Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SYMMETRICALLY DISUBSTITUTED FERROCENES
I. THE SYNTHESIS OF POTENTIAL BIDENTATE LIGANDS

J. J. BISHOP*, A. DAVISON**, M. L. KATCHER, D. W. LICHTENBERG, R. E. MERRILL AND J. C. SMART
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received August 14th, 1970; by publisher November 24th, 1970)

SUMMARY

Solutions of n-butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) readily dilithiate ferrocene in high yields. The 1,1′-dilithioferrocene can be used *in situ*, or when isolated as the pyrophoric adduct $[(C_5H_4Li)_2Fe]\cdot$TMEDA, to prepare the following complexes in high yields: ferrocene-1,1′-bis(dimethylarsine) (Fdma), ferrocene-1,1′-bis(diphenylarsine) (Fdpa), ferrocene-1,1′-bis(dimethylphosphine) (Fdmp), ferrocene-1,1′-bis(diphenylphosphine) (Fdpp). Elemental sulfur reacts with solutions of dilithioferrocene in refluxing glyme to give 1,2,3-trithia-[3]-ferrocenophane. This can be converted quantitatively to ferrocene-1,1′-dithiol (Fdt) by reduction with lithium aluminum hydride.

INTRODUCTION

The chemistry of symmetrically 1,1′-disubstituted ferrocenes, $(C_5H_4L)_2Fe$, where the substituents are potential donor groups, has been only superficially explored. The major difficulties in obtaining high yields of symmetrically disubstituted ferrocenes of the type $(C_5H_4L)_2Fe$, where $L = AsR_2$ or PR_2, were overcome by the discovery that ferrocene can be readily dimetalated[1,2]. Previous work by Sollott *et al.*[3] employing Friedel–Crafts reaction conditions, gave the first examples of substituted phosphino and arsino ferrocenes but did not yield symmetrically disubstituted derivatives. However, these workers[4] have obtained both mono- and disubstituted compounds, in very low yields, from the metalation reaction of ferrocene with n-butyllithium in ethers.

During the course of these studies two very brief reports[5,6] dealing with the chemistry of Fdpp have appeared. However, in one of these cases[5] no experimental conditions or properties of the complexes were given. Ref. 6 quotes unpublished information on the preparation of Fdpp without the use of TMEDA to assist the metalation.

---

* Petroleum Research Fund Graduate Fellow, 1968–1969.
** Fellow of the Alfred P. Sloan Foundation, 1967–1969.

This work describes a convenient synthesis of ferrocene-1,1′-bis(dimethylarsine) (Fdma), ferrocene-1,1′-bis(diphenylarsine) (Fdpa), ferrocene-1,1′-bis(dimethylphosphine) (Fdmp), ferrocene-1,1′-bis(diphenylphosphine) (Fdpp), ferrocene-1,1′-dithiol (Fdt) and some of their derivatives.

EXPERIMENTAL

General data

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany; Galbraith Laboratories, Inc., Knoxville, Tennessee; Midwest Microlab, Inc., Indianapolis, Indiana; Spang Microanalytical Laboratory, Ann Arbor, Michigan; and Scandinavian Microanalytical Laboratory, Herlev, Denmark; and, at M.I.T. by Dr. Stephen S. Nagy and Mrs. Nancy F. Alvord. Molecular weight determinations were carried out by Midwest Microlab, Inc.

All melting points are corrected and were determined using a Thomas Hoover "Unimelt" melting point apparatus on samples sealed in evacuated capillaries.

Where sensitive materials were involved, manipulations were carried out in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on Perkin–Elmer 337 and 521 spectrophotometers. Nuclear magnetic resonance spectra were recorded on Varian Ass. T-60, A-60 and HA-100 spectrometers with tetramethylsilane as an internal reference. Mass spectra were measured on a Hitachi Perkin–Elmer RMU-6D mass spectrometer.

Materials

Reagent-grade solvents were used and, when required, were degassed *in vacuo*. Hydrocarbon solvents were dried by distillation from calcium hydride under nitrogen. Dioxane, 1,2-dimethoxyethane and THF were distilled under nitrogen from sodium benzophenone ketyl prior to use.

