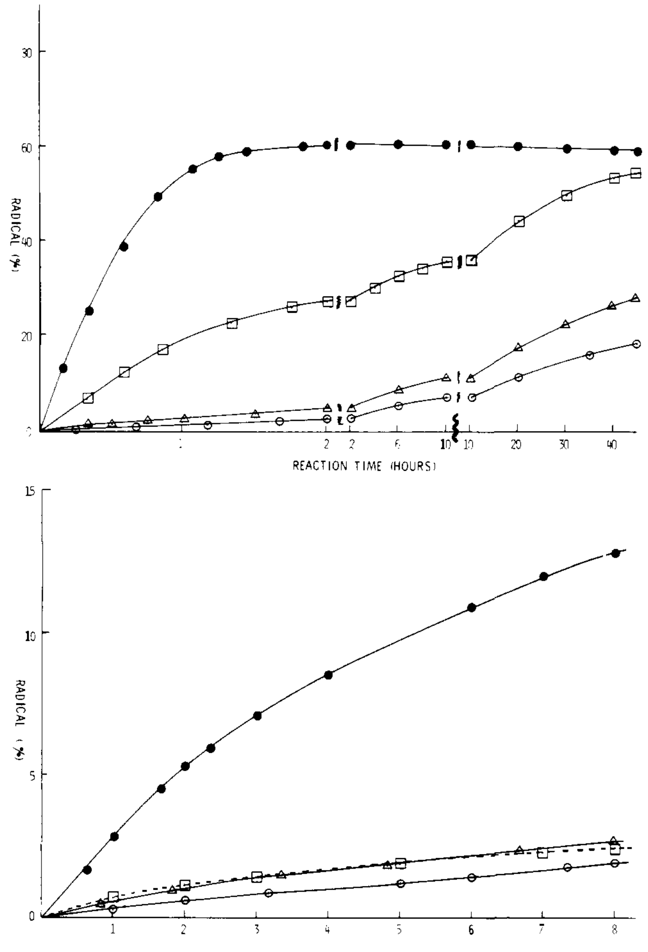

Figure 2. Formation of the radical intermediates with time determined by EPR and visible spectroscopy in the reaction of dimesityl ketone (DMK) with Grignard reagents. (a) *i*-PrMgCl (●), *sec*-BuMgCl (□), EtMgCl (△), 5-hexenylmagnesium bromide (○). (b) *i*-BuMgCl (●), *t*-BuCH$_2$MgBr (△), PhCH$_2$MgBr (□), MeMgBr (○).

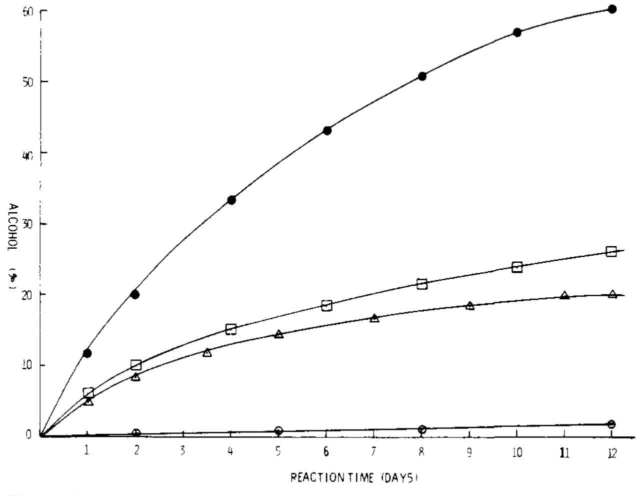

Figure 3. Formation of reduction product (Mes$_2$CHOH) with time determined by GLC in the reaction of DMK with Grignard reagents: (●) EtMgCl, (□) *i*-PrMgCl, (△) *sec*-BuMgCl, (○) *i*-BuMgCl.

reactions of Grignard reagents with aliphatic ketones but only with aromatic ketones or in special cases with aliphatic ketones that possess low reduction potentials (<−2.0 eV).

