Scheme I

(i) PhSCH₂Cl, NaOH, H₂O/CH₂Cl₂, catalyst, 0 °C, 8 h; (ii) TCIA, CCl₄, 0→20 °C, 6 h; (iii) AgBF₄, CdCO₃, MeOH, 0 °C, 4 h; (iv) LiC₁₀H₈, THF, CO₂; (v) SOCl₂, Et₂O, catalyst, DMF, Δ, 8 h; (vi) KFe(CO)₂Cp, THF, –78 →20 °C, 6 h; (vii) [(PPh₃)₂RhCl]₂ , CH₃CN, 20 °C, 48 h; (viii) Me₃SiOTf, CH₂Cl₂, –78 °C, 5.0 min.

Optically acitve σ-complex 11 was prepared from active acid 9 ([α]^{25}D –17.46 (c 0.24, ethanol)) that had been resolved with quinine. High optical purity (96% by ¹H NMR integration) of the acyl complex prepared from this acid was determined by using 5.0 mol % of the chiral shift reagent (–)-tris[3-[(heptafluoropropyl)hydroxymethylene]-d-camphorato]europium, (–)-Eu(hfc)₃.

Decarbonylation followed by low-temperature (–78 °C) methoxy abstraction gave the allene complex which was found to have, within experimental error, no optical rotation, i.e., [α]^{25}D 0.2, (c 0.013, CH₂Cl₂).[17] From these results we conclude that the Fp⁺ complex of *trans*-2,3-dimethylcyclopropylidene does, indeed, rapidly collapse to the allene complex. Further, from lack of rotation in the product from nearly optically pure σ complex it is likely[18] that the reaction proceeds by an allowed disrotatory ring opening to an achiral intermediate[19] (presumably the allyl cation that corresponds to 6) which then rapidly collapses to the allene complex 13.

(17) The error in this rotation is large due to light absorption by the complex which forced us to measure rotations on dilute solutions. Attempts to determine optical purity using a chiral shift reagent were not successful.

(18) Enantiomeric excess in allenes from concerted opening of *trans*-2,3-disubstituted cyclopropylidenes or their metal complexes is believed to be steric in origin. In principle it would therefore be possible that 12 could give optically inactive product without going through an achiral intermediate (if steric interactions of methyl vs. β-H exactly cancelled methyl vs. Fp). We have no data that can exclude this possibility.

(19) If the opening is disrotatory to an allyl cation, the intermediate is achiral in only one conformation. This is the conformation that would result from opening of the electronically preferred "upright" conformation of the carbene complex. Even if this conformer were not formed initially, rotation about the Fe–C bond should be fast due to the LUMO node on the central carbon of the allyl cation.

Possible Formation of Rhenabenzene. Lithium–Halogen Exchange Reactions in η1-4-Bromo-1,4-diphenyl-1,3-butadienyl Ligands To Form Rhenabenzene and Ferrabenzene

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Summary: Introduction of (E,E)-1,4-dilithio-1,4-diphenyl-1,3-butadiene (1) to (CO)₄PPh₃ReBr followed by protonation or methylation give (1,3-diphenyl-2-hydroxycyclopentadienyl)tricarbonylrhenium (5a) and (1,3-diphenyl-2-methoxycyclopentadienyl)tricarbonylrhenium (5b), respectively. A mechanism consistent with generation of 5 involves formation of an anionic acyl intermediate followed by alkyl migration to give (η1-4-lithio-1,4-diphenyl-1,3-butadienyl)rhenium complex 7. Cyclization by attack on a terminal carbonyl by the alkenyllithium moiety generates rhenabenzene 8 from 7. Reductive elimination, loss of triphenylphosphine, and protonation or methylation give 5a or 5b, respectively. A second synthetic approach to 8 is described. Preparation of (η1-4-bromo-1,4-diphenyl-1,3-butadienyl)rhenium complex 10 is reported. Lithium–halogen exchange with 10 using *n*-butyllithium gives 7. Intermediate 7 may convert to 5 as described above. Preparation of (η1-4-bromo-1,4-diphenyl-1,3-butadienyl)iron complex 11 is also reported. Lithium–halogen exchange and cyclization form an unstable ferrabenzene. Reductive elimination, loss of a terminal carbonyl, and methylation give 1,3-diphenyl-2-methoxyferrocene (4).

