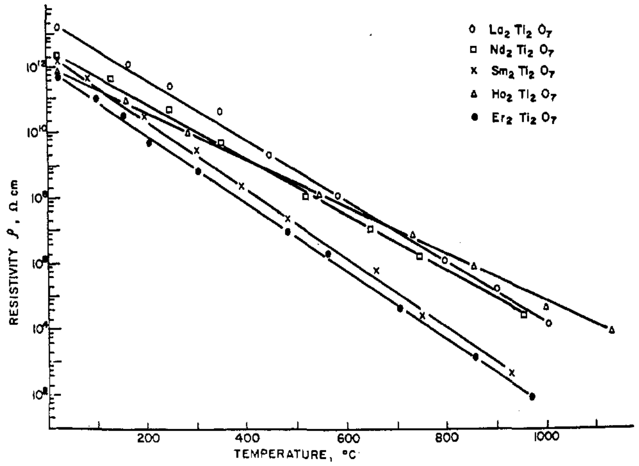

Fig. 1.—Electrical resistivities as a function of temperature for some rare earth titanates.

of about the same magnitude, and the reason for the somewhat lower resistivity (and high dissipation factor) for the Ce, Pr, and Tb compounds is probably a slight oxygen deficiency which came about during the firing of these compositions in an inert atmosphere. With the exception of these particular compounds, the dielectric constants of all other compositions were measured up to 300°. In each case, the dielectric constant stayed relatively constant up to this temperature. At higher temperatures, both the apparent dielectric constant and the dissipation factor increased, not because of any ferroelectric behavior but rather due to the exponential decrease of the electrical resistivity as demonstrated for $La_2Ti_2O_7$, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Er_2Ti_2O_7$ in Fig. 1. All these compounds exhibited p-type semiconduction at elevated temperatures.

Finally, we checked all of the compounds prepared for luminescence in the visible by irradiating them with both a 2537 Å. and a 3660 Å. ultraviolet source. None of the compounds fluoresced in the visible. This is somewhat surprising since most of the rare earths, at least in the configuration of their sesquioxides, absorb ultraviolet light in the region of the stated excitation. We could possibly have a case of concentration quenching or else the particular coordination of the cubic pyrochlore structure does not provide an appropriate host lattice for the excitation of the trivalent rare earths. Finally, the fact that TiO_2 is known to absorb ultraviolet light strongly, without re-emitting in the visible, could also be the cause for the nonluminescence of these rare earth titanates. Since it is established that there actually exists a photochemical interaction between ultraviolet light and TiO_2, this would also rule out the possibility of the excitation of fluorescent emission by energy transfer from the host structure because all incident energy would be dissipated through chemical reaction.

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Correspondence

Divergence in the Relative Shielding of Ring and Side-Chain Protons in Substituted Metallocenes

Sir:

We have recently examined the proton nuclear magnetic resonance spectra of several mono- and diacyl derivatives of the ferrocene–ruthenocene–osmocene triad and have observed that there is a gradual deshielding of all the corresponding ring protons proceeding from the iron to the ruthenium to the osmium analogs.[1] We have subsequently noted a gradual *shielding of the methyl protons* of acetylmetallocenes in this same series. In order to test the generality of this phenomenon, two series of substituted metallocenes with hydrogen atoms α and β to the ring have been synthesized and analyzed by proton n.m.r.

Ethylruthenocene [*Anal.* Calcd. for $C_{12}H_{14}Ru$: C, 55.85; H, 5.44; Ru, 38.98; mol. wt., 259. Found: C, 55.80; H, 5.53; Ru, 39.20; mol. wt., 258], m.p. 12–12.5°, and ethylosmocene [*Anal.* Calcd. for $C_{12}H_{14}Os$: C, 41.37; H, 4.05; Os, 54.59; mol. wt., 348. Found: C, 41.67; H, 4.21; Os, 52.54; mol. wt., 356], m.p. 33–33.5°, were both prepared in 88% yield by reduction of the appropriate acetylmetallocene with $LiAlH_4 + AlCl_3$ in ethyl ether.[2] Benzylruthenocene [*Anal.* Calcd. for $C_{17}H_{16}Ru$: C, 63.53; H, 5.02; Ru, 31.44; mol. wt., 321. Found: C, 63.68; H, 5.31; Ru, 31.25; mol. wt., 323], m.p. 86–87°, and benzylosmocene [*Anal.* Calcd. for $C_{17}H_{16}Os$: C, 49.74; H, 3.93; Os, 46.33; mol. wt., 410. Found: C, 50.00; H, 4.13; Os, 46.38; mol. wt., 409], m.p. 100–101°, were prepared in 87–90% yield by similar reduction of the corresponding benzoylmetallocenes. These alkylmetallocenes as well as ethylferrocene[3] and benzylferrocene[4] were purified by chromatography on activated alumina and subsequent recrystallization from methanol.

