

## PERHALOARYL-METAL CHEMISTRY III\*. $\sigma$ -(TRICHLORO-2-THIENYL) DERIVATIVES OF TRANSITION METALS AND RELATED STUDIES\*\*

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### SUMMARY

$\sigma$ -(Trichloro-2-thienyl) derivatives of iron, nickel and manganese have been prepared from 2-lithiotrichlorothiophene and various transition metal halides. These new compounds exhibit enhanced thermal and oxidative stabilities in a manner analogous to pentahalophenyl-transition metal derivatives. 2-Thienylpentacarbonylmanganese, a compound of limited stability, has been obtained from the reaction of thenoyl chloride and  $\text{Na}[\text{Mn}(\text{CO})_5]$ . Attempts to isolate Diels-Alder adducts which would indicate decomposition of 2-lithiotrichlorothiophene to 2,3-dichlorothiophyne have been largely unsuccessful. A reaction between bis(trichloro-2-thienyl)mercury and tetraphenylcyclopentadienone has produced 2,3-dichloro-4,5,6,7-tetraphenylthianaphthene in good yield. The latter may be formed via either an aryne or an addition-elimination process.

### INTRODUCTION

Heterocyclic compounds form extremely important metal coordination complexes in nature, occurring in chlorophyll, hemin, metallo-enzymes, etc. Certain heterocycles such as thiophene<sup>1</sup> form organometallic  $\pi$ -complexes in which a sextet of ring  $\pi$ -electrons participate in bonding with a metal, and several *N*- and  $\pi$ -pyrrolyl complexes of transition metals have likewise been recently described<sup>2</sup>. It is striking, therefore, that analogous complexes in which a transition metal is  $\sigma$ -bonded *directly* to a single carbon atom of a heterocyclic group are virtually unknown, the examples apparently being limited to a furyl-manganese complex<sup>3</sup>, two organoiron complexes derived from Schiff bases of furan- and thiophenecarboxaldehyde<sup>4</sup>, and several transition metal derivatives of perfluoropyridine<sup>5</sup>.

In conjunction with our program concerned with the formation, structure and relative stabilities of  $\sigma$ -(perhaloaryl) derivatives of the transition metals, it was of interest to determine if corresponding perhalogenated heterocyclic-transition metal compounds could be obtained, and to compare their properties, if possible, with non-halogenated analogs. In the present paper, we describe the isolation and prop-

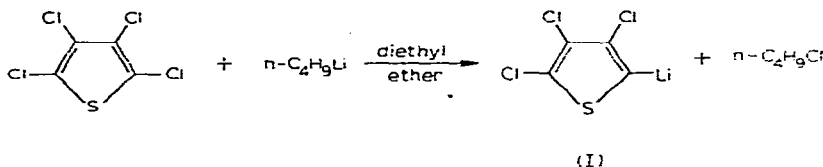
\* For Part II see ref. 6.

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erties of a new series of organometallic compounds which contain the thiophene ring system  $\sigma$ -bonded to various transition metals. Stability studies relating to certain organometallic precursors are also reported.

## RESULTS AND DISCUSSION

By analogy to pentachlorophenyl-transition metal chemistry<sup>6</sup>, the most logical route leading to  $\sigma$ -(trichlorothieryl) derivatives of transition metals would involve the reaction of either 2-lithiotrichlorothiophene (I) or the corresponding Grignard reagent with appropriate transition metal halides. Both of these intermediates have been previously reported, although the details concerning their formation, stabilities, and the scope of their reactivity are very limited. Steinkopf and coworkers<sup>7</sup> reported that the addition of tetrachlorothiophene\* to a refluxing solution of methyl bromide and magnesium in ethyl ether followed by hydrolysis gave 2,3,4-trichlorothiophene in 17% yield. Carbonation of the reaction mixture followed by hydrolysis was reported to produce trichlorothiophene-2-carboxylic acid in unspecified amount or yield. Bachman and Heisley<sup>9</sup> found that 2-lithiotrichlorothiophene (I) could be formed from tetrachlorothiophene and *n*-butyllithium in ethyl ether. The reagent was characterized by carbonation to the corresponding acid (55%) and by the alcohols formed upon its addition to carbonyl functions, followed



by hydrolysis. These workers also reported that "conversion of 2,3,4,5-tetrachlorothiophene to a Grignard reagent using a cohalide ( $\text{C}_2\text{H}_5\text{Br}$ ) proceeded less satisfactorily".