Solutions of n-butyllithium (1.6 *M* in hexane) were obtained from Foote Mineral Co. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (Eastman) was dried over sodium hydroxide or barium oxide and fractionated under nitrogen, b.p. 121–122°. Chlorodiphenylarsine was prepared by the method of Barker *et al.*[7] and fractionally distilled under vacuum, b.p. 148.5–149.5°/2.7 mm, m.p. 39–40°. Dimethyliodoarsine was obtained from cacodylic acid by the method of Burrows and Turner[8] as modified by Feltham *et al.*[9], and fractionally distilled under nitrogen at atmospheric pressure, b.p. 156–160°. Chlorodimethylphosphine was prepared from $(CH_3)_2PSCl$ by the method of Ulmer *et al.*[10] and distilled under nitrogen at atmospheric pressure, b.p. 73–75°, prior to use. Ferrocene (Alfa Inorganics) was purified by Soxhlet extraction from hexane. All other chemicals were of commercial reagent grade and, unless stated below, were used without purification.

Ferrocene-1,1′-bis(dimethylarsine) (Fdma)

A well-stirred mixture of 1.63 *M* n-butyllithium in hexane (250 ml, 0.40 mole), freshly distilled *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (44.6 g, 0.40 mole) and 50 ml of dry oxygen-free hexane, in a 3-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, nitrogen inlet, and pressure-equalizing dropping funnel, was treated under nitrogen during $3\frac{1}{2}$ h with a solution of ferrocene (37.2 g, 0.20 mole) in 1450 ml of the same solvent. Stirring was continued for 18 h. The resulting orange slurry of 1,1'-dilithioferrocene was added dropwise during $1\frac{1}{2}$ h to a vigorously stirred solution of dimethliodoarsine (83.6 g, 0.36 mole) and 150 ml of dry oxygen-free hexane. The mixture was maintained at −10° in a 3-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, mechanical stirrer and pressure equalizing dropping funnel. The funnel was also equipped with a mechanical stirrer to maintain the 1,1'-dilithioferrocene slurry. The yellow reaction mixture was stirred and allowed to warm at room temperature during 9 h. It was then cooled to 0°, and hydrolyzed with 200 ml of cold oxygen-free water. The organic layer was separated, dried over Drierite and filtered. The volatile components were removed *in vacuo* (0.5 mm) at 45°. The dark red-brown oily residue was fractionated *in vacuo*. An orange-yellow crystalline sublimate preceded the liquid fractions. This was removed and recrystallized from methanol to give ferrocene (3.9 g). The product was collected as a dark red oil (38.1 g, 54%, b.p. 137–140°/0.6 mm, m.p. 10.5°) and stored under nitrogen. (Found: C, 43.14; H, 5.12; As, 38.88. $C_{14}H_{20}As_2Fe$ calcd.: C, 42.68; H, 5.12; As, 38.03%.)

Fdma is insoluble in water and dissolved in all organic solvents to give very air-sensitive solutions.

Ferrocene-1,1'-*bis*(*dimethylarsine*) *monomethiodide*. When Fdma (1.05 g, 2.66 mmole) was treated with methyl iodide (10 ml, ca. 11.0 mmole) the product separated immediately. The mixture was allowed to stand for 1 h and the yellow crystals were removed by filtration. The crude product was recrystallized from hot butanol (30 ml), washed with petroleum ether (2 × 25 ml) and dried *in vacuo*. The filtrate was heated to boiling and treated with an equal volume of hot heptane to give a second crop of the fine yellow plates. The combined yield of the monomethiodide was 1.09 g (41%), m.p. 189–190.5 dec. (Found: C, 33.49; H, 3.98. $C_{15}H_{23}As_2FeI$: C, 33.62; H, 4.33%.)

Ferrocene-1,1'-*bis*(*dimethylarsine*) *dimethiodide*. The neat arsine Fdma (1.04 g, 2.64 mmole) was injected into a well-stirred solution of methyl iodide (10 ml, 11 mmole) in absolute ethanol (30 ml). The solution was refluxed with stirring for 14 h and allowed to cool. The solid was removed by filtration and extracted with hot butanol (4 × 25 ml) to remove traces of the monomethiodide. Recrystallization from hot methanol (200 ml), followed by washing with petroleum ether (3 × 25 ml) and drying *in vacuo* gave the product as golden needles (1.43 g, 80%), m.p. 252.5–254.0° dec. (Found: C, 28.22; H, 3.84. $C_{16}H_{26}As_2FeI_2$ calcd.: C, 28.35; H, 3.87%.)

