One can now write

$$\frac{3\cos^2\theta_i - 1}{|\mathbf{r}_i|^3} = \frac{3(\mathbf{r}_i\cdot\mathbf{R})^2 - |\mathbf{R}|^2|\mathbf{r}_i|^2}{|\mathbf{R}|^2|\mathbf{r}_i|^5} \quad (8)$$

but $\mathbf{r}_i = \mathbf{R} - \mathbf{r}_i'$, and $\mathbf{r}_i' = x_i\mathbf{i} + y_i\mathbf{j} + z_i\mathbf{k}$, where x_i, y_i, z_i are coordinates of the ith proton; $\mathbf{R} = |\mathbf{R}|\cdot\cos\Omega\mathbf{i} + |\mathbf{R}|\sin\Omega\cos\phi\mathbf{j} + |\mathbf{R}|\sin\Omega\sin\phi\mathbf{k}$. Substitution into eq 8 followed by some rearrangement gives the final result.

$$\frac{3\cos^2\theta_i - 1}{|\mathbf{r}_i|^3} = \frac{2|\mathbf{R}|^2 - 4|\mathbf{R}|Q + 3Q^2 - |\mathbf{r}_i'|^2}{(|\mathbf{r}_i'|^2 + |\mathbf{R}|^2 - 2|\mathbf{R}|Q)^{5/2}}$$

where $|\mathbf{r}_i'|^2 = x_i^2 + y_i^2 + z_i^2$, and $Q = x_i\cos\Omega + y_i\sin\Omega\cos\phi + z_i\sin\Omega\sin\phi$.

Macrocyclic Nuclear Magnetic Resonance Shift Reagents[1]

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Abstract: An account of work with macrocyclic nmr shift reagents is given. The reagents dealt with are dichlorogermanium tetraphenylporphine, dihydroxygermanium tetraphenylporphine, dichlorogermanium porphine, dihydroxygermanium porphine, dichlorogermanium phthalocyanine, and iron(II) phthalocyanine. The substrates dealt with are *cis*-4-*tert*-butylcyclohexanol, 4,4-dimethylcyclohexanol, *trans*-4-*tert*-butylcyclohexanol, 4-*tert*-butylphenol, 2,6-diisopropylphenol, 2,4-di-*tert*-butylphenol, 4-*tert*-butyl-2,6-dimethylphenol, 4-nitrophenol, acetic acid, methylmagnesium bromide, *n*-propylmagnesium bromide, *n*-octylmagnesium bromide, phenylmagnesium bromide, methylamine, *n*-butylamine, and *n*-hexylamine. Both the advantages and disadvantages possessed by the reagents and the ways in which they complement the familiar lanthanide reagents are discussed. The potential of certain additional macrocyclic reagents is also touched on.

The currently used group of β-diketone lanthanide shift reagents[2] is highly effective for many problems. However, none of these reagents are applicable to a number of important classes of compounds, and none of them show the degree of specificity sometimes desired.

A group of reagents, which are quite unlike these lanthanide reagents and which, as a consequence, are able to fill in some of the gaps left by them, is described in this paper.[3] These reagents are all metal porphines, metal tetraphenylporphines, or metal phthalocyanines.[6] All but one of them form the requisite reagent–substrate bonds by a reaction in which part or all of the functional group of the substrate is replaced by a portion of the reagent containing the porphyrin ring. The remaining reagent forms the requisite bond by a coordination reaction. The shifting ability of these reagents arises mainly from the ring currents of their macrocycles, although the substrate functional group alterations which they cause are sometimes also of importance.

These reagents, while unlike the β-diketone lanthanide reagents in mode of action and, to a considerable extent, in applicability, do resemble them in ease of use and effectiveness.

Experimental Section

Synthesis of Reagents. A. Dichlorogermanium Tetraphenylporphine. A mixture of tetraphenylporphine[11] (4.32 g), germanium tetrachloride (7.7 g), and quinoline (50 ml) was heated at 220° under nitrogen with stirring for 50 min and then was cooled and filtered. The resultant purple crystalline product was washed with quinoline and benzene and dried (5.33 g).

A portion of this product was recrystallized from benzene and vacuum dried at 80°. *Anal.* Calcd for $C_{44}H_{28}N_4GeCl_2$: C, 69.88; H, 3.73; Cl, 9.38. Found: C, 69.62; H, 3.69; Cl, 9.42.

The nmr spectrum of this tetraphenylporphine showed a singlet at τ 0.93 (β protons) and complex multiplets at τ 1.76 and 2.23 (ortho and meta–para protons).[12]

B. Dihydroxygermanium Tetraphenylporphine. A mixture formed by adding alumina (Woelm V, 5 g) to a suspension of dichlorogermanium tetraphenylporphine (200 mg) in chloroform (100 ml) was shaken for 10 min and evaporated to dryness under vacuum. The residue was placed on the top of a small column of alumina (Woelm V, 10 g) and the resultant was eluted with benzene and then with chloroform. Evaporation of the chloroform eluate gave the product as a purple solid (185 mg).

