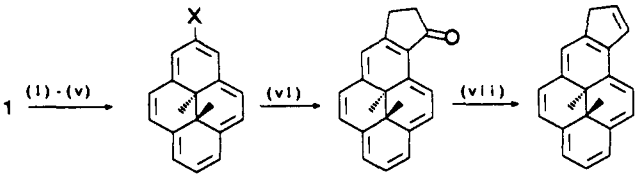
Scheme I^a



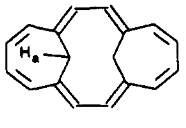
4a-e 5 6

^{a}4a–e: a, X = CHO; b, X = CH=CHCOOEt; c, X = CH_2CH_2COOEt; d, X = CH_2CH_2COOH; e, X = CH_2CH_2COCl. (i) $TiCl_4/Cl_2CHOMe$, 75%; (ii) $(EtO)_2P(O)CH_2COOEt/NaH$, >95%; (iii) Pd/H_2, >95%; (iv) aqueous NaOH, >90%; (v) $(COCl)_2$; (vi) $BF_3{\cdot}OEt_2$, 63% from 4e; (vii) LAH, then 20% aqueous HCl, room temperature, 81%.

Table I. ^1H NMR Data (δ) for Anion 3 and Benzannulene 2

proton	3^--K$^+$	3^--{K$^+$ cryptand}	3^- (corrected)^a	2
Me	-2.85	-3.17	-2.6	-1.62
A	7.79	7.92	8.71	8.09
B	7.61	7.70	7.97	7.36
C	7.55	7.58	8.10	7.50
D	6.90	6.83	7.50	7.13
E	7.39	7.41	8.13	7.35
F	7.57	7.59	8.39	7.61
G	7.70	7.71	7.93	7.68
H	8.25	8.35	8.08	7.88
I	6.67	6.76		
J	6.97	7.10		
K	7.30	7.43		

in similar positions with respect to the center of the aromatic rings, *and in a similar position to the methyl protons of 2 and 3 with respect to the 6π rings.*



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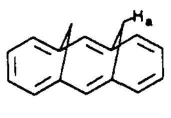

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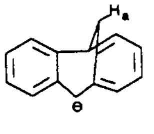

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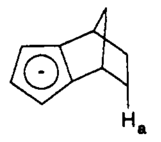

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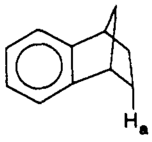

11

Finally, the coupling constants[16] of the macrocyclic rings in 2 and 3 give information on the bond orders[17] and hence on the delocalization.[18] The calculated chemical shift of the methyl protons of 3^-, based on the coupling constants, is −2.9 ppm. Thus, from the above estimates, δ_{Me} can be taken to be −2.8 ppm in comparison to the values of −1.6 ppm for 2 and −4.2 ppm for 1. On this basis Cp^- has about 54% of the effective bond-fixing ability ("effective aromaticity") of benzene. That the effective aromaticity of Cp^- is less than that of benzene is certain when one combines this shift data together with the alternance parameters[17] (ratio of adjacent bond orders) for the macrocyclic rings of 1.20 (5) for 3^- and 1.47 for 2, and the substantially more deshielded ring protons (corrected) for 3 than 2. Even if none of the charge were delocalized over the large ring, the chemical shift change is not enough to reach the value for 2. The fact that the charge is delocalized indicates that aromatic stabilization of the 6π anion is not large enough. According to the metalloaromaticity principle of Fenske,[19] complexation to give Cp–M derivatives should increase its aromaticity. We are currently investigating this.

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[16] 3: J_{CD} = 7.87 Hz; J_{DE} = 6.78 Hz; J_{FG} = 8.33 Hz; J_{AB} = 7.05 Hz. 2: J_{CD} = 8.79 Hz; J_{DE} = 6.44 Hz; J_{FG} = 8.67 Hz; J_{AB} = 6.20 Hz.

