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THE ISOLATION, CHARACTERIZATION AND SYNTHETIC UTILITY OF SEVERAL SOLID ORGANOLITHIUM COMPOUNDS

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SUMMARY

Pentachlorophenyllithium and ferrocenyllithium have been isolated and characterized as relatively air-stable solids. The chemical reactivity of these organolithium compounds has been investigated, and several carbene complexes of chromium and tungsten have been prepared. Pentachlorophenyllithium adds to furan and therefore represents a solid benzyne precursor. 1,1′-Dilithioferrocene·2TMEDA, ferrocenyllithium·TMEDA, and 2-lithio[(dimethylamino)methyl]ferrocene were isolated and characterized as air-sensitive solids. An attempted formation of 2,2′-dilithiobiphenyl from 2,2′-dibromobiphenyl and n-butyllithium yielded a mixture of ca. 80% of this dilithium reagent and ca. 20% of 2-bromo-2′-lithiobiphenyl.

INTRODUCTION

The synthetic utility of organolithium reagents in organic and organometallic chemistry has long been recognized, although these intermediates are generally prepared and utilized in solution, and are rarely isolated[1]. NMR data is available for several isolable aryllithium compounds[2] as well as for 4-tert-butylcyclohexyllithium[3], and X-ray crystallographic studies have been recently reported for benzyllithium·triethylenediamine[4] and for methyllithium[5]. During the course of some recent studies in synthetic and structural organometallic chemistry, we have had occasion to attempt the isolation and characterization of certain solid organolithium compounds.

CAUTION

Most organolithium compounds react vigorously with air and moisture, and several highly halogenated aryllithium reagents have been reported to explode in solution[6–8]. We wish to draw special attention to the potential explosion hazard associated with the preparation of pentachlorophenyllithium (I).

RESULTS AND DISCUSSION

Pentachlorophenyllithium (I) has been isolated as a white solid from a

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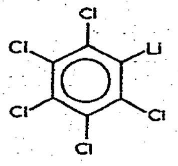
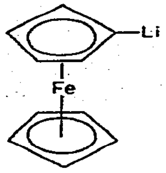


(I)



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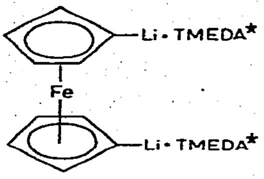

(III)

reaction between hexachlorobenzene and n-butyllithium at −78°[9]. The product must be filtered under nitrogen and dried at temperatures below ca. −40°, since on several initial attempts to isolate and dry (I) at room temperature, the product exploded during the drying process. Apparently at ambient temperatures in contact with an ethereal solvent, (I) undergoes spontaneous loss of lithium chloride, since it is known to be an excellent precursor to tetrachlorobenzyne[10]. When proper conditions are employed (see Experimental section), (I) can be safely isolated, and once it is dry, it was found to be *stable in air*. Attempted melting point determinations of (I) both in air and under nitrogen were unsuccessful, since the compound slowly decomposed on heating. It is significant that no explosion was observed on heating (I), suggesting that the carbon–lithium bond in (I) exhibits appreciable covalent character, and that the formation of tetrachlorobenzyne from (I) is solvent-assisted[11]. Small amounts of (I) could be dissolved in benzene or toluene under nitrogen and recovered unchanged.

Solid (I) was characterized by a total elemental analysis. Chemical characterization was carried out by reactions of solid (I) with dilute hydrochloric acid, with benzophenone, and with carbon dioxide followed by hydrolysis. The remarkable air-stability of (I) was also demonstrated by the following experiment. Four samples of (I) were weighed out in the air, and subsequently allowed to react with benzophenone after standing in the air for periods of 0, 2, 5, and 8 hours. These reactions resulted in isolated yields of purified diphenyl(pentachlorophenyl)methanol of 80, 77, 79, and 75%, respectively. The remarkable properties of (I) are undoubtedly due in part to the relatively large flanking *ortho*-chlorine atoms which tend to shield the carbon–lithium bond from chemical reaction. The enhanced stability of (I) relative to most other organolithium compounds is reminiscent of the highly stabilized carbonium ions, free radicals, and carbanions containing a pentachlorophenyl substituent which have been described in recent years by Ballester and his coworkers[12].

