

(PPh₃)X does not generate radical intermediates.

On the basis of these results, we conclude that photoinduced geometric isomerization reactions of *cis*- and *trans*-CpM(CO)₂(PPh₃)X occur via intramolecular rearrangements of the excited-state complexes. There are apparently three chemically distinct excited-state deactivation pathways available to these complexes, i.e., intramolecular isomerization, dissociation of carbon monoxide, and dissociation of PPh₃. However, knowledge concerning the electronic structures of the ground-state complexes and the character of the low-lying excited states and their conversion pathways to other electronic states is severely lacking. Hopefully, relationships between electronic structure and photochemical reactivity patterns for these complexes will be elucidated in the near future.

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Registry No. CpMo(CO)₃Cl, 12128-23-3; *cis*-CpMo(CO)₂(PPh₃)Cl, 32011-69-1; CpMo(CO)(PPh₃)₂Cl, 33152-14-6; CpMo(CO)₃Br, 12079-79-7; *cis*-CpMo(CO)₂(PPh₃)Br, 31851-05-5; *trans*-CpMo(CO)₂(PPh₃)Br, 31851-06-6; CpMo(CO)₃I, 12287-61-5; *cis*-CpMo(CO)₂(PPh₃)I, 57606-00-5; *trans*-CpMo(CO)₂(PPh₃)I, 32011-70-4; CpMo(CO)(PPh₃)₂I, 73104-92-4; CpW(CO)₃Cl, 12128-24-4; CpW(CO)₃Br, 37131-50-3; CpW(CO)₃I, 31870-69-6; CpMo(CO)(PPh₃)₂Br, 73208-29-4; [CpMo(CO)₃]₂, 12091-64-4; *cis*-CpW(CO)₂(PPh₃)Cl, 71425-48-4; *cis*-CpW(CO)₂(PPh₃)Br, 73173-84-9; *cis*-CpW(CO)₂(PPh₃)I, 53110-41-1; *trans*-CpW(CO)₂(PPh₃)I, 53110-40-0; [CpW(CO)₃]₂, 12566-66-4; [CpW(CO)₄]BF₄, 68868-84-8; *cis*-CpMo(CO)₂(¹³CO)Br, 73104-93-5; *trans*-CpMo(CO)₂(¹³CO)Br, 73175-01-6.

Contribution from the Department of Chemistry,
University of California, Los Angeles, California 90024

Chemistry via Metal Atom Cocondensation: Isomerization and Complexation Reactions of Organocyclopropanes and Spirocycles

A. J. LEE HANLAN, R. C. UGOLICK, J. G. FULCHER, S. TOGASHI, A. B. BOCARSLY, and J. A. GLADYSZ*

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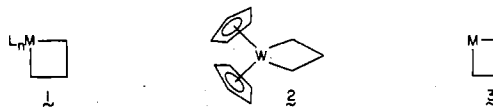
Reactions of metal atoms with structurally diverse organocyclopropanes have been studied. Quadricyclane (**4**) is isomerized to norbornadiene (**5**) upon cocondensation with a variety of metals, but control experiments suggest this reaction is heterogeneously catalyzed by metal aggregates which form upon warming the matrix. Norcarane (**6**), 2-norcarane (**7**), 3-carene (**8**), and 3-norcarene (**9**) give no reaction when cocondensed with a broad spectrum of metal atoms, despite the presence of an olefinic group in the latter three. When cyclopropylbenzene (**11**) is cocondensed with chromium, only bis(cyclopropylbenzene)chromium(0) (**12**) is formed. However, reaction of iron atoms with spiro[2.4]hepta-4,6-diene (**14**) yields a 14:64:6:17 ratio of 1,1'-diethylferrocene (**15**), 1-ethyl-1'-vinylferrocene (**16**), 1,1'-divinylferrocene (**17**), and [4]ferrocenophane (**18**) in 44% yield based upon iron. Cocondensations of iron with spiro[2.4]heptane (**20**; no reaction) and spiro[4.4]nona-1,3-diene (**23**; formation of bis(tetrahydroindenyl)iron (**24**) and 1,2-tetramethylene-1'-butylferrocene (**25**)) are also reported. Possible mechanisms of spirocycle (**14**, **23**) ring opening and product formation are discussed. No volatile bis(arene)chromium(0) complexes are formed when benzocyclopropene (**27**) and dispiro[2.2.2.2]deca-4,9-diene (**28**) are cocondensed with chromium, although the former is polymerized. The preparation of **18** from 1,1'-dilithioferrocene (**19**) and 1,4-dibromobutane is also described.

Introduction

The catalytic and stoichiometric interaction of inorganic and organometallic compounds with organocyclopropanes has been of substantial recent interest.^{1,2} Strained cyclopropanes such as bicyclobutanes have been isomerized to more stable valence isomers with a variety of catalysts.^{2,3} Numerous stoichiometric ring opening reactions have been observed. The involvement of metallocyclobutanes such as **1** has been suggested in many of these transformations. Metallocyclobutanes are also believed to be pivotal olefin metathesis intermediates,⁴ and their involvement in Ziegler-Natta olefin polymerization has recently been proposed.⁵

General preparative routes to metallocyclobutanes have not yet been developed. A few metallocyclobutanes have been

obtained by the oxidative addition of cyclopropanes to platinum complexes,⁶ and the tungsten metallocyclobutane **2** has been prepared from a cationic π -allyl precursor.⁷ Since improved accessibility of metallocyclobutanes would facilitate the study of their properties, we considered the possibility that the parent ring system **3** might result from the insertion of a transition-metal atom into a cyclopropane carbon-carbon bond.



Transition-metal atoms are highly reactive species by virtue of the 70-200 kcal/mol required for their formation.^{8a} Hence they can be utilized for the preparation of organometallic compounds whose synthesis would be difficult or impossible

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Table I. Quadricyclane (4) Reactions

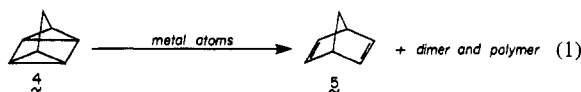
entry	metal, conditions ^a	mmol of 4: mmol of metal ^b	%			
			recovered 4 ^c	yield of 5 ^c	dimer + polymer ^{c,d}	turnover per metal ^e
1	Ti, cocondensation	185	88	8	1	16
2	Ti, cocondensation	13	82	15	1	2
3	Cr, cocondensation	41	25	70	1	29
4	Cr, surface	15	97	3	0	0.4
5	Cr, cocondensation ^f	13	98	2	1	0.4
6	Fe, cocondensation	7.4	0	61	1	5
7	Fe, surface	4.7	0	79	1	4
8	Fe, cocondensation ^f	5.9	77	18	2	1
9	V, cocondensation	17	18	71	4	13
10	Mo, cocondensation	56	96	2	1	2
11	Co, cocondensation	4.2	0	47	27	3
12	Ni, cocondensation	22	20	44	25	15

^a See also Experimental Section. ^b A correction factor, determined as described in the Experimental Section, was used to calculate the amount of evaporated metal reaching the reaction zone. Reaction scales: 11–22 mmol of 4. ^c Yields are based upon 4 and represent isolated materials. ^d Material of the formula (C₇H₈)_n (n ≥ 2) obtained by extraction of the reactor residue after pumping off 4 and 5. ^e mmol of 2 reacted: mmol of metal. ^f One-hour warm-up omitted; volatiles (4, 5) pumped directly into trap as matrix warmed.