We briefly attempted to develop an improved route to this Grignard reagent using techniques which have proved advantageous for the conversion of hexachlorobenzene to pentachlorophenylmagnesium chloride<sup>10,11</sup>. Unfortunately, neither a reaction in ethyl ether between tetrachlorothiophene, magnesium and a two-fold excess of 1,2-dibromoethane (as entraining agent), nor a similar reaction in tetrahydrofuran employing a catalytic amount of this entrainer indicated substantial conversion to the Grignard reagent, and this intermediate was abandoned in favor of the lithium reagent (I).

We have found that (I) is most suitably prepared and used at temperatures of *ca.*  $-20^\circ$  or less, since at this temperature the reagent exists as a light-colored, transparent solution which allows good visual evidence for the occurrence of a subsequent reaction. When (I) is formed at room temperature or above, the reagent is brown, although this discoloration apparently does not result in significantly reduced yields of subsequent reaction products. The stability of (I) in various solvents, as evidenced by standardized conversion to the corresponding acid, was examined as

\* Tetrachlorothiophene is a readily accessible starting material, since it is formed in quantitative yield from a reaction between hexachlorobutadiene and sulfur at elevated temperatures<sup>8</sup>.

TABLE I

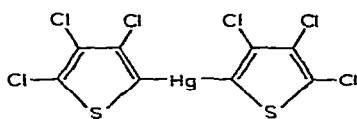
STABILITY OF 2-LITHIOTRICHLOROTHIOPHENE (I) IN ETHEREAL SOLUTIONS

Solvent	Temp. (°C)	Reaction period (h) <sup>a</sup>	Yield of 2-C <sub>4</sub> Cl <sub>3</sub> SCO <sub>2</sub> H (%)
Diethyl ether	0	0.5	68
		1.5	69
		3	68
		5	69
		26	65
		48	63
		99	55
Diethyl ether/ tetrahydrofuran (3/2)	-40	0.5	52
		2	46
		3	37
		5.5	39
Tetrahydrofuran	20 <sup>b</sup>	0.5	27
		1	15
		2	24

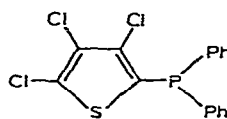
<sup>a</sup> Zero time is defined as the time at which the addition of n-butyllithium to tetrachlorothiophene is completed. <sup>b</sup> Studies conducted at -40° produced similar results.

a function of time and temperature. Representative results are summarized in Table I. It is apparent that (I) is somewhat more stable in ethyl ether solution than is pentachlorophenyllithium<sup>6</sup>. Even after four days at 0° in ethyl ether solution, the concentration of (I) was little altered, as evidenced by the amounts and the purity of the resulting carbonation product. As tetrahydrofuran was introduced into the solvent mixture, the yields of (I) were reduced significantly.

In preliminary studies, we observed that the hydrolysis of (I) produced 2,3,4-trichlorothiophene in yields of 67–75%, while a reaction of (I) with benzophenone afforded diphenyl(trichloro-2-thienyl)methanol in even higher yield (86%). The utility of (I) in the formation of organometallic compounds was also apparent from reactions of (I) with mercuric chloride and with diphenylchlorophosphine, which gave bis(trichloro-2-thienyl)mercury (II) and diphenyl(trichloro-2-thienyl)phosphine (III), respectively, in moderate yields.

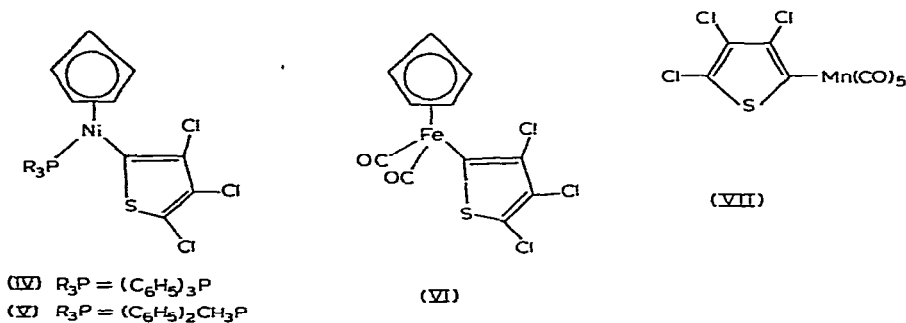


(II)



(III)