This solid was extractively recrystallized from benzene with a Soxhlet extractor and vacuum dried at 110°. *Anal.* Calcd for $C_{44}H_{30}N_4GeO_2$: C, 73.46; H, 4.18; Ge, 10.14. Found: C, 73.12; H, 4.38; Ge 9.74; Cl, 0.01.

The nmr spectrum of this compound in very dry $CDCl_3$ showed a singlet at τ 0.97, multiplets at τ 1.72 and 2.23 (β, ortho, and meta–para protons, respectively[12]), and a singlet (which disappeared upon addition of CH_3OD) at τ 17.35 (hydroxyl protons).

C. Dichlorogermanium Porphine. In a preparation modeled after Kane's,[9] a mixture of porphine (400 mg), germanium tetrachloride (0.80 ml), and quinoline (5 ml) was heated at 210° under

(1) Support for this work was provided by National Science Foundation Grant No. GP-22739 and by an NDEA Fellowship.

(2) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969), and subquent papers.

(3) Preliminary descriptions of this work have appeared.[4,5]

(4) J. E. Maskasky and M. E. Kenney, *J. Amer. Chem. Soc.*, **93**, 2060 (1971).

(5) J. E. Maskasky, J. R. Mooney, and M. E. Kenney, *ibid.*, **94**, 2132 (1972).

(6) Several accounts of the use of phthalocyanines as shift reagents appeared.[7-10]

(7) J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *Inorg. Chem.*, **5**, 1979 (1966).

(8) J. N. Esposito, L. E. Sutton, and M. E. Kenney, *ibid.*, **6**, 1116 (1967).

(9) A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, **7**, 2588 (1968).

(10) A. R. Kane, J. F. Sullivan, D. H. Kenny, and M. E. Kenney, *ibid.*, **9**, 1445 (1970).

(11) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

(12) The position of the ortho multiplet was taken as the mid-point of the two main inner peaks and the position of the meta–para multiplet as the position of the second largest peak.

nitrogen for 50 min, cooled, and centrifuged. The solids were washed with benzene (3 × 7 ml), and the washings were combined with the quinoline centrifugate. The resultant solution was washed with hot water (~5 × 20 ml), and the water washings were combined with the solids from the reaction mixture. This suspension was heated until solution of the solids was essentially complete. It was then centrifuged free of residues and was acidified with concentrated hydrochloric acid (25 ml). The resultant red precipitate was separated and dried at 120° (472 mg).

D. Dihydroxygermanium Porphine. Dichlorogermanium porphine (30 mg) was dissolved in hot water (~25 ml), and the resultant solution, after cooling, was passed through a column of 8 mesh Dowex 2 ion-exchange resin in the basic form. Evaporation of the eluate, first on a hot plate and later in an oven at 120°, gave the product as red crystals (28 mg).

With very dry $CDCl_3$ this porphine gave an nmr spectrum with singlets at τ −0.60, 0.32, and 17.81 (meso, β, and hydroxyl protons, respectively).

E. Dichlorogermanium Phthalocyanine and Iron(II) Phthalocyanine. Dichlorogermanium phthalocyanine was made by a previously described method.[13] Iron(II) phthalocyanine was purchased and was sublimed before use.

Application of the Reagents. A. General Remarks. Only a limited number of synthetic procedures were used in applying the reagents. Those described in the following are representative of the ones used. For convenience the procedures described are arranged according to the substrate involved.

The dihydroxygermanium tetraphenylporphine used was recrystallized from benzene while the dichlorogermanium tetraphenylporphine was generally not recrystallized.

B. Alcohols. Application of Dichlorogermanium Tetraphenylporphine to 4,4-Dimethylcyclohexanol. *n*-Butyllithium (0.33 ml of a 2.4 *M* solution) was slowly added under nitrogen to a solution of 4,4-dimethylcyclohexanol (102 mg)[14a] in ether (2 ml) and the mixture stirred for 10 min. Benzene (30 ml) and dichlorogermanium tetraphenylporphine (76 mg) were then successively added, and the resultant was refluxed for 1.5 hr and cooled. Finally water (1 ml) was added, and the mixture was stirred for 1 min. The benzene solution was separated, dried (Na_2SO_4), centrifuged, and taken to dryness under vacuum. The resulting purple crystals were washed with pentane and vacuum dried (72 mg).

The nmr spectrum of these crystals showed the expected resonances in the expected ratios along with resonances for ~7 wt % free alcohol.

Application of Dihydroxygermanium Tetraphenylporphine to *cis*-4-*tert*-Butylcyclohexanol. A mixture of *cis*-4-*tert*-butylcyclohexanol (108 mg),[14b] dihydroxygermanium tetraphenylporphine (25 mg), and benzene (15 ml) was refluxed for 12 hr, filtered, and taken to dryness under vacuum. The resulting purple microcrystalline solid was vacuum dried at 100°.

The nmr spectrum of this product showed the expected resonances in the expected ratios and in addition resonances corresponding to ~7 wt % alcohol.

