hydride complex [$Tp'W(CO)(PhC{\equiv}CMe)H$]. This contrasts sharply with the low-temperature reaction with $Li[BHEt_3]$, where azavinylidene formation is observed. The structure of this rare example of a group 6 d^4 alkyne hydride complex was confirmed by X-ray diffraction. In contrast to the $Tp^*W(CO)_3H$ complexes, the $^1J(^{183}WH)$ coupling constants for the alkyne derivatives are quite large, while the ^1H NMR chemical shifts for the hydride ligands are unusually low. A difference in reactivity is evident as well. Protonation of $Tp'W(CO)(RC{\equiv}CMe)H$ yields tungsten(II) products that retain the $Tp'W(CO)(RC{\equiv}CMe)$ unit, while $Tp^*W(CO)_3H$ complexes resist protonation and loss of H_2 does not occur.

Acknowledgment. We thank the National Science Foundation for support of this work (Grant CHE8907341).

Supplementary Material Available: Tables of anisotropic temperature factors, complete bond distances and angles, and calculated hydrogen positions for 7 and 10, as well as an ORTEP drawing of 7 and a PLUTO drawing of 10 with the complete atomic numbering schemes (10 pages); listings of observed and calculated structure factors for 7 and 10 (35 pages). Ordering information is given on any current masthead page.

Formation of Iron Carbonyl Complexes of Reactive Polyenes from Dihalides Involves the Free Polyene

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Iron carbonyl complexes of reactive polyenes are commonly prepared by reaction of dihalides with iron carbonyl reagents. In the case of *o*-xylylene, reaction of iron carbonyl reagents with 1,2-bis(halomethyl)benzenes generally forms tricarbonyl(5-8-η^4-*o*-xylylene)iron, but in poor yields. This results from formation of free *o*-xylylene, which predominantly eludes trapping by the iron carbonyl and forms dimers and oligomers. Formation of free *o*-xylylene is also supported by trapping with norbornene to form the Diels-Alder adduct at the expense of iron complex. Results from the dibromobenzocyclobutene and -cyclopentene systems support the analogous formation of free benzocyclobutadiene and 2*H*-indene upon reaction with iron carbonyls. Significant improvements in yield of the *o*-xylylene complex result when the reaction is run by using disodium tetracarbonylferrate under heterogeneous conditions or by using $Fe_2(CO)_8^{2-}$ in solution.

Stabilization of reactive polyenes through coordination to transition metals has been a paradigm of organometallic chemistry at least since the report of tricarbonyl(cyclobutadiene)iron in 1965.[1] Because of the reactivity of the free polyenes, derivatives such as dihalides have often been used as precursors to the transition-metal complexes, reaction with the iron carbonyl reagent resulting (somehow) in both dehalogenation and complexation. Yields in such reactions are highly variable, but there is little information in the literature on the reason(s) for the variability, which presumably involve the mechanism of the reaction. We here report some relevant results for the *o*-xylylene system and also for the related 2*H*-indene and benzocyclobutadiene systems.

Organic derivatives of *o*-xylylene (1) (also called *o*-quinodimethane; Chemical Abstracts name 5,6-dimethylene-1,3-cyclohexadiene) have enjoyed extensive use in organic synthesis[2,3] because of their high reactivity as Diels-Alder dienes. They have been generated for synthetic purposes by several means,[2] but notably absent from the commonly used precursors to *o*-xylylenes are transition-metal complexes. The tricarbonyliron complex of *o*-xylylene (2) has been known since 1967,[4] and many other complexes of *o*-xylylenes with iron[5] and with other tran-

Table I. Reported Yields of 2 from Reaction of 3 with Iron Carbonyls

reagent	solvent	temp, °C	yield of 2, %	ref
$Fe_2(CO)_9$	ether	35	6	4a
$Fe_2(CO)_9$	THF	22	4	8
$Fe(CO)_5$, Me_3NO	benzene	0-80	4	4b
$Na_2Fe(CO)_4$	?	?	35	9
$(R_4N)_2Fe(CO)_4$[a]	toluene/water	20	25	10
$Na_2Fe(CO)_4$[b]	THF	30	34	11

[a] Generated in situ from NaOH and $Fe(CO)_5$ under phase-transfer conditions, using $Bu_4N^+HSO_4^-$. [b] This paper also reported isolation, in 25% yield, of tetracarbonyl-2-ferraindane, convertible into 2 by refluxing at 80 °C or photolysis. This tetracarbonyl is a plausible intermediate in formation of 2, but we, like all previous workers, have seen no sign of it in any of our reactions.

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(2) Reviews of *o*-xylylene chemistry: (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873-89. (b) Wiersum, U. E. *Aldrichimica Acta* **1981**, *14*, 53-8. (c) Oppolzer, W. *Synthesis* **1978**, 793-802. (d) Physical studies of 1 are conveniently summarized by R. Schulz and A. Schweig in: Liebman, J. F.; Greenberg, A. *Structure and Reactivity*; VCH Publishers: Weinheim, Germany, 1988; pp 300-304. (e) The NMR spectrum of 1 in solution has recently been observed by an ingenious flow experiment: Trahanovsky, W. S.; Chou, C.-H.; Fischer, D. R.; Gerstein, B. C. *J. Am. Chem. Soc.* **1988**, *110*, 6579-81.