Ferrocenyllithium (II) as well as the chelated dilithium reagent, 1,1′-dilithioferrocene·2TMEDA (III), were isolated as orange solids and were characterized by total elemental analyses**. Surprisingly, (II) was also found to be moderately stable in air, showing no sign of hydrolysis to ferrocene, whereas (III) was pyrophoric

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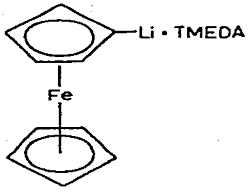
* TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

** Both solid (II) and (III) have been isolated previously. A reaction between ferrocene and 3 equivalents of n-butyllithium in ethyl ether solution afforded (II) admixed with 1,1′-dilithioferrocene, however, the products were not separated[13]. The chelated dilithium reagent (III) was isolated by Bishop *et al.* recently, and was indicated to contain only one TMEDA ligand on the basis of combustion analysis[14]. Our results, based on a *total* elemental analysis, suggest that structure (III) containing two TMEDA ligands is a more correct formulation.

in contact with air. When (II) was stirred in hexane solution with TMEDA, orange ferrocenyllithium·TMEDA (IV) was isolated. The chelated lithium reagent (IV) was air-sensitive, but was not pyrophoric, as might have been anticipated from the behavior of (III). Chemical characterization of (II) and (III) was effected by reactions with dilute sulfuric acid and with benzophenone, to give ferrocene and the respective ferrocenemethanol in high yields. Solid (II) was also carbonated to give, after hydrolysis, ferrocenoic acid in 75% yield.



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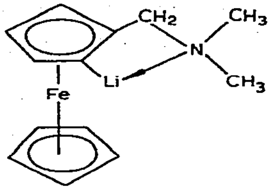
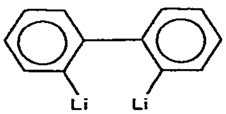


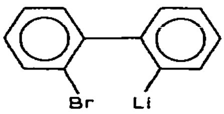
(V)

In view of the successful isolation of (II) and (III), it was of interest to attempt the isolation and characterization of 2-lithio[(dimethylamino)methyl]ferrocene (V). Lithium reagent (V) as formed in solution has been found to be a very important intermediate in the synthesis of 1,2-disubstituted ferrocenes[15]. 2-Lithio[(dimethylamino)methyl]ferrocene (V) was in fact isolated from a reaction between n-butyllithium and [(dimethylamino)methyl]ferrocene as an extremely air-sensitive pink solid, and was characterized by a total elemental analysis. The compound is not pyrophoric, but immediately decomposes and turns yellow when exposed to air.

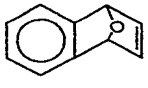
In connection with our studies in metallocycle chemistry, it was also of interest to attempt the isolation of a dilithium reagent, 2,2′-dilithiobiphenyl (VI). Dilithium reagent (VI) has been reported to be formed in good yield from a reaction between 2,2′-dibromobiphenyl and n-butyllithium in ethyl ether solution[16]. In our studies, total elemental analyses of the reaction product after filtration and evaporation of the solvent never gave satisfactory results for pure (VI). In each run, bromine was found to be present in the product, even when a five-fold ratio of n-butyllithium to 2,2′-dibromobiphenyl was used. The analytical results consistently indicated that the product was composed of ca. 70–80% (VI), with the remainder being the product of partial bromine–lithium exchange, 2-bromo-2′-lithiobiphenyl (VII).



(VI)



(VII)



(VIII)

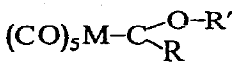
In order to confirm this result, a sample of the reaction product was subjected to controlled hydrolysis, and the products were analyzed by gas chromatography. Only two hydrolysis products, biphenyl and 2-bromobiphenyl, were found to be present, and were identified by comparing their retention times with those of authentic samples. Integration indicated that the hydrolysis product contained 81% biphenyl and 19% 2-bromobiphenyl, in good agreement with the results of elemental analysis.