Remarks. The syntheses of compounds of this class proved troublesome at times. However, it is clear that many such compounds can be made. Not surprisingly, compounds of this class were found to exhibit hydrolytic instability.

C. Phenols. Application of Dihydroxygermanium Tetraphenylporphine to 2,6-Diisopropylphenol. A mixture of 2,6-diisopropylphenol (248 mg), dihydroxygermanium tetraphenylporphine (50 mg), and benzene (15 ml) was refluxed for 16 hr and evaporated to dryness under vacuum. The resultant was heated under vacuum at 100°. This gave the product as purple crystals.

The spectrum of this product showed the expected resonances and gave the expected integration. It also showed resonances indicating ~6 wt % free phenol.

Application of Dihydroxygermanium Tetraphenylporphine to 4-Nitrophenol. A mixture of 4-nitrophenol (19 mg), dihydroxygermanium tetraphenylporphine (25 mg), and benzene (8 ml) was stirred for 1 min and then refluxed for 4 hr. The resultant was reduced in volume to 4 ml, cooled, and filtered. The red solid thus obtained was washed with pentane and vacuum dried at room temperature (27 mg).

The spectrum of this product showed the expected resonances in the expected ratios. No resonances for free phenol were observed.

Remarks. The stability of these compounds to hydrolysis was found to be variable. The 4-*tert*-butylphenol compound was found to be least stable, and the 4-nitrophenol compound to be most stable.

D. Acids. Application of Dihydroxygermanium Porphine to Acetic Acid. A suspension of acetic acid (1.5 ml) and dihydroxygermanium porphine (7 mg) was refluxed for several minutes and then evaporated to dryness under vacuum. The resultant red solid was vacuum dried at 100°.

The nmr spectrum of this product showed resonances having the expected positions and areas. Its mass spectrum, at a probe temperature of 230°, showed parent and parent minus ligand arrays, *i.e.*, $PGe(OAc)_2^+$, $PcGeOAc^+$, and PGe^+. It also showed arrays attributable to hydrolytic impurities, *i.e.*, $PGe(OAc)(OH)^+$, $PGe(OH)_2^+$, and $PGe(OH)^+$.

Remarks. Hydrolytic instability was found to be a characteristic of the compounds of this class.

E. Halides and Grignard-Type Compounds. Application of Dichlorogermanium Tetraphenylporphine to *n*-Octylmagnesium Bromide. With protection from light and under nitrogen, an ethereal solution of *n*-octylmagnesium bromide (1.1 ml of a 1.2 *M* solution) was slowly added to a suspension of dichlorogermanium tetraphenylporphine (100 mg) in tetrahydrofuran (30 ml). The resultant was stirred for 15 min and then water (0.25 ml) was added. After the mixture had been stirred for 1 min, the tetrahydrofuran layer was separated, dried (Na_2SO_4), filtered, and evaporated to dryness. The blue crystalline product was washed with pentane and vacuum dried (110 mg).

The nmr spectrum of this product showed the expected resonances. (and several minor impurity resonances). Integration indicated that two octyl groups were bonded to each germanium.

None of the compound was obtained from attempted syntheses in which benzene was used as a reaction solvent.

Application of Dichlorogermanium Porphine to *n*-Propylmagnesium Bromide. Under nitrogen and with protection from light an ether solution of *n*-propylmagnesium bromide (0.60 ml of an 0.83 *M* solution) was slowly added to dichlorogermanium porphine (25 mg) in benzene (15 ml). The resulting solution was stirred for 20 min, water (0.5 ml) was added, and the mixture was stirred for an additional 10 min. After separation the benzene layer was dried (Na_2SO_4), centrifuged, and taken to dryness under vacuum. The purple solid thus obtained was washed with pentane and vacuum dried (16 mg).

The nmr spectrum of this product yielded resonances having the expected positions. Its mass spectrum, using a probe temperature of ~130°, showed arrays for parent and parent minus ligand ions, *i.e.*, $PGePr_2^+$, $PGePr^+$, and PGe^+, along with arrays for parent minus fragmented ligand ions, *e.g.*, $PGePrC_2H_4^+$, $PGePrCH_2^+$, etc. The strongest arrays were those for $PGePr^+$ and PGe^+.

Remarks. All of the Grignard derived compounds of this group except the octyl tetraphenylporphine compound were prepared from reaction mixtures in which benzene was used as the reaction solvent. As noted above, the tetraphenylporphine compound was prepared from a mixture in which tetrahydrofuran was used. All of these mixtures except that for the octyl phthalocyanine compound gave at least acceptable yields.

Why this latter mixture gave a poor yield is uncertain. Also uncertain is why the benzene–tetraphenylporphine–octyl Grignard reaction mixtures gave no yields. It may be that attack on the macrocycles occurred in these mixtures.

All of the alkyl compounds of this class were found to be sensitive to light (as expected in view of the light sensitivity of similar compounds[7]). Because of this, exposure of the compounds to light, especially when in solution, was kept to a minimum.