Preliminary results concerning the reactions of Grignard reagents with mesityl phenyl ketone indicate a similar behavior. Kinetic studies of the reactions of Grignard reagents with DMK and mesityl phenyl ketone are in progress.

Mechanism of the Zr-Catalyzed Carboalumination of Alkynes. Evidence for Direct Carboalumination[1]

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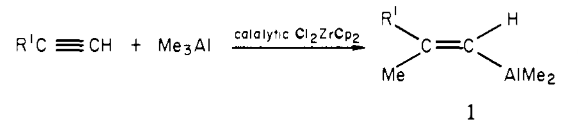
We wish to present unequivocal evidence for direct carboalumination in some representative reactions of terminal alkynes with organoalanes and zirconocene derivatives. We have recently discovered and developed controlled carbometalation of alkynes with Me$_3$Al and zirconocene dichloride[2] (eq 1) suitable for efficient

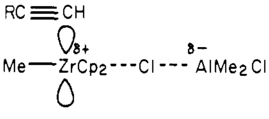


(1)

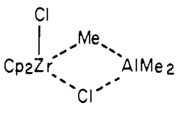
1

and highly stereo- and regioselective syntheses of trisubstituted olefins, especially those of terpenoid origin. In addition, this and related carboalumination reactions undergoing a clean single-state addition under homogeneous conditions appear to be well suited for detailed mechanistic studies that might be expected to shed useful light on the mechanism of carbometalation involving early transition-metal catalysts, such as the Ziegler–Natta polymerization.[3]

Since carbometalation of terminal alkynes requires the simultaneous presence of an organoalane and a Zr-containing species,[2] the reaction must involve an Al-assisted carbozirconation and/or a Zr-assisted carboalumination in the crucial carbon–carbon bond-forming step. We earlier suggested that the reactions shown in eq 1 might involve an Al-assisted carbozirconation as, for example, might be represented by **2**, on the basis of the following previous findings. First, Me$_3$Al and Cl$_2$ZrCp$_2$ undergo



2



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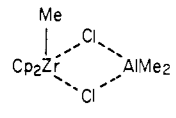

4

a Me–Cl exchange to form species containing the Me(Cl)ZrCp$_2$ moiety, such as **3** and **4**, which is rapid on the NMR time scale at ambient temperature.[2] Cleavage of a bridging Zr–Cl bond in **4** would give the Al–Zr species in **2**. Second, the reaction of a 1-alkynyldimethylalane, e.g., *n*-PrC≡CAlMe$_2$, with preformed Me(Cl)ZrCp$_2$[4] in a 1:1 ratio gives cleanly and quantitatively the carbozirconated product **5**, thereby providing a clean-cut example of carbozirconation of alkynes[5] (eq 2). It should be emphasized here again that no reaction is observed between 1-pentyne itself and Me(Cl)ZrCp$_2$ under comparable conditions. An Al–Zr species **6** analogous to **2** appears to be a plausible active species for this reaction. Third, although **5** itself is somewhat unreactive toward

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(1) Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 21. Controlled Carbometallation. 10. Part 9: Rand, C. L.; Van Horn, D. E.; Moore, M. W.; Negishi, E. *J. Org. Chem.*, in press.

(2) (a) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252–2254. (b) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, *100*, 2254–2256. (c) Okukado, N.; Negishi, E. *Tetrahedron Lett.* **1978**, 2357–2360. (d) Negishi, E.; King, A. O.; Klima, W. L.; Patterson, W.; Silveira, A., Jr. *J. Org. Chem.* **1980**, *45*, 2526–2582. (e) Negishi, E.; Valente, L. F.; Kobayashi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298–3299. (f) Kobayashi, M.; Negishi, E. *J. Org. Chem.* **1980**, *45*, 5223–5225. (g) Kobayashi, M.; Valente, L. F.; Negishi, E.; Patterson, W.; Silveira, A., Jr. *Synthesis* **1980**, 1034–1035. (h) Matsushita, H.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 2882–2884.

(3) For recent reviews, see: (a) Boor, J. "Ziegler-Natta Catalysts and Polymerization"; Academic Press: New York, 1978. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99–149.

