solution, we prefer doing this directly, without recourse to bond strength estimates. The data for ligand exchange reported in Table III are subject only to experimental errors such as those shown in Tables I and II and are typically accurate to ±1 kcal/mol. Uncertainties in bond strength assignments due to comparison between gas-phase and solution-phase values make the absolute bond strength assignments considerably less reliable, probably on the order of ±5 kcal/mol. However, these values have an internal relative accuracy which is considerably better.

(42) Daamen, H.; Van Der Poel, Stufkens, D. J.; Oskama, A. *Thermochim. Acta* 1979, 34, 69.

(43) Bleijerveld, R. H. T.; Vrieze, K. *Inorg. Chim. Acta* 1976, 19, 195.

(44) Adedegi, F. A.; Connor, J. A.; Demain, C. P.; Martinho-Simoes, J. A.; Zafarani Moattar, M. T. *J. Organomet. Chem.* 1978, 149, 333.

(45) Al-Takhin, G.; Connor, J. A.; Pilcher, G.; Skinner, H. A. *J. Organomet. Chem.* 1984, 265, 263.

Extensive solution thermochemical data, more readily comparable to our work, has appeared for three systems. Partenheimer⁴ has reported the enthalpies of reaction on the Pd-L system (eq 1). The order of bond strengths was triphenylphosphine > triphenyl phosphite > pyridine > cyclooctadiene. More extensive data have been reported for reactions 2 and 3. In both of these cases and in our system, P(OMe)₃ was the strongest ligand. In Table IV, we report the normalized enthalpies of substitution for ligands in our study which overlap with these systems. Dividing the enthalpies of reaction 29 by *n* gives an average

$$\text{AxM}[\text{P}(\text{OMe})_3]_n + n\text{L} \rightarrow \text{AxML}_n + n\text{P}(\text{OMe})_3 \quad (29)$$

relative bond strength for the different metals. Trimethyl phosphite is taken as the reference in eq 29, since it is the strongest ligand for all three systems and since the complexes in eq 2 and 3 do not form stable benzene complexes. Thus, the compounds in Table IV are listed in order of decreasing stability relative to their respective P(OMe)₃ complexes. There are some remarkable similarities but also some important differences in the three metals studied.⁴⁶ Preliminary work on the L₂Mo(CO)₄ and LMo(CO)₅ systems shows that even for complexes of the same metal and oxidation state, the changing steric and electronic factors of the metal can vary the order of stability.¹⁷ Extrapolation of results from this system to others is not yet warranted. Additional work in progress is aimed at determining a complete thermodynamic surface for the reactions of these organomolybdenum complexes.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE 8314497) is gratefully acknowledged. We also thank Dr. John Connolly of the University of Missouri at Kansas City for a gift of KTp. We also wish to thank Mr. Shakti Mukerjee for experimental assistance in some of the measurements.

(46) We wish to thank Dr. Chadwick Tolman, E. I. duPont de Nemours, for originally suggesting comparison similar to that in Table IV.

Lithiophosphinoferrocenes. A Route to Polyphosphines and Ring-Substituted Ferrocenophanes

Ian R. Butler and William R. Cullen*

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

Received October 29, 1985

The metalation of Fe(C₅H₄PPh₂)(C₅H₅) (7) by *n*-BuLi affords predominantly hetero-ring dilithiated products 8 best characterized by their reaction with S₈ which yields the [3]ferrocenophanes Fe(C₅H₃(P(S)Ph₂)S-1,*n*)(C₅H₄S₂) (*n* = 3 (~75%) or 2 (~25%). The PPh₂ group has some effect in directing the metalation of 7 to the 2-position. Reaction of 8 with ClPPh₂ affords tris(tertiary phosphines) and with Cl₂PPh affords [1]ferrocenophanes such as Fe(C₅H₃(PPh₂)PPh-1,3)(C₅H₄) (12a). Cleavage of 12a with RLi takes place so that the anion is formed predominantly in the PPh₂-substituted ring allowing the preparation of compounds such as Fe(C₅H₃(PPh₂)SiMe₃-1,3)(C₅H₄PPhMe). Some arsenic derivatives and related chemistry of Fe(C₅H₄PPh₂)₂ are also described.

Introduction

The lithiation of ferrocene has proven to be a useful initial reaction step in the synthesis of a wide range of substituted ferrocenes.¹⁻³ In particular this route is well

established for the preparation of ferrocenylphosphines which form many useful transition-metal complexes.

(2) Green, M. L. H. *Organometallic Compounds*; Chapman and Hall: London, 1968; Vol. 2.

(3) Slocum, D. W.; Engelmann, T. R.; Ernest, C.; Jennings, C. A.; Jones, W.; Koonsvitsky, B.; Lewis, J.; Shenkin, P. *J. Chem. Educ.* 1969, 46, 144.

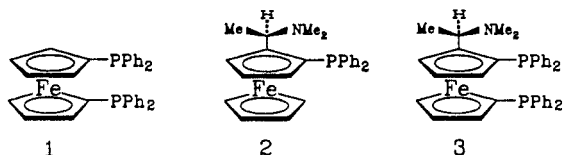
(1) Rosenblum, M. *Chemistry of the Iron Group Metallocenes* Wiley: New York, 1965.