F. Amines. Application of Iron(II) Phthalocyanine to *n*-Hexylamine. A mixture of *n*-hexylamine (12 mg), iron(II) phthalocyanine (35 mg), and benzene (10 ml) was stirred overnight and filtered. Evaporation of the resultant under vacuum gave the product as purple crystals.

The nmr spectrum of this product showed the expected resonances along with small free amine resonances.

Remarks. While the methylamine compound was found to be unstable to standing (probably because of dissociation), both the butylamine and hexylamine compounds were found to be stable. All three compounds were found to be nonhygroscopic.

G. Spectra. Except where noted, deuteriochloroform was used to make up the solutions used for obtaining the spectra. Generally the concentrations of these solutions were arranged to be in the 0.5–5% range (a range found to be high enough to give good spectra but

(13) R. D. Joyner, R. G. Linck, J. N. Esposito, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **24**, 299 (1962).

(14) (a) The 4,4-dimethylcyclohexanol was the generous gift of Dr. J. E. Nordlander. (b) The *cis*-4-*tert*-butylcyclohexanol was obtained from a commercial mixture of the cis and trans hexanols by preparative gas chromatography.

Table I. Data for Shift Compounds Derived from Alcohols[a,b] (τ)

Reagent	Alcohol	1-eq	1-ax	2-eq	2-ax	3-eq	3-ax	4-ax	Me-eq	Me-ax	Bu
$TPPGe(OH)_2$[c]	*cis*-4-*tert*-Butylcyclohexanol	13.26		13.17	11.57	10.69	12.29	*d*			10.14
$TPPGeCl_2$	4,4-Dimethylcyclohexanol		14.66	13.16	11.98	10.13	10.84		9.85[e]	10.35[e]	
$PGeCl_2$[c]	*trans*-4-*tert*-Butylcyclohexanol		15.34	13.63	12.71	11.0[b]	11.3[b]	*d*			9.93

[a] 100 MHz, $CDCl_3$ data. [b] Predominantly chair conformations. [c] TPP, tetraphenylporphine; P, porphine. [d] Overlapped. [e] May be inverted.

Table II. Data for Lanthanide and Porphyrin Shift Compounds Derived from *cis*-4-*tert*-Butylcyclohexanol (τ)

Reagent	1	2-eq	2-ax	3-eq	3-ax	4-ax	Bu
$TPPGe(OH)_2$	13.3	13.2	11.6	10.7	12.3		10.1
$Eu(dpm)_3$[a]	−24.7	−14.9	−8.2	−6.7	−13.6	−6.5	−2.8

[a] dpm, dipivaloylmethane.

Table III. Data for Shift Compounds Derived from Phenols[a] (τ)

Reagent	Phenol	2	2-α	2-β	6	6-α	6-β	3	5	4	4-β
$TPPGe(OH)_2$	2,6-Diisopropylphenol		13.35	10.75		13.35	10.75	4.53	4.53	4.25	
$TPPGe(OH)_2$	2,4-Di-*tert*-butylphenol			11.18	10.02			4.23	4.67		9.28
$TPPGe(OH)_2$	4-*tert*-Butyl-2,6-dimethylphenol		11.71			11.71		4.61	4.61		9.25
$TPPGe(OH)_2$	4-Nitrophenol	8.28			8.28			3.43	3.43		
$PGe(OH)_2$	4-*tert*-Butylphenol	9.00			9.00			4.73	4.73		9.30

[a] 100 MHz, $CDCl_3$ data.

not so high as to give significant concentration effects). Except for the spectrum of tetra-*n*-butylgermane, all spectra were obtained with either a Varian A-60A spectrometer or a Varian HA-100 spectrometer equipped for both continuous wave and Fourier transform operation. The germane spectrum was obtained with a Varian HR-300 spectrometer.

Discussion

Since many of the important properties of these macrocyclic reagents are functions of the macrocycles to a considerable extent, the discussion of the reagents and the results obtained with them is conveniently oriented in terms of the macrocycles concerned.

Germanium Tetraphenylporphine Reagents. Like the other germanium shift reagents, the tetraphenylporphine reagents dichlorogermanium tetraphenylporphine and dihydroxygermanium tetraphenylporphine displace part or all of the functional groups of the substrates with which they interact. Also like the other germanium reagents, these reagents are quite stable under ordinary handling and storage techniques. In addition, the reagents are readily accessible and give shift compounds which are relatively soluble and stable in deuteriochloroform.

The ability of these reagents to function effectively with alcohols is shown by the results obtained with 4,4-dimethylcyclohexanol (Figure 1 and Table I).[15] Further evidence as to this ability is provided by the data on *cis*-4-*tert*-butylcyclohexanol (Table I).

However, even though these reagents do function effectively with alcohols, they clearly do not give shifts which are as large as those given by the lanthanide reagents. The comparative data shown in Table II on the use of tris(dipivalomethano)europium(III)[16] and dihydroxygermanium tetraphenylporphine with *cis*-4-*tert*-butylcyclohexanol illustrate this point.