The starting material, 2,2′-dibromobiphenyl, could not be detected in the hydrolysis mixture.

The handling of these air-sensitive organolithium compounds in preparation for elemental analysis requires special comment. Reliable analyses were obtained only when a sample of the material to be analyzed was transferred in an inert atmosphere into a pre-weighed capsule. By carefully folding and crimping the capsule, it can be made air-tight and then re-weighed prior to elemental analysis. Tin capsules were used in connection with carbon–hydrogen determinations, since tin does not interfere with this analysis. The air-sensitive organolithium compounds were transferred into gelatin capsules under an inert atmosphere when samples were weighed for lithium and halogen analyses.

In addition to our interest in these solid organolithium compounds from structural and stability considerations, their utility as synthetic intermediates was also investigated. We have found, for example, that (I) can be weighed in air, dissolved in ethyl ether, and then treated with furan to afford a good yield of 5,8-epoxy-1,2,3,4-tetrachloro-5,8-dihydronaphthalene (VIII). Therefore (I) represents a stable solid benzyne precursor.

Both (I) and (II) have been used in the preparation of several ferrocenyl– and pentachlorophenyl–carbene complexes of Group VIB metals. The pentachlorophenyl–carbene complexes (IX) and (X) were prepared from (I) and tungsten hexacarbonyl in ethyl ether at −78°, followed by treatment with the appropriate trialkyloxonium tetrafluoroborate salt. Formation of the ferrocenylcarbene complex (XI) proceeded readily when (II) was allowed to react with chromium hexacarbonyl under similar conditions, followed by reaction with trimethyloxonium tetrafluoroborate. The proton NMR spectra of (IX), (X), and (XI) were consistent with their proposed structures in each case[*].



$$(CO)_5M-C\begin{matrix}\nearrow O-R' \\ \searrow R\end{matrix}$$

(IX) $R=C_6Cl_5, R'=C_2H_5, M=W$
(X) $R=C_6Cl_5, R'=CH_3, M=W$
(XI) $R=FeC_{10}H_9, R'=CH_3, M=Cr$
(XII) $R=FeC_{10}H_9, R'=C_2H_5, M=Cr$

(XIII) $R=C_6H_5, R'=C_2H_5, M=W$
(XIV) $R=C_6Cl_5, R'=C_2H_5, M=Cr$
(XV) $R=C_6Cl_5, R'=CH_3, M=Cr$
(XVI) $R=C_6H_5, R'=CH_3, M=Cr$

The metal–carbonyl stretching frequencies of these new carbene complexes are summarized in Table 1, together with frequencies obtained earlier for several similar complexes[17–19]. The effect of changing the alkoxy substituent from $R'=C_2H_5$ (XII) to $R'=CH_3$ (XI) does not change the ν(CO) frequency to any significant extent. The ν(CO) frequencies for the [(pentachlorophenyl)carbene]tungsten complexes (IX) and (X) are raised relative to the phenyl analog (XIII). This result is in accord with the highly electronegative nature of the pentachlorophenyl group, as was observed earlier in the chromium series of complexes[17]. On the other hand, the increase in the ν(CO) of the high energy A_1 mode of (IX) and (X) compared to

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[*] Two pieces of data in ref. 17 were unfortunately incorrectly reported. The NMR data for (ethoxyferrocenylcarbene)pentacarbonylchromium (XII) were recorded in $CDCl_3$, not in C_6D_6, and for the methyl proton triplet appearing at τ 8.38, J 7 Hz and not 12 Hz.

