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Synthesis and Properties of the Alkyl/Aryl Germanium Dioximates Containing Ge–O Bond: Stability Factors–A Theoretical Approach

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ABSTRACT: *The reactions of R_2GeCl_2 and R_3GeCl with 9,10-phenanthrenequinone dioxime in 1:1 and 1:2 molar ratios to form a series of organogermanium complexes of the general formula R_2GeL and $(R_3Ge)_2L$ [R=Me, Et, Ph] have been investigated. The physical and spectral properties of all derivatives are described. In addition, the nature of Ge—O bond has been studied by using the DFT/B3LYP method.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 23:545–550, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21048

INTRODUCTION

In the past two decades, the chemistry of divalent derivatives of germanium has developed into an active area of research [1–4]. Organogermanium compounds have many applications in the field of medicines [5,6], optics, and so on. Germanium compounds are also very attractive as potential precursors for obtaining the films by Metal Organic Chemical Vapor Deposition processes [7]. However, to the best of our knowledge, tetravalent germanium complexes containing Ge—O bonds have not been much explored and merited a detailed investigation. The organometallic and coordination chemistries of oximes constitute an active area of research, in which the oxime function (>C=N—O—) acts as a binucleating bridging unit to yield homo- and heterometallic complexes [8–11], which can be potentially useful for the development of new materials. Thus, in continuation to our interest in metal chelates of group IV elements [12–14], we have synthesized a series of tetravalent germanium derivatives and examined the nature of Ge—O bond by using the DFT/B3LYP method. The results are presented herein.

RESULTS AND DISCUSSION

The selected ligand, 9,10-phenanthrenequinone dioxime (H_2L), was prepared by the reaction of hydroxylamine hydrochloride with corresponding diketone in a 2:1 molar ratio in dry ethanol. It was then converted to its sodium salt by refluxing with sodium methoxide in methanol. The stoichiometric amount of sodium salt of 9,10-phenanthrenequinone dioxime was reacted with alkyl/aryl-germanium(IV) chloride in 1:1 and 1:2 molar ratios, respectively, to produce organogermanium complexes of the general formula R_2GeL and $(R_3Ge)_2L$ in 48–72% yield. The reactions are depicted in Scheme 1.

All the newly synthesized oxime complexes are crystalline solids, soluble in common organic solvents such as C_6H_6, $CHCl_3$, CH_2Cl_2, and DMSO and characterized by spectroscopic techniques.

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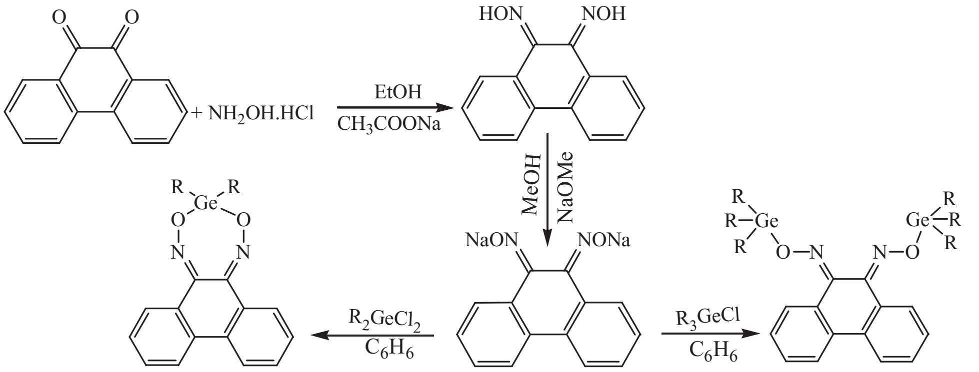


1: R=Me; **2**: R=Et; **3**: R=Ph

4: R=Me; **5**: R=Et; **6**: R=Ph

SCHEME 1 Preparation of complexes.