(15) The fact that all shifts are to high field in these and the other examples of this paper is to be expected since the substrates in all cases are bonded to the macrocycles at the apices of the shielding cones.

(16) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

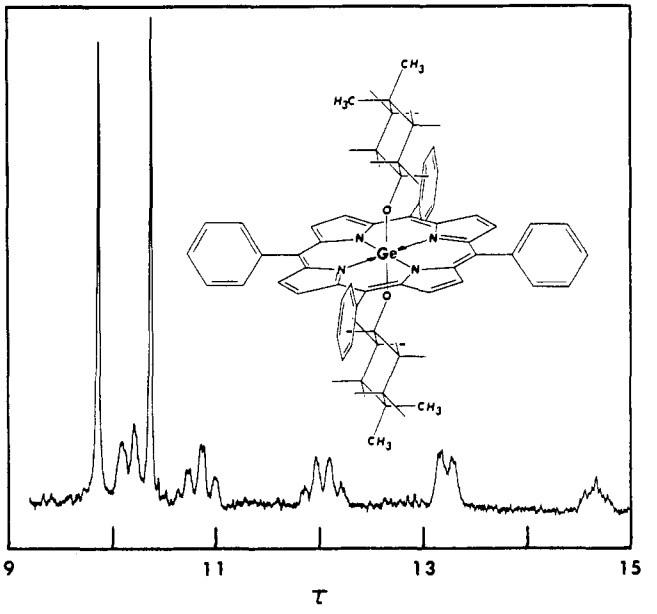

Figure 1. Upfield portion of 100-MHz spectrum of the shift compound derived from bis-4,4-dimethylcyclohexanol and dichlorogermanium tetraphenylporphine.

With phenols the situation is quite different. The lanthanide reagents are apparently only marginally effective (because of their instability in the presence of acids[17]), while one of the tetraphenylporphine reagents, dihydroxygermanium tetraphenylporphine, is quite effective. Data for some typical results obtained with this tetraphenylporphine reagent are given in Tables III and IV.

As might be expected, this reagent does not work with highly hindered phenols. Among such phenols are 2,4,6-tri-*tert*-butylphenol, 2,4-di-*tert*-butyl-6-iso-

(17) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

Table IV. Increments between Phenols and Shift Compounds Derived from Phenols[a] (ppm)

Reagent	Phenol	2	2-α	2-β	6	6-α	6-β	3	5	4	4-β
$TPPGe(OH)_2$	2,6-Diisopropylphenol		6.50	2.01		6.50	2.01	1.57	1.57	1.13	
$TPPGe(OH)_2$	2,4-Di-*tert*-butylphenol			2.59	6.58			1.52	1.73		0.56
$TPPGe(OH)_2$	4-*tert*-Butyl-2,6-dimethylphenol		3.96			3.96		1.60	1.60		0.53
$TPPGe(OH)_2$	4-Nitrophenol	5.20			5.20			1.60	1.60		
$PGe(OH)_2$	4-*tert*-Butylphenol	5.77			5.77			1.98	1.98		0.58

[a] 100 MHz, $CDCl_3$ data.

propylphenol, and 2-*tert*-butyl-6-methylphenol.

With carboxylic acids the situation is similar to that with phenols, the lanthanide reagents apparently being marginally effective[17] and dihydroxygermanium tetraphenylporphine being quite effective. An example of an application of the dihydroxide with an acid is provided by the work done with acetic acid (Tables V and VI).

Table V. Data for Shift Compounds Derived from Carboxylic Acids[a] (τ)

Reagent	Acid	Me
$TPPGe(OH)_2$	Acetic	11.08
$PGe(OH)_2$	Acetic	11.57

[a] 100 MHz, $CDCl_3$ data.

Table VI. Increments between Acids and Shift Compounds Derived from Acids (ppm)

Reagent	Acid	Me
$TPPGe(OH)_2$	Acetic	3.17
$PGe(OH)_2$	Acetic	3.66

Applicability of the reagent to acids other than carboxylic acids has not been investigated, but it is presumed that it will be found to be useful with at least some of them. With butyric acid the reagent is ineffective because of a chance overlap of the shifted resonances.

The use of dichlorogermanium tetraphenylporphine with Grignard reagents (another class of compounds for which the lanthanide reagents are not applicable) and by implication to organobromides and other compounds capable of yielding Grignard-type compounds is illustrated by work done with methyl, *n*-propyl, and *n*-octyl Grignard reagents. This work is summarized in Table VII.

Table VIII gives the incremental shifts between the shift compounds of the methyl and propyl Grignard reagents and the corresponding parent bromides. It also gives the incremental shifts for the octyl shift compound based on data for butyl bromide.