(4) Surtees, J. R. *Chem. Commun.* **1965**, 567.

(5) Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276–1277.

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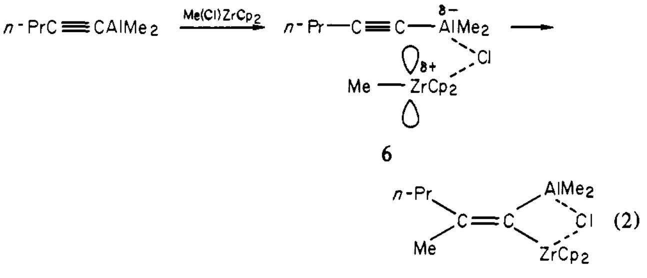
Table I. Me_mAlCl_{3-m}-$Me_n(Cl)_{2-n}ZrCp_2$ Systems.[a] Their ^1H NMR Data and Reaction with 1-Heptyne

reagent system		^1H NMR data[b]				reaction with 1-heptyne		
		Me		Cp		time for >95% completion at room temp, h	yield by GLC of protonolysis products, %	
Me_mAlCl_{3-m}	$Me_n(Cl)_{2-n}ZrCp_2$	chem shift, ppm	half-width, Hz	chem shift, ppm	half-width, Hz		n-C_5H_{11}-(Me)C=CH_2	n-C_5H_{11}-CH=CHMe
Me_2AlCl	Cl_2ZrCp_2	−0.38	3	6.45	2	48	60	5
Me_3Al	Cl_2ZrCp_2	−0.43[c]	6	6.45[c]	7	3	93	5
Me_3Al	$Me(Cl)ZrCp_2$	−0.76	2	6.24[d]	2	3	93	5
		−0.40	2					
		−0.33[e]						
Me_3Al	Me_2ZrCp_2	−0.97	2	6.00[d]	3	24	94	5
		−0.57	3					

[a] 1:1 mixtures of Me_mAlCl_{3-m} and $Me_n(Cl)_{2-n}ZrCp_2$ in $ClCH_2CH_2Cl$. The $MeAlCl_2$–Cl_2ZrCp_2 was not examined by ^1H NMR spectroscopy, as it did not undergo carbometalation with 1-heptyne. [b] The figures in the table are those observed at ca. 35 °C in $ClCH_2CH_2Cl$ with benzene (δ 7.32) as an internal standard. All systems except Me_2AlCl–Cl_2ZrCp_2 were examined by variable-temperature ^1H NMR spectroscopy (from −50 to 80 °C). [c] The Cp signal shows a broad shoulder at ca. δ 6.26. The two Cp signals coalesce at 59–60 °C. At −50 °C, the Me signal is split into three peaks at δ −0.60 (2 Hz), −0.43 (7 Hz), and 0.32 (2 Hz), while the Cp signal is split into two sharp peaks at δ 6.25 and 6.46. Similarly, the following peaks are observed after quenching Me_3Al–Cl_2ZrCp_2 with THF at room temperature: δ −0.98, −0.74, 0.22, 6.20, and 6.44. [d] No sign of broadening or splitting between −50 and 80 °C. [e] The peak remains sharp between −50 and 40 °C but broadens at or above 50 °C. At 80 °C its half-width is 12 Hz.



6

(2)

5

Al-containing compounds, (*E*)-1-alkenylchlorobis(η^5-cyclopentadienyl)zirconiums are known to be readily converted into the corresponding alkenylalanes on treatment with appropriate alanes,[6] providing a possible mechanism for in situ conversion of alkenylzirconium species into **1**.

Despite all these facts and interpretations, the results presented below provide unequivocal evidence for direct carboalumination, which must be assisted by a Zr-containing species, at least in some typical Zr-catalyzed carboalumination reactions of terminal alkynes. Furthermore the alkyl-halogen exchange, that we previously considered to be an essential step required for carbozirconation with alkylalanes and Cl_2ZrCp_2, not only is unnecessary for carboalumination but should even be prevented, if the undesirable hydrometalation,[7] that can occur competitively with the desired carboalumination, is to be avoided.