The IR spectra of all compounds were interpreted by comparing with those of the free ligand and related derivatives. A medium intensity band at 3140–3122 cm^{-1} in the free ligand due to $\nu_{(OH)}$ was absent in the spectra of complexes, confirming the deprotonation of oxime and synchronous formation of the Ge—O bond. There was no significant shifting for $\nu_{(C=N)}$ in the complexes that was observed at 1600 cm^{-1} in the ligand, clearly indicating that the imino group is not involved in coordination with germanium. In all complexes, new peaks were observed in the region 880–845 cm^{-1} assignable to Ge—O stretching [15] and in the region 689–630 cm^{-1} on account of different Ge—C stretchings for alkyl/aryl-germanium compounds [16]. The NMR spectra for complexes **1–6** did not show a characteristic signal for the =NOH protons observed at 12.24 ppm in the parent oxime. The aromatic protons of the phenanthrene moiety appeared in the region 8.68–7.27 ppm. For 1:1 complexes (**1–3**), the resonance due to methyl, ethyl, and phenyl protons were observed at 0.678 (s, CH_3), 0.97 (t, $CH_2C\mathbf{H}_3$), 1.14 (q, $C\mathbf{H}_2CH_3$), and 8.53–7.32 (m, Ar-H) ppm, whereas in the case of 1:2 complexes (**4–6**) the corresponding resonances were observed at 0.63 (s, CH_3), 0.91 (t, $CH_2C\mathbf{H}_3$), 1.17 (q, $C\mathbf{H}_2CH_3$), and 8.49–7.32 (m, Ar-H), respectively. In the ^{13}C NMR spectra of complexes, no significant shifting was observed for the C=N signal, suggesting no chelate formation through the imine nitrogen atom. For methyl derivatives **1** and **4**, methyl carbons resonated at 4.51 and 5.14 ppm [17] whereas for ethyl derivatives **2** and **5,** characteristic signals appeared at 7.18 ($CH_2\mathbf{C}H_3$), 9.02 ($\mathbf{C}H_2CH_3$), and 7.03 ($CH_2\mathbf{C}H_3$), 8.70 ($\mathbf{C}H_2CH_3$) respectively. Spectral characteristics of germanium oximates are presented in Table 1.

TABLE 1 Spectral Characteristics of Germanium Oximates

Compound	*IR(cm^{-1})*	*NMR (ppm)*	
		^1H	*^{13}C*
1	$\nu_{(C=N)}$ (1588), $\nu_{(NO)}$ (950) $\nu_{(Ge\text{–}O)}$ (879), $\nu_{(Ge\text{–}C)}$ (630)	8.66–7.36 (m, 8H, ArH), 0.678 (s, 6H, Ge-Me)	147.90 (C=N), 143.95–123.15 (C=C), 4.51 (Ge—Me)
2	$\nu_{(C=N)}$ (1596), $\nu_{(NO)}$ (948) $\nu_{(Ge\text{–}O)}$ (848), $\nu_{(Ge\text{–}C)}$ (648)	8.58–7.29(m, 8H, ArH), 1.14(q, 4H, Ge—$C\mathbf{H}_2CH_3$), 0.97(t, 6H, Ge—$CH_2C\mathbf{H}_3$)	148.10 (C=N), 136.21–123.29 (C=C), 9.02 (Ge—$\mathbf{C}H_2CH_3$), 7.18 (Ge—$CH_2\mathbf{C}H_3$)
3	$\nu_{(C=N)}$ (1598), $\nu_{(NO)}$ (945) $\nu_{(Ge\text{–}O)}$ (845), $\nu_{(Ge\text{–}C)}$(682)	8.53–7.32 (m, 18H, 8ArH + 10PhH)	156.17 (C=N), 134.6–121.2(C=C)
4	$\nu_{(C = N)}$ (1594), $\nu_{(NO)}$ (942) $\nu_{(Ge\text{–}O)}$ (855), $\nu_{(Ge\text{–}C)}$ (644)	8.68–7.37 (m, 8H, ArH) 0.63 (s, 18H, Ge—Me)	145.58 (C=N) 142.12–123.13 (C=C) 5.14(Ge—Me)
5	$\nu_{(C=N)}$ (1593), $\nu_{(NO)}$ (940) $\nu_{(Ge\text{–}O)}$ (860), ν $_{(Ge\text{–}C)}$(640)	8.25–7.27 (m, 8H, ArH) 1.17 (q, 12H, Ge—$C\mathbf{H}_2CH_3$), 0.91 (t, 18H, Ge—$CH_2C\mathbf{H}_3$)	148.48 (C=N), 133.00–123.05 (C=C) 8.70 (Ge–$\mathbf{C}H_2CH_3$), 7.03 (Ge—$CH_2\mathbf{C}H_3$)
6	$\nu_{(C=N)}$ (1597), $\nu_{(NO)}$ (942) $\nu_{(Ge\text{–}O)}$ (880), ν $_{(Ge\text{–}C)}$(689)	8.49–7.32 (m, 23H, 8ArH + 15PhH)	144.28 (C=N) 136.98–123.67 (C=C)

TABLE 2 Optimized Parameters of Compound **1–6**

Compound	*R (Ge—O^1)*	*R (Ge—O^2)*	*R (Ge—C)*	*R (N—O)*	*θ (C—Ge—C)*	*θ (O—Ge—O)*
1	1.83	1.83	1.93	1.44	119.69	96.63
2	1.75	1.81	1.86	1.44	118.82	99.55
3	1.82	1.82	1.90	1.44	116.44	95.91
4	1.86	1.86	1.95	1.43	117.17	–
5	1.88	1.85	1.96	1.43	108.97	–
6	1.85	1.85	1.93	1.43	113.34	–