Work carried out with dichlorogermanium tetraphenylporphine and phenyl magnesium bromide offers a further example of the applicability of the dichloride to Grignard-type compounds. Figure 2 shows the upfield portion of the 100-MHz spectrum of the shift compound which dichlorogermanium tetraphenylporphine gives with this Grignard reagent. With LAOCN3[18] and a plotting routine, the chemical shifts found for the Grignard derived phenyl protons are τ 2,6, 9.55; 3,5, 5.15; and 4,4.66. The corresponding coupling constants (Hz) are 2,3, 7.8; 3,4, 7.4; 2,4, 1.3; 2,6, 1.8; 3,5, 1.5; and 2,5, 0.3.

Still another example of the use of dichlorogermanium tetraphenylporphine with Grignard-type compounds is provided by the previously described work done with ferrocenyllithium.[4,19] The observed chemical shifts of the ferrocenyl protons in the shift compound formed by ferrocenyllithium and dichlorogermanium tetraphenylporphine are τ 2,5, 12.23; 3,4, 8.26; and 1′–5′, 8.02.

Table VII. Data for Shift Compounds Derived from Alkyl Grignard Reagents[a] (τ)

Reagent	Grignard	α	β	γ	δ	ε	ζ
$TPPGeCl_2$	*n*-Octylmagnesium bromide	17.05	15.01	11.80	10.79	10.15	9.61
$PGeCl_2$	Methylmagnesium bromide	17.98					
$PGeCl_2$	*n*-Propylmagnesium bromide	17.92	15.74	12.34			
$PGeCl_2$	*n*-Octylmagnesium bromide	17.95	15.77	12.19	11.13	10.35	9.79
$PcGeCl_2$[b]	*n*-Octylmagnesium bromide	16.05	14.03	11.47	10.72	10.13	*c*

[a] 100 MHz, $CDCl_3$ data. [b] Pc, phthalocyanine. [c] Overlapped.

Table VIII. Increments between Selected Bromides and Shift Compounds Derived from Grignard Reagents (ppm)

Reagent	Grignard	Reference bromide	α	β	γ	δ	ε	ζ
$TPPGeCl_2$	*n*-Octylmagnesium bromide	*n*-Butyl bromide[a,b]	10.46	6.69	3.27	2.14	1.45	0.91
$PGeCl_2$	Methylmagnesium bromide	Methyl bromide[c]	10.63					
$PGeCl_2$	*n*-Propylmagnesium bromide	*n*-Propyl bromide[d]	11.31	7.63	3.36			
$PGeCl_2$	*n*-Octylmagnesium bromide	*n*-Butyl bromide[b]	11.36	7.72	3.66	2.48	1.65	1.09
$PcGeCl_2$	*n*-Octylmagnesium bromide	*n*-Butyl bromide[b]	9.46	5.98	2.94	2.07	1.43	

[a] τ($CDCl_3$): α, 6.59; β, 8.05; γ, 8.53; δ, 9.07. [b] Comparisons: α,α; β,β; γ,γ; 8.65 (arbitrary), δ; 8.70 (arbitrary), ε–ζ. [c] τ($CDCl_3$): 7.35. [d] τ($CDCl_3$): α, 6.61; β, 8.11; γ, 8.98.

Germanium Porphine Reagents. Dichlorogermanium porphine and dihydroxygermanium porphine, like their

(18) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, Chapter 3.

(19) The spectrum of the ferrocenyllithium shift compound in deuteriochloroform is shown in ref 4.

tetraphenylporphine analogs, yield shift compounds which have generally good solubility and stability. In addition they contribute only two singlets to the spectra of the shift compounds (and these are at very low field). However, these features of the reagents are at present partly balanced by the reagents' high cost (which is caused by the high cost of porphine).

The applicability of these reagents is similar to that of their tetraphenylporphine analogs. Work summarized in Tables I and III–VIII illustrates the use of the dichloro reagent with an alcohol and three Grignard reagents[20] and the use of the dihydroxy reagent with a phenol and an acid.

Germanium Phthalocyanine Reagent. Like its tetraphenylporphine analog, dichlorogermanium phthalocyanine is readily accessible. In addition it yields ring-current effects which have been described in detail by equations,[21,22] graphs,[21,22] and data tabulations[22] (*i.e.*, by Johnson–Bovey-type tables[23]).

The single use made of this reagent in this work was that with *n*-octylmagnesium bromide (Tables VII and VIII). While the reagent performed well in this application and can be expected to perform well in additional applications, it is anticipated that its use will be restricted somewhat by the low solubilities to be expected of some of its shift compounds.

On the basis of the work done with this reagent, the work described above with the tetraphenylporphine and porphine germanium reagents, and some work done earlier with dihydroxygermanium phthalocyanine,[8,24,25] it is clear that dihydroxygermanium phthalocyanine also can be expected to be an effective reagent in several types of applications. However, its use as a reagent, like that of dichlorogermanium phthalocyanine, probably will be limited by solubility problems.

Iron(II) Phthalocyanine Reagent. Iron(II) phthalocyanine differs from the germanium reagents in that it forms bonds with substrates by coordination rather than by displacement. It also differs because it acts very selectively, being useful, as far as is known, only for unhindered amines (such selectivity is of considerable potential value, of course).[26]

Since the reagent itself is paramagnetic,[29] a very important property of it is its insolubility in organic solvents. Also important are its resistance to oxidation and decomposition under ordinary handling techniques and its ready availability from supply houses.[30]

(20) The spectrum of the octyl Grignard shift compound in deuteriochloroform is shown in ref 4.