The proton n.m.r. spectra of the ethyl- and benzylmetallocenes, together with pertinent n.m.r. spectra for monoacetyl- and 1,1′-diacetylmetallocenes, are abstracted in Table I. It is apparent that the introduction of an ethyl or benzyl substituent generally effects shielding of the ring protons with respect to the parent unsubstituted metallocene. As in the case of the various acylmetallocene series, both the ethyl- and benzylmetallocenes show a gradual deshielding of all the corresponding ring protons proceeding from the

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[1] M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963).

[2] K. L. Rinehart, Jr., A. F. Ellis, C. J. Michejda, and P. A. Kittle, *J. Am. Chem. Soc.*, **82**, 4112 (1960); K. Schlogl, A. Mohar, and M. Peterlik, *Monatsh.*, **92**, 921 (1961).

[3] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955); M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

[4] M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

TABLE I

PROTON N.M.R. SPECTRA OF SOME ALKYLMETALLOCENES

Metallocene[c]	Chemical shifts and multiplicity[a,b]				
	C_5H_5 ring	Substituted ring[d]		CH_2	CH_3
Ethylferrocene	5.91 (s)	5.96 (u)	5.96 (u)	7.66 (q)	8.84 (t)
Ethylruthenocene	5.48 (s)	5.48 (t)	5.57 (t)	7.78 (q)	8.93 (t)
Ethylosmocene	5.32 (s)	5.29 (t)	5.38 (t)	7.76 (q)	8.98 (t)
Benzylferrocene	5.90 (s)	5.94 (u)	5.94 (u)	6.32 (s)	...[e]
Benzylruthenocene	5.52 (s)	5.52 (t)	5.60 (t)	6.44 (s)	...[f]
Benzylosmocene	5.37 (s)	5.31 (t)	5.41 (t)	6.43 (s)	...[g]

[a] Determined as 10% (wt. to vol.) solutions in CCl_3D on a Varian A-60 spectrometer and given in τ units (estimated accuracy ±0.02 p.p.m.). [b] s, singlet; t, triplet; q, quadruplet; u, unresolved. [c] Ferrocene, ruthenocene, and osmocene resonate at τ 5.86, 5.45, and 5.30, respectively.[1] The methyl resonances for the ferrocenes, ruthenocenes, and osmocenes in the monoacetyl series occur at τ 7.62, 7.72, and 7.79 and in the 1,1′-diacetyl series at τ 7.65, 7.80, and 7.91, respectively. Analogous trends were noted in other solvents, such as acetone and dioxane. [d] The high-field resonances are attributed to protons adjacent to the alkyl group. [e,f,g] The aromatic proton resonances are centered at τ 2.79, 2.75, and 2.76, respectively.