We recently reported that (E,E)-1,4-dilithio-1,4-diphenyl-1,3-butadiene (1)[2] reacts with (η5-C₅H₅)Fe(CO)₂I to possibly form metal–alkyl and metal–carbene bonds giving an unstable ferrabenzene intermediate 3 (eq 1).[3]

(1)
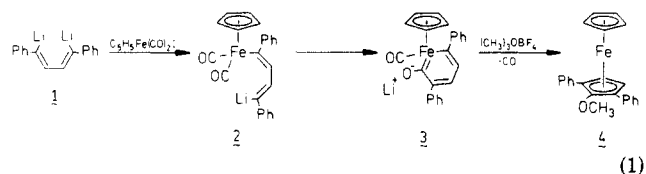
We now report [1] reaction of 1 with another transition-metal carbonyl halide, (CO)₄PPh₃ReBr, and [2] probable generation of metallabenzenes by lithium–halogen exchange with η1-4-bromobutadienyl ligands of transition metals containing electrophilic carbonyl ligands. These reactions support the hypothesis[3] that metallabenzenes are intermediates leading to η5-cyclopentadienyl complexes.

The success of generating 4 from 1 prompted us to test the generality of this method with other transition metals. A solution of 1 in ethyl ether was added to a refluxing

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(2) Barton, T. J.; Nelson, A. J.; Clardy, J. *J. Org. Chem.* 1972, *37*, 895–901. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *Ibid.* 1967, *32*, 885–888.

(3) Ferede, R.; Allison, N. T. *Organometallics* 1983, *2*, 463–465.

Scheme I
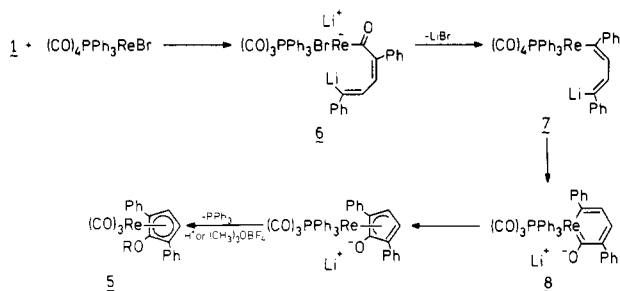
solution of $(CO)_4PPh_3ReBr$ in ethyl ether.[4] Chromatography[5] (silica gel; pentane/ethyl ether) yielded a yellow oil identified as **5a** (84%, eq 2).[6] Alternatively, an ether solution of **1** can be added to a refluxing solution of $(CO)_4PPh_3ReBr$ in ethyl ether.[4] Addition of solid $(CH_3)_3OBF_4$ at room temperature followed by chromatography (silica gel; pentane/ethyl ether) yielded two yellow oils identified as **5b** (29%) and **5a** (7%, eq 2).[6]

$$1 + (CO)_4PPh_3ReBr \xrightarrow{35°} \xrightarrow{H^+ \text{ or } (CH_3)_3OBF_4} \quad (2)$$

5a R = H
5b R = CH₃
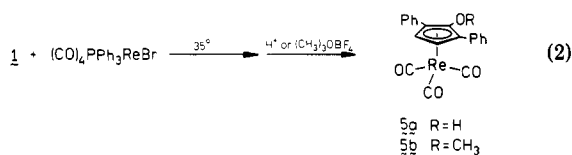
A mechanism consistent with the formation of **5a** and **5b** and the known chemistry of $(CO)_4PPh_3ReBr$[7] is given in Scheme I. Formation of the anionic acyl complex **6** is followed by alkyl migration to give **7**. Cyclization of **7** generates rhenabenzene **8**. Reductive elimination, loss of triphenylphosphine, and either protonation or alkylation give **5**.[8]

Formation of acyl anion **6** and its conversion to alkenyl complex **7** is precedented. Generation of the methyl complex $(CO)_4PPh_3ReCH_3$ via an anionic acetyl intermediate in the reaction of CH_3Li with $(CO)_4PPh_3ReBr$ has

been investigated by Gladysz and co-workers.[7] However, since the acyl ligand in **6** contains an alkenyllithium moiety, we felt that an intraligand cyclization to give **9** (eq 3) may be a viable reaction path.[9] A more direct approach,