Ferrocene-1,1'-*bis*(*dimethylarsine sulfide*). A mixture of Fdma (1.01 g, 2.56 mmole), sulfur (0.17 g, 5.3 mmole) and absolute alcohol (50 ml) was refluxed with stirring for $11\frac{1}{2}$ h. The product, which formed slowly during reflux, was removed by filtration and recrystallized from hot butanol (50 ml). Subsequent washing with petroleum ether (2 × 25 ml) and drying *in vacuo* gave 0.63 g of tiny golden flakes, which darkened gradually between 212–226° and melted sharply at 231.5°. (Found: C, 36.96; H, 4.52; S, 14.00. $C_{13}H_{20}As_2FeS_2$ calcd.: C, 37.84; H, 4.65; S, 14.19%.)

Ferrocene-1,1'-*bis*(*diphenylarsine*) (*Fdpa*).

The product was obtained in 57% yield utilizing a slurry of 1,1'-dilithioferrocene, as described above, and chlorodiphenylarsine. However, the isolation after hydrolysis was straightforward and carried out in air. The crude product was separated by filtration, washed with cold absolute ethanol (2 × 75 ml) and dried by suction. Two recrystallizations from dry heptane gave the pure product as long orange needles, m.p. 150–151° (lit.[4] 145–146.5°). The complex is air stable both in the solid and in solution. It is soluble in acetone, benzene and chloroform, sparingly soluble in aliphatic hydrocarbons and hot higher alcohols, and insoluble in water and lower alcohols. (Found: C, 63.67; H, 4.07; As, 23.71. $C_{34}H_{28}As_2Fe$ calcd.: C, 63.58; H, 4.39; As, 23.33%.)

Ferrocene-1,1'-*bis(diphenylarsine) dimethiodide.* The dimethiodide was obtained by refluxing Fdpa (2.0 g, 3.1 mmole) in excess methyl iodide (20 ml) for 9 h. The crude product obtained by decantation was recrystallized from ethanol (150 ml) to give clusters of golden needles (1.7 g, 59%), m.p. 166.5–167.5° dec. (Found: C, 46.46; H, 4.03. $C_{36}H_{34}FeAs_2I_2$ calcd.: C, 46.69; H, 3.70%.)

Ferrocene-1,1'-*bis(diphenylarsine sulfide).* An intimate mixture of the arsine Fdpa (1.01 g, 1.57 mmole) and sulfur (0.57 g, 16.0 mmole) was heated, under nitrogen, to 190° for 20 min. The pulverized product was extracted with small amounts of hot acetone until extracts were colorless. The combined extracts (*ca.* 100 ml) were evaporated slowly to *ca.* 50 ml. Cooling to −15° and filtration removed most of the sulfur. The filtrate was further concentrated to ca. 25 ml and slow cooling gave the product as large orange crystals (0.77 g). Two additional recrystallizations from hot methanol (*ca.* 140 ml) gave 0.34 g (33%) of pure product, m.p. 173.5–175.0°. (Found: C, 58.10; H, 4.33; S, 8.74. $C_{34}H_{28}As_2FeS_2$ calcd.: C, 57.81; H. 4.00; S, 9.08%.)