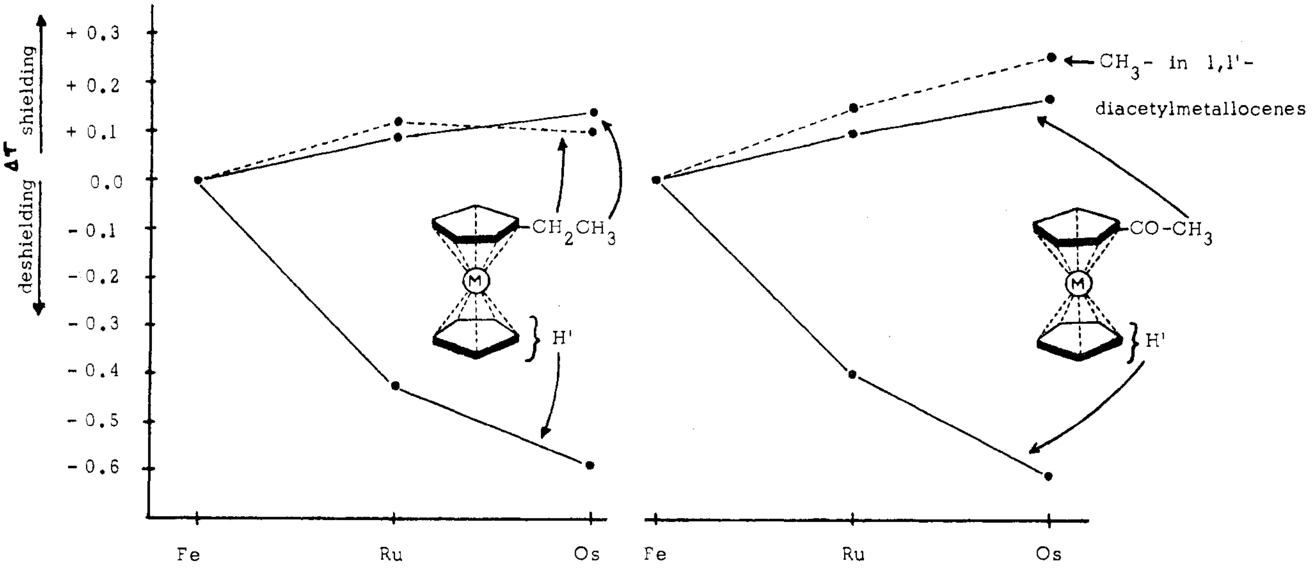

Fig. 1.—Divergence in the shielding of protons in substituted metallocenes.

ferrocene to the ruthenocene and osmocene derivatives. In addition, protons α to the cyclopentadienyl ring in alkylmetallocenes exhibit appreciably greater shielding in both ruthenium and osmium derivatives relative to the iron analog, while corresponding β-protons in acylmetallocenes and methyl protons in acetylmetallocenes experience gradually increased shielding in the same sequence. The quantitative relationships are conveniently illustrated in Fig. 1, in which the differential shieldings ($\Delta\tau$) of both the unsubstituted ring protons and side-chain protons are plotted as a function of the metal to indicate the direction and magnitude of the effect.

It is recognized that differences in proton chemical shifts can be due to a variety of factors, including both diamagnetic and paramagnetic contributions to the shielding constant.[5] Variations in the magnitude of ring current effects, providing such ring currents are indeed present in metallocenes,[6] might be expected to alter the degree of shielding of the ring protons in particular, and could account at least in part for the effects observed. The *divergence* in relative shielding of the ring and side-chain protons in substituted metallocenes, which we now report, needs further explanation, however.[7]

Since the differences in proton chemical shifts described above are dependent on the nature of the metal, the variations in the resonances may likewise be related to variations in shielding effects of the respective metal orbitals. Based on the analogy of enhanced shielding by electron-rich zones of anisotropic organic moieties (π-electron systems, comprising olefins, carbonyl functions, and heterocyclic and aromatic nuclei), the orbitals effecting any selective shielding are, very likely, the filled d-orbitals of the metals. Maximum shielding of the ring protons in the iron analogs and in particular the maximum shielding of the β-protons in osmium analogs may indicate the closest proximities of these areas to the metal orbitals effecting the shielding. Studies of this nature may thus provide an indication of the variation in orbital size and shape with respect to a fixed reference system, namely, the carbon skeleton of the substituted cyclopentadienyl ring. The gradual deshielding of

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[5] W. D. Phillips, "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press, New York, N. Y., 1962, pp. 403–413.

[6] L. N. Mulay and Sr. M. E. Fox, S.N.D., *J. Am. Chem. Soc.*, **84**, 1308 (1962).

[7] Electronegativity alone, which has the same value for both ruthenium and osmium (*i.e.*, 2.2: L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 93), is not sufficient to account for the differences in shielding or reaction rates.

the ring protons and the concomitant gradual increased shielding of the β-protons may conceivably indicate a progressively increasing radial expansion in the size of the d-orbital(s) responsible for the shielding, proceeding from the iron to the ruthenium to the osmium derivatives.[8] The effects observed and the interpretation advanced can be compared with the information obtained from the comparative chemistry of these metallocenes.[9] Since the proton shifts indicate selective shielding or deshielding in certain regions of the molecule, any comparison of the chemistry of these compounds must also be made between equivalent regions only. If done accordingly, the deductions drawn from chemical shifts appear to parallel many of the conclusions concerning relative electron densities derived from the chemistry of this metallocene triad.