TABLE 1

ν(CO) STRETCHING FREQUENCIES OF SOME CARBENE COMPLEXES OF CHROMIUM AND TUNGSTEN[a]

Complex	*R'*	*R*	*M*	A_1	A_1	*E*	B_1	*Ref.*
(IX)	C_2H_5	C_6Cl_5	W	2074	1967	1947	1994	[b]
(X)	CH_3	C_6Cl_5	W	2077	1970	1946	1997	[b]
(XI)	CH_3	$FeC_{10}H_9$	Cr	2054	1952	1940	1979	[b]
(XII)	C_2H_5	$FeC_{10}H_9$	Cr	2055	1947	1934	1976	17
(XIII)	C_2H_5	C_6H_5	W	2070.5	1958.0	1948.0 1941.0	1984.5 calcd.	18
(XIV)	C_2H_5	C_6Cl_5	Cr	2070	1972	1955	1998	17
(XV)	CH_3	C_6Cl_5	Cr	2070	1973	1955	1996	17
(XVI)	CH_3	C_6H_5	Cr	2060	1963	1952	1986	19

[a] Measured in n-hexane and given in cm^{-1}. [b] This work.

their respective chromium analogs (XIV) and (XV) reflects the influence of a change in the metal atom. The increase in this symmetric mode in the tungsten complexes suggests that backdonation of the metal to the antibonding orbitals on the carbonyl ligand is reduced for tungsten compared to chromium, thereby formally increasing the carbon–oxygen bond order and hence the stretching frequency. The same trend is observed in the case of the phenyl–carbene complexes (XVI) and (XIII). While the R' group is different in these latter two complexes, it has been shown in this and earlier work[17] that such a change does not appreciably affect the frequency of the A_1 mode, and hence the observed values largely reflect electronic effects due to a change in the metal atom.

EXPERIMENTAL

Ethyl ether was purified by drying over calcium chloride followed by distillation under nitrogen from benzophenone sodium radical. Hexane was purified by distillation under nitrogen from calcium hydride. Hexachlorobenzene (Fluka AG), ferrocene (Alfa Inorganics), chromium hexacarbonyl (Strem), and tungsten hexacarbonyl (Climax) were used without further purification. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (Eastman) was distilled through a Vigreux column, collecting the fraction that distilled between 120–121°; the diamine was protected from the light while stored. Commercial n-butyllithium in hexane was obtained from Alfa Inorganics, Inc., while trimethyloxonium tetrafluoroborate was a gift from Prof. Dr. E. O. Fischer. Triethyloxonium tetrafluoroborate[20], [(dimethylamino)-methyl]ferrocene[21], 2,2'-dibromobiphenyl[22], 2-bromobiphenyl[23], and bromoferrocene[24] were prepared according to literature methods. NMR spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard, while IR spectra were recorded on a Perkin–Elmer Model 21 spectrophotometer and were calibrated with polystyrene. Elemental analyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass.

Isolction of pentachlorophenyllithium (I)

A slurry of hexachlorobenzene (3.00 g, 10.5 mmoles) in 50 ml of anhyd. ethyl ether was cooled to −78° in a nitrogen-purged 100-ml round-bottom flask. n-Butyllithium (4.7 ml, 10.5 mmoles) was added dropwise from a syringe over a period of 10 min. Stirring was continued at −78° for 2 h during which time the slurry of hexachlorobenzene disappeared to give a slightly straw-colored solution. This solution was filtered through a glass-fritted (25–50 μ) Schlenk-type nitrogen filtration apparatus, equipped with a Dewar-jacket, at −78° under nitrogen, and collected in a purged, pre-cooled (−78°) Schlenk tube. The Schlenk tube was then transferred to a cooling bath maintained at −40° to −45°, and the ether was removed under reduced pressure. When only a small amount of ether remained, 10 ml of hexane (cooled to −78°) was added, causing the separation of a slightly cream-colored crystalline solid. This solid was filtered on a glass frit under nitrogen at −78°, using the filtration apparatus described above. The solid was washed eight times with 10-ml portions of hexane. The fitration apparatus was maintained at −78°, transferred to a vacuum system, and the solid was dried for ca. 8 h. This step is very critical, and at no time until the solid is completely dry should the temperature be raised above ca. −40°. Attempts to isolate and dry (I) at ambient temperatures resulted in a rather powerful explosion on several occasions. Once (I) is completely dry, it may be handled at room temperature in air without complications. This procedure produced 2.12 g (79%) of white, solid (I). (Found: C, 28.20; H, 0.12; Cl, 69.10; Li, 2.36. C_6Cl_5Li calcd.: C, 28.12; H, 0; Cl, 69.17; Li, 2.71%.)