Table I. Mass Spectral Data for Phosphinoferrocenes^a

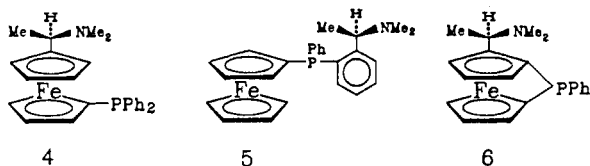
compd	mass spectrum, <i>m/e</i> (relative intensity)
7	371 (27.9), 370 (100.00, M ⁺), 294 (6.6), 293 (33.3)
7a ^b	373 (66.39), 372 (100.00, M ⁺), 296 (34.34), 295 (84.39), 294 (13.70), 393 (14.42), 264 (21.18), 227 (15.13), 198 (6.45)
9a	498 (8.99), 497 (11.82), 496 (41.85, M ⁺), 462 (2.23), 432 (7.62), 403 (9.55), 402 (36.87), 400 (17.56), 368 (6.29), 337 (37.03)
9b	498 (20.82), 497 (29.97), 496 (100.00, M ⁺), 432 (13.79), 402 (5.04), 401 (6.06), 400 (26.82), 368 (11.22), 211 (8.64), 260 (11.61)
10	835 (10.00), 834 (26.00, M ⁺), 802 (10.00), 650 (13.12), 650 (24.10), 434 (76.92), 432 (81.87), 402 (43.79), 370 (88.55)
11a	741 (13.38), 740 (51.63), 738 (100.00, M ⁺), 663 (3.67), 662 (15.46), 661 (31.90), 555 (12.18), 554 (33.77), 553 (13.70), 447 (9.02), 369 (10.33)
11b	741 (12.44), 740 (50.53), 738 (100.00, M ⁺), 662 (19.38), 661 (44.55), 554 (20.92), 553 (48.57), 489 (8.00), 476 (16.63), 369 (5.20)
12a	477 (28.66), 476 (88.58, M ⁺), 400 (8.30), 399 (27.53), 367 (11.37), 291 (45.53), 233 (23.38), 226 (10.92), 203 (11.26), 202 (20.86)
13a	521 (26.72), 520 (94.59, M ⁺), 477 (5.16), 443 (13.59), 371 (18.18), 370 (73.80), 369 (15.24), 367 (33.05), 366 (22.23), 335 (56.68), 293 (72.71), 291 (71.76)
18	565 (20.00), 564 (60.15, M ⁺), 549 (10.19), 514 (60.25), 503 (11.19), 468 (9.78), 452 (71.15), 442 (97.00), 381 (52.00)
21	924 (12.28), 923 (36.59), 922 (60.15, M ⁺), 921 (12.23), 846 (11.67), 845 (20.54), 738 (25.10), 737 (26.81), 558 (10.46)
22a	661 (1.30), 660 (3.54, M ⁺), 555 (23.52), 554 (70.49), 478 (12.95), 477 (38.39), 445 (1.33), 381 (5.18), 369 (20.18), 303 (10.84), 292 (26.43)
22b	705 (13.01), 704 (27.31, M ⁺), 627 (1.82), 555 (40.30); 554 (100.00), 519 (6.71), 478 (24.04), 477 (69.13); 445 (2.90), 369 (21.19), 367 (12.10), 292 (41.78)
Fe[C ₅ H ₃ (PPh ₂)(AsPh ₂)] [C ₅ H ₄ AsPh ₂] ^c	828 (1.95), 827 (7.33), 826 (13.65, M ⁺), 750 (9.49), 749 (20.50), 598 (6.27), 597 (5.40), 521 (4.26), 520 (5.66)
Fe[C ₅ H ₃ (PPh ₂)(AsPh ₂)] [C ₅ H ₃ (AsPh ₂) ₂] ^c	1056 (3.23), 1055 (9.55), 1054 (14.91, M ⁺), 979 (2.79), 978 (9.53), 977 (16.34), 827 (12.22), 824 (26.79), 825 (9.66)
Fe[C ₅ H ₂ (PPh ₂) ₃] [C ₅ H ₃ (PPh ₂) ₂] ^d	1109 (1.99), 1108 (6.80), 1107 (19.97), 1106 (25.54, M ⁺), 1032 (1.52), 1031 (5.05), 1030 (7.04), 925 (5.92), 924 (30.08), 923 (89.65), 922 (100)

^a Probe temperature, 150 °C. ^b D₂O quench of lithiated 7. ^c From 8 + ClAsPh₂ see experiment 2b. ^d From 1 + BuLi/TMED followed by ClPPh₂ see experiment 5a.

Probably the most widely used ligands of this class at present are the compounds 1–3.^{4–6}



Some of our recent studies have been concerned with augmenting the available range of ferrocenylphosphines. For example, 4 and 5 have been synthesized; both are



isomers of 2 and both are readily prepared in optically pure form.⁷ The best route to 4 utilizes the PhLi cleavage of the [1]ferrocenophane 6. The prototype of this very useful reaction, (eq 1) was first described by Seyferth and



(4) (a) Davison, A.; Bishop, J. J. *Inorg. Chem.* **1971**, *10*, 826. (b) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972.

(5) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsomoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

(6) Cullen, W. R.; Einstein, F. W. B.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988.

(7) (a) Butler, I. R.; Cullen, W. R. *Can. J. Chem.* **1983**, *61*, 147. (b) Butler, I. R.; Cullen, W. R.; Rettig, S. J., unpublished results.

Table II. Selected Microanalytical Data of Phosphinoferrocenes

compd	mol formula	anal. calcd (found)	
		C	H
9a ^a	C ₂₂ H ₁₈ FePS ₄	53.22 (53.02)	3.63 (3.57)
9b ^b	C ₂₂ H ₁₈ FePS ₄	53.22 (52.43)	3.63 (3.36)
10	C ₄₄ H ₃₆ Fe ₂ P ₂ S ₃ ·CH ₂ Cl ₂	59.40 (59.50)	4.11 (4.15)
11a	C ₄₆ H ₃₇ FeP ₃	74.80 (74.91)	5.01 (4.81)
12a	C ₂₈ H ₂₂ FeP ₂	70.61 (70.15)	4.66 (4.74)
13a	C ₂₈ H ₂₂ AsFeP	64.65 (64.18)	4.27 (4.58)
16b ^d	C ₃₄ H ₂₈ AsFeP	68.25 (68.69)	4.72 (4.70)
19 ^c	C ₃₂ H ₃₁ FeNP ₂	70.21 (69.16)	5.71 (5.93)
21	C ₅₈ H ₄₆ FeP ₄	75.50 (75.25)	5.02 (5.34)

^a S, 25.79 (25.90). ^b S, 25.79 (26.20). ^c N, 2.56 (2.28). ^d Described previously in ref 8.