[17] Cremer, D.; Gunther, H. *Justus Liebigs Ann. Chem.* **1972**, *763*, 87–108.

[18] Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571–2578.

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Entrainment by R•/R′MgBr Exchange

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Bromocyclopropane (CpBr) in pure diethyl ether (SH) reacts completely with magnesium metal, but the yield of the Grignard reagent (CpMgBr) is limited to about 50% by the formation of cyclopropane (CpH) and other byproducts.[2] The CpMgBr yield is enhanced by the presence of hexylmagnesium bromide (HxMgBr), by coreaction with 1-bromohexane (HxBr) or both (Table I).

The effect of HxBr is an example of "entrainment", a technique introduced in 1934 by Victor Grignard to induce RMgX formation in difficult cases.[3-5] In entrainment, the yield of RMgX is enhanced by allowing magnesium to react with a mixture of RX and an auxiliary halide R′X that readily forms a Grignard reagent R′MgX.[6] Explanations involving halogen–metal exchange (eq 1) have been ruled out in several cases, and no other chemical

$$RX + R'MgX \rightarrow RMgX + R'X \qquad (1)$$

basis has been found.[7] Instead, physical effects such as surface cleaning have been suggested.[3b,7] Since CpBr does not react with HxMgBr in SH (7 h at 34 °C) in the absence of magnesium, reaction 1 is also ruled out here, but the product distributions in Table I indicate another chemical basis for at least part of the entrainment effect.

The yield of CpMgBr is diminished by the attack of intermediate radicals Cp• on SH [giving CpH, CpS, SS, and S(−H) (ethyl vinyl ether)].[2] In contrast, 1-bromohexane (HxBr) gives HxMgBr without significant solvent attack.[2] When CpBr reacts in the presence of HxMgBr (preformed, formed during the reaction, or both), the increase in the yield of CpMgBr is accompanied by a decrease in that of SS, the appearance of CpHx and HxS, and the disappearance of some HxMgBr. These results are consistent with reaction 2 (R = Cp, R′ = Hx) (or its equivalent) and Scheme I.[8]

$$R^\bullet + R'MgBr \rightarrow RMgBr + R'^\bullet \qquad (2)$$

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[2] Garst, J. F.; Ungváry, F.; Batlaw, R.; Lawrence, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 5392.

[3] (a) Grignard, V. *Compt. Rend.* **1934**, *198*, 625. (b) Grignard, V. *Compt. Rend.* **1934**, *198*, 2217.

[4] The general synthetic problem of reluctant RMgX formation has been successfully attacked with finely divided and especially reactive magnesium metal.[5]

[5] (a) Rieke, R. D. *Science* **1989**, *246*, 1260. (b) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

[6] Subsequently, "entrainment" has also been used to describe reactions with auxiliary halides, such as 1,2-dibromoethane, that do not form Grignard reagents.[5]

[7] Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954, pp 38–45. About two dozen examples of entrainment of reluctant aryl halides and one alkyl halide are cited: Tables II–VIII, pp 41–42.

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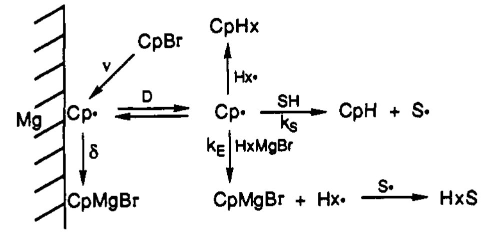
Table I. Yields of Products of Reactions of Magnesium with Bromocyclopropane and 1-Bromohexane, Separately and Together, in Diethyl Ether, under Nitrogen, and at Reflux (≈34 °C)[a]

HxBr	CpBr	CpH	CpMgBr	HxMgBr	SS	CpHx	HxS	ΣCp	ΣHx
1		0	0	82	0	0	0		98
	1	40	51	0	7.5	0	0	98	
2	1	40	51	68	7.0	0	0	98	99
1	2	29	64	68	2.2	2.0	6.0	99	99
1	1	28	58	39	1.0	6.6	6.6	95	95
1, 2	2	17	74	58	<1	4.2	5.2	97	97