Hydrolysis of (I)

Solid pentachlorophenyllithium (I) (0.300 g, 1.16 mmoles) dissolved in 30 ml of ethyl ether was stirred in a 100-ml round-bottom flask. Under nitrogen, 5% hydrochloric acid was added dropwise, and stirring was continued for 8 h. The organic layer was separated and dried over anhyd. magnesium sulfate. Evaporation of the ether afforded crude pentachlorobenzene, which when recrystallized from pentane gave 0.272 g (93%) of white needles, m.p. 87° (lit.[9] m.p. 87.8–88.6°).

Diphenyl(pentachlorophenyl)methanol

Solid pentachlorophenyllithium (I) (0.300 g, 1.16 mmoles) dissolved in 30 ml of ethyl ether was stirred in a 100-ml round-bottom flask. Benzophenone (0.213 g, 1.16 mmoles) in 25 ml of ethyl ether was added dropwise, and stirring was continued for 8 h. The ether solution was poured into 50 ml of water, the layers were separated, the ether portion was washed with water, and was dried over anhyd. magnesium sulfate. Evaporation of the ether yielded a white solid which was recrystallized from hexane to give 0.416 g (80%) of pale-yellow crystals of diphenyl(pentachlorophenyl)-methanol, m.p. 152° (lit.[9] m.p. 152.5–153.8°).

At the same time, three additional 0.300 g samples of solid pentachlorophenyllithium were prepared and allowed to stand in the air. After periods of 2, 5, and 8 h, one of these samples was allowed to react with benzophenone under identical conditions as described above, resulting in isolated yields of purified diphenyl-(pentachlorophenyl)methanol of 77, 79, and 75%, respectively.

Pentachlorobenzoic acid

A large amount of crushed dry ice was added to a purged 250 ml round-bottom flask fitted with a nitrogen inlet and covered with anhyd. ethyl ether. Solid pentachlorophenyllithium (I) was dissolved in ether, carefully added to this stirred slurry, and the mixture was allowed to warm to room temperature. After stirring for 24 h, the ether was extracted with water (3 × 10 ml). Acidification of the aqueous extracts with 10% sulfuric acid produced 0.224 g (66%) of pale-yellow pentachlorobenzoic acid, m.p. 207° (lit.[9] m.p. 208.5–210°).

5,8-*Epoxy*-1,2,3,4-*tetrachloro*-5,8-*dihydronaphthalene* (*VIII*)

Solid pentachlorophenyllithium (I) (0.300 g, 1.16 mmoles) dissolved in 30 ml of anhyd. ethyl ether was cooled to −78° in a nitrogen atmosphere and 5.0 ml of freshly distilled furan was added dropwise over a 15 min period. The reaction mixture was allowed to warm to room temperature at its own rate, and stirring was continued for 40 h. After this time, the solvent was removed at reduced pressure to yield a dark-tan solid. Column chromatography (alumina, 5% water added, 2 cm × 40 cm) with 50% hexane/benzene elution produced a colorless fraction, presumably pentachlorobenzene, and a slightly yellow band. Evaporation of the solvent from the latter band followed by vacuum sublimation ($90°/10^{-3}$ mmHg) afforded 0.217 g (67%) of 5,6-epoxy-1,2,3,4-tetrachloro-5,8-dihydronaphthalene, m.p. 119° (lit.[10] m.p. 119.5–120.5°).

[*Alkoxy*(*pentachlorophenyl*)*carbene*]*pentacarbonyltungsten complexes*

A solution of solid pentachlorophenyllithium (I) (0.512 g, 2.0 mmoles) in 40 ml of anhyd. ethyl ether was cooled to −78° and added in one step under nitrogen to 250 ml of ether containing tungsten hexacarbonyl (0.705 g, 2.0 mmoles) which had also been cooled to −78°.