(3) Some recent synthetic applications of *o*-xylylene chemistry include: Nemoto, H.; Fujita, S.; Nagai, M.; Fukumoto, K.; Kametani, T. *J. Am. Chem. Soc.* **1988**, *110*, 2931-8. Jung, M. E.; Brown, R. W.; Hagenah, J. A.; Strouse, C. E. *Tetrahedron Lett.* **1984**, *25*, 3659-62. Ito, Y.; Amino, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1983**, *105*, 1586-90. Mann, J.; Piper, S. E. *J. Chem. Soc., Chem. Commun.* **1982**, 430-2.

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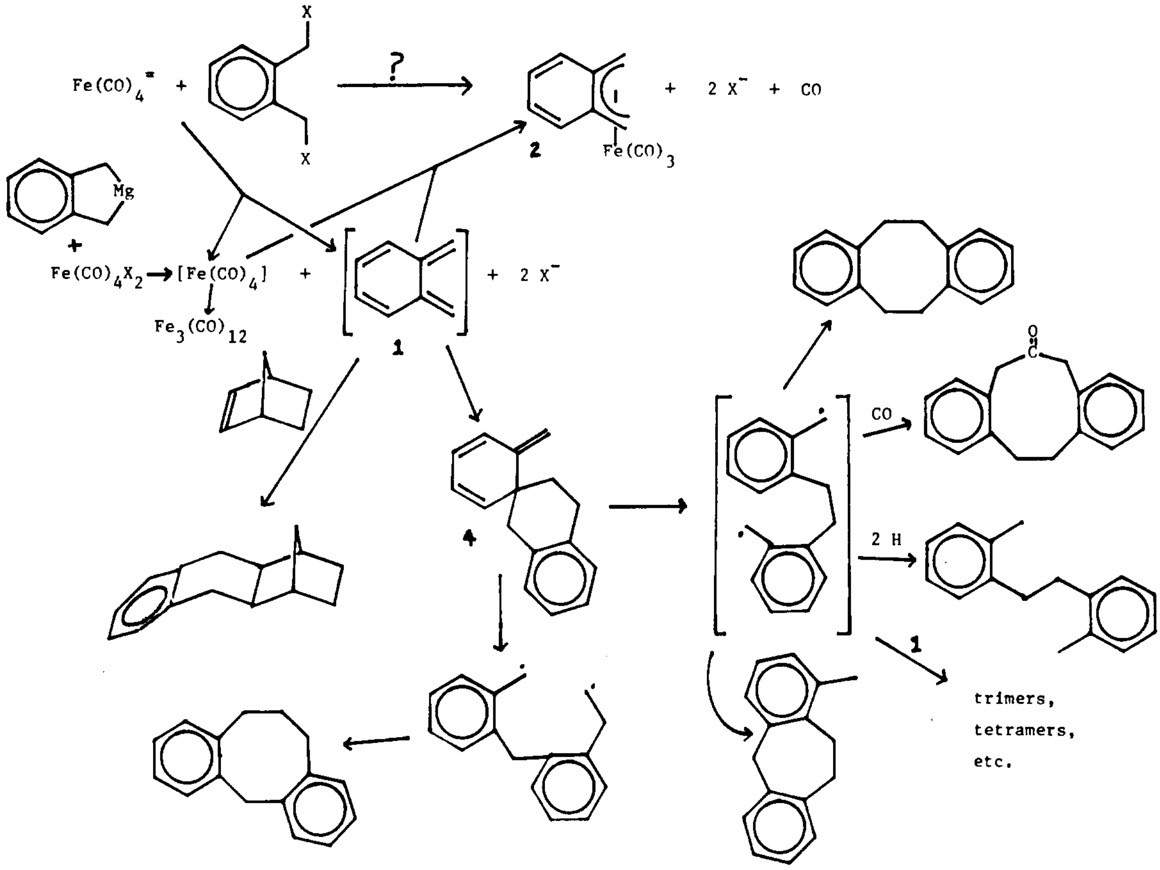
Scheme I. Formation of *o*-Xylylene Complex and Oligomers



sition metals[6] are also known. However, none of these appears to have seen use as a synthetic precursor to free *o*-xylylene (1). This is a surprising contrast to the time-honored use of, for example, tricarbonyl(cyclobutadiene)iron as a precursor to free cyclobutadiene.[7]

One reason may be that formation of 2 by reaction of 1,2-bis(bromomethyl)benzene (3) with iron carbonyl reagents proceeds in very poor to, at best, moderate yields. Literature data are summarized in Table I. These data show a clear preference for use of the anionic reagent, disodium tetracarbonylferrate, over neutral iron carbonyls; but they do not indicate what factors limit the yield and how the yield might be further improved. We therefore undertook to answer these questions by experimental study.

Results

Table II summarizes the results of numerous runs studying the reaction of disodium tetracarbonylferrate with 1,2-bis(halomethyl)benzenes. Yields of 2 shown were obtained by isolation of 2 by flash chromatography on silica and were corrected for small amounts of recovered dihalide in runs 1, 9, 13, 16, and 17. In THF, temperature (runs 1, 3, 4, and 5) had a modest effect on the yield of 2, with the higher temperatures giving the best results. The leaving group (runs 2, 12, and 18; 13 and 20) also showed a modest effect. Neither the manner of preparing the ferrate reagent (as the dioxanate[12] or dioxane-free[13]) nor slow addition of 3 to the ferrate solution (run 11) had significant effect. In even the best case using THF as solvent, the yield of 2 was only 14%.