by conventional methods.^{8–10} Reaction types observed between organic molecules and metal atoms include direct π complexation,¹⁰ oxidative addition,⁹ and oxygen abstraction.¹¹ Experimentally, metal vapor and excess (tenfold or greater) organic compound are cocondensed on a 77 K surface.¹² The concentration of metal atoms must be kept low because metal atom reaggregation is a low activation energy process which can compete with complex formation. Klabunde has generalized that unless the organic reactant has nonbonding or π electrons, metal atom repolymerization will be rapid at 77 K.⁹ However, we felt that cyclopropanes would be sufficiently reactive due to their strain energy and high lying Walsh orbitals to afford metallocyclobutanes such as 3. While such highly coordinatively unsaturated products would undoubtedly react further upon warming, trapping via the introduction of additional ligands (CO, PPh₃, etc.) to the matrix might afford complexes with some stability at room temperature. Hence we initiated an extensive study of the chemistry observed when metal atoms are cocondensed with organocyclopropanes, the results of which are reported in this paper.¹³

Results

Quadricyclane (4)¹⁴ was cocondensed with a variety of metal

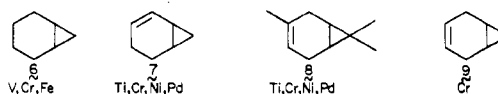


atoms at 77 K over a 0.5–1.0 h period in the reactor described in the Experimental Section. The matrix was allowed to warm for 1 h under static vacuum (unless noted) before workup. Volatiles (C₇H₈ material) were then pumped into a cold trap, weighed, and analyzed by NMR and GC. In all cases, some norbornadiene (5) was present, as summarized in Table I. Less volatile products were isolated by extracting the residue remaining in the reactor after pump-off of 4 and 5. A portion of this extract was nonvolatile, formed a cream-colored precipitate, and analyzed approximately for (C₇H₈)_n. This ma-

terial was presumed to be polymeric. The volatile components of the reactor extract were shown to be C₁₄H₁₆ dimers by GC/MS; GC retention times were identical with those of dimers obtained from the cocondensation of chromium and molybdenum atoms with norbornadiene. The combined yield of dimers and polymer is given in Table I.

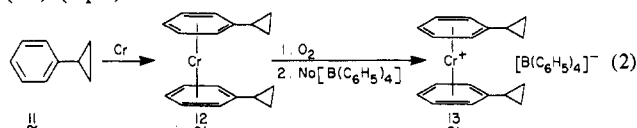
Several control experiments were conducted. Condensation of 4 onto the walls of the reactor with hot, nonevaporating tungsten filaments in place of the normal metal atom sources did not result in any reactions. When chromium alone was evaporated onto the reactor walls (77 K), followed by deposition of 4 (Table I, entry 4), little isomerization was observed. However, when a cocondensation was conducted as usual but the volatile products pumped directly into a trap as the matrix warmed (entry 5), virtually no isomerization was observed. The important implications of these observations will be discussed below. In experiments conducted with iron, a preformed iron surface (entry 7) was as active as codeposited iron (entry 6). Again, when the 1 h matrix warm-up was eliminated (entry 8), less isomerization was observed.

Reactions of norcaradiene (6) and the structurally related vinylic and allylic cyclopropanes 7–9 were investigated next.



When cocondensed with metal atoms (see formulas) as described for 4, 6–9 were recovered in nearly quantitative yields; no isomers could be detected by GC or ¹H NMR, even in the reactor residue. No distinctive colors (other than pale yellow) were observed in the cocondensation matrices.

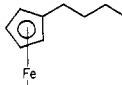
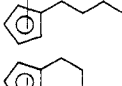
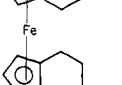
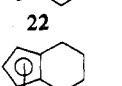
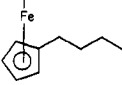
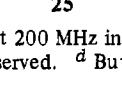
The cocondensation of cyclopropylbenzene (11) with chromium atoms afforded a 45% yield (based upon chromium) of bis(cyclopropylbenzene)chromium(0) (12), which was characterized by mass, ¹H NMR, and ¹³C NMR spectroscopy. Air oxidation produced the bis(cyclopropylbenzene)chromium(I) cation, which was isolated as its tetraphenylborate salt (13) (eq 2).



When nickel was cocondensed with cyclopropylbenzene, a yellow-orange matrix was formed, which when warmed afforded only starting material. Cocondensation of 11 with vanadium yielded a small amount of an air-sensitive, unstable oily red product, which upon decomposition gave cyclo-

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Table II. NMR Data on C₁₈ Ferrocenes

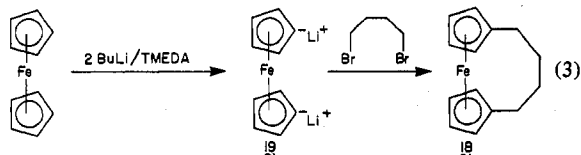
compd		butyl chain	cyclohexyl methylene	cyclopentadienyl ring
	¹ H NMR ^a	2.24 (t, <i>J</i> = 8 Hz, 4 H) 1.33 (m, 8 H) 0.84 (t, <i>J</i> = 7 Hz, 6 H)		3.90 (s, 8 H)
	¹³ C NMR ^b	33.3, 29.1, 22.7, 14.0		68.7, 67.7 ^c
	¹ H NMR		2.61 (m, 4 H) 2.27 (m, 4 H) 1.89 (m, 4 H) 1.60 (m, 4 H)	3.82 (d, <i>J</i> = 2 Hz, 2 H) 3.71 (t, <i>J</i> = 2 Hz, 4 H)
	¹³ C NMR		24.2, 23.7	84.7, 68.5, 67.7
22				
	¹ H NMR	2.29 (m, 4 H, overlapped) ^d 1.47 (m, 6 H, overlapped) ^d 0.90 (t, <i>J</i> = 7 Hz, 3 H)	2.58 (m, 2 H) 2.29 (overlapped) ^d 1.85 (m, 2 H) 1.47 (overlapped) ^d	3.91, 3.88 (br s, 7 H total)
	¹³ C NMR	33.5, 28.7, 22.7, 14.0	24.5, 23.7	69.8 (br), 66.4 (br) ^c
25				

^a δ, at 200 MHz in CDCl₃ relative (CH₃)₄Si. ^b Ppm, at 50 MHz in CDCl₃ relative (CH₃)₄Si. ^c Alkyl-substituted ferrocene carbon(s) not observed. ^d Butyl-chain protons not resolved from cyclohexyl methylene protons.

propylbenzene. No allylbenzene, methylstyrene, or styrene were detected in any of these reactions.

The cocondensation of spiro[2.4]hepta-4,6-diene (**14**)¹⁵ with iron atoms resulted in a dark orange syrup after matrix thawing. Recovered ligand was found by GC and ¹H NMR to be devoid of isomerized material. The reactor residue was extracted with benzene and chromatographed on silica gel. A fast moving orange band was collected and shown by GC to contain four major products in a 14:64:6:17 ratio (in order of elution). Samples of each were purified by preparative GC. Spectroscopic properties suggested the structures 1,1'-diethylferrocene (**15**), 1-ethyl-1'-vinylferrocene (**16**), 1,1'-divinylferrocene (**17**), and [4]ferrocenophane (**18**), respectively (see Scheme I below). The total isolated yield of ferrocenes (based upon iron and an average product formula of C₁₄H₁₆Fe) was 44%.

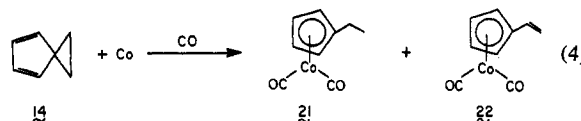
Chemical evidence was obtained for the proposed structures **15**–**18**. When a portion of the reaction mixture was hydrogenated, **16** and **17** were converted to **15**. Pure **15** was identical with an authentic sample. An independent synthesis of **18** was achieved (33% yield) by the reaction of 1,1'-dilithioferrocene (**19**)¹⁶ with 1,4-dibromobutane (eq 3).