Withers.⁸ Further examples are given in this paper which also describes some studies on the lithiation of ferrocenylphosphines.

The ultimate objectives of this work are to establish routes for the preparation of novel multidentate ligands and to develop methodology for polymer preparation and for use in attaching the ligands to inert supports. Some related studies of aminoferrocenes have been recently described.⁹

Experimental Section

Freshly distilled and purified solvents were used in the lithiation reactions and chromatographic separations of ferrocenophanes; otherwise solvents used were of reagent grade. Commercially available (Aldrich) solutions of *n*-butyllithium and phenyllithium

(8) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275.

(9) Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1986**, *5*, 1320.

Table III. Selected ^1H and ^{31}P NMR Data for Ferrocenylphosphines^a

compd	^1H		^{31}P
	ferrocenyl resonances	phenyl resonances	
1	4.02 (pq, 4); 4.28 (pt, 4)	7.23-7.38 (b m, 20)	-157.47
1 ^b	4.30 (pq, 4); 4.65 (pt, 4)	7.30-7.50 (m, 12); 7.59-7.67 (d,d,d, 8)	-100.24
7	4.07 (s, 5); 4.11 (pq, 2); 4.37 (pt, 2)	7.27-7.33 (m, 6); 7.33-7.38 (m, 4)	-134.07
7a	4.16 (s, 5); 4.45 (pq, 2); 4.49 (pq, 2)	7.37-7.50 (m, 6); 7.78-7.85 (d,d,d, 4)	-99.30
9a	3.83, 4.05, 4.44, 4.48, 4.70, 4.79, 4.83 (major isomer) 3.72, 4.01, 4.27, 4.51, 4.63, 4.83, 4.92 (minor isomer)	7.50-7.60 (m, 6); 7.80-7.90 (m, 4)	-100.81
9b	3.83 (m, 1); 4.11 (m, 1); 4.25 (m, 1); 4.39 (m, 1); 4.42 (m, 1); 4.66 (m, 1); 5.32 (m, 1) (major isomer)	7.40-7.55 (m, 6); 7.58-7.80 (m, 4)	-99.68
11a	3.89 (pq, 2); 4.03 (b d, 2); 4.06 (b, m, 1); 4.09 (pt, 2)	7.20-7.35 (m, 30)	-133.03 (b)
11b	3.73 (pq, 2); 4.07 (pqn, 2); 4.28 (b t, 1); 4.39 (pt, 2)	7.20-7.35 (m, 30)	
12a	4.19 (m, 1); 4.33 (m, 1); 4.36 (ms, 2); 4.47 (m, 1); 4.58 (m, 1); 4.80 (m, 1)	7.22-7.36 (m, 10); 7.40 (m, 3); 7.58 (m, 2)	-126.4 (b), -158.1
13a	4.15 (m, 1); 4.20 (m, 1) f 4.89 (m, 1); 4.69 (m, 1); 4.66 (m, 1)	7.25-7.40 (m, 10); 7.50-7.60 (m, 5)	

^a Chemical shifts in ppm from external Me_4Si (^1H) and external $\text{P}(\text{OMe})_3$ (^{31}P). Abbreviations: pq = pseudo quartet; pt = pseudo triplet; pqn = pseudo quintet. ^b Disulfide.

were used. All manipulations were performed under an argon atmosphere by using conventional Schlenk glassware. Manipulation of compounds other than ferrocenophanes was carried out without special precautions.

Column chromatography was carried out by using neutral alumina. The activity grade used in each separation is given in brackets, e.g., (I) for Grade I. Preparative plate separations were carried out by using commercial silica gel coated glass plates (2.0-mm thickness). Mixtures of hexanes and diethyl ether were usually used as eluents. Product mixtures were monitored routinely throughout all experimental procedures by using TLC on aluminum-backed alumina or silica gel coated plates.

^1H NMR spectra were obtained by using either Bruker WP80 or WH400 instruments. Mass spectral data were recorded by using a Kratos MS-50 instrument. Elemental analyses were performed by Mr. Peter Borda of this department and are listed in Table II. Spectroscopic data are given in Tables I and III.

1. Preparation of (Diphenylphosphino)ferrocene (7) and 1,1'-Bis(diphenylphosphino)ferrocene (1). These compounds were prepared by the reaction of the appropriate lithioferrocene with chlorodiphenylphosphine;⁴ chromatographic workup was used. Larger amounts of 7 are best purified by column chromatography in small batches (~1 g).