$$6 \longrightarrow (3)$$
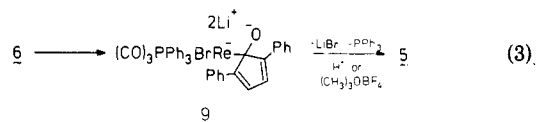
therefore, for generating transition metallacycles was sought. An alternate preparation of rhenium complex **7** (Scheme I) and iron complex **2** (eq 1) could serve this purpose. With this in mind, stable η^1-4-bromo-1,4-diphenylbutadienyl complexes of rhenium **10** and iron **11** were prepared (eq 4). Treatment of $(1Z,3Z)$-1,4-di-

$$ (4)$$

10 M = $(CO)_4PPh_3Re$
11 M = $C_5H_5(CO)_2Fe$
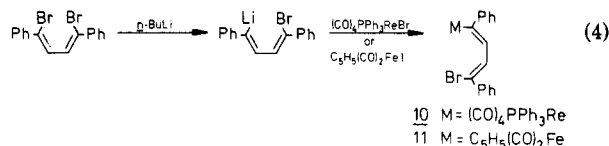
bromo-1,4-diphenyl-1,3-butadiene[2] with 1 equiv of *n*-butyllithium gives $(1Z,3E)$-1-bromo-4-lithio-1,4-diphenyl-1,3-butadiene. Addition of $(CO)_4PPh_3ReBr$ or $C_5H_5(C-O)_2FeI$ yielded, after chromatography, **10** (18%)[6] or **11** (32%),[6] respectively. ^{13}C NMR carbonyl absorptions[6] establish a cis geometry about the rhenium in **10**. Lithium–halogen exchange[10] in **10** and **11** would thus give intermediates **7** and **2**, respectively.

Addition of 1 equiv of *n*-butyllithium to a cold (dry ice/2-propanol bath) solution of **10** in ethyl ether followed by warming to room temperature and addition of $(CH_3)_3OBF_4$ gave after column chromatography **5b** (14%) and **5a**.[11] Similarly, introduction of *n*-butyllithium to **11** in ethyl ether (dry ice/2-propanol bath) followed by $(CH_3)_3OBF_4$ (25 °C) and chromatography yielded **4** (10%).

These reactions support [1] that lithium–bromine exchange (**10** to **7**; **11** to **2**) can occur in the presence of electrophilic terminal carbonyls, [2] interligand attack at a terminal carbonyl (**7** to **8**; **2** to **3**), rather than intraligand attack of an acyl carbonyl (i.e., **6** to **9**) can occur to generate metallabenzenes of iron and rhenium which then convert to cyclopentadienyl complexes, and [3] in the reaction of $(CO)_4PPh_3ReBr$ with **1**, acyl to alkyl conversion (**6** to **7**), may occur faster than an unprecedented intraligand attack (**6** to **9**).

Generation of lithiobutadienyl complexes **7** and **2** by lithium–bromine exchange is quite remarkable even with these modest yields. Similar acyl complexes (which do not contain vinyl bromide moieties) of rhenium and iron, when introduced to alkyllithium reagents, react at terminal carbonyls to give bis(acyl) complexes.[12] Our reactions, on the other hand, show that lithium–halogen exchange is competitive with this type of reaction. Furthermore,

(4) This reaction also proceeds at low temperatures (-78 to 0 °C); however, yields of **5a** and **5b** are reduced.

(5) Protonation is accomplished on the silica gel column.