The ether solution was allowed to warm to room temperature during which time it became yellow. After 1 h of rapid stirring at room temperature, the ether was removed at reduced pressure to yield a light yellow solid. This solid was dissolved in 100 ml of deoxygenated water, and trimethyloxonium tetrafluoroborate (0.294 g, 2.0 mmoles) was added in one step to yield a flesh pink solution. Rapid stirring was continued for 30 min after which time the orange aqueous solution was extracted with nitrogen-saturated ethyl ether (3 × 50 ml). The ether extracts were dried over anhyd. magnesium sulfate, and the ether was evaporated to give an orange solid. Recrystallization of the product from benzene/heptane gave 0.468 g of deep-red crystals of [methoxy(pentachlorophenyl)carbene]pentacarbonyltungsten (X), m.p. 129°. (Found: C, 25.52; H, 0.52; Cl, 28.53; O, 15.60. $C_{13}H_3Cl_5O_6W$ calcd.: C, 25.33; H, 0.49; Cl, 28.76; O, 15.58%.) NMR spectrum (C_6H_6): τ 6.42 (s, $-OCH_3$). Mol. wt.: found, 612 (mass spectrometry); calcd., 612.

[Ethoxy(pentachlorophenyl)carbene]pentacarbonyltungsten (IX) was prepared in a similar manner with the exception that triethyloxonium tetrafluoroborate (0.380 g, 2.0 mmoles) was used. The product was recrystallized from heptane to give 0.412 g (33%) of orange-red crystals, m.p. 117.5°. (Found: C, 26.99; H, 0.77; Cl, 26.92; O, 15.50; W, 29.55. $C_{14}H_5Cl_5O_6W$ calcd.: C, 26.68; H, 0.80; Cl, 28.12; O, 15.23; W, 29.17%.) NMR spectrum (C_6D_6): τ 8.89 (t, 3, J 7 Hz, $-OCH_2CH_3$); 5.72 (m, 2, $-OCH_2CH_3$).

Isolation of ferrocenyllithium (*II*)

Ferrocenyllithium (II) was prepared from n-butyllithium in hexane (0.85

ml, 1.89 mmoles) and bromoferrocene (0.500 g, 1.89 mmoles) in 25 ml of ethyl ether under nitrogen as described in the literature[25]. As the reaction mixture warmed to room temperature, an orange solid was observed to separate from the ether layer. The solid was collected on a glass frit under a nitrogen atmosphere, washed with hexane until the washings were colorless (5 × 20 ml), and dried *in vacuo* to yield 0.314 g (87 %) of orange (II). (Found: C, 62.38; H, 4.65; Fe, 29.15; Li, 3.60. $C_{10}H_9FeLi$ calcd.: C, 62.56; H, 4.73; Fe, 29.09; Li, 3.61 %.)

Hydrolysis of (II)

Solid ferrocenyllithium (II) (0.192 g, 1.0 mmole), suspended in 20 ml of ethyl ether under nitrogen, was shaken with 20 ml of 10% sulfuric acid. The aqueous layer was extracted with ethyl ether and the extracts were dried over anhyd. magnesium sulfate. The orange solid remaining after evaporation of the ether was sublimed to produce 0.169 g (91 %) of ferrocene, m.p. 173° (lit.[26] m.p. 173–174°).

(Diphenylhydroxymethyl)ferrocene

Solid ferrocenyllithium (II) (0.384 g, 2.0 mmoles) was suspended in 50 ml of anhyd. ethyl ether. A solution of benzophenone (0.473 g, 2.60 mmoles) in 100 ml of ethyl ether was added and the reaction mixture was allowed to stir for 6 h at room temperature. After hydrolysis with 100 ml of cold water, the organic layer was separated, dried, and chromatographed on alumina. Elution with hexane removed ferrocene (0.010 g, 3 %), while (diphenylhydroxymethyl)ferrocene (0.624 g, 82 %) was obtained with benzene elution; m.p. 135° (lit.[27] 133–136°.)