2. Lithiation of 7 in the Presence of TMED. General Procedure for the Preparations of 8. *n*-Butyllithium in hexane (2.1 mol equiv of a 1.55 M solution) was added to a rapidly stirred solution of 7 (1 mol equiv) in diethyl ether (10 mL/mmol of 7). TMED (1 mol equiv with respect to *n*-BuLi) was subsequently added. The reaction mixture was stirred for a minimum of 20 h. The resulting reaction suspension of 8 was generally used without purification. When necessary, the precipitated lithio derivative, a pale orange solid, was isolated by filtration, washed with hot hexane (2 × 30 mL), and vacuum dried.

a. Reaction of 8 with D_2O . D_2O (5 mL) was added to a slurry of the lithio derivatives 8 prepared as above from 1.0 g of 7. The organic fractions were separated and dried (MgSO_4) to give the deuterated products 7_{D} .

b. Reactions of 8 with ClAsPh_2 and ClSiMe_3 . To a cooled slurry of 8 prepared from 7 (1.0 g) was added either chlorodiphenylarsine (1.60 g, 6.0 mmol) or chlorotrimethylsilane (0.7 g, 6.5 mmol). The solution was allowed to warm to room temperature and was further stirred for 6 h. The reaction mixture was then hydrolyzed with aqueous sodium bicarbonate solution and worked up as follows.

i. Reaction with ClAsPh_2 . The organic layer was combined with a dichloromethane extract (30 mL) of the solid products remaining in the reaction vessel. The solvent was removed to give a yellow orange oily solid. This product gave four rather diffuse bands, A-D, on column chromatography (alumina (III)): fraction A, M^+ 598, monosubstituted 7; fraction B, M^+ 826, disubstituted 7; fraction C, M^+ 826, disubstituted 7; fraction D, a mixture containing trisubstituted 7, M^+ 1054, and a compound with M^+ 1346. All fractions are oils and have resisted attempts at crystallization.

ii. Reaction with ClSiMe_3 . The ether fraction was concentrated and the mass spectrum of the oily residue showed peaks

at M^+ 442, 514, 586, and 658 corresponding to mono-, di-, tri-, and tetrasubstituted 7. Separation by TLC (hexane eluent) combined with mass spectroscopy showed that the major product was the bis(trimethylsilyl) derivative. Only a trace of the tetrasubstituted and a small amount of the trisubstituted (<5%) were present.

c. Reaction of 8 with ClPPh_2 . Preparation of 11. To a cooled slurry of 8 (-30 °C) prepared from 7 (1.5 g, 4.0 mmol) was added excess chlorodiphenylphosphine (2.0 g, ~10 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for a further 10 h. The reaction mixture was hydrolyzed with aqueous sodium bicarbonate solution (25 mL). The organic fraction was separated and combined with the extracts (CH_2Cl_2 , 25 mL) of the residual solid. The solvent was removed to give an orange oil. Examination of this oil by TLC (hexanes/diethyl ether eluent, 80/20), indicated the presence of four compounds: 7, 1 (by comparison with authentic samples), and two orange bands with lower but similar R_f values. On column chromatography (alumina (I)) the phosphine byproducts were removed by elution with hexanes/diethyl ether (80/20). The product ferrocenes diffused on the column and were eluted without separation. Preparative plate chromatography (hexanes/diethyl ether eluent, 80/20, *low loading is essential*), allowed the isolation of all compounds including two compounds identified as 11a and 11b (ratio ~3:1) (total yield ~40%).

d. Reaction of 8 with S_8 . Preparation of 9. A slurry of 8 prepared from 3.0 g of 7 was treated with S_8 (0.5 g, 15.6 mmol (S), excess). The reaction mixture was stirred for 6 h. The organic layer was isolated following hydrolysis as described above. Concentration of this fraction gave an orange oil. Chromatographic examination, TLC, showed two major products. However, many other compounds were present in trace quantities. The two major products (~40% total) were isolated as a mixture by column chromatography (alumina (V)). Compound separation was achieved by preparative TLC (hexane/diethyl ether eluent, 60/40). The ratio of 9a (higher R_f) to 9b was approximately 75:25. 9a crystallized (diethyl ether/hexane, 30/70) as yellow microcrystals while 9b initially yielded yellow/brown nodules which on recrystallization (CH_2Cl_2 layered with *n*-hexane) gave orange crystals. Several byproducts were subjected to mass spectral analysis. These were shown to consist of ferrocene coupled products such as 10 (M^+ 834).

e. Reaction of 8 with Cl_2EPH . Preparation of 12 and 13 (E = P, As) To a chilled (-70 °C) slurry of 8 prepared from 3.0 g of 7 was added either Cl_2PPH or Cl_2AsPh (1.53 g or 1.90 g, 8.5 mmol). The mixture was allowed to warm to room temperature, stirred for 1 h, and hydrolyzed with aqueous sodium bicarbonate (10 mL). The deep red orange organic layer was separated and concentrated by solvent removal under vacuum, yielding a red oil. TLC examination (75/25 hexane/diethyl ether) showed the presence of two red compounds with almost identical R_f values as the major solution components as well as traces of several orange compounds. Both red compounds elute together on column chromatography (alumina (III)). The compound with the higher R_f value in each case comprised ~70% of the oil. Repeated recrystallization (diethyl ether/hexane, 50/50) gave 12a or 13a

the major components, as deep red/black crystals (yield ranges from 20 to 45%).

f. Reaction of 8 with Ph_2SiCl_2 . A chilled (-70°C) suspension of 8 prepared from 3.0 g of 7 was treated with Cl_2SiPh_2 2.20 g, 8.7 mmol). The reaction mixture was worked up in a similar fashion to the above. Chromatographic examination (TLC) showed the major reaction products to be orange/red; these were isolated as a mixture by column chromatography. Attempted crystallization yielded the product as an orange oil which solidified on drying to give a fluffy pale orange solid. Crystals could not be obtained from a range of hexane/diethyl ether mixtures.