2-Lithiotrichlorothiophene (I) was also found to be a valuable intermediate in the formation of  $\sigma$ -bonded (trichloro-2-thienyl)-transition metal derivatives. A reaction between (I) and  $\pi$ -cyclopentadienyl(triphenylphosphine)nickel chloride readily produced the green complex  $\pi$ -cyclopentadienyl- $\sigma$ -(trichloro-2-thienyl)(triphenylphosphine)nickel (IV), in analogy to a similar reaction involving pentachlorophenyllithium<sup>12</sup>. The corresponding diphenylmethylphosphine complex (V) could



be obtained in an analogous manner from (I) and  $\pi$ -cyclopentadienyl(diphenylmethylphosphine)nickel chloride. Treatment of  $\pi$ -cyclopentadienyldicarbonyliron iodide with (I) afforded yellow-green crystals of  $\pi$ -cyclopentadienyl- $\sigma$ -(trichloro-2-thienyl)-dicarbonyliron (VI), while the reaction between (I) and pentacarbonylmanganese bromide resulted in the formation of  $\sigma$ -(trichloro-2-thienyl)pentacarbonylmanganese (VII). Reactions occurred readily between (I) and a variety of other transition metal halides, but the products have not yet been fully characterized.

The  $\sigma$ -(trichloro-2-thienyl) complexes (IV)–(VII), like their corresponding pentafluorophenyl and pentachlorophenyl analogs<sup>6,12,13</sup>, exhibit enhanced thermal and oxidative stabilities when compared to most other  $\sigma$ -bonded organo-transition metal compounds. All the complexes (IV)–(VII) were stable in air for indefinite periods at room temperature, and all exhibited no noticeable decomposition when heated for a week at 75° under nitrogen. Both (VI) and (VII) could be heated through their melting points under nitrogen, cooled, and remelted without apparent change, and a sample of (VII) remained virtually unchanged in the liquid state after heating for 24 hours under nitrogen at 110°. Attempts to prepare non-chlorinated analogs of (IV)–(VI) using 2-thienyllithium in place of (I) resulted in immediate reactions at low temperatures, although the resulting complexes were apparently too unstable to allow their separation and characterization at room temperature.

We have, however, successfully carried out a reaction between the manganese carbonyl anion  $Na[Mn(CO)_5]$  and thenoyl chloride to *directly* produce  $\sigma$ -(2-thienyl)-(pentacarbonyl)manganese (VIII) as a light-yellow liquid of limited stability in 42%

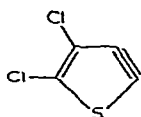


yield. In marked contrast to (VII),  $\sigma$ -(2-thienyl) complex (VIII) gradually decomposes under nitrogen at room temperature, and extensive decomposition occurs in less than one hour in air at this temperature. When a sample of (VIII) was heated to 110° under nitrogen, it appeared to decompose in a matter of minutes.

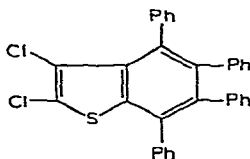
The striking stabilities of (IV)–(VII) may be related to a number of factors. The presence of strongly  $\pi$ -bonding ligands (CO,  $R_3P$ , etc.) coordinated to a transition metal is known to stabilize  $\sigma$ -bonded groups attached to that same metal<sup>14</sup>. Moreover, organotransition metal complexes containing highly electronegative  $\sigma$ -bonded ligands are frequently stable and isolable compared to their hydrocarbon analogs, presumably in part as the result of increased ionic resonance energy associated with

the carbon-transition metal bond<sup>13</sup>. It seems likely that both of these stabilization processes are operative in complexes (IV)–(VII). A  $\sigma$ -(trichloro-2-thienyl) ligand might be expected to remove electron density from the transition metal by inductive as well as  $d_{\pi}$ - $p_{\pi}$ \* effects, and both processes should result in an increase in the metal-ligand bond strength. Steric effects imposed by bulky chlorine atoms may also protect the molecule from attack by chemical reagents<sup>14</sup>. We hope to gain a better understanding of the relative importance of these and other stabilization factors by means of joint quantitative stability and X-ray crystallographic studies which are currently in progress\*.

Both pentachlorophenyllithium and pentafluorophenyllithium are known to undergo reasonably facile elimination of lithium halides at room temperature and above to form the corresponding tetrahalobenzynes<sup>16</sup>. Tetrahalobenzynes generated in this manner behave as powerful dienophiles and readily undergo Diels-Alder reactions with furan, anthracene, and even benzene and mesitylene. Although the stability of (I) compared to perhaloaryllithium reagents in ethereal solutions indicated little tendency for (I) to eliminate lithium chloride and form 2,3-dichlorothiophyne (IX), recent interest in hetaryne chemistry<sup>17-19</sup> prompted an attempt to detect a



(IX)