(21) T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Amer. Chem. Soc.*, **91**, 5210 (1969).

(22) T. R. Janson, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971; *Diss. Abstr. B*, **32**, 3237 (1972).

(23) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Spectroscopy," Vol. I, Pergamon Press, Oxford, England, 1965, p 595.

(24) R. D. Joyner and M. E. Kenney, *J. Amer. Chem. Soc.*, **82**, 5790 (1960).

(25) R. Rafaeloff, F. J. Kohl, P. C. Krueger, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **28**, 899 (1966).

(26) It should be noted, however, that iron(II) phthalocyanine apparently forms compounds with hydroxides[27] and cyanides.[28]

(27) H. B. Charman, *Nature (London)*, **201**, 1021 (1964).

(28) A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, 7, 58 (1965).

(29) C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, **53**, 1643 (1970).

(30) It is interesting to note that iron(II) phthalocyanine has long been accessible. In fact it was the first phthalocyanine reported by Linstead.[31] Recognition of copper(II) phthalocyanine and its subsequent application as a pigment grew out of the early work on iron compounds.

(31) R. P. Linstead, *J. Chem. Soc.*, 1016 (1934).

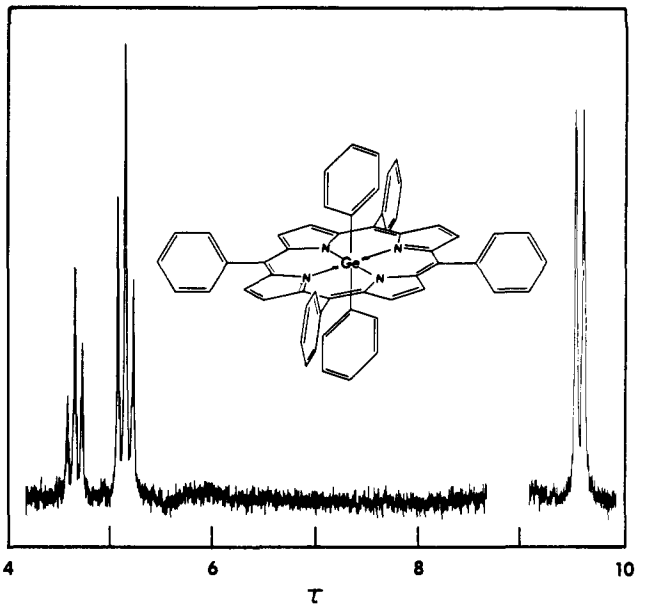

Figure 2. Upfield portion of 100-MHz spectrum of the shift compound derived from phenylmagnesium bromide and dichlorogermanium tetraphenylporphine.

Of significance with regard to the shift compounds formed by this reagent are the absence in them of unpaired electrons and the lack of substantial amine nitrogen to amine hydrogen coupling. Also of significance are the slowness of the exchange between the bound amines of these compounds and any free amines, the slowness of the exchange between the hydrogens of the bound amines and the hydrogens of any free amines, and the slowness of the intermolecular exchange of the hydrogens of the bound amines (in deuteriochloroform). Data for some typical unhindered amines are given in Tables IX and X.[32]

Table IX. Data for Shift Compounds Derived from Amines[a] (τ)

Reagent	Amine	NH_2	α	β	γ	δ
PcFe	Methylamine	17.28	12.73			
PcFe	*n*-Butylamine	17.44	13.01	11.41	10.68	10.37
PcFe	*n*-Hexylamine	17.42	13.00	11.42	10.77	10.08

[a] 100 MHz, $CDCl_3$ data.

Of some interest with regard to the butylamine shift compound is the 1.11 ppm downfield shift of its amino resonance when dimethyl sulfoxide is used as a solvent instead of deuteriochloroform and the further 0.45 ppm downfield shift when butylamine is used instead of dimethyl sulfoxide. The upfield shift of the resonance when a butylamine solution of the compound is heated and the very exceptional solvent power of butylamine for the compound are also of interest. All of these properties are, of course, consistent with a marked ability on the part of the amino protons of the compound for hydrogen bonding.

Not surprisingly the ruthenium analog of this reagent[33] is also found to be a good shift reagent for

(32) Spectra of the methylamine shift compound in deuteriobenzene and the butylamine shift compound in deuteriochloroform are shown in ref 5.

(33) P. C. Krueger and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **25**, 303 (1963).