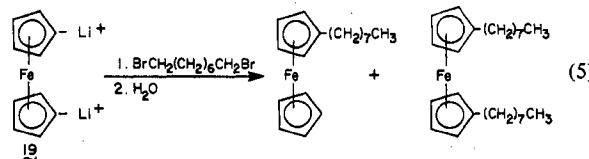
No volatile products formed when spiro[2.4]heptane (**20**) was cocondensed with iron atoms. When mixtures of **14** and P(OCH₃)₃ were cocondensed with iron atoms (ratios as high as 1:4), only ferrocenes **15**–**18** were produced.

When **14** was cocondensed with chromium atoms and nickel atoms, brightly colored volatile products formed. Because of their sensitivity, these complexes were not characterized. When **14** was cocondensed with cobalt atoms, a brownish matrix was obtained. While the matrix was warmed to room temperature, 1 atm of CO was introduced into the reactor. Excess **14** was then fractionated from a volatile orange oil.

Subsequently isolated was a ca. 1:1 mixture of the known compounds **21** and **22** (eq 4).¹⁷ However, in multiple runs, yields of **21** and **22** never exceeded 1% (based on cobalt).



The cocondensation of spiro[4.4]nona-1,3-diene (**23**)¹⁵ with iron atoms also resulted in the formation of ferrocene products but in lower (5–20%) yields. The two major products obtained (in 1:5 to 1:9 ratios) were purified by preparative GC and spectroscopically characterized. The product with the longer retention time (major product) was shown to be bis(tetrahydroindenyl)iron (**24**)¹⁸ by comparison to an authentic sample. The other product was a new compound. Its mass spectrum indicated a molecular weight 2 greater than that of **24**. Its 200-MHz ¹H NMR spectrum and 50.32-MHz ¹³C NMR spectrum were virtually identical with the superimposed spectra of **24** and 1,1'-dibutylferrocene, as summarized in Table II. Hence the structure **25** was assigned. No 1,1'-dibutylferrocene was detected in the reaction mixture by GC. A reaction mixture was exposed to PtO₂/H₂, but the GC trace was unaffected. These conditions would have hydrogenated any 1-butyl-1'-butenylferrocenes to 1,1'-dibutylferrocene. An attempt was made to synthesize an authentic sample of [8]-ferrocenophane (**26**) by the reaction of 1,1'-dilithioferrocene (**19**) with 1,8-dibromooctane. However, the major non-polymeric products obtained were octylferrocene and 1,1'-dioctylferrocene (eq 5).



Two other organocyclopropanes were cocondensed with chromium atoms. Benzocyclopropane (**27**, contaminated with

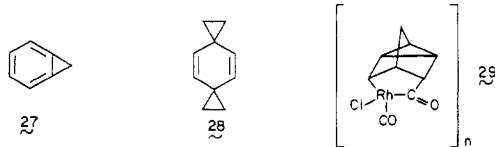
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a trace of toluene and a small (<5%) amount of styrene from its preparation)¹⁹ did not afford any volatile π complexes. Recovered **27** contained a slightly greater amount of toluene than was present in the original sample. Substantial amounts of material could be extracted from the reactor residue after exposing it to air. An oily component of this extract was shown by mass spectrometry to be a C_7H_6 polymer (see Experimental Section).

The cocondensation of highly crystalline **28**²⁰ (neat or dis-



solved in decane) with chromium similarly did not result in the formation of any volatile π complexes. Starting material was recovered unchanged.

Discussion

Although quadricyclane (**4**) is thermally robust (half-life 14 h at 140 °C),²¹ rapid isomerization to **5** can be effected by a variety of catalysts.²² Metallocyclobutanes have been postulated as intermediates in these isomerizations; when $[Rh(CO)_2Cl]_2$ was employed in stoichiometric quantities, rhodacyclopentanone **29** was obtained.²³ Direct 2+2 cyclo-reversion of **4** to **5** by metal-induced attenuation of orbital symmetry imposed energy barriers has also received mechanistic consideration.²

Mechanistically, our results with **4** and chromium and iron atoms (Table I, entries 3–7) are the most informative. Notably, a predeposited chromium surface does not efficiently isomerize **4** (entry 4). However, much less isomerization is observed when the cocondensation is conducted as usual but the 1-h matrix warm-up eliminated (entry 5). During the warm-up period the matrix melts, and if no stable complexes are formed, the metal aggregates. Klabunde has shown that finely dispersed metal particles which have superior catalytic properties are produced under these conditions.²⁴ Since contact time between the aggregated chromium and organic reactant is therefore important, we believe it probable that most of the isomerization observed with chromium (entry 3) is heterogeneously catalyzed.

Surface-catalyzed isomerization is more evident in the experiments conducted with iron atoms, in which lower ratios of **4**:metal were employed. A preformed iron surface (entry 7) was as active as codeposited iron (entry 6). When the organic material was pumped from the reactor as the matrix warmed (entry 8), much less isomerization was observed.

While surface control experiments were not conducted with the other transition metals utilized in Table I, most of the observed reactions are believed to be heterogeneously catalyzed. Thus strictly speaking, the turnover numbers in Table I should be restated in terms of surface atoms to provide more accurate reactivity comparisons. However, the isomerization

of quadricyclane to norbornadiene via a discrete metallocyclobutane cannot be ruled out as a minor reaction pathway. We believe that if a metallocyclobutane was formed, it would not quantitatively revert to **4**; decomposition to less strained norbornadiene does not require any atom transfer and seems the more likely reaction upon warming. From this premise, our results indicate that at 77 K and higher temperatures, metal atom aggregation is faster than quadricyclane bond insertion.

The two experiments with titanium (Table I, entries 1 and 2) provide an interesting example of how "yields" can be manipulated. At the 185:1 ratio of **4** to titanium employed in entry 1, only 8% of the quadricyclane was isomerized. However, each titanium atom deposited isomerized (or dimerized) an average of 16 quadricyclane molecules (turnover number). When a higher matrix concentration of titanium was employed (entry 2, **4**:Ti = 13:1), twice as much norbornadiene was formed, but each titanium atom averaged only two isomerizations. Thus, depending upon whether the investigator is predisposed toward organic synthesis (yield of **5**) or catalysis (turnover number), the reaction conditions can be adjusted accordingly.

The C_7H_8 dimers and polymers formed as tabulated in Table I may arise from initially produced norbornadiene or directly from quadricyclane.^{22b} Norbornadiene dimers have been obtained via cocondensation of nickel, molybdenum, and tungsten with norbornadiene.^{8,10} Polymers have also been formed with molybdenum and tungsten.¹⁰ We have observed dimer and polymer formation upon cocondensation of norbornadiene with chromium and iron. No norbornadiene complexes have yet been prepared by metal atom cocondensation, and attempts to obtain spectroscopic or trapping evidence for their existence have not been successful.^{8,25} Hence it is possible that these reactions are surface catalyzed. Skell has suggested that polymer formation may be via olefin metathesis of norbornadiene.^{8,10}

Although the structurally related cyclopropanes **6–9** lack the strain energy of **4**, easily identified products would result if isomerization occurred. Since olefinic binding groups are present in **7–9**, we thought metal atom reagggregation would be retarded relative to **4**. 2-Norcarene is ring opened to a cationic π -allyl complex upon treatment with $PdCl_2(C_6H_5CN)_2$,²⁶ and a wide variety of other vinyl cyclopropanes have been observed to undergo rhodium(I)-catalyzed isomerization^{1e} or stoichiometric ring-opening reactions with iron carbonyls.^{1a} However, recoveries of **6–9** after cocondensation with metal atoms were in the 80–100% range. We believe that any metallocyclobutanes formed from **6–9** would give subsequent reactions (isomerization) upon warming rather than revert solely to a metal atom and organocyclopropane. Indeed, thermolysis of isolable metallocyclobutanes gives rise mainly to olefinic products,^{7,27} although cyclopropanes are formed as minor products in some cases. From this premise, we conclude that no carbon-carbon bond insertion occurs with substrates **6–9** prior to metal atom reagggregation.