3. Ring Cleavage Reactions of the [1]Ferrocenophanes. General Procedure. A solution of the ferrocenophane 12 or 13 (1 mol equiv), in the minimum volume of diethyl ether required for complete solution, was added dropwise to a chilled (-70°C) solution of phenyllithium (5 mol equiv) in the same solvent. The solution was allowed to warm to room temperature during which time the characteristic red color of the ferrocenophane discharged to give a clear orange-yellow solution. The cooled reaction mixture was treated carefully with water (20 mL), and the ether layer was separated and dried over anhydrous MgSO_4 . The mixture was then filtered, the MgSO_4 washed with diethyl ether, and the combined solution (filtrate plus washings) reduced in volume, under vacuum, to a few milliliters.

a. Reaction of 12a. The TLC examination of the product mixture showed the presence of two products, one of which was present in trace quantities. Crystallization from hexanes afforded 1 (16, E = P) (yield >80%).

b. Reaction of 13a. Investigation by TLC showed an almost identical result to 3.a. Crystallization of the product oil from hexanes gave 1-(diphenylarsino)-1'-(diphenylphosphino)ferrocene (16, E = As) as orange crystals in 85% yield.

4. Reaction of 12a with MeLi and ClSiMe_3 . Preparation of 18. The lithiation of 12a (0.1 g) with methyl lithium was carried out as described above for phenyllithium. Treatment of the resulting solution carefully with ClSiMe_3 gave one major product. This was isolated by preparative TLC and was identified as 18 by ^1H NMR and mass spectroscopy.

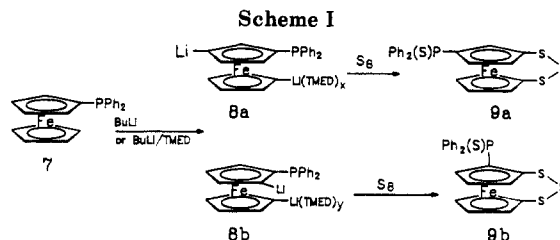
5. Reaction of 1 with *n*-Butyllithium/TMED. General Procedure. A solution of *n*-butyllithium in hexanes (2.2 or 3.0 mol equiv with respect to 1) was added to a rapidly stirred slurry of 1 in diethyl ether (20 mL/1.0 g of 1). TMED (1.5 mol equiv with respect to 1) was then added. The resulting slurry was stirred for a minimum of 40 h. The solid can be isolated if desired.

a. Reactions with ClPPh_2 and ClSiMe_3 . Preparation of 21. A suspension of the lithio derivative prepared from 1 (3.0 g, 5.4 mmol) was treated with either chlorodiphenylphosphine or chlorotrimethylsilane (3.0 g, 13.6 mmol, or 1.5 g, 13.8 mmol) at 20°C . The resultant solution was hydrolyzed (H_2O , 20 mL) after 3 h. The ether layer and an extract of the solid residues (dichloromethane, 50 mL) were combined, and the solvent volume was reduced to 3–4 mL. The remaining oil was chromatographed (alumina (III)) without clean separation.

i. Phosphine Reaction. Preparative plate chromatography of the reaction mixture (hexanes/diethyl ether, 60/40) revealed a number of fractions which were identified by mass spectroscopy as 1: two trisubstituted, 11a and 11b; tetrasubstituted (major products, overlapping orange bands); and pentasubstituted derivatives (orange bands). The order of elution followed the substitution number. The major product 21 was isolated as a fluffy orange solid (~45% yield).

ii. Silane Reaction. Preparative plate chromatography revealed many bands which were characterized by mass spectroscopy as mono-, di-, tri-, and tetrasilylated products. The major band contained the disubstituted derivatives which were isolated as an orange oil. Further separation and crystallization was unsuccessful.

6. Reaction of 2 with *n*-Butyllithium/TMED. Preparation of 19. A solution of 2 (2.0 g, 4.5 mmol) in diethyl ether (25 mL) was treated with a solution of *n*-butyllithium (6 mL of a 1.55 M solution) and TMED (0.6 g, 5.2 mmol). The reaction mixture was stirred overnight at 20°C , cooled to -30°C , and treated with dichlorophenylphosphine (0.85 g, 4.7 mmol) in diethyl ether (20 mL). The mixture was allowed to warm to 20°C and stirred for a further 30 min before being hydrolyzed (H_2O , 25 mL). The ether layer was separated, reduced in volume to a few milliliters, and



subjected to column chromatographic separation (alumina (III)). The red fraction was isolated. Removal of solvent afforded 19 as a powder.

Results and Discussion

The reaction of ferrocene with *n*-butyllithium has been studied extensively in a variety of solvents.^{3,4,10–15} When an equimolar or molar excess of the alkyl lithium is employed, mixtures of monolithio- and 1,1'-dilithioferrocene result. When a twofold excess of *n*-butyllithium is used in the presence of an equivalent amount of the bidentate amine tetramethylethylenediamine (TMED), 1,1'-dilithioferrocene in the form of its TMED adduct(s) predominates (<90%).^{11–15}

The results of the present investigation show that the reaction of (diphenylphosphino)ferrocene (7) with a 2:1 molar ratio of *n*-butyllithium/TMED proceeds smoothly to form principally the dilithiated compounds 8 (Scheme I).¹⁶ The isomer ratio 8a:8b \approx 78:22 can be established by integration of the cyclopentadienyl region of the ^1H NMR spectrum of the product 7a obtained following treatment with D_2O . This same spectrum reveals that disubstitution predominates over mono by more than 9:1.^{10,15} As described above ferrocene itself behaves similarly.

Metalation of alkylferrocenes with two or more equivalents of metalating agent favors dimetalation over mono by a factor of 2.2–3.0:1.¹⁵ The present results for 7 show an even greater preference. Again, in the alkylferrocenes (Fc-R) metalation at the 3-position is favored over the 2-position by factors of 8 (R = Me) to 98 (R = CMe_3).^{18,19} This is attributed to a combination of electronic and steric

(10) Slocum, D. W.; Sugarman, D. I. In *Polyamine-Chelated Alkali Metal Compounds*; Langer, A. W., Ed.; ACS Publication 130; American Chemical Society: Washington, DC, 1974; p 222.