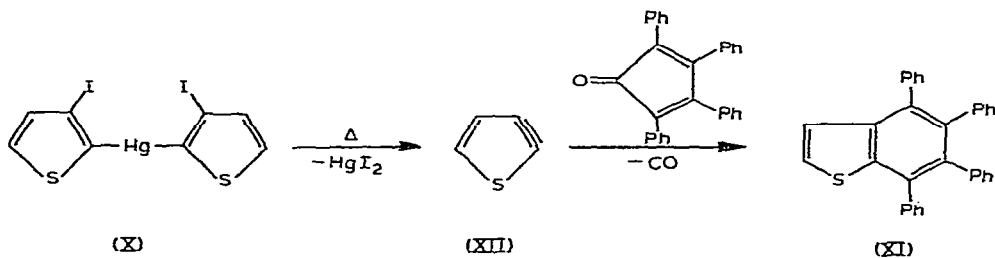
(XIII)

species such as (IX) in solution. In separate experiments, solutions of (I) were heated to reflux with anthracene in diethyl ether, anthracene in di-n-butyl ether, furan in diethyl ether, and benzene in diethyl ether (1 : 1). Although reactions apparently occurred at elevated temperatures, as was evidenced by the formation of dark, insoluble, polymeric material and inorganic residues, no products which could be attributed to Diels-Alder addition to an intermediate such as (IX) could be detected.

1,3-Diphenylisobenzofuran, one of the most powerful dienes known in the Diels-Alder reaction, has been shown to react with norbornene and norbornadiene<sup>20</sup>, unconjugated olefins such as cyclopentene<sup>21</sup>, as well as benzyne<sup>22</sup> and cyclopentyne<sup>23</sup>. Two experiments were conducted using this reactive diene. One investigation involved the preparation of (I) in ethyl ether to which was added a benzene solution of 1,3-diphenylisobenzofuran. The ethyl ether was subsequently removed by distillation, allowing a higher reflux temperature. After a prolonged reflux period, a TLC slide indicated the presence of large amounts of unreacted 1,3-diphenylisobenzofuran and chlorothiophenes, together with trace amounts of two more polar substances and a substantial amount of an immobile residue. In a control experiment in which tetrachlorothiophene was substituted for (I), similar results were obtained, and very small amounts of these same two polar components were again present as determined by TLC. The nature of these two products was not determined, due to the very small quantities of each present, although it seems unlikely that either was formed from an intermediate such as (IX) and 1,3-diphenylisobenzofuran.

\* For a recent evaluation of stabilization effects as applied to *trans*-bis(triethylphosphine)- $\sigma$ -bis(phenylethynyl)nickel, see ref. 15.

Wittig and coworkers have recently reported that bis(3-iodo-2-thienyl)mercury (X), when heated in the presence of tetraphenylcyclopentadienone, gave 4,5,6,7-tetraphenylthianaphthene (XI), the reaction presumably proceeding via thiophyne



(XII)<sup>23,24</sup>. We have likewise examined a reaction between (II) and tetraphenylcyclopentadienone at elevated temperatures, and have been able to isolate a product in good yield which on the basis of elemental and mass spectral analysis is assigned as 2,3-dichloro-4,5,6,7-tetraphenylthianaphthene (XIII). Although (IX) or a closely related organometallic species may be an intermediate in this reaction, such pyrolytic processes need not necessarily proceed via arynes intermediates, as has been recently discussed by Rasheed<sup>25</sup>. Direct addition of tetraphenylcyclopentadienone to (II) followed by subsequent elimination of mercuric chloride and carbon monoxide would lead to the same result.

#### EXPERIMENTAL SECTION

Infrared spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated *versus* polystyrene. NMR spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as internal standard. Melting points of all organo-transition metal compounds were taken in sealed capillaries under nitrogen and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Diethyl ether and tetrahydrofuran were purified by drying over sodium wire and potassium hydroxide, respectively, followed by distillation from calcium hydride or lithium aluminum hydride. Tetrachlorothiophene was the generous gift of Hooker Chemical Corp. and was used as received. *n*-Hexane used for the preparation of analytical samples was washed with sulfuric acid and distilled from sodium wire. Benzene used for the preparation of analytical samples was dried by azeotropic distillation and stored over sodium wire. Thin-layer chromatography (TLC) experiments were performed with CAMAG silica gel containing ultraviolet-sensitive fluorescent indicator.