The variable that most affected the yield of 2 was the solvent (runs 7, 12, 13, 14, and 15). DMF and THF, in which the ferrate salt is reasonably soluble, gave comparable results (9–11% yield). But in ether or hexane, *in which the ferrate is not visibly soluble*, much better yields of 2 (28–30%) resulted.

The favorable effect of nonpolar solvents is synthetically useful, but even under these conditions, most of the starting material gets diverted to products other than the desired 2. What are the other products formed?

Addition of dihalide to a nearly colorless solution or suspension of the ferrate salt results in rapid reaction, with evolution of heat and instantaneous darkening of the reaction mixtures to dark green or brown. TLC and, eventually, isolation show formation of significant quantities

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Table II. Yields of 2 from Reaction of $C_6H_4(CH_2X)_2$ with $Na_2Fe(CO)_4$

run	X	prep[a]	solvent	temp, °C	time, h	yield, %
1	Br	D	THF	−90 to 20	18	4.2
2	Br	D	THF	22	24	11.2
3	Br	D	THF	−50 to −30	45	3.1
4	Br	D	THF	22	20	11.8
5	Br	D	THF	80	0.33	14.2
6	Br	D	THF	22	48	9.3
7	Br	D	DMF	22	15	11.3
8	Br	F	THF	22	21	11.5
9[b]	Br	F	THF	22	16.5	13.6
10[c]	Br	F	THF	22	16.5	10.0
11[d]	Br	F	THF	22	26	11.0
12	Cl	F	THF	22	15	9.3
13	Cl	F	hexane	22	16	28.
14	Cl	D	ether	22	48	29.
15	Br	D	hexane	22	48	29.5
16	Cl	F	hexane[e]	22	12	21.4[e]
17	Cl	F	THF[e]	22	12	6.3[e]
18	$OCOCF_3$	D	THF	65	0.2	1.8
19	Br	D	heptane	98	1.25	13
20	Br	D	hexane	22	24	27

[a] Preparation of $Na_2Fe(CO)_4$ reagent: D = dioxanate[12] and F = freshly prepared in situ. [b] Run used excess 3: initial ratio of 3:$Fe(CO)_4^{2-}$ was 1.67. [c] Run used excess iron reagent: initial ratio of $Fe(CO)_4^{2-}$:3 was 1.50. [d] Run involved very slow addition of 3 to reaction mixture. [e] Solution also contained 1.0 M norbornene, and 8–12% of Diels–Alder adduct was also isolated.

(10% isolated yields in runs 10 and 12) of dodecacarbonyltriiron. This product clearly derives from two-electron oxidation of the tetracarbonylferrate dianion, indicating intervention of electron-transfer chemistry. Two-electron reduction of 3 should produce free 1, some of which may be trapped by reaction with neutral iron carbonyl fragments, but much of which must escape to form dimers, trimers, and oligomers of 1. (See Scheme I).

In fact, chromatographic separation of some of the lower R_f components of the reaction mixtures, especially from runs 7–9, led to mixtures of products, which were characterized by IR, NMR, and GC/MS methods. These revealed the formation of three dimers of 1, a dihydro dimer (1,2-di-*o*-tolylethane) and a dihydro trimer; the same products were also produced by reaction of 3 with zinc in refluxing ethanol.[14] The reaction of 3 with disodium tetracarbonylferrate also produced carbonyl-containing products. Higher molecular weight materials, insoluble in hexane or THF, were consistently produced in quantities corresponding to 30–60% of the starting 3. IR and NMR spectra of these materials were consistent with data previously reported for oligomers and polymers of *o*-xylylene.[15]

An umpolung of the reaction was also attempted. This involved formation of the organomagnesium species (o-$CH_2C_6H_4CH_2Mg)_3$[16] and its reaction with tetracarbonyldiiodoiron. This reaction produced 2 in 5% yield and also produced the dimer and dihydro dimer of 1, along with the same carbonyl-inserted dimers as obtained in the reaction of 3 with disodium tetracarbonylferrate. The conclusion that both reactions proceed through the same manifold, forming free 1 and $Fe(CO)_4$ in electron-transfer processes, is difficult to avoid.

Further support for the hypothesis that free 1 was produced in these reactions was adduced from trapping experiments. Unfortunately, the electron-deficient dienophiles commonly used to trap 1[2] would be expected to react rapidly with the highly basic and nucleophilic tetracarbonylferrate dianion and could not be used. However, Rickborn[17] has shown that norbornene can effectively trap 1 to form an *exo* Diels–Alder adduct. In our hands, this adduct was formed in 24% yield upon reaction of 3 with zinc metal in refluxing THF containing 1 M norbornene.

Reaction of 1,2-bis(chloromethyl)benzene with disodium tetracarbonylferrate in THF or hexane containing 1 M norbornene did in fact product both 2 (6% and 21% yields in THF and hexane, respectively) and the Diels–Alder adduct (8% and 12% yields). GC/MS study of the low-R_f oligomeric material clearly indicated incorporation of norbornene units. The reduced yields of 2 formed in the presence of norbornene support the view (Scheme I) that some or all of the 2 is formed from free 1, with norbornene effectively intercepting some of the 1 before reaction with $Fe(CO)_4$.