(11) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberger, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* 1971, 27, 242.

(12) Rausch, M. D.; Moser, G. A.; Meade, C. F. *J. Organomet. Chem.* 1973, 51, 1.

(13) Walczak, M.; Walczak, K.; Mink, R.; Rausch, M. D.; Stucky, G. *J. Am. Chem. Soc.* 1978, 100, 6382.

(14) Butler, I. R.; Cullen, W. R.; Ni, J.-J.; Rettig, S. J., *Organometallics* 1985, 4, 1296.

(15) Rausch, M. D.; Sarnelli, A. J. In *Polyamine-Chelated Alkali Metal Compounds*; Langer, A. W., Ed.; ACS Publication 130; American Chemical Society: Washington, DC, 1974; p 248.

(16) Solid 8 can be isolated as an orange powder, but attempts to prepare a crystalline sample were unsuccessful possibly because of the presence of isomers. The number of TMED molecules in each molecule of 8 must be left open in view of the result found for 1,1'-dilithioferrocene, namely, $[(\eta\text{-C}_5\text{H}_4\text{Li})_2\text{Fe}]_2[\text{TMED}]_2$.¹⁴

(17) The 3- and 4-positions, with respect to a monosubstituted ferrocene ring, are actually enantiomeric because of the presence of planar chirality. The distinction needs to be made when the 1-position is occupied by an optically active group or when the molecule is highly substituted as in a ferrocenophane. These conditions can result in the formation of diastereomers. The same remarks hold for substituents in the 2- or 5-positions.

(18) Simple alkylferrocenes are not metalated on the side chain even with *n*-amylpotassium¹⁹ although the dilithiated derivative of $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{Me}_6)$ is substituted at one C_5H_5 position and the CMe_6 .²⁰

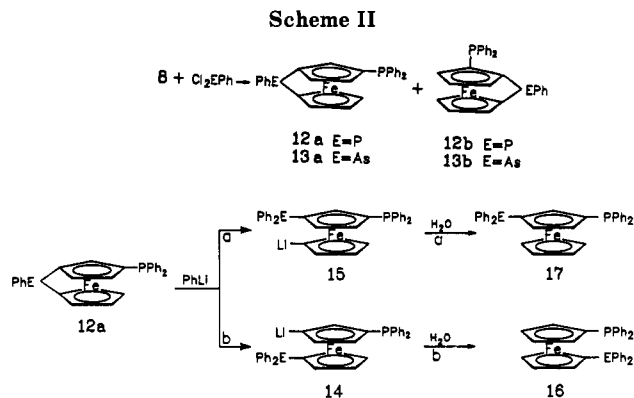
(19) Benkeser, R. A.; Bach, J. L. *J. Am. Chem. Soc.* 1964, 24, 769.

(20) Chao, S.; Robbins, J. L.; Wrighton, M. S. *J. Am. Chem. Soc.* 1983, 105, 181.

effects. The much lower ratio found in the case of 7 strongly suggests that the $-PPh_2$ group has some directing effect to the 2-position as is found to high specificity in amino derivatives such as $Fc-CHNR'_2$.^{3,10,11,21-24} The presence of traces of mono-, tri-, and tetralithiated derivatives in addition to 8 formed in the presence of TMED²⁵ is revealed when the reaction mixture is treated with chlorotrimethylsilane. The corresponding volatile mono-, tris-, and tetrakis(trimethylsilyl) derivatives are easily identified by their mass spectra.^{9,26-29}

In order to prepare derivatives from 8 which could be better characterized, attention was given to reactions which would produce ferrocenophanes since these are conveniently prepared from dilithiated species. Equation 1 illustrates the preparation of a [1]ferrocenophane;^{8,30} [3]-ferrocenophanes result from reaction with sulfur³¹⁻³⁴ (Scheme I).

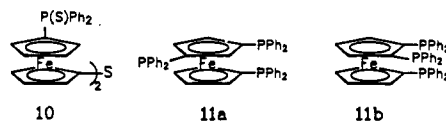
The products from the reaction of 8 with S_8 consist mainly of two isomers 9a and 9b, which can be isolated in a ratio of $\sim 3:1$ as expected from the deuteration studies described above. The oxidation of the PPh_2 groups by sulfur is normal. Both isomers show clear parent ions in their mass spectra, and the analytical data are consistent with the formulation. The solid-state structures confirm the substitution pattern³⁴ and reveal that the rings are eclipsed with the $-S_3-$ bridges in a pseudochair conformation. This same structure is found in the parent [3]-ferrocenophane $Fe(C_5H_4)_2S_3$.³¹ Because the barrier to chair-chair interconversion (bridge reversal) is high,^{32,33} both 9a and 9b exist as mixtures of diastereomers at ambient temperature.¹⁷ The 1H NMR spectrum of a crystalline sample of 9a reveals the presence of a mixture ($\sim 60:40$) of these diastereomers in solution.³⁵ Fourteen multiplets are seen in the cyclopentadienyl region. The



1H NMR spectrum of crystals of 9b indicate that there is a preponderance of one diastereomer in solution. A full treatment of the relevant NMR data including the application of the "SUPER COSY" 2D technique to assign the spectra will be published elsewhere.³⁴

The byproducts from the reaction of 8 with sulfur include traces of 10 as well as several compounds which contain more than two ferrocenyl groups. The latter presumably results from the coupling of 8 with sulfur to give sulfur-bridged oligomers of the ferrocenylphosphine. Compound 10 can be synthesized independently and cleanly by treating $Fe(C_5H_4Li)(C_5H_4PPh_2)$ (eq 1) with S_8 . The appropriate characterization data are listed in the tables.