Ferrocene-1,1'-*bis(diphenylphosphine) (Fdpp)*

A mixture of *N,N,N',N'*-tetramethylethylenediamine (60.3 g, 0.520 mole) and a 15.20% (ca. 1.63 *N*) solution of n-butyllithium in hexane (315 ml, 0.513 mole) was added with stirring over a half-hour period to a solution of ferrocene (46.5 g, 0.250 mole) in 1500 ml dry hexane under nitrogen in a 3-liter, three-necked flask equipped with a stirrer, nitrogen inlet and reflux condenser. The solution was stirred for 4½ h at room temperature under nitrogen and then a solution of chlorodiphenylphoshine (95 ml, 0.51 mole) in 100 ml hexane was added dropwise over a 20 minute period with constant stirring. During this procedure the temperature of the solution rose to 48°. The reaction mixture was further stirred under nitrogen for two hours and then carefully quenched with 100 ml distilled water. The supernatant hexane layer was decanted from the brownish-orange solid and the solid was washed three times with 250 ml portions of distilled water and finally dissolved in 400 ml hot dioxane. Cooling this dioxane solution gave orange crystals (63.7 g, 46.0%), m.p. 181–183°. Concentration of the mother liquor on a rotary evaporator gave a second crop of slightly less pure product. The total yield was 70.0 g (51.0%). Recrystallization from 1/2 benzene/-heptane gave a purer sample, m.p. 183–184° (lit.[4] m.p. 182–184°). (Found: C, 73.84; H, 5.46; P, 11.19. $C_{34}H_{28}FeP_2$ calcd.: C, 73.66; H, 5.09; P, 11.17%.)

Ferrocene-1,1'-bis*(diphenylphosphine oxide).* A solution of bromine (0.9 ml, ca. 0.017 mole) in 25 ml benzene was added to a solution of Fdpp (4.98 g, 9 mmole) in benzene. After stirring for 15 min, the supernatant benzene solution was decanted from the resulting dark orange-red oil. The oil was hydrolyzed by heating in a solution of NaOH (3 g) in 50 ml water on a steam bath for 30 min, giving a tan-orange solid. This product was dissolved in 100 ml chloroform, dried over anhydrous $MgSO_4$, and filtered. Finally 200 ml hexane was added to the heated filtrate. Cooling gave a tan-orange crystalline product. Yield, 2.94 g (61%).

Recrystallization from absolute ethanol, followed by drying at 0.1 mm for 3 h at 70° gave dark orange crystals, m.p. 252–254.5°. (Found: C, 69.74; H, 4.94; P, 10.94. $C_{34}H_{28}FeO_2P_2$ calcd.: C, 69.64; H, 4.81; P, 10.56%.)

*Ferrocene-*1,1'*-bis(methyldiphenylphosphonium) diiodide.* The addition of CH_3I (1.0 ml, 1.1 mmole) to Fdpp (1.279 g 0.230 mmole) resulted in a lightly exothermic reaction. Benzene (20 ml) was added to the solids and the mixture was refluxed to complete the reaction and to dissolve any unreacted ligand. The hot benzene was decanted and the orange product was recrystallized from absolute ethanol (50 ml) to give a partially crystalline solid. Yield 1.09 g, 65.5%.

The crude product was recrystallized from absolute ethanol and washed with ethanol (2 × 10 ml) followed by pentane (3 × 20 ml) to give orange crystals, m.p. 244–245° (lit.[4] 223–228°). (Found: C, 51.82; H, 4.38. $C_{36}H_{34}FeI_2P_2$: calcd.: C, 51.58; H, 4.09%.)

*Ferrocene-*1,1'*-bis(diphenylphosphine sulfide).* A solution of sulfur (0.10 g, 3 mmole) in 25 ml hot butanol was added to a solution of Fdpp (0.60 g, 0.95 mmole) in 50 ml hot n-butanol and the mixture was refluxed for 15 min. On cooling, filtration, and washing with butanol and pentane, a yellow crystalline product was isolated. Yield 0.55 g (85%). Recrystallization from butanol and washing with butanol and pentane gave golden-yellow crystals, m.p. 244–246°. (Found: C, 66.25; H, 4.72; P, 9.90; S, 10.08. $C_{34}H_{28}FeP_2S_2$ calcd.: C, 66.02; H, 4.56; P, 10.02; S, 10.37%.)

The isolation of the adduct of 1,1'*-dilithioferrocene with N,N,N',N'-tetramethylethylenediamine*

To a 1-liter round-bottomed flask, equipped with a side-arm and a magnetic stirrer, ferrocene (85 g, 0.457 mole) was added. After the neck was sealed with a rubber septum, the flask was evacuated and refilled with nitrogen. A solution of n-butyllithium in hexane (1 mole ca. 750 ml, 11% excess) was added to the flask via a cannula. The suspension was rapidly stirred and freshly distilled *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (82.5 ml, 0.55 mole, 20% excess) was added dropwise during 1 h. During the addition the reaction mixture became quite warm, ca. 50°, and the ferrocene slurry reacted to give a deep cherry red solution. The reaction mixture was allowed to cool slowly with stirring for 10 h. The fine orange precipitate was filtered through a medium porosity sintered disc, using Schlenk tube techniques, and washed with hot, dry oxygen-free hexane (2 × 200 ml). Drying *in vacuo* (0.5 mm, 12 h) yielded a fine orange pyrophoric powder (120 g, 90%). (Found: C, 61.07; H, 7.38. $C_{16}H_{24}FeLi_2N_2$ calcd.: C, 61.18; H, 7.71%.)