Although a phenyl substituent might be expected to facilitate cyclopropane ring rupture, no evidence for ring opening was obtained in any of the experiments involving cyclopropylbenzene (**11**). Toluene forms an unstable complex with nickel atoms upon cocondensation,²⁸ so the yellow-orange matrix obtained from **11** and nickel is probably due to a

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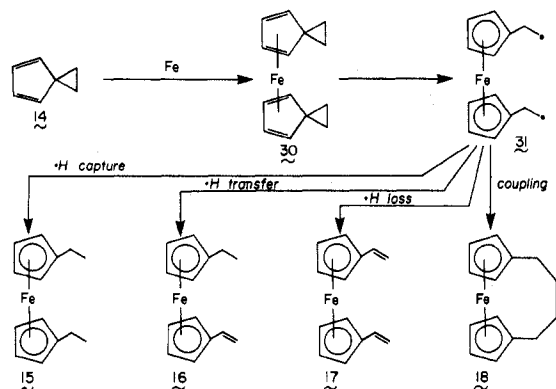
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Scheme I. Proposed Mechanism for the Formation of Ferrocenes 15-18



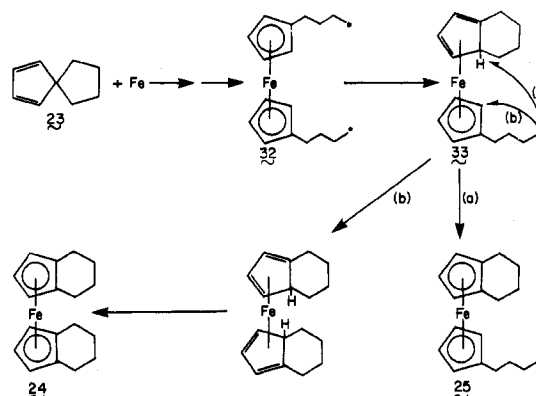
transient π -arene species. Bis(benzene)vanadium(0) has been prepared in 2% yield by the cocondensation of vanadium with benzene.^{29a} Like the material obtained from **11** and vanadium, it is red and extremely air sensitive.²⁹ Interestingly, cyclopropylbenzene has been observed to give a rhodacyclopentanone (75%) when reacted with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ for 48 h at 60 °C.³⁰

Metal atoms are well-known to efficiently complex 1,3-dienes.³¹ Furthermore, many metal atoms, including iron, yield metallocenes when cocondensed with cyclopentadiene.^{8b} This requires the expulsion of H_2 , presumably after cyclopentadiene coordination. The results obtained when **14** is cocondensed with iron atoms can be rationalized along similar lines (Scheme I). A possible initially formed species is **30**. Since the saturated homologue, spiro[2.4]heptane (**20**), failed to react with iron atoms, the diene functionality in **14** must play an important role in iron binding and/or cyclopropane activation.

The products **15-18** can be rationalized as arising from the biradical **31**, as depicted in Scheme I. The major product, **16**, would then form via an intramolecular transfer of a quasi-benzylic hydrogen. The existence of other species on the reaction coordinate between **30** and the products, such as intermediates with iron-carbon σ bonds, constitutes an open question. An independent means of generating the biradical **31**, perhaps from an azo precursor, would be desirable. A biradical intermediate is apparently formed when 6,6-dimethylfulvene is cocondensed with iron atoms: products obtained include tetramethyl[2]ferrocenophane (30%) and the hydrogen abstraction product 1,1'-diisopropylferrocene (25%).³²

Complexes of the formula (diene) FeL_3 are commonly available by adding phosphites to diene-iron matrices or by cocondensing iron with diene-phosphite mixtures.^{31b,33} Our failure to obtain such products from **14** suggests that cyclopropane ring opening occurs shortly after (or perhaps synchronously with) the coordination of **14** to iron. With a single exception involving η^2 complexation,^{34a} reactions of **14** with a variety of metal-carbonyl compounds yield exclusively ring-opened products.^{17,34}

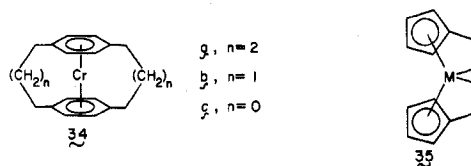
Scheme II. Proposed Mechanism for the Formation of Ferrocenes 24 and 25



The successful reaction of **23** with iron atoms (Scheme II) indicates that cyclopropane ring strain is not a primary driving force for the reactions of **14**. Hence the ring opening of coordinated **14** and **23** is most likely driven by the formation of an aromatic cyclopentadienyl ring and the formal oxidation of iron(0). Products **24** and **25** (Scheme II) can be rationalized as arising from the cyclization-prone biradical **32**.^{34d} As depicted in Scheme II, the intermediate **33**, in which the iron is formally in the +1 oxidation state, may also be common to both products. The reaction of **23** with $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$, $\text{Fe}_2(\text{CO})_9$, and $\text{Co}_2(\text{CO})_8$ also results in the formation of complexed tetrahydroindene.^{17,34c}

The formation of some [4]ferrocenophane (**18**) upon cocondensation of **14** with iron atoms is significant in that metal atoms are generally not efficient templates for the formation of phane or cage-like structures.³⁵ A more direct synthesis of **18**, however, can be realized from 1,1'-dilithioferrocene (**19**; eq 3). Surprisingly, **19** has not to our knowledge been previously employed in the synthesis of carbon-bridged ferrocenophanes, although sulfur-^{15b} and silicon-bridged³⁶ ferrocenophanes have been prepared from **19**.

Although we failed to obtain any organometallic products from **28** and chromium, **28** is highly crystalline (but hydrocarbon soluble) and better results might be realized in a solution-type reactor. By analogy to the reaction of **14** with iron, we had hoped that some **34a** might be formed. Recently, **34b** and **34c** have been isolated in low yield from the cocondensation of [3.3]- and [2.2]paracyclophane with chromium atoms.^{37,38}



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Because of its foul odor, extensive experiments were not conducted with benzocyclopropane (**27**). Since chromium atoms rapidly react with aromatic hydrocarbons at 77 K,³⁹ it is probable that some type of π complex, which decomposes upon warming, is formed. Since control experiments with chromium surfaces were not conducted, the origin of the C_7H_6 polymer is uncertain. Previously, naphtho[*b*]cyclopropane has been observed to undergo a ring-insertion reaction with $Fe_2(CO)_9$.⁴⁰

Conclusion

This study has established that metal atoms will reaggregate at a much faster rate than they undergo reaction with organocyclopropanes unless a functional group is present that the metal atoms can strongly interact with. Metal atom reaggregation yields from 89 (Pd) to 123 (Ti) kcal/mol for all of the metals employed in this study except molybdenum (ΔH_{298K} for the formation of molybdenum atoms is 159 kcal/mol).^{8a} Metal atom insertion into a cyclopropane destroys one strained carbon-carbon bond and forms two new metal-carbon bonds. In light of known transition metal-carbon bond strengths (generally 28–62 kcal/mol),⁴⁰ insertion is probably not as exothermic as, and certainly has a higher orientational requirement (lower ΔS^\ddagger) than, metal atom reaggregation. The platinum-carbon bond energies in metallocyclobutanes of the type $L_2X_2Pt(CH_2CH_2CH_2)$ have been determined to be in the range of 27–30 kcal/mol,^{27a} some 5–9 kcal/mol weaker than those for acyclic platinum-carbon bonds. Nonetheless, under the high dilution matrix conditions of the type employed in this study, a wide variety of insertion reactions have been observed.⁹

The isolation of **12** indicates that strong binding of the metal atom to the organic substrate is not in itself sufficient to achieve cyclopropane ring opening; the three-membered ring must be provided with additional activation as in **14**. While metallocyclobutane products are not formed when **14** is reacted with iron atoms, other metals might afford cyclic complexes such as **35**.^{34d} Indeed, preparative extension of these reactions (Schemes I and II) to other spirocycles and metals should provide entry into otherwise difficultly accessible metallocenes. The synthesis of **21** and **22** from **14**, cobalt, and CO (eq 4), albeit in low yield, illustrates another type of preparative application.