Table X. Increments between Selected Amines and Shift Compounds Derived from Amines (ppm)

Reagent	Amine	Reference amine	NH_2	α	β	γ	δ
PcFe	Methylamine[a]	Methylamine	8.12	5.18			
PcFe	*n*-Butylamine[b]	*n*-Butylamine	8.54	5.71	2.81	2.08	1.29
PcFe	*n*-Hexylamine	*n*-Butylamine[c]	8.52	5.70	2.82	2.17	1.43

[a] $\tau(CDCl_3)$: NH_2, 9.16; α, 7.55. [b] $\tau(CDCl_3)$: NH_2, 8.90; α, 7.30; β, ~8.60; γ, ~8.60; δ, 9.08. N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, High Resolution NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum 89. [c] Comparisons: α,α; β,β; γ,γ; 8.65 (arbitrary), δ.

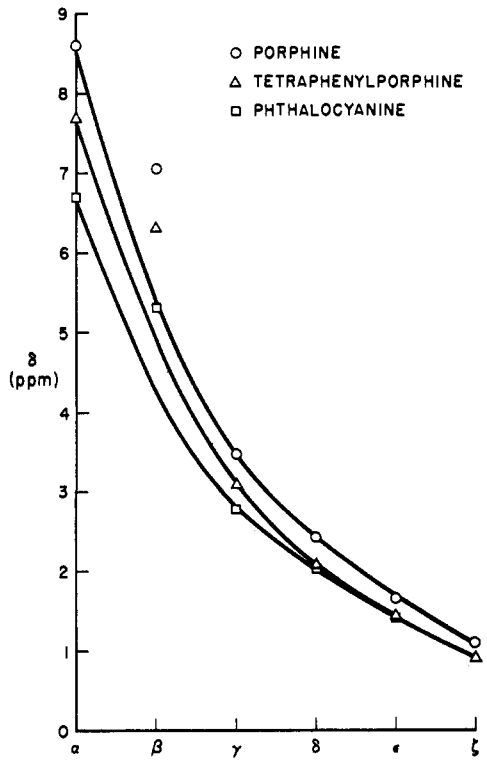

Figure 3. Graph of ring-current-only incremental shifts *vs.* octyl proton chain positions for shift compounds derived from octylmagnesium bromide and dichlorogermanium porphine, dichlorogermanium tetraphenylporphine, and dichlorogermanium phthalocyanine.

amines. However, because it is relatively unavailable and because it behaves in the same way as its iron analog, it appears to lack promise as a reagent.

Ring–Substrate Interactions. The presence of substantial ring–substrate interactions in several of the shift compounds is clearly indicated by some of the data obtained.[34] For example, the presence of significant steric interactions between the tertiary butyl groups and the ring in the 2,4-di-*tert*-butylphenol shift compound is indicated by the inequality of the incremental shifts associated with its 3 and 5 protons (Table IV). Similarly strong interactions between the isopropyl groups and the ring in the 2,6-diisopropylphenol shift compound are suggested by the large difference between the incremental shift associated with the central protons of the isopropyl groups of this compound and the incremental shift associated with the singlet of the methyl protons of the 4-*tert*-butyl-2,6-dimethylphenol compound (Table IV).

Also indicating steric interactions are the ring-current-only portions of the incremental shifts associated with the methylene protons of the octyl Grignard shift compounds. These data, which were obtained by taking the differences between the methylene resonances and comparable resonances in tetra-*n*-butylgermane, Table XI and Figure 3, indicate strong γ-methylene ring interactions since the β-methylene increments are disproportionately large.

Table XI. Increments between Tetra-*n*-butylgermane[a,b] and Shift Compounds Derived from *n*-Octyl Grignard Reagent (ppm)

Reagent	α	β	γ	δ	ϵ	ζ
$TPPGeCl_2$	7.73	6.31	3.10	2.09	1.45	0.91
$PGeCl_2$	8.63	7.07	3.49	2.43	1.65	1.09
$PcGeCl_2$	6.73	5.33	2.77	2.02	1.43	

[a] $\tau(CDCl_3)$: α, 9.32; β, ~8.70; γ, ~8.70; δ, 9.12. [b] Comparisons: α,β; β,β–ζ.

Relative Shielding Abilities of the Rings. The ring-current-only methylene incremental shifts of Table XI also obviously contain information about the relative shielding abilities of the rings. Unfortunately, however, the positions of the methylenes cannot be specified accurately and hence the full value of the information cannot be realized.

Nevertheless, it can be reasonably assumed that the methylenes occupy elements of cone-like shells extending out from the ring centers and that the smaller shielding ability of the tetraphenylporphine ring relative to the porphine ring for these elements is due mainly to the net result of phenyl-ring inductive and anistropy effects. The smaller shielding ability of the phthalocyanine ring relative to the porphine ring for these elements can be ascribed mainly to the result of perturbations of the central porphine-like ring by the azo nitrogen atoms and the benzo rings and to effects from the anisotropy of the benzo rings.[35]

Acknowledgment. The help of Mr. Everett R. Santee of the University of Akron in obtaining the spectrum of tetra-*n*-butylgermane is gratefully acknowledged.

(34) Indications of steric interactions in complex phthalocyanines have been noted previously.[9]

(35) A similar rationalization has been used previously to explain observed shielding differences for like protons under the influence of porphine and phthalocyanine rings.[9]