The complex can be stored for long periods under oxygen-free nitrogen at room temperature.

1,2,3-*Trithia-*[3]*-ferrocenophane*

To a dry, nitrogen filled, 500 ml round-bottomed flask, equipped with a side arm, reflux condenser and a magnetic stirrer, was added 1,1'-dilithioferrocene · TMEDA (9.5 g, 30.5 mmole). The addition of dry oxygen-free 1,2-dimethoxyethane (300 ml) gave a clear, deep orange red solution. The addition of sublimed sulfur (6 g, 187 mmole) to the rapidly stirred solution caused it to warm and darken. The resulting mixture was refluxed for 12 h, cooled and then filtered through a bed of "Celite". The filtrate was treated with diethyl ether (150 ml) and washed with 10% aqueous sodium hydroxide (5 × 100 ml). The combined aqueous fractions were washed with diethyl ether (3 × 200 ml). The combined ether fractions were dried ($MgSO_4$) and the solvent removed by vacuum distillation to give a dark semi-solid. Vacuum sublimation of this material (0.3 mm, 160°, water cooled probe) gave dark orange crystals (4.4 g, 52%). Further purification was accomplished by dissolving small amounts of this material in a minimum of cold acetone and filtering to remove any remaining sulfur. Evaporation of the filtrate and recrystallization of the residue from benzene gave orange crystals of the analytically pure material, m.p. 149.5–150.5°. (Found: C, 42.95; H, 2.99; S, 34.15. $C_{10}H_8FeS_3$ calcd.: C, 42.98; H, 2.89; S, 34.42%.)

The mass spectrum (70 eV) showed peaks corresponding to the ions $[C_{10}H_8FeS_x]^+$, $x = 3$, 1 and 0, with other prominent peaks at *m/e* 246, 159, 152, 149, 100 and 56.

1,2,3-Trithia-[3]-ferrocenophane is air stable and readily soluble in both polar and non-polar organic solvents.

Ferrocene-1,1'-dithiol (Fdt). To a suspension of $LiAlH_4$ (1 g, 0.026 mole) in diethyl ether (200 ml) was added, in small portions, 1,2,3-Trithia-[3]-ferrocenophane (3.55 g, 0.127 mole). The reaction mixture became warm and evolved hydrogen sulfide. After stirring, for 2 h, under reflux the reaction mixture was poured onto 300 ml of ice-cold oxygen-free water. The addition of potassium hydroxide (5 g) gave an orange aqueous layer and a yellow ether layer. The aqueous layer was separated, extracted with diethyl ether (2 × 50 ml) and then acidified with concentrated HCl which caused the product to separate as a bright yellow suspension. The suspended material was extracted into 300 ml of ether and the solvent was removed *in vacuo*, to give the product as bright yellow crystals (3.05 g, 95%). This material proved to be pure enough for most purposes. However, an analytical sample was prepared by sublimation (0.3 mm, 80°, water cooled probe) to give clear yellow crystals, m.p. 59–60°. (Found: C, 48.00; H, 4.07; S, 25.61. $C_{10}H_{10}FeS_2$ calcd.: C, 48.13; H, 4.03; S, 25.63%.)

The mass spectrum (70 eV) showed prominent peaks corresponding to the ions $[(C_5H_4)_2Fe(SH)_x]^+$ ($x = 2$–0), other prominent peaks at *m/e* 154, 97, and 56.

The complex is moderately air sensitive in the solid; solutions, however, are more sensitive.