The Use of 8 in the Preparation of Bis- and Tris-(tertiary phosphines). The dilithio derivatives 8 react with $ClPPh_2$ to afford the tris(diphenylphosphino)ferrocenes 11a and 11b which are separable by TLC.³⁶ The analytical and spectroscopic data listed in the tables support the formulation. The isomer assignment can be made independently on the basis of NMR decoupling experiments which easily identify the unique proton in the 2-position in 11a. The ratio of 11a to 11b is $\sim 3:1$ which is in agreement with the other derivatization results described above.



Another less obvious route to this type of derivative is outlined in Scheme II.

The phosphorus- and arsenic-bridged [1]-ferrocenophanes 12 and 13 are obtained from 8 by treatment with Cl_2EPh ($E = As$ or P).³⁷ Generally the yields of the compounds are only moderate (30–40%) presumably due in part to the formation of oligomeric and polymeric byproducts. Seyferth and co-workers encountered similar problems in their preparation of the simple [1]-ferrocenophanes (eq 1).^{8,38}

The new products are isolated as oils from which the major isomers 12a and 13a can be crystallized. The analytical data and spectroscopic evidence confirm the formulation of both 12 and 13. In particular, the ^{31}P NMR

(36) The arsenic analogues of 11 are obtained in a similar way but are difficult to separate from traces of other substituted products; apart from mass spectra and 1H NMR these compounds are uncharacterized.

(37) The reaction of 8 with Cl_2SiPh_2 affords oily products which can be separated into oily fractions by column chromatography. The major product shows parent ions corresponding to the expected ferrocenophanes but the presence of isomers (distribution unestablished) seems to hinder the crystallization of the fraction.

(38) Withers, H. P.; Seyferth, D.; Fellman, G. D.; Garrou, P. E.; Martin, S. *Organometallics* 1982, 1, 1283.

(21) Gokel, G. V.; Ugi, I. K. *J. Chem. Educ.* 1972, 49, 294.

(22) Battelle, L. F.; Bau, R.; Gokel, G. W.; Oyakawa, R. T.; Ugi, I. K. *J. Am. Chem. Soc.* 1975, 95, 482.

(23) Butler, I. R.; Cullen, W. R.; Herring, F. G.; Jagannathan, N. R. *Can. J. Chem.* 1986, 64, 667.

(24) Appleton, T. D.; Cullen, W. R.; Evans, S. V.; Kim, T.-J.; Trotter, J. *J. Organomet. Chem.* 1985, 279, 5.

(25) Metalation of 7 by *n*-BuLi (two or more mole equivalents, 40 h) in diethyl ether in the absence of TMED proceeds in a similar manner as indicated by the products isolated after D_2O or $ClSiMe_3$ quenching experiments. The presence of TMED seems to encourage more extensive metalation.

(26) This volatility has been noted previously as it can erroneously lead to conclusions that higher proportions of higher substituted derivatives are present in mixtures if mass spectroscopy is used as the only indicator of composition.²⁷ In the present case TLC shows that the major products are the expected bis(trimethylsilyl) derivatives (identified by mass spectroscopy). The NMR spectra show the presence of isomers but distinction between 2,1'- and 3,1'-substitution cannot be made. Likewise, the substitution pattern of the tri- and tetrasilylated derivative is not known. The mono(trimethylsilyl) compound isolated by chromatography, proved to be a mixture of isomers with the principal component being 1,1'-substituted on the basis of its NMR spectrum.²⁸

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

(28) The monosubstitution ($SiMe_3$) products isolated after the metalation of alkylferrocenes, R₂FC, show a preference for 1,1' structures over 1,3 ranging from 3 for ($R = CMe_3$) to 2.4 ($R = Me$).¹⁹

(29) The 1H NMR spectrum of the disubstituted compound $Fe[C_5H_4(PPh_2)(SiMe_3)]_2[C_5H_4SiMe_3]$, the major product, showed that isomers were present, but assignment was not possible. Mass spectrum: m/e 516 (18.53), 515 (49.70), 514 (100.00, M⁺), 442 (9.21), 421 (5.38), 377 (5.21), 314 (16.68), 229 (17.65).

(30) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. *J. Organometallics* 1983, 2, 128.

(31) Davis, B. R.; Bernal, I. *J. Cryst. Mol. Struct.* 1972, 2, 107.

(32) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* 1981, 208, 213.

(33) Davison, A.; Smart, J. *J. Organomet. Chem.* 1969, 5, 83.

(34) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Herring, F. G.; Jagannathan, N. R.; Jones, R. H. *Inorg. Chem.*, in press.

(35) Although pure diastereomers can be obtained by crystallization on redissolution, a mixture of diastereomers results in solution due to the rapid equilibration process.

spectrum of **12a** shows the expected two resonances; that of the PPh_2 group is much sharper than that of the bridging $-\text{PPh}$. The major isomer is assigned to **12a** on the basis of the results described above.³⁹

Both compounds **12a** and **13a** are readily cleaved by PhLi according to Scheme II; however, the products isolated in high yield after hydrolysis are those, **16**, from the less desirable route b. The more interesting product **17** which would have planar chirality if $\text{E} = \text{As}^{17}$ would be difficult to obtain by other routes.⁴⁰ The products **16** are better prepared from 1,1'-dilithioferrocene or from monolithiated derivatives prepared as outlined in eq 1.

Nevertheless, this situation can be turned to advantage in a number of ways. A monolithiated species such as **14** could be used to prepare compounds with 1,3,1'-substituents possessing planar chirality.⁴⁰ **14** could also be used to attach 1,1'-disubstituted ferrocene ligands to inert supports since specific monolithiation of a derivative like **1** is difficult to achieve as will be seen from results presented below.