#### 2-Lithiotrichlorothiophene (I)

The reagent was conveniently prepared in a 250-ml four-necked flask which was equipped in the usual manner and which had been purged at least three times with nitrogen. Liquid tetrachlorothiophene dissolved in the required amount of purified diethyl ether (usually 0.25–0.40 *M*) was introduced under nitrogen. An equimolar amount of commercial *n*-butyllithium in hexane solution (Alfa Inorganics, Inc.) was added to an addition funnel by means of a nitrogen-flushed syringe. The reaction flask was cooled to *ca.*  $-25^{\circ}$ , exercising care that precipitation of tetrachloro-

thiophene did not occur, and the *n*-butyllithium solution was added dropwise over a period of 15–30 min to the rapidly stirred solution. The initially colorless reaction mixture turned yellow immediately, subsequently changing to green and returning to yellow at the end of the addition. After an additional stirring period of one hour at  $-25^{\circ}$ , the reagent was ready for use.

*Stability studies of 2-lithiotrichlorothiophene (I) in solution*

A solution of (I) was prepared from tetrachlorothiophene (6.80 g, 30.7 mmoles) in diethyl ether (125 ml) and *n*-butyllithium solution (14.75 ml, 30.7 mmoles) at  $-20^{\circ}$ . Additional solutions of (I) were prepared in tetrahydrofuran at  $20^{\circ}$  and in diethyl ether/tetrahydrofuran (3/2) at  $-40^{\circ}$ . Five-ml aliquots of the solutions were carbonated and hydrolyzed in the usual manner at specified times. The resulting white precipitate was filtered and dried several hours in an oven. Melting point comparisons indicated essentially pure trichlorothiophene-2-carboxylic acid in each case. The times of aliquot removal and yields of acid are given in Table 1.

*Bis(trichloro-2-thienyl)mercury (II)*

A solution of (I) was prepared from tetrachlorothiophene (13.22 g, 60 mmoles) in diethyl ether (160 ml) and *n*-butyllithium solution (28.6 ml, 60 mmoles) at  $-30^{\circ}$ . Solid mercuric chloride (8.15 g, 30 mmoles) was added under nitrogen in one portion to the solution at  $-55^{\circ}$ . Rapid stirring at this temperature was continued for 1 h. The reaction mixture was allowed to warm to room temperature over 1 h and stirred at this temperature for an additional 2 h. The reaction mixture was then evaporated to dryness and was washed twice with water. The resulting white solid was subjected to extraction in a Soxhlet extractor with 350 ml of 95% ethanol for 6 h; addition of water to the ethanol extracts precipitated bis(trichloro-2-thienyl)mercury (II) (6.8 g, 40%), m.p.  $239-241^{\circ}$ . A subsequent recrystallization from ethanol/water afforded (II) of m.p.  $241-243^{\circ}$  (lit.<sup>7</sup>  $241^{\circ}$ ).

Continued extraction of the remaining residue with ethanol followed by addition of water precipitated a small amount (1.08 g, 9%) of crude (trichloro-2-thienyl)mercuric chloride, m.p.  $190-200^{\circ}$  (lit.<sup>7</sup>  $211^{\circ}$ ).

*Diphenyl(trichloro-2-thienyl)phosphine (III)*

A solution of (I) was prepared from tetrachlorothiophene (4.44 g, 20 mmoles) in diethyl ether (75 ml) and *n*-butyllithium solution (9.55 ml, 20 mmoles) at  $-30^{\circ}$ . After an additional 1 h period, diphenylchlorophosphine (4.42 g, 20 mmoles) in diethyl ether (20 ml) was added dropwise with stirring at  $-55^{\circ}$ . The reaction mixture was allowed to stir at  $-45^{\circ}$  for 30 min and subsequently at room temperature overnight. After hydrolysis with 100 ml of water, the layers were separated, the ether layer was dried, and the filtrate was evaporated to dryness, affording 3.74 g of a tan solid. The latter was chromatographed on a column of dry-packed Florisil, elution being made with hexane/benzene (10/1). The colorless eluent, containing only (III) as monitored by TLC, was collected and evaporated to dryness, giving 2.47 g (34%) of diphenyl(trichloro-2-thienyl)phosphine, m.p.  $112-114^{\circ}$ . An analytical sample was prepared by recrystallization of this solid from hexane, affording a product of m.p.  $115-116^{\circ}$ . (Found: C, 51.60; H, 2.91; Cl, 28.50; P, 8.18.  $C_{16}H_{10}Cl_3PS$  calcd.: C, 51.71; H, 2.69; Cl, 28.62; P, 8.34%.)