Ferrocene-1,1'-bis(dimethylphosphine) (Fdmp)

To a suspension of 15 g (0.478 mmole) of dilithioferrocene tetramethylenediamine in 100 ml of anhydrous hexane was added 1 ml (0.95 g, 1.015 mmole) of chlorodimethylphosphine in 25 ml of the same solvent. The resulting orange suspension was allowed to stir for 1 h and the mixture was then treated with an excess of solid carbon dioxide. The reaction mixture was first washed with aqueous sodium hydroxide (2 × 100 ml, 10%) and then extracted with aqueous hydrochloric acid (2 × 100 ml, 10%). Neutralization of the yellow aqueous layer caused the product to separate as an emulsion. It was extracted with 100 ml of diethyl ether. The ether layer was dried ($MgSO_4$) and fractionally distilled. The product was collected as a dark red oil (1.25 g, 84%, b.p. 104–108°/0.05 mm) and stored under nitrogen. (Found: C, 54.38; H, 6.60. $C_{14}H_{20}FeP_2$ calcd.: C, 54.95; H, 6.54%.)

Nuclear magnetic resonance spectral data (τ)

Fdma: 5.93, triplet, *J* 1.6, (1); 5.86, triplet, *J* 1.7, (1); 8.86, singlet, (3); (CCl_4).
Fdpa: 2.75, singlet, (5); 5.87, triplet, *J* 1.7, (1); 6.08, triplet, *J* 1.7, (1); (CCl_4).
Fdmp: 5.83, singlet (2); 8.87, doublet, $J(P\text{–}CH_3)$ 17.0 (3); ($CDCl_3$).

Fdpp: 3.29–3.38, multiplet, (5); 6.13, triplet, *J* 1.6, (1); 6.35, triplet, *J* 1.6 (1); (CCl_4).

Fdt: 5.83, complex (4); 7.18, singlet, (1); ($CDCl_3$).

Infrared spectra

Fdma (*neat*): 3086 m, 2978 vs, 2908 s, 2850 w, 2805 w, 1418 s, 1410 s, 1373 m, 1314 w, 1255 m, 1237 w, 1192 m, 1150 vs, 1049 w, 1026 vs, 882 m, 841 s, 821 s, 610 w, 577 m, 563 m, 500 s, 484 m.

Fdma (CH_3I) (*Kel-F and Nujol Mulls*): 3066 m, 2965 s, 2895 m, 1420 m, 1380 w, 1327 w, 1317 w, 1279 m, 1270 w, 1259 w, 1195 w, 1172 m, 1163 m, 1149 m, 1036 s, 1019 m, 939 vs, 926 s, 885 s, 861 m, 844 s, 835 vs, 829 s, 815 s, 800 m, 640 m, 614 w, 594 m, 581 w, 561 m, 505 s, 495 s, 487 vs.

Fdma $(CH_3I)_2$ (*Kel-F and Nujol*): 3070 m, 3056 m, 2975 s, 2897 m, 1410 w, 1390 m, 1330 w, 1300 w, 1290 w, 1279 w, 1270 w, 1178 w, 1166 s, 1070 w, 1045 w, 1031 m, 937 vs, 926 s, 918 (sh), m, 892 m, 867 m, 847 s, 862 w, 815 m, 648 w, 639 w, 606 w, 594 w, 486 vs.

FdmaS_2 (*Kel-F and Nujol*): 3070 w, 3060 w, 2970 w, 2895 w, 1402 w, 1380 m, 1328 w, 1269 w, 1252 m, 1162 s, 1039 w, 1022 s, 901 s, 868 s, 882 s, 878 (sh), s, 842 w, 828 m, 819 m, 619 m, 601 s, 508 m, 490 m, 475 vs.

Fdpa (CCl_4): 3140 w, 3090 (sh), m, 3075 vs, 3060 vs, 3030 m, 3015 m, 3000 m, 2700 vw, 2650 vw, 2600 vw, 1960 m, 1945 m, 1885 m, 1870 m, 1810 m, 1750 w, 1690 w, 1645 m, 1575 m, 1485 vs, 1450 sh, w, 1440 vs, 1410 w, 1380 m, 1330 m, 1307 m, 1275 w, 1235 w, 1195 m, 1187 m, 1152 vs, 1082 s, 1077 vs, 1069 m, 1058 m, 1027 vs, 1000 m, 908 w, 882 m, 876 (sh), w, 860 vw, 827 w, 694 vs, 660 w, 612 w, 499 s.