Ferrocenoic acid

Solid ferrocenyllithium (II) (0.288 g, 1.5 mmoles) was added to a slurry of 20 ml of anhyd. ethyl ether and an excess of dry ice. The reaction mixture was allowed to warm to room temperature. The ether solution was extracted with water (2 × 30 ml) and the orange aqueous portion was acidified. The solid when formed was filtered and dried to yield 0.260 g (75 %) of ferrocenoic acid, m.p. 205° dec. (lit.[28] 208.5° dec.).

[Methoxyferrocenylcarbene]pentacarbonylchromium (XI)

A slurry of ferrocenyllithium (II) (0.480 g, 2.50 mmoles) in 35 ml of anhyd. ethyl ether was cooled to −78°. Chromium hexacarbonyl (0.55 g, 2.50 mmoles) and 250 ml of ethyl ether were cooled to −78° under nitrogen. The slurry of (II) was added in one portion to the chromium hexacarbonyl/ether mixture. Stirring was continued for 12 h as the orange reaction mixture was allowed to warm to room temperature. The ether was removed under reduced pressure to give an orange solid. Nitrogen-saturated water (150 ml) was added, and trimethyloxonium tetrafluoroborate (0.370 g, 2.50 mmoles) was also added in one portion, producing a deep-purple solution. Hexane (100 ml) was added and stirring was continued for 15 min. The hexane and aqueous layers were separated, and the latter was extracted with ethyl ether (2 × 100 ml). The combined hexane and ether layers were evaporated to dryness to produce purple crystals. Recrystallization of the product from benzene/heptane yielded 0.380 g of purple (XI), m.p. 170° dec. (softens at 135°). The yield was 36 %. (Found: C, 48.73; H, 3.05; Cr, 12.40; Fe, 13.32; O, 22.69. $C_{17}H_{12}CrFeO_6$ calcd.: C, 48.60; H, 2.88; Cr, 12.38; Fe, 13.29; O, 22.85 %.) NMR spectrum ($CDCl_3$):

τ 5.75 (s, 5, π-C_5H_5); 5.32 (s, 3, $-OCH_3$); 5.00 (t, 2, J 2 Hz, π-C_5H_4); 5.22 (t, 2, J 2 Hz, π-C_5H_4). NMR spectrum (C_6D_6): τ 6.06 (s, 5, π-C_5H_5); 5.87 (s, 3, $-OCH_3$); 5.20 (t, 2, J 2 Hz, π-C_5H_4); 5.69 (t, 2, J 2 Hz, π-C_5H_4).

Reaction of ferrocenyllithium (II) and TMEDA

Solid ferrocenyllithium (II) was suspended in 25 ml of anhyd. hexane under nitrogen. TMEDA (0.232 g, 2.0 mmoles) in 10 ml of anhyd. hexane was added dropwise, and the reaction mixture was allowed to stir for 24 h. An orange solid which remained in the reaction flask was filtered under nitrogen, washed with hexane, and dried at room temperature *in vacuo*. This solid (IV) was handled under inert conditions. (Found: Fe, 18.10; Li, 2.24. $C_{16}H_{25}FeLiN_2$ calcd.: Fe, 18.12; Li, 2.25%.)

Isolation of 1,1'-*dilithioferrocene·2TMEDA (III)*

1,1'-Dilithioferrocene·2TMEDA was prepared as described in the literature[2,9]. After stirring for 6 h, the orange crystals which had separated were filtered under nitrogen onto a glass frit, washed with hexane until the washings were colorless, and dried under high vacuum. The reaction was essentially quantitative and produced an orange pyrophoric solid. (Found: C, 61.48; H, 9.40; Fe, 12.98; Li, 3.65; N, 13.00. $C_{22}H_{40}FeLi_2N_4$ calcd.: C, 61.40; H, 9.37; Fe, 12.98; Li, 3.23; N, 13.02%.)