(6) Compound **5a**: yellow oil; exact mass calcd (^{187}Re) *m/e* 504.037, found 504.039, calcd (^{185}Re) *m/e* 502.0344, found, 502.0334; mass spectrum (CID NH₃), *m/e* 505 (M⁺ + 1, ^{187}Re), 503 (M⁺ + 1, ^{185}Re); ¹H NMR (acetone-*d₆*) δ 4.0 (br s, 1 H, OH), 5.7 (s, 2 H, C₅H₂), 7.5 (m, 10 H, C₆H₅); ¹³C NMR (acetone-*d₆*) δ 196.8 (s, CO), 138.0, 132.8, 129.8, 129.6, 128.6, 91.8, 78.8; IR (neat) 2010, 1920 (CO) cm⁻¹. **5b**: yellow oil; exact mass calcd (^{187}Re) *m/e* 518.053, found 518.063, calcd (^{185}Re) *m/e* 516.050, found 516.059; ¹H NMR (acetone-*d₆*) δ 3.5 (s, 3 H, CH₃O), 5.7 (s, 2 H, C₅H₂), 7.5 (m, 10 H, C₆H₅); ¹³C NMR (acetone-*d₆*) δ 196.6 (s, CO), 132.8, 132.3, 129.4, 129.4, 129.0, 97.2, 78.8, 64.6; IR (neat) 2020, 1930, (CO) cm⁻¹. **10**: yellow oil; mass spectrum (CID NH₃), *m/e* 847 (M⁺ + 1, ^{187}Re^{81}Br), 845 (M⁺ + 1, ^{185}Re^{81}Br, ^{187}Re^{79}Br), 843 (M⁺ + 1, ^{185}Re^{79}Br); ¹H NMR (acetone-*d₆*) δ 6.1–7.6 (m, (C₆H₅)₂BrC₄H₂); ¹³C NMR (acetone-*d₆*) δ 190.8 (d, *J* = 8.6 Hz, 2CO, cis to PPh₃), 188.9 (d, *J* = 7 Hz, CO, cis to PPh₃), 188.5 (d, *J* = 41 Hz, CO, trans to PPh₃), 167.2 (d, *J* = 10 Hz, CRe), 158.2, 143.2 (d, *J* = 5 Hz), 141.1, 134.8, 134.3, 132.3, 131.9, 129.9, 129.4, 129.0, 128.5, 128.4, 127.7, 125.9, 125.5, 124.9, 119.0; IR (neat) 2090, 2050, 1990, 1940 (CO) cm⁻¹. Anal. Calcd for C₂₈H₂₇O₄BrPRe: C, 54.03; H, 3.22. Found: C, 54.01; H, 3.42. **11**: yellow oil; exact mass calcd (⁸¹Br) *m/e* 461.9740, found 461.9778, calcd (⁷⁹Br) *m/e* 459.9760, found 459.9787; mass spectrum (CID NH₃), *m/e* 463 (M⁺ + 1, ⁸¹Br), 461 (M⁺ + 1, ⁷⁹Br); ¹H NMR (acetone-*d₆*) δ 5.1 (s, 5 H, C₅H₅), 7.0–7.8 (m, 13 H, (C₆H₅)₂BrC₄H₂); ¹³C NMR (acetone-*d₆*) δ 216.3 (CO), 167.0, 160.0, 141.7, 141.1, 133.7, 129.3, 128.9, 128.4, 127.8, 126.5, 125.6, 123.9 ((C₆H₅)₂BrC₄H₂), 87.3 (C₅H₅); IR (neat) 2020, 1940 (CO) cm⁻¹.

(7) Parker, D. W.; Marsi, M; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *194*, C1–C4.

(8) η^5-[(HO)Ph₂C₅H₂]Re(CO)₂PPh₃ or η^5-[(MeO)Ph₂C₅H₂]Re(CO)₂PPh₃, the dicarbonyl(triphenylphosphine) analogue of **5** was not observed. Casey and co-workers have reported that (η^5-C₅H₅)₅Re(CO)₃, with prolong heating in the presence of P(CH₃)₃ converts to (η^5-C₅H₅)-Re(CO)₂P(CH₃)₃, this latter product being the apparent thermodynamic product. Cf. Casey, C. P.; O'Conner, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535–538.

(9) Attack of alkyllithium on acyl complexes occurs preferably at a terminal carbonyl ligand. Cf. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 303.

(10) For a general discussion of Li–Br exchange reactions: Cf. Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Elmsford, NY, 1974.

(11) Some **5a** was observed by ¹H NMR; however, purification from this reaction mixture proved difficult thus percent yield was not obtained.

(12) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1977**, *99*, 4368–4372. Lukehart, C. M.; Zeile, J. V. *Ibid.* **1976**, *98*, 2365–2367. Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Ibid.* **1975**, *97*, 6903–6904. Darensbourg, M. *J. Organomet. Chem.* **1972**, *38*, 133–138. Casey, C. P.; Bunnell, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 733. Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436–441.

successful lithium–bromine exchange reactions in two different metal systems hint that other carbene–alkyl metallacycles may be generated, albeit in low yields, in a similar fashion.

We are presently exploring reactions of 1 as well as other alkyl- and alkenyldilithium reagents with transition-metal carbonyl halides. Further work regarding initial alkyl bond formation followed by reactions which give metallacycles

is also being pursued.