Treatment of 0.5 g of (III) in 5 ml of benzene with a ten-fold excess of methyl iodide at reflux for 15 min afforded a nearly quantitative yield of diphenylmethyl-(trichloro-2-thienyl)phosphonium iodide. The solid was washed with ether and recrystallized twice from hot ethanol/diethyl ether to produce an analytical sample of m.p. 199–201°. (Found: C, 39.81; H, 2.66.  $C_{17}H_{13}Cl_3IPS$  calcd.: C, 39.76; H, 2.53%.)

*Diphenyl(trichloro-2-thienyl)methanol*

A solution of (I) was prepared from tetrachlorothiophene (6.70 g, 30 mmoles) in diethyl ether (100 ml) and n-butyllithium solution (14.6 ml, 30 mmoles) at  $-35^\circ$ . Benzophenone (5.51 g, 30 mmoles) in ethyl ether (35 ml) was added dropwise with stirring, during which time a white precipitate was formed. After gradual warming to room temperature, 100 ml of water was added, the layers were separated, and the ether layer was washed with water and was dried. The solution was concentrated to dryness giving a tan solid (9.52 g, 86%). An analytical sample was prepared by recrystallization of the solid from hexane; the m.p. was  $97.5-98.5^\circ$ . (Found: C, 55.22; H, 2.75.  $C_{17}H_{11}Cl_3OS$  calcd.: C, 55.21; H, 2.98%.)

The NMR spectrum ( $CCl_4$  soln.) of diphenyl(trichloro-2-thienyl)methanol exhibited a sharp singlet at  $\tau$  2.69, intensity 10, attributed to the phenyl protons, and a sharp singlet at  $\tau$  6.51, intensity 1, attributed to the hydroxyl proton.

*$\pi$ -Cyclopentadienyl- $\sigma$ -(trichloro-2-thienyl)(triphenylphosphine)nickel (IV)*

A solution of (I) was prepared from tetrachlorothiophene (1.32 g, 5.90 mmoles) in diethyl ether (50 ml) and n-butyllithium solution (2.81 ml, 5.90 mmoles) at  $-30^\circ$ .  $\pi$ -Cyclopentadienyl(triphenylphosphine)nickel chloride<sup>26</sup> (1.48 g, 3.50 mmoles) was added under nitrogen in one portion to the stirred solution at  $-60^\circ$ , and 70 ml of additional ethyl ether was also introduced. The brown reaction mixture was maintained at  $-60^\circ$  for 2 h and then allowed to warm to room temperature with stirring overnight. The green solution was filtered under nitrogen through a transfer tube containing glass wool. The filtrate was hydrolyzed with 25 ml of a saturated aqueous solution of ammonium chloride and the layers were separated. The ether layer was washed with water, dried, and evaporated to a solid. The latter was washed several times with hexane to remove 2,3,4-trichlorothiophene. Following recrystallization from hexane, there remained 0.58 g (29%) of green crystals of (IV), m.p. 196–197°. (Found: C, 56.29; H, 3.61; Ni, 9.83; P, 5.84.  $C_{27}H_{20}Cl_3NiPS$  calcd.: C, 56.63; H, 3.52; Ni, 10.25; P, 5.41%.)

The NMR spectrum ( $CDCl_3$  soln.) of IV exhibited an aromatic multiplet centered at  $\tau$  2.50, intensity 15, and a sharp singlet at  $\tau$  4.72, intensity 5, attributed to the  $\pi$ -cyclopentadienyl protons.

*$\pi$ -Cyclopentadienyl- $\sigma$ -(trichloro-2-thienyl)(diphenylmethylphosphine)nickel (V)*

In a manner similar to that described above, solid  $\pi$ -cyclopentadienyl(diphenylmethylphosphine)nickel chloride<sup>12</sup> (3.60 g, 10 mmoles) was added to a solution of 2-lithiotrichlorothiophene prepared from tetrachlorothiophene (3.73 g, 16.7 mmoles), diethyl ether (75 ml), and n-butyllithium solution (80 ml, 16.7 mmoles) at  $-30^\circ$ . Hydrolysis, chromatography on Florisil, and recrystallization of the product from hexane afforded 1.84 g (36%) of green (V), m.p. 92–94°. An analytical sample



melted at 93.5–94°. (Found: C, 51.46; H, 3.67; Ni, 11.22; P, 6.09.  $C_{22}H_{18}Cl_3NiPS$  calcd.: C, 51.76; H, 3.55; Ni, 11.50; P, 6.07%.)

An NMR spectrum ( $CDCl_3$  soln.) of (V) exhibited an aromatic multiplet centered at  $\tau$  2.52, intensity 10, a sharp singlet at  $\tau$  4.82, intensity 5, attributed to the  $\pi$ -cyclopentadienyl protons, and a doublet ( $J(H-P)$  10 Hz) at  $\tau$  8.48, intensity 3, attributed to the methyl protons.