The formation of organometallic species such as bis(arene)chromium complexes upon metal atom/arene cocondensation has been firmly established as proceeding via atomic metal.³⁹ However, our demonstration of surface-catalyzed quadricyclane isomerization indicates that caution must be exercised in interpreting the results of metal atom/organic molecule cocondensations in which only *organic* products are formed. For instance, Green has noted the oligomerization of butadiene upon metal atom cocondensation,⁴² and several reports of acetylene cyclotrimerizations have appeared.^{35a,43} These may in fact be catalyzed by metal particles instead of metal atoms.

Finally, we wish to speculate that the spectroscopic monitoring of cyclopropane/metal atom cocondensation matrices may reveal additional valuable information. Ozin and Hanlan have noted⁴⁴ that the cocondensation of cyclopropane and

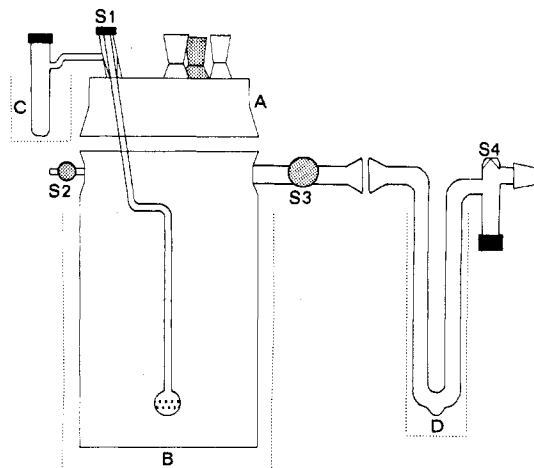


Figure 1. Reactor with electrodes omitted.

rhodium ($10^4:1$) at 10 K gives rise to an intense UV absorption at 225 nm with a shoulder at 330 nm. These absorptions are independent of rhodium concentration and disappear upon warming. Only spectral bands attributable to cyclopropane remain. This is suggestive of a charge-transfer interaction. Coupled with the data herein, it appears that other preparative routes for matrix generation of metallocyclobutanes will have to be sought.

Experimental Section

General Procedures. Melting points were determined on a Büchi Schmelzpunktbestimmungsapparat and were not corrected. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer. Mass spectra were obtained on an AEI MS9 instrument. NMR spectra were obtained on Varian T-60, Varian CFT-20, and Bruker WP-200 spectrometers. All chemical shifts are relative (CH_4)₄Si internal standard. Microanalyses were performed by Galbraith Laboratories.

Organic Substrates. Quadricyclane was prepared by a literature procedure¹⁴ and purified by spinning band distillation. Cyclopropylbenzene and norcarene were purchased from Aldrich Chemical Co.; although used without purification, both were checked by ¹H NMR and GC for isomeric contaminants. 2-Norcarene was prepared by the reaction of 1.3 equiv of Simmons-Smith reagent with 1,3-cyclohexadiene⁴⁵ and purified by preparative gas chromatography. An identical procedure was followed for the preparation of 3-norcarene from 1,4-cyclohexadiene. 3-Carene was purchased from Pfaltz and Bauer. Spirocycles were prepared by published procedures.^{15,20} Benzocyclopropane was obtained via a standard preparation.¹⁹

Other Reagents and Materials. Tetramethylethylenediamine (TMEDA) was freshly distilled from KOH (117 °C) before use. 1,4-Dibromobutane and 1,8-dibromooctane were purchased from Aldrich Chemical Co. and used without purification. Authentic samples of 1,1'-diethylferrocene, 1,1'-dibutylferrocene,⁴⁶ and bis-(tetrahydroindenyl)iron¹⁸ were prepared by published procedures.

Metal Atom Reactor. A view of the metal atom reactor utilized in this study (with electrodes omitted) is provided in Figure 1. It is based upon designs previously described by Skell, Timms, and Klabunde.^{8-10,12}

The reactor top A (Figure 1) is a heavy glass bowl with a 100-mm O-ring joint on the rim. Two stainless-steel electrodes are inserted through 24/40 glass joints in the top. A pressure gauge (Penning-type) can be inserted into a third joint. The ligand reservoir (C) (capacity 15 mL) is attached to the top via a glass inlet tube which passes through a 5-mm Teflon stopcock (S1) and runs down the center of the reactor. The inlet tube is wrapped over its entire length with nichrome wire, which is attached by alligator clips to tungsten leads which pass through the reactor (see Figure 2, supplementary material).

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The reactor bottom (B) is a thick-walled glass cylinder which is sealed to top A by a 100-mm O-ring joint. The reactor walls furnish a surface area of approximately 3000 cm² for cocondensation. A small stopcock (S2) near the top rim permits the introduction of argon during product workup. A glass side arm supports a 20-mm stopcock (S3) and an O-ring joint for the attachment of a U-tube (D). U-Tubes can be joined in series to fractionate volatile products; ampules and NMR tubes can be attached to the bottoms of the U-tubes for isolating sensitive materials under vacuum. A 20-mm stopcock (S4) in the last U-tube allows the apparatus to be shut off from the diffusion pump. The entire assembly is clamped to a lattice and is supported with lab jacks.

Metal Evaporation. Metal atoms are produced by resistive heating of alumina crucibles (E) or coated tungsten rods which are securely clamped by split bolts (F) to the electrodes, as detailed in Figure 2, supplementary material. The hollow, stainless-steel electrodes (G) circulate cooling water in cold-finger fashion. A stainless-steel 24/40 joint (H) near the top of the electrode ensures a tight metal-glass seal. Heavy copper cables leading from a step-down transformer are bolted to studs in the electrodes. Current to the transformer is controlled by a variac.

Coated tungsten rods are the most convenient metal source when <200 mg of metal is required. Chromium-coated tungsten rods (2 in. × 0.05 in. diameter, coated to a diameter of 0.080 in.) were obtained from GTE Sylvania. Coated rods of Ti, V, Ni, Fe, and Co were obtained from Materials Research Corp. The transformer output during metal evaporation varies from 1.6 V, 55 A for Cr to 3 V, 95 A for Ti. Larger quantities of metal can be evaporated from tungsten/alumina spiral crucibles (2-in. length × 0.5-mL volume) obtained from GTE Sylvania. The transformer output during the evaporation of chromium from a crucible is 6 V, 40 A.

Some of the metal evaporated from the filament is intercepted by structures within the reactor. The fraction of metal reaching the walls was determined in a blank run in which only chromium was evaporated. The total amount of chromium evaporated was determined by weighing the coated rod before and after evaporation. The amount of chromium deposited on the walls was determined by dissolving the chromium film in hot 70% perchloric acid, heating to oxidize to Cr(VI), and titrating by standard methods.⁴⁷ The fraction of metal reaching the walls was found to be 0.76.

Cocondensate Vapor Delivery. Various reactor tops, which differ in the shape of the inlet tube, are utilized, depending upon the amount and properties of the organic material being employed. The top employed in this study (Figures 1 and 2) is designed to accommodate 1–12 g of material with a bp <250 °C (760 mm). The inlet tube terminates in a glass bulb which is symmetrically pierced to spray vapor evenly on the reactor walls. During a cocondensation the entire length of the tube is gently heated with nichrome wire (J, Figure 2) to aid vapor transfer and prevent substrate freezing.