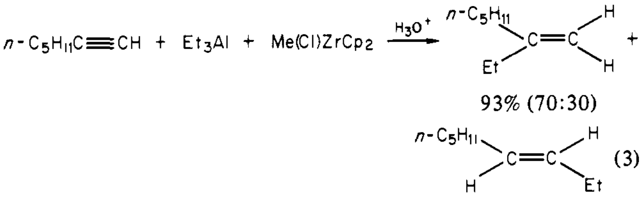
In the hope of clarifying mechanistic details of the Zr-catalyzed carboalumination, we have varied *m* and *n* in the reagent systems **7** and examined their ^1H NMR spectra (from −50 to 80 °C) as

$$Me_mAlCl_{3-m}\text{-}Me_n(Cl)_{2-n}ZrCp_2$$

7 ($m = 1, 2$, or 3; $n = 0, 1$, or 2)

well as their reaction with 1-heptyne. As indicated by the results shown in Table I, Me–Cl exchange that is rapid on the NMR time scale at ambient temperature (ca. 35 °C) is observed only with the Me_3Al–Cl_2ZrCp_2 system. And yet all four reagent systems undergo the desired carbometalation. The rate and the product yields observed with Me_3Al–$Me(Cl)ZrCp_2$ are comparable with those observed with Me_3Al–Cl_2ZrCp_2. These results clearly indicate that the rapid Me–Cl exchange is not required for carbometalation.

To further probe the critical question of Al-assisted carbozirconation vs. Zr-assisted carboalumination, we have reacted 1-heptyne with a 1:1 mixture of Et_3Al and $Me(Cl)ZrCp_2$[4] and found that the reaction procedures, after protonolysis, a 70:30 mixture of 2-ethyl-1-heptene and *trans*-3-nonene in 93% combined yield with only traces, if any, of the corresponding methylated alkenes (eq 3). The results are not only consistent with direct carboalumination but inconsistent with direct carbozirconation.



(3)

To rule out any special effect, if any, due to the difference between Me and Et, we have then run the reaction of 1-heptyne with a 1:1 mixture of Me_3Al and $CD_3(Cl)ZrCp_2$[8] prepared by the reaction of Cl_2ZrCp_2 with 2 equiv of CD_3MgI followed by treatment with 1.5 equiv of $PbCl_2$ in benzene (room temperature, 1 h). The product obtained in essentially quantitative GLC yield (~80% by isolation) after iodination[9] is stereochemically pure (≥98%) (*E*)-1-iodo-2-methyl-1-heptene contaminated with a small amount (2%) of (*Z*)-3-iodo-2-octene. The extent of deuterium incorporation is <4%.

Although the precise role of Zr-containing reagents remains to be unclear, we may now conclude that the Zr-catalyzed carboalumination of terminal alkynes, at least in some typical cases, proceeds by a Zr-assisted carboalumination. Since, however, the reaction shown in eq 2 does appear to provide a genuine, albeit highly special, example of the Al-assisted carbozirconation of alkynes, we must view that the Al–Zr reagent systems may undergo either carboalumination or carbozirconation of alkynes, depending on the reaction parameters involved.

One of the practical difficulties associated with the Zr-catalyzed carboalumination with alkylalanes other than methylalanes is the competitive hydrometalation. Thus, for example, the reaction of 1-alkynes with n-Pr_3Al and Cl_2ZrCp_2 induces a Zr-catalyzed hydroalumination to the extent of 30–50%.[7,10] If the Zr-catalyzed hydroalumination occurs via transmetalation–elimination–

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(6) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521–3531.

(7) Negishi, E.; Yoshida, T. *Tetrahedron Lett.* **1980**, *21*, 1501–1504.