Discussion

Clearly, reaction of 1,2-dihalides with iron carbonyl reagents results in reductive dehalogenation to form the free alkene, when the alkene is a stable compound.[1,18] This process is often thought to involve oxidative addition of $Fe(CO)_4$ to a carbon–halogen bond, perhaps by analogy to results from monohalogenated systems or other metals.[19] Whatever the mechanistic details, it appears that *o*-xylylene (1), although reactive, is sufficiently stable[20] to be formed from reaction of 3 with $Fe(CO)_4^{2-}$ or neutral iron carbonyls. The generally superior yields of cyclobutadiene complexes produced in the analogous reactions of dihalocyclobutenes suggest that free cyclobutadiene, significantly less stable thermodynamically than 1, is not released into the medium during the reaction. As Pettit observed, "It is not considered necessary that a free cyclobutadiene molecule appear as an intermediate in the reaction."[1] Neither, of course, is it precluded (see below).

Dimerization and oligomerization of 1 have been studied by a number of workers. The second-order rate constant for dimerization of 1 at 25 °C is about 10^4 L mol^{-1} s^{-1}.[20,21] Our finding that the yield of 2 improves at higher temperatures is consistent with the low activation energy reported for dimerization of 1 (5.9 kcal/mol[21]); the formation of 2 from 1, having a higher activation energy, competes more effectively at higher temperatures.

It is probable that the spirodimer 4 forms most rapidly, via an allowed Diels–Alder reaction. 4 is not very stable at temperatures above 0 °C; its rearrangement reactions[15,22]

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(14) We thank Ms. Angela Tesoriero for performing this experiment.

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(20) The standard enthalpy of formation of 1 in the gas phase has been estimated to be 60.8 kcal/mol, which may be compared to 47.7 kcal/mol for its isomer benzocyclobutene: Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741–50. 1 is thus thermodynamically more stable than its isomer cyclooctatetraene, H_f° = 71.5 kcal/mol: Prosen, E. J.; Johnson, W. H.; Rossini, F. D. *J. Am. Chem. Soc.* **1950**, *72*, 626–7. Turner, R. B.; Meador, W. R.; Doering, W. von E.; Knox, L. H.; Mayer, J. R.; Wiley, D. W. *J. Am. Chem. Soc.* **1957**, *79*, 4127–33.

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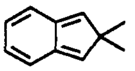
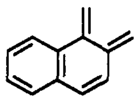
may occur as shown in Scheme I. Although dibenzo[*a*,*e*]cycloocta-1,5-diene is often reported as the sole dimeric product,[2,17,20] GC/MS analyses of our mixtures consistently show three stable $C_{16}H_{16}$ products, possible structures for which are shown in Scheme I. Hydrogen abstraction from solvent also generates *o*-tolylmethyl radicals, which dimerize to form 1,2-bis(*o*-tolyl)ethane or react further with 1 to form dihydro trimers and higher oligomers.[15,23]

Why are better results obtained with $Na_2Fe(CO)_4$ under heterogeneous conditions? We hypothesize ad hoc that under these conditions the *o*-xylylene produced remains adsorbed to the solid surface long enough to be trapped by iron carbonyls; when it desorbs, it must predominantly undergo oligomerization as in the homogeneous mixtures.

Fortunately for the prospects of using iron carbonyl complexes as precursors to synthetically useful *o*-xylylenes, the parent 1 is probably a worst case. Rates of dimerization are very sensitive to substitution on the exocyclic carbons. Such close derivatives of 1 as 2,2-dimethylisoindene (5)[24] and the benzo derivative 6[21] dimerize sufficiently slowly as to allow their characterization by NMR spectroscopy. Formation of complexes from the corresponding dibromides should therefore proceed much more successfully than for the parent system. Indeed, Roth and Meier[4a] reported in 1967 that the tricarbonyliron complex of 5 was formed from the dibromide in 40% yield under conditions in which 2 was obtained in only 6% yield. We infer that the slow dimerization of 5 allows it ample time to react with the iron carbonyl reagent, in contrast to the more transient 1.



5



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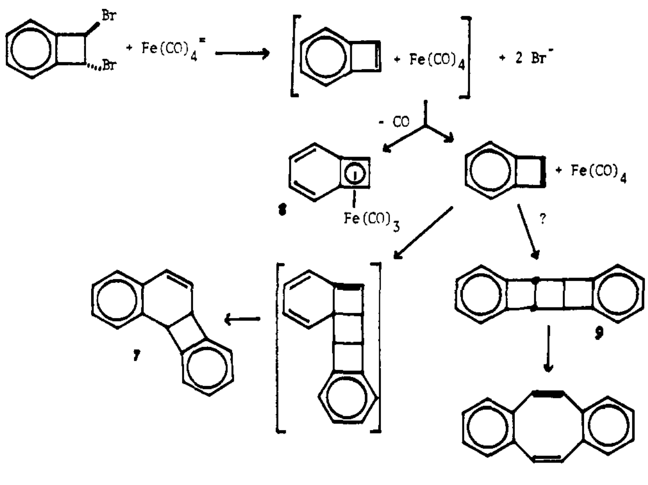
In order further to improve the yield of 2, one might consider including additional quantities of a reactive, neutral iron carbonyl reagent in the reaction medium along with the $Na_2Fe(CO)_4$ in order to increase the probability of intercepting free 1. Unfortunately, any such reagent will react rapidly with the tetracarbonylferrate. In the case of nonacarbonyldiiron, the reaction would be[25]

$$2Fe(CO)_4^{2-} + Fe_2(CO)_9 \rightarrow 2Fe_2(CO)_8^{2-} + CO$$

The use of $Fe_2(CO)_8^{2-}$ as a reagent for preparation of 2 is suggested by this equation, since 2-electron reduction of the dihalide by this species would produce 1 in the presence of 2 equiv of reactive, unsaturated iron carbonyl species ($2Fe(CO)_4 \rightleftharpoons Fe_2(CO)_8$),[26] increasing the chance of 1 being converted to 2 rather than oligomerizing. In fact, Ioset and Roulet[27] have recently reported (in a footnote) a 40% yield of 2 from reaction of 3 with $(Bu_4N^+)_2Fe_2(CO)_8^{2-}$ in acetone. We confirm the effectiveness of this reagent; in our hands, yields of 34% (acetone solution) and 33% (ether suspension) were obtained. The beneficial effect of the additional iron carbonyl species present on the yield of 2 is both synthetically useful and supportive of our proposed mechanism.