General Reaction Procedure. In a typical run, the apparatus is assembled and evacuated to 10⁻⁵ torr. Stopcock S1 is closed, and the reservoir (C) is opened and filled with 2–10 g of organic material. After the reactor and U-tubes are trapped in liquid N₂ and the reservoir is trapped in dry ice-acetone, the system is reevacuated. The organic material is degassed by several freeze-thaw cycles. The nichrome inlet coil and the metal evaporation source are degassed by heating to a dull red glow. The dry ice-acetone bath surrounding the reservoir is warmed until organic material begins to condense on the reactor walls. The rate of deposition is regulated by the bath temperature. Water or oil is used for bath temperatures of 25–200 °C.

As organic material begins to deposit, the current through the metal source is gradually increased until metal begins to evaporate. The rate of metal deposition is controlled by adjusting the transformer output with a variac. Typical deposition rates are 4 g/h for organic material and 100 mg/h for metal. Much higher evaporation rates can be employed. The progress of the cocondensation can be observed by briefly removing the liquid N₂ trap from the reactor, after turning off the current to the metal source.

When the addition of organic material is complete, stopcock S3 is closed and the liquid N₂ trap is removed. The reactor is allowed to warm to room temperature under static vacuum. After 1 h, S3 is opened and volatile material (usually excess substrate) is collected

in U-tube D. If the desired product is less volatile, S3 is closed and argon is introduced through S2. Top A is then removed and replaced with a sublimator top. Material can be collected by sublimation to the cold finger; alternatively the reactor can be extracted with a solvent. Air-sensitive materials can be isolated by detaching the reactor from the U-tube and transferring the assembled reactor into a drybox. The metal source is weighed before and after cocondensation to determine the amount of metal vaporized.

Quadricyclane (4) Reactions. All cocondensations with this substrate were conducted in an identical fashion. The quantities of reactants employed can be inferred from Table I. A typical procedure is as follows (entry 2, Table I):

The reactor was assembled and evacuated as previously described with a titanium-coated tungsten rod (1.3610 g) clamped to the electrodes. Quadricyclane (1.5 mL, 1.48 g, 16.1 mmol) was loaded in the side arm reservoir, which was then cooled in dry ice-acetone and reevacuated to 10⁻⁵ torr via two freeze-thaw cycles. The temperature of the acetone bath was raised to -16 °C to distill in quadricyclane. Titanium was evaporated with transformer output 3V, 95 A. After 35 min, the cocondensation was halted and the reactor was allowed to warm to room temperature under static vacuum. After 1 h, volatile material (1.44 g) was collected in the U-tube and was analyzed neat by ¹H NMR. The signals for the norbornadiene vinyl protons and the quadricyclane cyclopropyl protons were well separated from the other signals in the mixture; integration indicated a 15:82 ratio. In most experiments GC analysis was performed as well; care must be taken because quadricyclane can isomerize on hot GC injector ports. The reactor residue was extracted with ether and filtered. Solvent was removed to yield 11 mg (0.12 mmol of "C₇H₈") of a residue, which was analyzed by GC/MS. The titanium rod was reweighed (1.2810 g) to calculate the amount of titanium evaporated (0.0800 g). The correction factor (0.76) determined above was applied to this figure to yield the amount of titanium reaching the walls of the reactor (61 mg, 1.27 mmol).

Reactions of chromium and iron surfaces (Table I, entries 4 and 7) with quadricyclane were conducted as described above, except that quadricyclane was distilled onto the reactor walls *after* the metal had been evaporated.

Norcarane (16) Cocondensations. Norcarane (2.0 mL, 18.9 mmol) was distilled into the reactor from a 20 °C bath. Chromium (14 mg, 0.27 mmol, uncorrected) and vanadium (78 mg, 1.53 mmol, uncorrected) were evaporated from coated rods. Iron (31 mg, 0.56 mmol, uncorrected) was evaporated from a W/Al₂O₃ crucible. The volatiles (92–95% mass recovery) collected after the cocondensation were analyzed neat by ¹H NMR and contained only norcarane. No ether-soluble material was obtained upon extraction of the reactor residue.

2-Norcarene (7) Cocondensations. 2-Norcarene (0.51 g, 5.4 mmol) was collected in a glass tube during preparative gas chromatography. The glass tube was placed in the side arm reservoir, cooled to -78 °C during evacuation, and warmed to -5 °C to admit 2-norcarene to the reactor over 25 min. Chromium (6.3 mg, 0.12 mmol) was evaporated concurrently from a coated rod. After warm-up, 0.50 g of volatile material was collected in a ¹H NMR tube attached to a U-tube in the line.

¹H NMR and GC analyses showed no new products. Ether extraction of the reactor residue afforded no additional hydrocarbon material. In other runs, 0.37–0.46 g of 2-norcarene was cocondensed with nickel (85 mg, 1.43 mmol), titanium (3 mg, 0.06 mmol), and palladium (48 mg, 0.45 mmol). The weights of metal are uncorrected.

3-Carene (8) Cocondensations. 3-Carene (2.0 mL, 12.6 mmol) was distilled into the reactor at room temperature over a period of 0.5 h. Chromium (98 mg, 1.88 mmol, uncorrected), nickel (83 mg, 1.41 mmol, uncorrected), and titanium (11 mg, 0.23 mmol, uncorrected) were evaporated from coated rods. Palladium (133.5 mg, 1.25 mmol, uncorrected) was evaporated from a W/Al₂O₃ crucible. After 1-h warm-up, the volatile fraction (80–100% mass recovery) was collected in a U-tube and analyzed neat by ¹H NMR and GC; no new products were observed. No products were obtained from ether extraction of the reactor residue.

3-Norcarene (9) Cocondensation. 3-Norcarene (0.87 g, 9.3 mmol) was loaded in the side-arm reservoir, freeze-thaw degassed, and distilled into the reactor at -19 °C over a 15-min period. Chromium (34 mg, 0.65 mmol, uncorrected) was simultaneously evaporated from a coated rod. After warm-up (0.5 h) a volatile fraction (0.68 g) was collected in an ampule attached to a U-tube in the vacuum line. ¹H NMR analysis (neat) showed only starting material. The reactor

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residue was extracted with ether and acetone, but no products were present by ^1H NMR.

Bis(cyclopropylbenzene)chromium(0) (12). Cyclopropylbenzene (7.8 mL, 7.3 g, 62 mmol) was distilled into the reactor at room temperature over 2 h. Chromium (164 mg, 3.1 mmol, uncorrected; 2.3 mmol, corrected) was evaporated from a coated rod. After 1-h warm-up, a volatile fraction (6.42 g) was collected in the U-tube and analyzed (neat) by ^1H NMR. The NMR spectrum was identical with that of the starting material, and GC analysis showed no new products.

The reactor, which contained a dark green residue, was taken into a drybox and extracted with ether. The extract was filtered and the ether removed to yield 300 mg (1.0 mmol, 45% yield based upon chromium) of bis(cyclopropylbenzene)chromium(0) (12) as a dark green oil (melting point below room temperature). ^{13}C NMR (ppm, C_6D_6): 94.8, 75.3, 75.1, 74.9 (arene carbons); 15.4, 8.3 (cyclopropane carbons). Mass spectrum (m/e , 70 eV): 288 (18%), 170 (47), 142 (14), 118 (100), 117 (100), 103 (19). Satisfactory ^1H NMR spectra could not be obtained with this sample, presumably due to paramagnetic impurities. Hence in a separate experiment, 12 was distilled directly from the reactor into a ^1H NMR tube attached to a U-tube on the vacuum line. ^1H NMR (δ , C_6D_6): 4.23 (5 H, s, br), 1.48 (1 H, m), 0.55 (2 H, m).