(8) The reaction of Cl_2ZrCp_2 with CD_3MgI in a 1:2 ratio in ether (room temperature, 0.5 h) gives $(CD_3)_2ZrCp_2$ in 90% yield: ^1H NMR (C_6H_6, Me_4Si) δ 5.74 (s). Treatment of $(CD_3)_2ZrCp_2$ with 1.5 equiv of $PbCl_2$ produces ca. 95% pure $CD_3(Cl)ZrCp_2$ in 90% yield: mp 194–195 °C dec (lit.[4] mp for $CH_3(Cl)ZrCp_2$ 191–193 °C); ^1H NMR (C_6H_6, Me_4Si) δ 5.75 (s).

(9) Negishi, E.; Van Horn, D. E.; King, A. O.; Okukado, N. *Synthesis* **1979**, 501–502.

(10) Van Horn, D. E. Ph.D. Dissertation, Syracuse University, 1978.

hydrozirconation[11]–transmetalation,[6] as we suggested recently, this side reaction should be prevented by choosing an Al–Zr reagent system which does not readily undergo transmetalation to form an *n*-Pr–Zr species. Examination of a 1:1 mixture of *n*-Pr_3Al and Cl_2ZrCp_2 in 1,2-dichloroethane by ^{1}H NMR spectroscopy at ambient temperature reveals, as expected, the formation of *n*-Pr(Cl)$ZrCp_2$[12] (≤60%) along with Cl_2ZrCp_2 (40–45%). On the other hand, a 1:1 mixture of *n*-Pr_2AlCl and Cl_2ZrCp_2 does not show any sign of *n*-Pr–Cl exchange, as judged by ^{1}H NMR spectroscopy. We have therefore treated 1-heptyne with *n*-Pr_2AlCl and Cl_2ZrCp_2 in a 1:1:1 ratio and have indeed obtained, after protonolysis, 2-*n*-propyl-1-heptene and (*E*)-4-decene in 76 and 21% yield, respectively, with no more than a trace of 1-heptene. Although the generality of this modified procedure is yet to be explored, we may now have at hand a means of circumventing the undesirable hydrometalation. This and other aspects of the Zr-catalyzed carboalumination are under active investigation.

Acknowledgment is made to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[11] For a review, see: Schwartz, J. *J. Organomet. Chem. Libr.* **1976**, *1*, 461–488.

[12] The reaction of $(Cp_2ZrCl)_2O$ with 2 equiv of *n*-Pr_3Al in CH_2Cl_2 in a manner reported for the preparation of Me(Cl)$ZrCp_2$[4] gives *n*-Pr(Cl)$ZrCp_2$ in ~40% yield: ^{1}H NMR ($ClCH_2CH_2Cl$, Me_4Si) δ 0.7–1.1 (m with a triplet at 0.82 ppm, $J = 7$ Hz, 5 H), 1.2–1.8 (m, 2 H), and 6.16 (s, 10 H).

Book Reviews*

Infrared Characteristic Group Frequencies. By G. Socrates (Brunel University). John Wiley & Sons, New York. 1980. xi + 153 pp. $72.00.

When using infrared as an analytical tool to solve chemical problems, it is important to have a number of references available that correlate absorption regions with structural units. This book is clearly intended for that purpose. It contains only charts and tables listing regions where large numbers of organic and inorganic compounds absorb, accompanied by a textual discussion of these patterns of absorption organized largely by types of bonds, functional groups, and/or compound class. There is also a brief chapter on the near infrared. About two-thirds of the book is devoted to a chapter-by-chapter rendition of compounds traditionally associated with organic chemistry and the remainder is devoted to inorganic compounds, organometallic compounds, etc. The book has an unusual page size (they are much wider than they are tall), very probably in an effort to accommodate the charts. One of the charts (Chart 1) has a novel approach: it is a "negative" correlation chart, that is the absence of a band in the so-noted region implies the absence of the functional group or chemical class listed. Charts 2 and 3 are more like the usual correlation charts: Chart 2 (seven pages) lists absorption regions (from high to low wavenumber) and the functional groups likely to cause absorption in that region. Chart 3 (thirteen pages) is, on the contrary, listed in order of functional groups and *all* regions in which that particular functional group might absorb are listed, as well as the vibration that causes each absorption.