1,1'-*Bis(diphenylhydroxymethyl)ferrocene*

Solid 1,1'-dilithioferrocene·2TMEDA (III) (0.430 g, 1.0 mmole) was added to 50 ml of anhyd. hexane under an atmosphere of nitrogen. A solution of benzophenone (0.473 g, 2.60 mmoles) in 200 ml of anhyd. hexane was added and the reaction mixture was allowed to stir for 12 h at room temperature. Cold water (200 ml) was added to the reaction mixture and the resulting insoluble material was filtered and washed with cold hexane. This filtration yielded 0.505 g (92%) of 1,1'-bis(diphenylhydroxymethyl)ferrocene, m.p. 179° (lit.[29] m.p. 179–181°).

Hydrolysis of (III)

1,1'-Dilithioferrocene·2TMEDA (0.430 g, 1.0 mmole) was suspended in 30 ml of anhyd. hexane under nitrogen. Hydrochloric acid (50 ml, 5%) was added dropwise and stirring was continued for 4 h. The reaction mixture was extracted with ethyl ether (3 × 40 ml), and the extracts were dried over anhyd. magnesium sulfate. Evaporation of the solvent gave ferrocene, 0.174 g (94%), m.p. 172° (lit.[26] m.p. 173–174°).

Isolation of 2-lithio[(dimethylamino)methyl]ferrocene (V)

[(Dimethylamino)methyl]ferrocene (2.43 g, 10 mmoles) was dissolved in 45 ml of anhyd. ethyl ether under nitrogen and treated with n-butyllithium in hexane (4.76 ml, 10 mmoles). Stirring was continued for 24 h after which time the red-orange crystals which had formed were allowed to settle. The crystalline substance was filtered under nitrogen onto a glass frit and was washed with hexane until the washings were colorless (5 × 20 ml). The red-orange solid was dried under high vacuum to yield 1.15 g (47%) of pink (V). This organolithium compound is extremely air-sensitive and undergoes decomposition with the slightest contact with air. Decomposition is accompanied with the appearance of a yellow color. (Found: C, 62.48; H, 6.54; Fe, 22.15; Li, 2.80; N, 5.32. $C_{13}H_{16}FeLiN$ calcd. C, 62.69; H, 6.48; Fe, 22.42; Li, 2.79; N, 5.62%.)

Reaction of 2,2'-dibromobiphenyl and n-butyllithium

In a nitrogen-purged 200 ml round-bottom flask, 2,2'-dibromobiphenyl (1.00 g, 3.20 mmoles) was dissolved in 60 ml of anhyd. ethyl ether and cooled to −10°. n-Butyllithium in hexane solution (3.05 ml, 6.40 mmoles) was added dropwise from a syringe while the reaction mixture was rapidly stirred. The mixture was maintained at −10° for 1 h, allowed to warm to room temperature, and stirred an additional 4 h. The ether was concentrated under reduced pressure to ca. 2 ml and 10 ml of anhyd. hexane was added to produce a cream-colored solid. The solid was filtered under nitrogen and dried to a constant weight under high vacuum. (Found: Br, 13.44; Li, 7.38. $C_{12}H_8Li_2$(VI) calcd.: Br, 0; Li, 8.36%. $C_{12}H_8BrLi$ (VII) calcd.: Br, 33.43; Li, 2.90%.)

A sample of this solid was subjected to a controlled hydrolysis, and the products were analyzed by gas chromatography. GC conditions: Perkin–Elmer 990 Gas Chromatograph, 10% SE 30 on Anakrom ABS 70/80, flow rate 55 ml/min, flame ionization detector, column temperature 200°, injection port temperature 240°, detector temperature 230°. Retention times: biphenyl, 1.7 min; 2-bromobiphenyl, 2.6 min; 2-aminobiphenyl, 3.3 min; 2,2'-dibromobiphenyl, 6.7 min. The hydrolysis mixture contained only two products, with retention times of 1.7 min and 2.6 min.

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