Scheme II. Reaction of Dibromobenzocyclobutene with Tetracarbonylferrate



Extension to Cyclic *o*-Xylylene Derivatives. The low yield of the *o*-xylylene complex 2 (compared to those of other polyene complexes) appears to arise from an unfortunate combination of properties of 1: it is sufficiently stable to be formed readily by dehalogenation of 3, but it is very reactive toward di- or oligomerization. A less stable polyene might not be released in free form, and a less reactive polyene, even though released, might be intercepted more effectively by iron carbonyl reagent.

In search of evidence for formation of free polyenes in related systems, we have looked at two in which the free hydrocarbons formed by iron carbonyl induced dehalogenation would be expected to form products more readily characterized than the oligomers that result from 1.

Reaction of *cis*-1,3-dibromoindane with bis(tetraethylammonium) octacarbonyldiferrate in ether produced indene almost quantitatively. The indene must arise by 1,5-hydride shift in isoindene (2*H*-indene), formed by initial debromination of the starting material. The rate of conversion of isoindene to indene does not seem to be known; hydride shift in a diphenylisoindene at 23.4 °C occurred with a first-order rate constant of 42 s^{-1}.[29] Formation of isoindene (and thence indene) under conditions that produce optimal yields of 2 from 3 strongly supports our conclusion that these reactions proceed by initial debromination. In the case of isoindene, the fast intramolecular rearrangement process obviates intermolecular trapping by reactive iron carbonyl species.

In contrast to isoindene, benzocyclobutadiene deactivates itself in solution by formation of a dimer. Under favorable conditions, benzocyclobutadiene, from metal-induced dehalogenation of *trans*-1,2-dibromobenzocyclobutene, forms the dimer, 7, 6*a*,10*b*-dihydrobenzo[*a*]biphenylene (Scheme II) in over 80% yield.[30] Thus, formation of this dimer, free of isomers and oligomers as

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[23] Brickwood, D. J.; Ollis, W. D.; Stephanatou, J. S.; Stoddart, J. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1398–1406.

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[25] $Fe(CO)_4^{2-}$ and $Fe(CO)_5$ react to form $Fe_2(CO)_8^{2-}$ with a rate constant of 6 × 10^8 at 25 °C: Amatore, C.; Verpeaux, J.-N.; Krusic, P. J. *Organometallics* **1988**, *7*, 2426–8.

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[30] (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701–5. (b) Nenitzescu, C. D.; Avram, M.; Dinu, D. *Chem. Ber.* **1957**, *90*, 2541–4. (c) Trahanovsky, W. S.; Fischer, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 4971–2. The NMR data reported (Rampazzo, L.; Inesi, A.; Bettolo, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *83*, 341–6) for this dimer (solvent not given) are different from the expected values and from our data. Reviews of benzocyclobutadiene: Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press; New York, 1967; Chapter 6. Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and Their Valence Isomers*; CRC Press, Inc.: Boca Raton, FL, 1987; pp 117–23.

formed by 1, should be a useful diagnostic for formation of free benzocyclobutadiene.

In their pioneering paper describing formation of complexes from reactions of dihalides with iron carbonyls, Emerson, Watts, and Pettit[1] included the formation of the tricarbonyliron complex of benzocyclobutadiene (8), although in unstated yield. We have studied the reaction of *trans*-1,2-dibromobenzocyclobutene with three iron carbonyl reagents,[31] with the particular intent of looking for the dimer 7 as evidence of formation of free benzocyclobutadiene. Reaction of the dibromide with a 2-fold excess of $Fe_2(CO)_9$ in ether at room temperature gave a 17% conversion (35% yield, correcting for recovered dibromide) to the iron complex 8. A benzocyclobutadiene dimer also formed; but it was dibenzocyclooctatetraene[32] rather than the canonical dimer 7. With $Na_2Fe(CO)_4$ reagent, the complex 8 was formed in 12% yield, and both dimers formed, with 7 in greater amount. Small amounts of 1-bromobenzocyclobutene and benzocyclobutene were also formed in these reactions, as shown by NMR spectroscopy. With $(Et_4N^+)_2Fe_2(CO)_8{}^{2-}$ in THF, the yield of complex 8 was only 6%; again both dimers formed, with 7 in greater amount, along with significant amounts of bi(benzocyclobutyl). The latter product was not formed in the other reactions of dibromobenzocyclobutene but is formally analogous to the ditolylethane formed from 3.