The strengths of this book are the charts as well as the extensive tables that are spread throughout the chapters. A spot check indicates that the references listed that support the tables frequently supplement (rather than reproduce) the references listed for the same functional groups listed by Bellamy and by Colthup et al. A scan of the references listed at the end of each chapter does raise an eyebrow; these references are rarely recent (very few are publications that have appeared since 1974). A similar scan of the two books listed above does, however, yield essentially the same result.

In summary, it does appear that this book represents a worthwhile addition to an institutional library (although, at $0.50 per page it is unlikely to be added to many personal libraries). Finally, there is a section added in appendix form titled Further Reading. This seems to be a collection, in no particular order, of general reading that could serve to supplement the text. My concern about up-to-date references again surfaces. Due to this concern and due to the fact that above I have mentioned some of these books, I will list below some books that certainly should be considered as supplements or alternates to this text. I also note that none of these were cited in the text by Socrates (although earlier editions of some were cited).

L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Vol. 1, 3rd ed., Halsted Press (Wiley), New York, 1975.

N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy", 2nd ed., Academic Press (Harcourt, Brace Jovanovich Publishers), New York, 1975.

K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley-Interscience, New York, 1978.

E. Maslowsky, Jr., "Vibrational Spectra of Organometallic Compounds", Wiley-Interscience, New York, 1977.

D. Dolphin and A. Wick, "Tabulation of Infrared Spectral Data", Wiley-Interscience, New York, 1977.

Terence C. Morrill, *Rochester Institute of Technology*

Manual of Economic Analysis of Chemical Processes. By A. Chauvel, P. Leprince, Y. Barthel, C. Raimbault, and J.-P. Arlie (Institut Francais du Petrole). Translated by R. Miller and E. B. Miller. McGraw-Hill Book Company, New York. 1981. xiv + 462 pp. $37.95.

This excellent translation of the 1976 French original is a valuable handbook of cost estimation methods widely used in the petroleum and petrochemical industry. More than a mere compendium of equations, it is a readable step-by-step description of the techniques of economic analysis. These techniques, gathered, developed, and refined over the years by the staff at IFP, will be very useful for cost estimators, market researchers, process development engineers, and consultants. Cost estimation methods developed by operating companies, consultants, and contractors are usually jealously guarded, and IFP is one of the few leading research organizations that would consider publishing the results of many years work in this way. Founded 35 years ago and funded by a portion of the French gasoline tax, IFP is also obliged to promote the dissemination of knowledge and know-how through publication.

The 228-page text is divided into five chapters: (1) Market Research, (2) Elements of Economic Calculation, (3) Investment Costs, (4) Cost Estimating for Industrial Projects, and (5) Evaluating Research Projects. Each chapter is followed by one or two detailed examples, illustrating the book's subtitle, "Feasibility Studies in Refinery and Petrochemical Processes".

The first chapter on Market Research serves as a reminder that the availability and price of raw materials and products must be ascertained before a detailed design project can be undertaken, and changes in any of these factors must be constantly monitored during the project.

Chapter 2 gives methods for calculating investments and operating costs (fixed costs and variable costs) and details of all the most widely used techniques for calculating profitability of a project (payout time, discounted cash flow, return on investment, etc.). Chapter 3 gives additional details on investment costs, including estimates of accuracy, effects of location, and how to adjust for inflation.

Chapters 4 and 5 show how to apply these principles to industrial projects and research projects, respectively.

Thirteen appendixes occupy 211 pages. Eleven of the appendixes deal with sizing and cost estimation of major types of processing equipment. Pricing data and pricing methods (useful for scale-up) are presented in detail. The prices are given in dollars, as of 1975, for a U.S. location. Incidentally, all of the methods given in the text apply primarily to plants in the United States. Short-cut design methods for sizing process equipment have been compiled from standard sources and presented in a convenient way. Reflecting European practice, metric units are used in most cases, and this provides a good source of methods for the engineer trained in their use, or for anyone who would like to become accustomed to designing in metric units.

A bibliography gives the sources of the sizing and cost estimation data and methods. It is selective, but gives all the most important references up to 1976.

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* Unsigned book reviews are by the Book Review Editor.