Bis(cyclopropylbenzene)chromium(I) Tetraphenylborate (13). A sample of bis(cyclopropylbenzene)chromium(0) (33 mg, 0.11 mmol) was exposed to air and dissolved in H_2O (15 mL). A solution of sodium tetraphenylborate (44 mg, 0.13 mmol) in H_2O (5 mL) was added, precipitating a yellow solid. The solid was collected by centrifugation and recrystallized from 1:1 acetone-ethanol. When the salt was heated in a melting point capillary, it darkened at 160 $^\circ\text{C}$ and did not melt to 210 $^\circ\text{C}$. Anal. Calcd for $\text{C}_{42}\text{H}_{40}\text{CrB}$: C, 83.03; H, 6.64; Cr, 8.56. Found: C, 82.73; H, 6.75; Cr, 8.32. IR (KBr): 3068 (m), 3052 (s), 3032 (m), 2998 (m), 2980 (m), 1575 (m), 1475 (m), 1472 (m), 1423 (m), 1138 (m), 1062 (m), 1024 (m), 892 (m), 842 (m), 798 (s), 740 (s), 732 (s), 702 (s) cm^{-1} .

Cocondensation of Cyclopropylbenzene with Nickel and Vanadium. Cyclopropylbenzene (10 mL, 9.35 g, 79 mmol) was cocondensed with nickel (38 mg, 0.66 mmol, uncorrected) evaporated from a $\text{W}/\text{Al}_2\text{O}_3$ crucible. A bright yellow-orange matrix was produced which faded upon warm-up. After warm-up (1 h) volatiles (9.2 g) were collected in a U-tube trap. ^1H NMR and GC analyses showed only starting cyclopropylbenzene to be present.

Cyclopropylbenzene (5.7 g, 48 mmol) was cocondensed with vanadium (27 mg, 0.53 mmol, uncorrected) evaporated from a coated W rod. A dark green matrix was formed in the initial stages of the cocondensation. After warm-up (1 h) a volatile fraction (5.2 g) was collected in the U-tube trap. No new products were found by ^1H NMR analysis. The red-orange residue which remained was dissolved in petroleum ether and concentrated to a dark red oil. During the course of routine manipulations in a drybox, the material decomposed. Extraction with petroleum ether and GC analysis indicated only cyclopropylbenzene.

Reaction of Spiro[2.4]hepta-4,6-diene (14) with Iron Atoms. Spirodiene 14 (10 mL, ca. 100 mmol) was distilled into the reactor at room temperature over 1.5 h. Iron (419 mg, 7.51 mmol uncorrected; 5.71 mmol corrected) was simultaneously evaporated from a $\text{W}/\text{Al}_2\text{O}_3$ crucible. The matrix was kept under static vacuum at -196°C for an additional 0.5 h before warming to room temperature. The excess ligand was then pumped over to a U-tube and GC analyzed (no organic products detected). The reactor residue was extracted and chromatographed on a silica gel column. A fast moving orange band was collected (0.600 g, 2.5 mmol of $\text{C}_{14}\text{H}_{16}\text{Fe}$) which was homogeneous by TLC but contained four major products by GC analysis. Area ratios: 14:62:6:17. Retention times (min; 6 ft \times $1/8$ in. 10% DC-710 on Chrom W, 205 $^\circ\text{C}$): 4.3, 4.5, 5.2, 11.9. These were separated by preparative GC (5 ft \times $1/4$ in. DC-710, 160 $^\circ\text{C}$) and identified as 15-18 by mass spectrometry and NMR data. 15: ^1H NMR (δ , C_6D_6) 3.97 (d, 8 H), 2.25 (q, $J = 8$ Hz, 4 H), 1.10 (t, $J = 8$ Hz, 6 H); ^{13}C NMR (ppm, C_6D_6) 68.3, 68.0, 22.5, 15.3 (heights ca. 2:2:1:1). 16: ^1H NMR (δ , C_6D_6) 6.45 (d of d, $J = 18$, 11 Hz, 1 H), 5.33 (d of d, $J = 18$, 2 Hz, 1 H), 5.05 (d of d, $J = 11$, 2 Hz, 1 H), 4.13 (m, 4 H), 3.93 (s, 4 H), 2.23 (q, $J = 8$ Hz, 2 H), 1.10 (t, $J = 8$ Hz, 3 H); ^{13}C NMR (ppm, C_6D_6) 135.0, 110.7, 69.5, 69.0, 68.7, 67.5, 22.0, 15.1 (heights ca. 1:1:2:2:2:1:1). 17: ^1H NMR (δ , C_6D_6) 6.35 (d of d, $J = 18$, 9 Hz, 1 H), 5.28 (d of d, $J = 18$, 2 Hz, 2 H), 5.02 (d of d, $J = 9$, 2 Hz, 2 H), 4.07 (m, 8 H); ^{13}C NMR (ppm, C_6D_6) 134.6, 111.2, 70.2, 68.3. 18: ^1H NMR (δ , C_6D_6) 3.95 (s, 8 H), 2.32 (m,

4 H), 1.73 (m, 4 H); ^{13}C NMR (ppm, C_6D_6) 68.5, 67.9, 29.8, 27.5 (heights ca. 2:2:1:1). The ^1H NMR spectrum of 18 closely matched one previously reported.⁴⁸

Hydrogenation of 16 and 17. Approximately 100 mg of the mixture of 15-18 obtained by column chromatography above was dissolved in 2 mL of 1:1 benzene-ethyl acetate. A few milligrams of PtO_2 was added and the mixture stirred for 2 h under 48 psi of H_2 in a Fischer-Porter bottle. The reaction mixture was filtered and analyzed by GC. The 16 and 17 originally present had been converted to 15.

Cocondensation of Trimethyl Phosphite and Spiro[2.4]hepta-4,6-diene (14) with Iron Atoms. Spirodiene 14 (5 mL, ca. 50 mmol) was cocondensed with iron (121 mg, uncorrected) as described above. Trimethyl phosphite (11 mL, ca. 88 mmol) was then distilled into the cold (77 K) reactor. The matrix was allowed to warm to room temperature over the course of 20 min, and the volatiles were removed. The reactor was extracted with hexanes and filtration was done through alumina (all under N_2). The orange fraction obtained contained only ferrocenes 15-18 by TLC and GC.

Similar experiments were conducted in which premixed 14 (3 mL, ca. 30 mmol) and trimethyl phosphite (15 mL, ca. 120 mmol) were cocondensed with iron (135 mg, uncorrected). Yields of 15-18 were greatly decreased, but new products were not observed.

Cocondensation of Spiro[2.4]heptane (20) with Iron Atoms. Spiro[2.4]heptane (2.0 mL, 1.60 g, 16.7 mmol) was distilled into the reactor at -8°C over the course of 15 min. Iron (55 mg, 1.0 mmol; 0.76 mmol, corrected) was simultaneously evaporated from a crucible. The matrix was allowed to warm over a 30-min period, after which all volatile material was pumped into a U-tube. The contents of the U-tube (1.27 g) were shown by ^1H NMR and GC to be unreacted 20. Ether was added to the reactor residue, but no organic material was extracted.

Synthesis of [4]Ferrocenophane (18) from 1,1'-Dilithioferrocene (19). To 15 mL of dry hexane in a three-necked flask under N_2 was added 11 mL (74 mmol) of tetramethylethylenediamine (TMEDA, freshly distilled from KOH at 117 $^\circ\text{C}$) and 35 mL of 2.1 M $n\text{-C}_4\text{H}_9\text{Li}$. After 10 min of stirring, 5.6 g (30 mmol) of ferrocene dissolved in 250 mL of hexane was slowly added. The mixture was stirred overnight, during which time a light orange precipitate (19) formed. To this reaction mixture was added, over a period of several hours, 3.5 mL (29 mmol) of 1,4-dibromobutane dissolved in 50 mL of hexane. After being stirred 4 days at room temperature (during which time the formation of 19 was GC monitored), the reaction mixture was quenched with H_2O and the hexane layer separated. The hexane was evaporated and the residue taken up in 1:20 ethyl acetate-hexane (some material, presumably polymeric, failed to dissolve) and column chromatographed on silica gel. Thus obtained was 6.28 g of a ferrocene-[4]ferrocenophane mixture. A 2.71-g (10 mmol, 33%) yield of [4]ferrocenophane was determined to be present by measuring GC peak areas. A portion of this material was subsequently purified by preparative GC.