Fdpa $(CH_3I)_2$ (*Nujol*): 1607 m, 1574 w, 1481 s, 1439 vs, 1403 m, 1310 m, 1215 m, 1187 m, 1174 m, 1163 vs, 1089 vs, 1066 m, 1051 w, 998 vs, 927 m, 920 m, 915 s, 899 s, 894 vs, 880 m, 860 m, 847 m, 829 m, 820 s, 739 vs, 687 vs, 633 vw, 625 w, 609 vw, 599 m, 492 m, 475 s, 456 vs.

FdpaS_2 (*Nujol*): 3126 w, 3046 w, 1959 w, 1886 w, 1816 w, 1761 w, 1656 w, 1576 m, 1478 vs, 1459 m, 1438 s, 1433 vs, 1379 m, 1351 w, 1324 w, 1310 m, 1201 w, 1187 m, 1164 s, 1157 s, 1083 vs, 1068 m, 1033 s, 1023 vs, 1000 m, 973 w, 924 w, 917 w, 906 w, 888 w, 878 w, 868 w, 835 m, 825 s, 742 vs, 738 vs, 690 vs, 673 w, 607 w, 495 vs, 483 s, 470 s, 454 vs.

Fdpp (*Nujol*): 3055 w, 1580 w, 1475 s, 1430 s, 1309 m, 1195 m, 1181 w, 1165 vs, 1092 m, 1068 m, 1029 s, 998 w, 890 w, 880 w, 844 m, 828 vs, 745 vs, 698 vs, 629 m, 526 s, 509 s, 491 vs, 472 vs, 444 vs, 410 s.

FdppO_2 (*Nujol*): 3095 w, 3070 w, 1580 w, 1475 w, 1440 s, 1317 w, 1209 s, 1190 s, 1180 (sh), 1167 s, 1117 vs, 1097 m, 1075 m, 1057 m, 1041 m, 1027 m, 993 w, 890 w, 866 w, 842 w, 825 s, 754 s, 719 s, 697 s, 565 vs, 524 s, 486 s, 476 (sh), w, 440 m, 419 w.

FdppS_2 (*Nujol*): 3065d w, 1575 w, 1475 w, 1435 s, 1310 m, 1197 m, 1186 w, 1176 vs, 1161 w, 1103 vs, 1067 w, 1034 m, 1024 m, 995 w, 828 s, 751 vs, 740 m, 712 vs, 689d s, 645d s, 620 m, 609 m, 537 vs, 497 m, 482 s, 470 s, 456 m, 423 s.

Fdpp $(CH_3I)_2$ (*Nujol*): 3055 w, 1580 vs, 1470 w, 1430 m, 1319 w, 1187 s, 1120 s, 1040 m, 995 w, 926 m, 909 m, 822 w, 780 w, 751 (sh), 743 vs, 719 w, 685 s, 615 w, 522 s, 474 m, 460 vs, 423 w.

1,2,3-*Trithia*-[3]-*ferrocenophane* (*Nujol*): 1202 w, 1195 w, 1175 w, 1160 m, 1155(sh), 1025 s, 1015 s, 1007 (sh), 891 m, 877 w, 866 w, 855 w, 845 w, 832 m, 817 s, 717 w.

Fdt (*Nujol*): 2521 m, 2491 w, 1169 m, 1023 m doublet, 898 m, 880 w, 844 w, 826 w, 812 m.

Fdmp (*neat*): 3090 s, 2960 vs, 2900 s, 2809 m, 1422 vs, 1382 s, 1312 m, 1287 s, 1272 s, 1192 s, 1162 s, 1032 s, 942 s, 907 s, 862 (sh), 710 s, 670 s.