Formation of the canonical dimer 7 in reactions of the carbonylferrate anions with the dibromide supports the hypothesis that free benzocyclobutadiene is generated in these reactions, as shown in Scheme II. The unexpected formation of its isomer, dibenzocyclooctatetraene, which has not been reported to form upon dimerization of free benzocyclobutadiene, may be attributed to the influence of iron carbonyl species in the reaction mixture. Nenitzescu and co-workers[33] have reported that nickel carbonyl causes formation of the dimer 9 from benzocyclobutadiene and isomerization of 9 to dibenzocyclooctatetraene. A similar effect of iron carbonyls is plausible.

Conclusions

Reaction of organic dihalides with iron carbonyls to form complexes of reactive polyenes is a useful route to otherwise unobtainable complexes, but the yields are limited by escape of the reactive polyene. The free polyene may undergo complexation in part, or it may form dimers, oligomers, polymers, or tautomers, depending on its intrinsic reactivity. The fact that reaction of the dihalides with carbonyl reagents, especially the strongly reducting $Fe(CO)_4{}^{2-}$, results in dehalogenation *even when the hydrocarbon formed is as unstable as benzocyclobutadiene* suggests that the result initially obtained in the *o*-xylylene case is a general one.

Experimental Section

Ether and THF solvents were freshly distilled under nitrogen from benzophenone ketyl. Other solvents were redistilled from appropriate drying agents before use. Evaporations were done on a rotary evaporator at aspirator pressure and temperatures below 40 °C. Infrared spectra were recorded as liquid films on sodium chloride plates or KBr pellets, using Perkin-Elmer 567 or 1600 (FT) spectrometers. NMR spectra were obtained in $CDCl_3$ solutions containing internal TMS standard, unless otherwise indicated, on Varian CFT-20 or Nicolet QE-300 spectrometers. Mass spectra were obtained on a Hewlett Packard 5980 instrument.

1,2-Bis(bromomethyl)benzene, 1,2-bis(chloromethyl)benzene, 1,2-bis(dibromomethyl)benzene, norbornene, and indane were used as obtained from Aldrich Chemical Co. Iron pentacarbonyl (Pressure Chemical Co.) was filtered under nitrogen before use; other iron carbonyls were used as obtained. *N*-Bromosuccinimide (Crescent Chemical) was recrystallized from water, dried over P_4O_{10}, and stored at −20 °C. Disodium tetracarbonylferrate,[12,13] bis(tetraethylammonium) octacarbonyldiferrate,[34] *trans*-1,2-dibromobenzocyclobutene,[30a] *o*-xylylmagnesium trimer,[16] tetracarbonyliron diiodide,[35] and the dimer 7[30] were prepared by literature methods. 1,2-Bis((trifluoroacetoxy)methyl)benzene was prepared by reaction of the diol with trifluoroacetic anhydride in ether containing triethylamine; an oil, it showed a CH_2 proton resonance at δ 5.48 and aromatic protons at δ 7.47.

Reaction of 1,2-Bis(bromomethyl)benzene (3) with Disodium Tetracarbonylferrate (Run 8). A sample, theoretically 25.9 mmol, of $Na_2Fe(CO)_4$, freshly prepared by sodium naphthalene reduction of $Fe(CO)_5$,[13] was suspended in 30 mL of fresh THF, and a solution of 9.239 g of 1,2-bis(bromomethyl)benzene (3) (35.0 mmol) in 100 mL of THF was added slowly over a period of 15 min. A deep purple coloration was observed, and the solid dissolved as the dibromide was added. After 16 h of stirring at room temperature, the solution was filtered under nitrogen by using Schlenkware. After washing with THF, there remained 4.120 g of light brown solid (principally sodium bromide). The filtrate was evaporated under pump vacuum at room temperature. The yellow distillate showed the presence of $Fe(CO)_5$ by IR spectroscopy. Complete evaporation of the volatiles from the filtrate left 8.356 g of dark brown oil. TLC of this material showed iron complex 2, unreacted dibromide, and slower moving materials. This material was dissolved in ether, and hexane was added to form a solid precipitate (1.097 g) of polymeric material. IR spectra of this solid mulled in Nujol or hexachlorobutadiene showed peaks at 2860–3030, 1710, 1540–1600, 1490, 1450, 1370, and 750 cm^{-1}, consistent, except for the carbonyl peak at 1710, with data reported for poly(*o*-xylylene).[15] The soluble material was dissolved in ether, 5 g of degassed silica gel was added, and the solution evaporated. The resulting material was placed atop a silica gel column and eluted with hexane, which yielded 0.603 g of complex 2 (2.47 mmol, 9.5% conversion, 13.4% yield)[36] and then 2.873 g of unreacted dibromide (29% recovery, 10.9 mmol). Further elution with ether/hexane mixtures of increasing polarity yielded a total of 1.922 g of brown resinous material. IR spectra of these materials were similar to those of poly(*o*-xylylene). NMR spectra showed broad peaks at about δ 2.2 (ArMe), 2.8 ($ArCH_2CH_2Ar$), 3.6 ($ArCH_2CO$), and 7.0 (Ar). GC–MS analysis of the two largest fractions of this material showed, in the earlier fraction, three dimers of *o*-xylylene, M_r = 208, and a dihydro trimer, M_r = 314, presumably 1,2-bis[2-(*o*-tolyl)ethyl]benzene. All these products were also formed in the reaction of 3 with zinc in ethanol.[14] The later fraction showed carbonyl-containing components, especially ones of apparent M_r = 238, possibly 1,3-bis(*o*-tolyl)-2-propanone and M_r = 236, possibly dibenzocyclononanone.