As a test of the first suggestion **12a** was treated with MeLi , and the resultant product mixture reacted with chlorotrimethylsilane. The major product is identified as **18** on the basis of its ^1H NMR and mass spectra. This compound, because of the presence of planar chirality and an asymmetric phosphorus atom, can exist as a mixture of diastereomers. The ^1H NMR spectrum shows the anticipated doubling of the PMe (two doublets) and SiMe_3 resonances.

The difference in stability of the two intermediate anions in Scheme II is probably due to the electronegativity of the $-\text{PPh}_2$ group.⁴¹ If this conclusion is correct, the cleavage of the ferrocenophanes **19** by PhLi followed by hydrolysis should produce **3** as the major product. This is indeed found. Other monor products include one, **20**, in which the ring has opened the other way. An authentic sample of **20** has previously been isolated as one of the products of the stepwise reaction of **2** with BuLi and ClPPh_2 .⁹

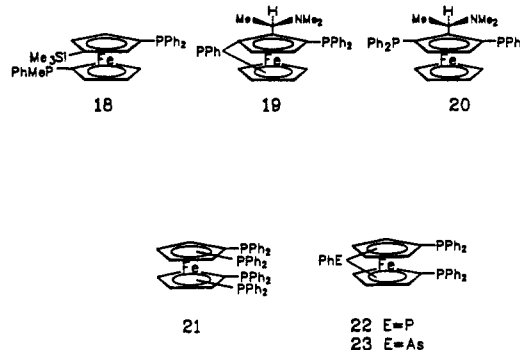
Tris- and Tetrakis(tertiary phosphines) from 1 and 2. In principle the chemistry developed above for **7** could be applied to **1** and **2**. Thus, the sequence, lithiation followed by reaction with ClPPh_2 , should afford tetra-substituted ferrocenes. The sequence lithiation, reaction with Cl_2EPh followed by cleavage of the product ferrocenophane with PhLi , should afford tris(tertiary phosphines).

Lithiation of **1** with 2 equiv of BuLi/TMED affords mainly the hetero-ring dilithiation product as determined from quenching experiments with both D_2O and ClSiMe_3 .⁴² When lithiated **1** was treated with ClPPh_2 , problems with mixtures of isomers precluded the isolation of useful

quantities of individual tetrakis(tertiary phosphines). The available analytical and spectroscopic data show that the major product **21** is a mixture of the three possible isomers of this formulation. The [1]ferrocenophanes **22** and **23** formed as part of the second sequence are very sensitive in solution, and again it is difficult to isolate individual compounds from the mixture of isomers. Thus **1**, unlike **7**, is not a useful precursor to multidentate phosphines. Similar observation can be made for **2** although, as mentioned above, the mixture of diastereomers **19** can be isolated.

Mass spectral data for some new compounds are summarized in Table I and footnotes. All compounds show clear parent ions and loss of phenyl groups and EPh_2 moieties ($\text{E} = \text{P}, \text{As}$). Loss of the latter group usually occurs with concurrent proton abstraction to give fragment ions of the type $(\text{M} - \text{PPh}_2 + \text{H})^+$. Compounds with Me_3Si substituents show stepwise loss of this group so the spectra of mixtures are difficult to interpret.⁹

^1H NMR spectra of the more highly substituted ferrocenyl compounds, e.g., the tetrakis(tertiary phosphines) **21** obtained from **1**, are less useful since the ratio of ferrocenyl proton resonances to those of the substituent groups is small, making analysis difficult.



In summary, the lithiation of ferrocenylphosphines with $n\text{-BuLi}$ is a facile process. The phosphorus substituents have only a limited effect in directing lithiation to the adjacent position. Subsequent reaction of the lithio compounds with ClQ ($\text{Q} = \text{PPh}_2, \text{AsPh}_2, \text{SiMe}_3$) affords a range of substituted ferrocene derivatives which are potentially of interest as multidentate ligands although, as the number of substituents increases, the problem of obtaining pure compounds from mixtures of isomers is compounded. Isomer problems can be reduced by treating the lithio derivatives with reagents such as S_8 and Cl_2EPh which afford more easily characterized [3]- and [1]-ferrocenophanes. These compounds are useful for establishing substitution patterns.

The cleanest method of preparing monolithioferrocenylphosphines is by RLi cleavage of [1]-ferrocenophanes. Ring opening takes place so that the anion is formed in the ring which carries the original phosphine substituent. This provides a facile route to specifically substituted multidentate ligands from **7** which would be difficult to obtain by any other route.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada for funding this research as well as the staff of the U.B.C. mass spectroscopy and NMR laboratories for spectroscopic measurements and Mr. Peter Borda for microanalytical data.

(39) Diastereomers can arise from the combination of the planar chirality of the disubstituted cyclopentadienyl ring with the asymmetric phosphorus atom.¹⁷ The ^1H NMR spectra of **12a** and **13a** as isolated after careful recrystallization show seven multiplets in the cyclopentadienyl region, indicating the presence of only one diastereomer.

(40) This feature would be more desirable in a 1,2-substituted product. In fact this possibility was the motive for attempting much of the synthetic work described in this paper.

(41) The ^1H NMR spectra of cyclopentadienyl rings substituted with PPh_2 groups are shifted downfield of unsubstituted rings in ferrocene derivatives.

(42) $\text{Fe}[\text{C}_5\text{H}_3(\text{PPh}_2)(\text{SiMe}_3)]_2$: mass spectrum, m/e (relative intensity) 700 (22.09), 699 (54.88), 698 (100.00, M^+), 627 (26.77), 626 (59.46), 625 (11.22), 622 (14.12), 621 (28.74), 549 (21.43), 514 (18.81), 513 (11.15), 436 (13.87), 364 (11.37), 349 (15.18).