*$\pi$ -Cyclopentadienyl- $\sigma$ -(trichloro-2-thienyl)dicarbonyliron (VI)*

A solution of (I) was prepared from tetrachlorothiophene (4.44 g, 20 mmoles) in diethyl ether (75 ml) and n-butyllithium solution (9.55 ml, 20 mmoles) at  $-30^\circ$ . Powdered  $\pi$ -cyclopentadienyldicarbonyliron iodide<sup>27</sup> (5.45 g, 18 mmoles) was added under nitrogen to the stirred solution at  $-60^\circ$ . The deep-brown reaction mixture was maintained at this temperature for 90 min, then allowed to warm to room temperature with stirring overnight. The mixture was filtered through a transfer tube containing glass wool, and the filtrate was evaporated to dryness, giving a viscous oil. This material was dissolved in a small amount of benzene, and the solution was chromatographed on a column of dry-packed Florisil, elution being made with hexane/benzene (2/1). The initial red-brown eluent was discarded since it contained 2,3,4-trichlorothiophene. The following yellow-green band was collected and evaporated to produce a green oil. Addition of a small amount of hexane and subsequent cooling of the resulting solution to  $-78^\circ$  afforded (VI) in the form of yellow crystals (1.1 g, 17%), m.p. 81–84°. An analytical sample was prepared by recrystallization from hexane; m.p. 88–89°. (Found: C, 36.09; H, 1.37; Cl, 28.85; Fe, 15.27.  $C_{11}H_5Cl_3FeO_2S$  calcd.: C, 36.35; H, 1.38; Cl, 29.27; Fe, 15.37%.)

The NMR spectrum ( $CDCl_3$  soln.) of (VI) exhibited a single sharp resonance at  $\tau$  4.98.

*$\sigma$ -(Trichloro-2-thienyl)pentacarbonylmanganese (VII)*

A solution of (I) was prepared from tetrachlorothiophene (2.34 g, 10.5 mmoles) in diethyl ether (80 ml) and n-butyllithium solution (5.05 ml, 10.5 mmoles) at  $-35^\circ$ . Pentacarbonylmanganese bromide<sup>28</sup> (2.93 g, 10.5 mmoles) was added under nitrogen in one portion to the stirred solution at  $-65^\circ$ , and the mixture was maintained at this temperature for 18 h. A TLC slide [hexane/benzene (4/1) as eluent] indicated nearly complete disappearance of pentacarbonylmanganese bromide and the presence of a product contaminated with slightly less polar dimanganese decacarbonyl. The mixture was transferred to a rotary evaporator and concentrated to a deep-red oil. Benzene (15 ml) was added and the solution was chromatographed on a column of dry-packed Florisil, which was eluted with hexane. The initial eluent contained substantial amounts of dimanganese decacarbonyl, while subsequent portions progressively contained lesser amounts of this product, as monitored by TLC. Fractions containing the desired product and minimum amounts of dimanganese decacarbonyl were collected and combined, evaporated to a red oil, and the latter was dissolved in a small amount of hexane. When this solution was cooled to  $-78^\circ$  with rapid stirring, precipitation of 0.51 g (13%) of a deep-orange powder, m.p. 88–96°, resulted. An analytical sample was prepared by recrystallization of the powder from hexane (5–10 ml) which was cooled to  $-78^\circ$ . This procedure afforded 100 mg of white crystals of (VII), m.p. 100–101°. (Found: C, 28.58; Cl, 28.11; Mn, 14.78.  $C_9Cl_3MnOS$  calcd.: C, 28.34; Cl, 27.88; Mn, 14.40%.)

### $\sigma$ (2-Thienyl)pentacarbonylmanganese (VIII)

2-Thenoyl chloride<sup>29</sup> (5.4 g, 37 mmoles) was added to an equimolar amount of  $\text{NaMn}(\text{CO})_5$  prepared in tetrahydrofuran solution<sup>30</sup>. The color changed immediately from the gray-green color of the  $\text{Mn}(\text{CO})_5^-$  ion to red-brown. After the reaction mixture had been allowed to stir overnight at room temperature, the precipitated sodium chloride was separated by filtration under nitrogen and the solvent was removed *in vacuo*. The residue was subjected to chromatography under nitrogen on Florisil using a mixture of benzene/hexane (1/1) as eluent. After removal of the solvent from the first yellow zone, the resulting product was distilled at 79° (2 mm) to produce (VIII) as a light-yellow liquid (4.2 g, 42%). The material was best stored under nitrogen at -20° away from light. (Found: C, 38.61; H, 0.96; Mn, 20.24; S, 10.98.  $\text{C}_9\text{H}_3\text{MnO}_5\text{S}$  calcd.: C, 38.86; H, 1.08; Mn, 19.76, S, 11.52%.)