Book Reviews

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Si-Silicon. Supplement Volume B2. Properties of Crystalline Silicon Carbide. Diodes. Molecular Species in the Gas Phase. Amorphous Silicon-Carbon Alloys. J. Schlichting, G. Czack, E. Koch-Bienemann, P. Kuhn, and F. Schröder, volume authors. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin/Heidelberg/New York. 1984. xiv + 314 pages. DM 1080, $393.20.

A purist might consider silicon carbide to be the simplest organosilicon compound, and actually, it is a species that is of some interest to some organosilicon chemists today. The pyrolysis of various organosilicon monomers and polymers gives SiC or, at least, SiC-containing ceramic materials. Silicon carbide fibers are now produced commercially in Japan by such a pyrolysis route. Thus a book about this inorganic cousin of organosilicon compounds, although of primary interest to the materials scientist, merits mention in this journal.

The present Gmelin volume, the first of two on silicon carbide to be issued, covers for the most part, in 245 pages, the properties of crystalline silicon carbide: crystallographic properties (there are nearly 170 known, different polytypes), bonding, the mechanical properties that make SiC such a useful material, thermal properties and diffusion, electrical and magnetic properties, optical properties and spectra, and surface interactions.

Short sections follow on silicon carbide diodes (25 pages) and on molecular binary silicon/carbon species such as SiC, SiC_2, Si_2C, and others (4 pages). These are generated at very high temperatures and observed in the gas phase or in low-temperature argon matrices. The final section deals with amorphous silicon–carbon "alloys": both hydrogen-free and hydrogen-containing films, as well as the much less studied fluorine - and oxygen-containing films.

The literature cited in this book in great detail is much different from that which is found in the more usual Gmelin chemical volumes which we have reviewed: few references to the chemical literature; rather mainly solid-state, ceramics, and physics journals, reviews, monographs, conference reports, dissertations, and patents are cited. This literature has been covered through the middle of 1983, and quite a few later references are included.

This excellent book, with its well-nigh exhaustive coverage of SiC, a material of major commercial importance, should be well received. Its companion volume (Silicon Suppl. Vol. B3), due to appear later in 1985, will cover the Si/C phase diagram, the formation, preparation, and manufacture, and the chemical reactions of silicon carbide. That volume should bring much more that will be of interest to organosilicon chemists.

Dietmar Seyferth, *Massacachusetts Institute of Technology*

The Chemistry of Ruthenium. By E. A. Seddon and K. R. Seddon. Elsevier, Amsterdam/New York. 1984. xxxix + 1373 pages. $250.00.

The intent of this massive book (~3 in. thick) is to present a systematic and comprehensive coverage of the inorganic and organometallic chemistry of the element ruthenium. Emphasis is on the *chemistry* of ruthenium, and no attempt has been made to cover any aspect of its metallurgy, alloys, analysis, binary compounds other than halides and chalcogenides and catalytic uses of the metal in a heterogeneous form. Literature coverage is through the end of 1978, and approximately 3200 references are cited.

The book begins with an Introductory chapter which outlines the organization of what is to follow and presents such things as the discovery and history of the element, its extraction, purification, applications, and a general overview of its physical and chemical properties. The principal organization of the rest of the text is by oxidation state, and Chapter 2 appropriately discusses oxidation state assignments. This chapter also gives an excellent accounting and illustration of the use of the MLX classification scheme devised by M. L. H. and J. C. Green. This chapter is followed successively by chapters on compounds containing Ru(VIII) (20 pp), Ru(VI) (6 pp), Ru(VI) (14 pp), Ru(V) (14 pp), Ru(IV) (64 pp), Ru(III) (186 pp), Ru(II) (550 pp), Ru(I) (36 pp), Ru(0) (48 pp), and "low" oxidation states, mainly Ru(–II) (2 pp). Then comes a 128-page chapter on ruthenium carbonyl clusters, a 68-page chapter on ruthenium nitrosyl complexes, and a 88-page chapter on the photophysics and photochemistry of tris(diimine)ruthenium(II) complexes, primarily $[Ru(2,2'-bipyridine)_3]^{2+}$.

Although the book is produced from camera-ready copy, it is very well done and is not unpleasant to read. The authors have written the book in an agreeable style that makes the subject matter easy to digest. The very high price of this book will surely restrict its purchase for personal libraries but it should prove to be an invaluable library resource for anyone interested in the chemistry of this element.

Gregory L. Geoffroy, *The Pennsylvania State University*