[a] "1" denotes that RBr was present initially and "2" that it was added, after completion of the initial reaction, for reaction with excess Mg (99.99%, Alfa). Yields are mol of product per 100 mol of CpBr consumed, except that HxMgBr is based similarly on HxBr. The initial concentration of each halide at each reaction stage was 0.18–0.20 M. Mass balances (last two columns) are based on all of the products determined, including HxH, Hx(–H), CpS, and HxHx. Analyses were by titration and gas chromatography, augmented by spectroscopic methods and independent syntheses of unknown compounds, as described in detail elsewhere.[2]

Scheme I



Although there appear to be no previous reports of the occurrence of reaction 2 during Grignard reagent formation, Lawler and co-workers detected it (through CIDNP) in iron-promoted reactions of Grignard reagents with alkyl halides.[10] Kharasch and Fuchs had suggested this possibility earlier.[11] In addition, trapping of polarized $R^{\bullet}$ in reaction 2 could account for the appearance of CIDNP in RMgBr during Grignard reagent formation.[12]

Lehr and Lawler estimate the rate constant as $>10^5$ M^{-1} s^{-1} in THF for reaction 2 with R = isobutyl, R′ = ethyl, and X = Br.[10b] According to D-model calculations,[13] a rate constant of 10^5 M^{-1} s^{-1} would not be sufficient to make the reaction very significant during the formation of a 1 M solution of a Grignard reagent. A rate constant as large as 10^6 M^{-1} s^{-1}, however, could lead to significant reaction. The rate constant for the reaction of $Cp^{\bullet}$ with SH is probably near 10^6 s^{-1}.[2,14] The present data indicate that reaction 2 (R = Cp, R′ = Hx) is competitive with solvent attack by $Cp^{\bullet}$ when [HxMgBr] ≈ 0.2 M. so the rate constant for reaction 2 probably approaches 10^7 M^{-1} s^{-1}. Rate constants for related reactions of alkylborons, -aluminums, -mercuries, etc. can have similar values.[15]

Historically, entrainment has been most often used with aryl halides.[7] Cyclopropyl and aryl radicals, which are σ radicals, are more electronegative than typical alkyl (π) radicals. Since $R^{\bullet}/R'MgX$ exchange can be regarded as a net electron transfer, reaction of σ radicals with alkylmagnesium halides such as ethyl- and hexylmagnesium halides are expected to be thermodynamically favored. Conversely, the $Hx^{\bullet}/CpMgBr$ exchange reaction is expected to be thermodynamically unfavored and therefore relatively slow. Consistent with this, no effects on the yields of CpMgBr, CpH, and SS are found when magnesium reacts with HxBr in the presence of CpMgBr, and no CpHx or HxS is formed.

The scope of $R^{\bullet}/R'MgX$ exchange reactions, their mechanistic details, accurate values of their rate constants, the extents of their contributions to entrainment in other examples, solvent, halogen, and other effects on $R^{\bullet}/R'MgX$ exchange, and the possible roles of transition-metal impurities all remain to be established.[16]

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(8) Scheme I uses the D model, in which intermediate radicals diffuse freely in solution. For a recent summary of another view of the mechanism of RMgX formation, see ref 9.

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$C_{60}^{\bullet-}$ with Coordination Compounds. (Tetraphenylporphinato)chromium(III) Fulleride

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Recent reports of the reductive electrochemistry of C_{60},[1-4] the isolation of the first fulleride salt,[5] the conductivity and superconductivity of alkali metal doped fullerenes,[6,7] and the lithiation of C_{60}[8] suggest that the anions of the buckminsterfullerenes ("bucky balls") have a very rich chemistry. With the charac-

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