An infrared spectrum of (VIII) ( $\text{CCl}_4$  solution) exhibited strong terminal carbonyl bands at 2110, 2010, 2000 and 1985  $\text{cm}^{-1}$ . An NMR spectrum of (VIII) ( $\text{CDCl}_3$  soln.) exhibited multiplet absorption attributable to the thienyl protons between  $\tau$  2.3-3.2.

### Attempted conversion of 2-lithiotrichlorothiophene (I) to 2,3-dichlorothiophene (IX) and subsequent Diels-Alder adduct formation with 1,3-diphenylisobenzofuran

A solution of (I) was prepared from tetrachlorothiophene (0.82 g, 3.7 mmoles) in diethyl ether (15 ml) and n-butyllithium solution (1.75 ml, 3.7 mmoles) at -15°. After the solution had been allowed to stir for 1 h at -15°, 1,3-diphenylisobenzofuran (K and K Labs., Inc.) (1.0 g, 3.7 mmoles) in dry benzene (25 ml) was added over a 5-min period at room temperature. The diethyl ether was distilled from the yellow fluorescent mixture and the benzene was heated to reflux. A TLC slide [hexane/benzene (4/1) as eluent] after 24 h indicated the presence primarily of unreacted 1,3-diphenylisobenzofuran and chlorothiophenes. After a 6-day reflux period, TLC indicated chlorothiophenes and 1,3-diphenylisobenzofuran as the major components, together with minute amounts of two relatively polar products (which appeared blue under ultraviolet light) and a residue which did not elute. Chromatographic separation of the reaction mixture was not feasible.

### Control reaction between tetrachlorothiophene and 1,3-diphenylisobenzofuran

Tetrachlorothiophene (0.16 g, 0.74 mmole) and 1,3-diphenylisobenzofuran (0.20 g, 0.74 mmole) in dry benzene (15 ml) were refluxed under nitrogen for 72 h. A TLC slide of the reaction mixture indicated 1,3-diphenylisobenzofuran as the major component, together with lesser amounts of chlorothiophenes and very small amounts of the same polar products observed in the previous experiment.

### 2,3-Dichloro-4,5,6,7-tetraphenylthianaphthene (XIII)

Tetraphenylcyclopentadienone (7.50 g, 19.6 mmoles) and (II) (4.35 g, 7.6 mmoles) were mixed and placed in a 100-ml, nitrogen-flushed flask, equipped with a condenser attached to a bubbler. The reaction mixture was maintained at 245° for 18 h by means of a Woods metal bath heated on a hot plate. A violet melt was formed, and slow but regular evolution of a gas was noted. Upon cooling, 9.95 g of a purple solid was obtained. Chromatographic purification of 3.6 g of this residue on a dry-packed Florisil column, using hexane/benzene (1/1) as eluent, afforded 1.9 g of a

pale-yellow solid, m.p. 238–244° [crude yield of 68% based on the expected product (XIII)]. Two recrystallizations of this solid produced a product of m.p. 253–256° which appeared by TLC to be contaminated with trace amounts of (II). The product was accordingly sublimed until the sublimate contained both (II) and (XIII), while the residue consisted only of (XIII), as indicated by TLC. An analytical sample was prepared by subsequent recrystallization of the residue from hexane, yielding off-white crystals of m.p. 254–256°. (Found: C, 75.98; H, 4.11; Cl, 13.58; S, 5.80.  $C_{32}H_{20}Cl_2S$  calcd.: C, 75.74; H, 3.97; Cl, 13.97; S, 6.32%.)

The mass spectrum of (XIII) determined on a Bendix Time-of-Flight instrument (sample introduced directly into probe at 146°) indicated a molecular ion peak at  $m/e$  506  $\pm$  1 (the presence of chlorine atoms prevented the exact assignment due to the chlorine isotope effect). There were no discernible  $m/e$  peaks greater than 507. At 68°, only a peak at  $m/e$  78 was observed. An NMR spectrum of (XIII) ( $CS_2$  soln.) exhibited multiplet absorption between  $\tau$  2.7–3.4, attributed to the protons of a phenyl group. An infrared spectrum ( $CCl_4$  soln.) exhibited major absorption bands (phenyl group) at 3060, 3030, 1603, 1495, 1445, 695 and 670  $cm^{-1}$ .

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