Attempted Synthesis of [8]Ferrocenophane. To 15 mL of dry hexane in a three-necked flask under N_2 was added 5.5 mL (4.25 g, 37 mmol) of TMEDA and 17.6 mL of 2.1 M $n\text{-C}_4\text{H}_9\text{Li}$. Ferrocene (2.8 g, 15 mmol) in 150 mL of hexane was then slowly added and the mixture stirred overnight, during which time an orange precipitate (19) formed. To this reaction mixture was added 2.8 mL of 1,8-dibromooctane (4.1 g, 15 mmol) dissolved in 30 mL of hexane over a 6-h period. After 19 h of stirring, a small portion of the reaction mixture was quenched with H_2O . GC analysis indicated only ferrocene to be present. The reaction mixture was then refluxed for 21 h, followed by quenching with 120 mL of H_2O . Ether was added, and the organic phase was separated and dried with Na_2SO_4 . The solvent was removed, affording an oil from which some ferrocene precipitated. The oil was slowly passed through a silica gel column with hexane, under which conditions a pure ferrocene fraction was obtained, followed by a second fraction containing a mixture of substituted ferrocenes. The second fraction (1.66 g) was analyzed by GC and shown to contain two major products in a 2.6:1 ratio. Pure samples of these were obtained by preparative GC on a DC-710 column at 250 $^\circ\text{C}$. Mass and NMR spectra indicated these materials to be octylferrocene (m/e (16 eV): $\text{M}^+ = 298$, 100%) and 1,1'-dioctylferrocene (m/e (16 eV): $\text{M}^+ = 410$, 100%).

Reaction of Spiro[4.4]nona-1,3-diene (23) with Iron Atoms. Spirodiene 23 (5 mL, ca. 42 mmol) was distilled into the reactor at room

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temperature over the course of 1–1.5 h. Iron (100 mg, 1.8 mmol uncorrected, 1.4 mmol corrected) was simultaneously evaporated from a crucible. The orange-brown matrix was allowed to warm to room temperature under a static vacuum. After 1 h, excess **23** was distilled into a U-tube and the reactor extracted with benzene. The extract was filtered and passed through silica gel. After solvent removal, a dark orange oil remained (51.3 mg, 0.173 mmol of "C₁₈H₂₄Fe", 13% yield based upon iron). GC analysis indicated two major products (ratios varying from 1:5 to 1:9 in different runs) and three minor products. The summed areas of the minor products were less than the area of the least abundant major product. Pure samples of the major products were obtained by preparative GC and assigned structures **24** (longer retention time material, most abundant) and **25** as described in the Results (NMR data, Table II). MS (*m/e*, 16 eV): **24**, M⁺ = 294 (100%); **25**, M⁺ = 296 (100%).

Reaction of Spiro[2.4]hepta-4,6-diene (14) with Cobalt Atoms. Approximately 5 mL of a 14-hexane mixture (2:3 molar ratio) was distilled into the reactor at room temperature while cobalt (179 mg, 3.0 mmol, corrected) was evaporated from a W/Al₂O₃ crucible. A brown matrix, with some blue-purple spots, formed. While at 77 K, 1 atm of CO was admitted to the reactor. The matrix was then warmed to room temperature, forming an orange melt. After an additional 20 min, the CO was pumped off and starting **14** fractionated from a volatile orange red product by careful trap-to-trap distillation. Traces of **14** were removed from the orange-red oil by alumina chromatography (hexane, followed by ether elution) under N₂. Under these conditions, two orange-red products separated. These were identified as **21** (least polar) and **22**, respectively, by their ¹H-NMR, IR, and mass spectra.¹⁷ MS (*m/e*, 70 eV): **21**, M⁺ = 208 (100%), 180 (85), 152 (76); **22**, M⁺ = 206 (46%), 178 (42), 150 (100). In multiple runs on approximately the same scale (some using pure **14** instead of 14-hexane), the combined weight of **21** and **22** never exceeded 10 mg.

Cocondensation of Dispiro[2.2.2]deca-4,9-diene (28) with Chromium Atoms. Dispirodien **28** (1.0 g, 7.6 mmol) was sublimed into the reactor by heating the ligand reservoir (C) with heating tape. Chromium (46 mg, 0.88 mmol, uncorrected) was simultaneously evaporated from a coated tungsten rod. After matrix warm-up, excess ligand (unchanged by ¹H NMR and GC) was pumped off over a 24-h period. The reactor residue was exposed to air and washed with H₂O; an aqueous solution of KI was added and this mixture extracted with CHCl₃. Solvent evaporation yielded ca. 30 mg of a yellow-green oil which was homogeneous by TLC on alumina.

In an alternative procedure, ca. 0.7 g of **24** was dissolved in decane (ca. 10 mL) and this solution cocondensed with chromium (36 mg, 0.69 mmol, uncorrected). The reactor residue was extracted with benzene and worked up as described above. A similar green product was isolated and purified by alumina column chromatography. Crystallization could not be induced.

The green product gave a precipitate when treated with ethanolic AgNO₃. However, it was benzene soluble and water insoluble. Such behavior is atypical of bis(arene)chromium(I) iodides.⁴⁹ A portion

of the green oil was reduced (overnight, under N₂) by using a standard recipe⁴⁹ of Na₂S₂O₄ (100 mg), KOH (67 mg), H₂O (2 mL), CH₃OH (0.5 mL), and benzene (5 mL). The benzene layer was then separated and dried. Solvent was removed (all under N₂) and a mass spectrum of the residue obtained. No ions characteristic of bis(arene)chromium species were present.

Cocondensation of Benzocyclopropene (27) with Chromium Atoms. Benzocyclopropene (2.1 mL, 23.4 mmol) was distilled into the reactor over a 70-min period from a -10 °C reservoir while chromium (100 mg, 1.93 mmol, uncorrected) was evaporated from a coated tungsten rod. The reactor was allowed to warm under static vacuum for 1.5 h, and volatile material (1.4 mL) was then distilled into a trap. This material was shown by NMR to be unreacted **27** containing a slightly greater percentage of toluene than before the condensation. The reactor top was replaced with a sublimator head under argon and the reactor residue heated to 90 °C under 5 × 10⁻⁵ mm vacuum. No material sublimed from the residue.

The reactor was then opened to air and extracted with benzene (100 mL). Water (30 mL) was then added. Air was bubbled through this mixture for 1.5 h, and the layers then separated. The benzene was evaporated to yield 327 mg of a green oil, a portion of which was purified by preparative TLC on alumina. The mass spectrum of this material (16 eV, 220 °C) showed a base peak at *m/e* 179 (100%, 2(C₇H₆) - 1), and peaks of lower intensity at ascending increments of approximately 90: *m/e* 269 (60.0%), 359 (22.0), 449 (11.6), 539 (6.4), 629 (4.9), 720 (9.5), 810 (20.9). Higher mass ranges were not scanned.

Dry KI was added to the water layer, which was subsequently extracted with CHCl₃. The CHCl₃ was dried over Na₂SO₄ and evaporated to yield 66 mg of a brown oil. To this oil was added H₂O (2 mL), CH₃OH (0.5 mL), benzene (5 mL), KOH (67 mg), and Na₂S₂O₄ (100 mg).⁴⁹ This mixture was stirred under N₂ for 1 day and the benzene layer separated. After the solution was dried with Na₂SO₄, the benzene was removed in a glovebox to yield a brown oil which was submitted for mass spectrometry. No ions characteristic of bis(arene)chromium species were present.

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Supplementary Material Available: Figure 2, a side-on view of the assembled reactor (1 page). Ordering information is given on any current masthead page.

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