RESULTS AND DISCUSSION

In hexane solutions ferrocene can be dilithiated quite smoothly[1,2] by mixtures of n-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The red-orange crystalline solid which separates during this procedure can be readily isolated and has been shown to be $(C_5H_4Li)_2Fe \cdot TMEDA$. It is pyrophoric but can be handled using standard Schlenk or glove box techniques. This adduct is readily soluble in 1,2-dimethoxyethane to give deep orange-red solutions. The use of the solid lithium reagent has been found superior in some preparations to the *in situ* use of the slurries produced in the metalation reaction. The phosphine and arsine complexes, Fdpp, Fdma, and Fdpa were prepared in good ca. 50% yields by reacting the hexane slurry of dilithioferrocene with the appropriate halophosphine or arsine. The distinct advantages in these preparations over those discussed previously[3,4] for Fdpa are the high yields and that no monosubstituted products are obtained. Thus the procedure represents a convenient "one pot" reaction for producing large amounts of these potential ligands from readily available materials. By utilizing solid $(C_5H_4Li)_2Fe \cdot TMEDA$ the overall yields can be substantially improved to ca. 85–90%.

The methyl derivatives, Fdma and Fdmp, are dark red malodorous liquids, moderately air stable as neat liquids, but they are extremely air sensitive in solution. Their IR and NMR spectra are clearly in accord with their formulation as symmetrically disubstituted ferrocenes. The diarsine Fdma was converted quantitatively to ferrocene by refluxing ethanolic hydrochloric acid solutions.

The phenyl complexes Fdpa and Fdpp were obtained as orange, crystalline, non-volatile solids, which are air stable in both the solid and solution. In contrast to Fdma, Fdpa is not degraded to ferrocene by refluxing alcoholic hydrochloric acid solutions. Unlike Fdpp, Fdpa did not give a well-characterized dioxide.

Under a variety of conditions the hexane slurries of dilithioferrocene did not give tractible products with elemental sulfur. However, refluxing $(C_5H_4Li)_2Fe \cdot TMEDA$ and sulfur in 1,2-dimethoxyethane gave good yields of 1,2,3-trithia-[3]-ferrocenophane. The complex is an air stable, orange crystalline material which can be readily sublimed. Its NMR spectrum is temperature dependent and the fluxional behavior has been described previously[11]. Reduction with $LiAlH_4$ and subsequent work-up gives an almost quantitative conversion to ferrocene-1,1'-dithiol (Fdt) as a volatile, moderately air sensitive solid whose NMR and IR spectrum are in accord with its formulation. The complexes function as bidentate ligands with metals in a variety of oxidation states and the chemistry of these complexes will be described elsewhere.

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support by the National Science Foundation (Grants GP-6672 and GP-11001): The American Chemical Society, a Petroleum Research Fund Graduate Fellowship, 1968–1969 (J.J.B.).

REFERENCES

1 M. L. KATCHER, *B.S. Thesis, M.I.T.*, 1967.
2 M. D. RAUSCH AND D. J. CIAPPENELLI, *J. Organometal. Chem.*, 10 (1967) 127.
3 G. P. SOLLOTT AND E. HOWARD JR., *J. Org. Chem.*, 27 (1962) 4034; G. P. SOLLOTT, H. E. MERTWOY, S. PORTNOY AND J. L. SNEED, *J. Org. Chem.*, 28 (1963) 1090.
4 G. P. SOLLOTT, J. L. SNEED, S. PORTNOY, W. R. PETERSON JR. AND H. E. MERTWOY, *U.S. Dep. Comm. Office Tech. Services, A.D. G11869*, Vol. II, (1965) 441.
5 W. J. CELLAND AND P. L. PAUSON, unpublished work, as quoted by W. E. WATTS, *Organometal. Chem. Rev.*, 2 (1967) 231.
6 W. J. CELLAND AND P. L. PAUSON, unpublished information quoted by G. MARR AND T. HUNT, *J. Chem. Soc. C.*, (1969) 1070.
7 R. L. BARKER, E. BOOTH, W. E. JONES AND F. N. WOODWARD, *J. Soc. Chem. Ind., (London)*, 68 (1949) 277.
8 G. J. BURROWS AND E. E. B. TURNER, *J. Chem. Soc.*, (1920) 1373.
9 R. D. FELTHAM, A. KASENELLY AND R. S. NYHOLM, *J. Organometal. Chem.*, 7 (1967) 285.
10 H. E. ULMER, L. C. D. GROENWEGHE AND L. MAIER, *J. Inorg. Nucl. Chem.*, 20 (1961) 82.
11 A. DAVISON AND J. C. SMART, *J. Organometal. Chem.*, 19 (1969) P7.