We are pursuing the implications of these findings in order to understand better the "topography" of metal d-orbitals and specific metal effects in metallocene chemistry. The results of such a study might also prove useful in clarification of the bonding in metallocenes, since this topic is presently the subject of some controversy.[10]

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[8] There is conceivably a parallelism between the plots of Fig. 1 and similar plots using either the covalent radii (1.165, 1.241, and 1.255 Å.) or the atomic volumes (7.10, 8.18, or 8.38 cc.) of iron, ruthenium, and osmium, respectively. The values are from T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, pp. 870–872.

[9] For a review, see M. D. Rausch, *Can. J. Chem.*, **41**, 1298 (1963).

[10] G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959); J. P. Dahl and C. J. Ballhausen, *Kgl. Danske Videnskab. Selkab Mat.-fys. Medd.*, **33**, 5, 111 (1961); E. M. Shustorovich and M. E. Dyatkina, *Zh. Strukt. Khim.*, **3**, 345 (1962).

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Book Reviews

Teaching Chemistry with Models. By R. T. SANDERSON. D. Van Nostrand and Co., Princeton, N. J. 1962. 175 pp. 15 × 23 cm. Price, $5.75.

Models of organic and inorganic molecules and of various crystal types have been available commercially for many years now. However, due mainly to their size, the small models are not satisfactory for lecture demonstrations. Consequently, there have been numerous articles discussing "do it yourself" methods of constructing larger models using styrofoam or other suitable materials. Articles by J. A. Campbell: "Structural Molecular Models," *J. Chem. Educ.*, **25**, 200 (1948), and "Some Simple Solid State Models," *ibid.*, **34**, 210 (1957), have been particularly useful among some 40 papers on this subject.

In this book R. T. Sanderson, of the State University of Iowa, summarizes some methods of making and using models. He has developed his own scale of electronegativities and shows this for each element by using a color-coded scale from blue to green to yellow to orange to red for the atoms from fluorine to cesium. The atomic models also show the relative size of atoms (using covalent radii only), the distribution of electrons, and the valence orbitals.

The molecular models show the geometric structure, the multiplicity of bonding, and the charge distribution. Sanderson uses tangent spheres with the appropriate covalent radii, rather than using both van der Waals and covalent radii as used in most models such as the Fisher–Hirschfelder type which are preferred by most chemists. His rationalization of his personal preference, on p. 21 of the book, was not particularly convincing to this reviewer, who has constructed over 300 atomic, molecular, and solid state models using both radii without any of the difficulties mentioned in this book.

In addition to the one chapter of model construction, there are nine chapters on possible uses of the models to explain the properties of various substances. There is a useful bibliography of articles on model building from the *Journal of Chemical Education* and 55 pages of tables giving the dimensions and other data necessary for the construction of the Sanderson type models. The book also contains 16 pages of black and white photographs and a like number of pages of color plates which probably contributed to the relatively high cost of this small volume.

It is the hope of this reviewer that teachers who use the Sanderson and other types of models will stress the many limitation and dangers of over-emphasizing the use of models in teaching so that their students will not be carried away by the glib accounts of their usefulness that characterize many of the articles written by model building enthusiasts.

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Mathematical Crystallography and the Theory of Groups of Movements. By HAROLD HILTON. Dover Publications, Inc., 180 Varick St., New York 14, N. Y. 1963. xii + 262 pp. 13.7 × 21.6 cm. Price, $2.00.

A review of this book was originally published in the *Philosophical Magazine*, **7**, 605 (1904), and some of the reviewer's comments are still appropriate today.

"Crystallography is a science which in its practical aspect concerns the mineralogist and the chemist; but very few of those who are familiar with the forms and classifications of crystals will find Mr. Hilton's pages easy reading."

"The book is . . . . a treatise on the theory of a set of finite groups of a special type, involving certain operations of translation, reflexon, and rotation."

"The argument is frequently very condensed, and every line demands the closest attention on the part of the reader if he really wishes to follow the demonstration. . . . There is a steady strain upon the geometrical and kinematical imagination, a strain which comparatively few of those who are practically interested in crystallographic questions will care to undergo."

The listing of point groups, space groups, and their subgroups and equivalent points are, of course, more adequately presented in the modern "International Tables for X-Ray Crystallography." There are also a number of modern books presenting the applications of symmetry groups to crystallography which should be preferred by a student of crystallography. Another style of presentation is always valuable for deeper insight, however, and a modern reader may be intrigued by the extent of the development of the symmetry concepts before von Laue's discovery of the X-ray diffraction phenomenon and the present