Reaction of 1,2-Bis(chloromethyl)benzene with Disodium Tetracarbonylferrate in the Presence of Norbornene (Run 16). Solid disodium tetracarbonylferrate was prepared in situ as in run 8. It was slurried in 40 mL of hexane, and 11.901 g (116 mmol) of norbornene was added. A solution of 3.501 g (20.0 mmol) of 1,2-bis(chloromethyl)benzene in 60 mL of hexane was added slowly from the dropping funnel. After 3 days of stirring at room temperature, the mixture was filtered under nitrogen, yielding a brown precipitate (4.390 g) and a filtrate that left 5.006 g of residue upon evaporation. Chromatography on silica yielded the

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[31] The experiments involving benzocyclobutadiene were carried out by Mr. Michael A. Newman.

[32] Wong, H. N. C.; Sondheimer, F. *Tetrahedron*, **1981**, *37, Suppl. No. 1*, 99–109. Wittig, G.; Koenig, G.; Clauss, K. *Liebigs Ann. Chem.* **1955**, *593*, 127–56.

[33] Avram, M.; Dinu, D.; Nenitzescu, C. D. *Chem. Ind.* (*London*) **1959**, 257. Mateescu, G. D.; Avram, M.; Dinu, D.; Nenitzescu, C. D. *Rev. Chim.* **1963**, *8*, 13–22. 9 was also reported formed in the reaction of diiodobenzocyclobutene with magnesium: Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 2646–50.

[34] Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350–60.

[35] Hieber, W.; Bader, G. *Ber. Deutsch. Chem. Ges.* **1928**, *61*, 1717–22.

[36] Complete spectroscopic data for 2 are given in: Ribakove, E. C.; Kerber, R. C. *Organometallics* **1990**, *9*, 531–4.

following: (a) unreacted norbornene; (b) 1.238 g of a mixture of iron complex **2** and the *o*-xylylene–norbornene Diels–Alder adduct, which was analyzed by proton NMR spectroscopy as containing 0.844 g of **2** (17.3% conversion, 21.4% yield) and 0.394 g of adduct (9.8% conversion, 12.3% yield); (c) 0.660 g of unreacted dichloride (18.9% recovery); (d) 0.537 g of brown resinous material. GC–MS analysis of the latter showed several peaks whose spectra indicated incorporation of norbornyl (C_7H_{11}) and carbonyl units: M_r = 140 ($C_7H_{11}COOH$), 218 [$(C_7H_{11})_2CO$], 228 ($C_7H_{11}COCH_2C_6H_4CH_3$), and 226 ($C_7H_{10}COCH_2C_6H_4CH_2$), and others.

Reaction of [o-$C_6H_4(CH_2)_2Mg(THF)_2]_3$ with Tetracarbonyliron Diiodide. The magnesium reagent was prepared in THF solution from 1,2-bis(chloromethyl)benzene and 40–80-mesh magnesium metal by a literature method.[16] The filtered THF solution (20.0 mmol of magnesium reagent in 300 mL of THF) was added dropwise from a dropping funnel into a 500-mL 3-neck flask fitted with magnetic stirrer, nitrogen gas inlet, and reflux condenser and charged with 8.445 g (20.2 mmol) of tetracarbonyliron diiodide in 50 mL of THF. Gas evolution was observed, and a precipitate formed. After 3 days of stirring, 2.5 mL of ethanol was added to destroy any remaining Grignard reagent, and the mixture was filtered under nitrogen, leaving 8.709 g of precipitate. The filtrate was evaporated and stirred with 50:50 hexane/ether to form further precipitate, filtration of which left 5.026 g of green oil. This was chromatographed on silica as before to yield 0.233 g (5%) of complex **2**, followed by traces of unreacted dichloride and then resinous materials (2.569 g.) GC–MS analysis of one fraction of this material showed components of M_r = 120 [probably dihydrobenzo[c]furan, 210 [1,2-bis-(*o*-tolyl)ethane], 208 (an *o*-xylylene dimer), 238 [1,3-bis(*o*-tolyl)-2-propanone], and 236 (probably dibenzocyclononanone); all peaks but the benzofuran were identical in retention time and mass spectrum with peaks observed from reaction of disodium tetracarbonylferrate with **3**.

Dibromination of Indane. A mixture of 21.36 g (120 mmol) of *N*-bromosuccinimide, 7.090 g (60.0 mmol) of freshly distilled indane, and a pinch of benzoyl peroxide in 300 mL of carbon tetrachloride was refluxed under nitrogen for 20 min. Gravity filtration and evaporation of the filtrate left 18.345 g of pale orange oil, whose proton NMR spectrum indicated the presence of both trans (δ 3.04, t, J = 5.53 Hz; 5.54, *t*, J = 5.53 Hz) and cis (δ ca. 2.9, 3.3, m; 5.47 dd, as previously reported[28]) 1,3-dibromides in a 2:1 ratio. Recrystallization by slow addition of hexane to a concentrated ether solution of the dibromides at −78 °C resulted in formation of 2.67 g of white crystals, mp 87–9 °C, of *cis*-1,3-dibromoindane.[28] Photobromination with molecular bromine gave similar results.

Reaction of *cis*-1,3-Dibromoindane with $Fe_2(CO)_8^{2-}$. A solution of 0.800 g (2.90 mmol) of *cis*-dibromide in 50 mL of ether was cannulated into a round-bottom flask containing 2.08 g (3.50 mmol) of solid bis(tetraethylammonium) octacarbonyldiferrate. After several hours' stirring at room temperature, a sample was removed, and the solvent was evaporated under a stream of nitrogen. GC and NMR analysis of the residue showed indene to be the only significant component. A run using durene as an internal standard indicated an 82% yield of indene.

Reaction of *trans*-1,2-Dibromobenzocyclobutene with $Fe_2(CO)_9$.[32] Dibromobenzocyclobutene[30a] (2.00 g, 7.63 mmol) and 5.50 g (15.26 mmol) of nonacarbonyldiiron in 75 mL of ether were stirred for 4 days at room temperature. The mixture was filtered through Celite, the filter cake washed with ether, and the ether filtrate evaporated, leaving 2.767 g of oily product. Chromatography on degassed silica gel gave 1.328 g of an inseparable mixture of unreacted dibromide and iron complex **8**; analysis by proton NMR spectroscopy showed this to consist of 1.07 g (53% recovery) of dibromide and 0.26 g of complex **8** (17% conversion, 35% yield). Further elution of the column with hexane yielded 0.064 g of dibenzocyclooctatetraene (8% conversion, 16% yield), identified by NMR, GC, and MS comparison with an authentic sample prepared by reaction of 1,2-bis(dibromomethyl)benzene with powdered zinc,[37] and traces of *cis*-1,2-dibromo- and 1-bromo-2-iodobenzocyclobutene. Further reaction of the dibromide–complex **8** mixture with an additional 5.50-mmol portion of nonacarbonyldiiron, this time by refluxing in ether for 31 h, produced additional **8** but still did not result in consumption of all the dibromide. Small amounts of benzocyclobutene (δ 3.16) and 1-bromobenzocyclobutene (δ 3.9 dd, J's = 14.5, 4.6 Hz; 3.5 d, J = 14.5 Hz) were visible in the NMR spectrum of the first chromatography fractions.[38]

Reaction of the same quantities of reagents in THF at room temperature for 7 days also failed to consume all the dibromide. Gas chromatographic (3 ft OV-17 column, 150–250 °C) analysis of the crude product mixture showed, in decreasing quantity order, unreacted dihalide, iron complex **8**, and dibenzocyclooctatetraene. No trace of canonical dimer **7** was visible.

Reaction of *trans*-1,2-Dibromobenzocyclobutene with Collman's Reagent. Disodium tetracarbonylferrate sesquidioxanate (3.80 g, 11.0 mmol) was suspended in 40 mL of ether and cooled to 0 °C, and a solution of 2.62 g of dibromide in 15 mL of ether was cannulated in. The mixture was allowed to warm to room temperature and stirred for 19 h. The reaction was quenched with 10 mL of 10% aqueous sulfuric acid, and then the hexane solution was extracted with 3 × 50 mL of water, dried, and evaporated. TLC and IR and NMR spectroscopy showed substantial unreacted dibromide, dodecacarbonyltriiron, and some iron complex **8**. Column chromatography in hexane, with increasing quantities of methylene chloride, gave an inseparable mixture of unreacted dibromide and complex **8**, which was analyzed by NMR spectroscopy and found to contain 0.954 g (36% recovery) of dibromide and 0.168 g (0.77 mmol, 8% yield, 12% conversion) of **8**; a trace of 1-bromobenzocyclobutene was also indicated. Further elution yielded a mixture of dimers, of which canonical dimer **7** predominated over dibenzocyclooctatetraene by about 4:1, as indicated by GC.

Reaction of *trans*-1,2-Dibromobenzocyclobutene with Bis(tetraethylammonium) Octacarbonyldiferrate. The iron salt (4.55 g, 7.63 mmol) was dissolved in 30 mL of THF, and a solution of 1.00 g (3.82 mmol) of dibromide in 10 mL of THF was introduced by syringe and washed in with an additional 5 mL of THF. The mixture was stirred at room temperature for 47 h, refluxed for 5 h, cooled, and quenched with 5 mL of 10% aqueous sulfuric acid. The material was partitioned between 50 mL of water and 100 mL of ether, the layers were separated, and the aqueous layer was extracted with two additional portions of ether. Drying and evaporating the ether layers left 1.672 g of product. Chromatography of the hexane-soluble portion of this material with hexane on silica yielded complex **8** (0.047 g, 5%) and 0.082 g (ca. 21%) of a dimer mixture. NMR spectroscopy of this material showed a complex aromatic region, the four multiplets of dimer **7**, a trace of dibenzocyclooctatetraene (δ 6.76), a broad singlet at δ 3.88, and broad doublets at 3.02 and 2.95 (J = 13.2 Hz). The latter three peaks, equal in area, were consistent with formation of an unknown benzocyclobutyl compound. GC–MS analysis of this material showed the two dimers, **7** predominating, and also a material of apparent molecular weight 206, consistent with the structure 1,1′-bi(benzocyclobutyl) [m/z 205 (100%), 206 (88%), 191 (86%), 91 (60%), 178 (39%), 89 (30%), 115 (29%), 128 (27%)].

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(37) This reaction was discovered by Ms. Angela Tesoriero in these laboratories in 1985; it is a much more convenient synthesis of dibenzo[*a*,*e*]cyclooctatetraene than those previously reported.[32]

(38) Fraenkel, G.; Asahi, Y.; Mitchell, M. J.; Cava, M. P. *Tetrahedron* **1964**, *20*, 1179–84. Bubb, W. A.; Sternhell, S. *Aust. J. Chem.* **1976**, *29*, 1685–97.