TABLE 3 BE of Complexes

	Compound					
Characteristics	***1***	***2***	***3***	***4***	***5***	***6***
BE (anti) (Kcal/mol)	−27.76	−19.58	−28.58	−31.40	−28.47	−39.20
BE (syn) (Kcal/mol)	−1.30	−6.87	−2.12	−4.94	−2.02	−12.75

Theoretical Calculations

Geometry Optimizations. To understand the nature of the Ge—O bond, the structures of ligand as well as the complexes were optimized at the DFT/B3LYP level. The ligand may exist in syn (−704447.765 kcal/mol) and anti (−704474.220 kcal/mol) conformations and the anti isomer appeared to be the most stable. The N—O bond length in all the complexes increased compared to ligand (1.40 Å), whereas the C=N bond length decreased from 1.32 to 1.30–1.31 Å. All other optimized parameters of the complexes are summarized in Table 2.

Binding Energy. Binding energy of complexes is an important factor to account their stabilization. Greater the negative value of binding energy, the stronger the binding capacity, resulting in formation of the most stable complexes. The details are presented in Table 3, and it is evident that 1:2 molar complexes have greater binding capacity than 1:1 molar complexes.

Thermodynamic Stability. The frequency calculations on optimized structures gave a zero imaginary frequency, and it was used to calculate thermodynamic stability constants by the equation $\Delta G = -RT \ln K$. The results are summarized in Table 4, and it was observed that the stability constants of 1:1 complexes (**1–3**) are larger than that of 1:2 (**4–6**).

TABLE 4 Thermodynamic Stability Data of the Complexes

Compound	*ΔH (kJ/mol)*	*ΔG (kJ/mol)*	*ln K*
1	− 96.41	− 131.70	10.01
2	− 83.12	− 117.85	8.96
3	− 116.28	− 144.25	10.96
4	− 125.36	− 104.33	7.93
5	− 108.85	− 84.60	6.43
6	− 111.356	− 109.83	8.35

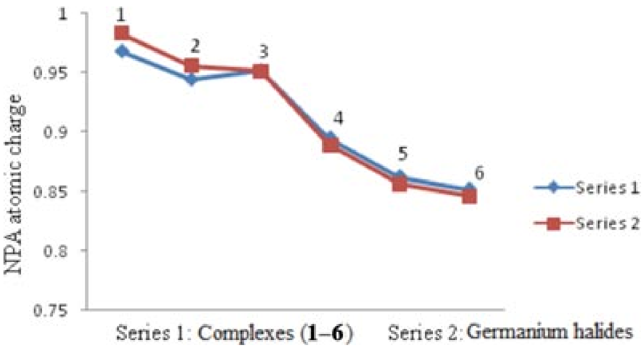


FIGURE 1 Variation of NPA charges on Ge atom in reactants and products.

Natural Bond Orbital Calculations. Among theoretical methods, natural bond orbital (NBO) analysis is a unique approach to evaluate the delocalization effects [18]. Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the NBO approach.

The positive charge on the germanium atom in the reactant changes due to delocalization of electrons upon complex formation is shown in Fig. 1. In the case of 1:1 complexes (**1–3**), there is a decrease in the positive charge on germanium upon substitution of halide with two oxygen atoms. However, in 1:2 complexes (**4–6**) there is not much variation because of unavailability of interaction of lone pairs from both the oxygen. Nearly 97.79% of the electrons are located in the Lewis orbitals. Remaining

TABLE 5 Possible Interactions in Dimethylgermanium Dioximate

Donor	*Acceptor*	*E(2) (Kcal/mol)*
$\sigma(\mathrm{O_{25}{-}Ge_{27}})$	$\Pi^*(\mathrm{C_7{-}N_{24}})$	4.97
$\sigma\ (\mathrm{O_{26}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{N_{23}{-}O_{26}})$	6.37
$\sigma\ (\mathrm{O_{25}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	7.16
$\sigma\ (\mathrm{O_{26}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	3.60
$\sigma\ (\mathrm{O_{25}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{28}})$	3.22
$\sigma\ (\mathrm{O_{25}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{32}})$	3.84
$\sigma\ (\mathrm{O_{26}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{28}})$	3.23
$\sigma\ (\mathrm{O_{26}{-}Ge_{27}})$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{32}})$	4.20
$\sigma\ (\mathrm{Ge_{27}{-}C_{28}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	7.46
$\sigma\ (\mathrm{Ge_{27}{-}C_{28}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	6.75
$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	4.77
$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	3.53
$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{28}})$	4.24
LP $\mathrm{N_{23}}$	$\sigma^*\ (\mathrm{O_{26}\ {-}Ge_{27}})$	3.25
LP $\mathrm{O_{25}}$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{32}})$	3.01
LP $\mathrm{O_{25}}$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	24.49
LP $\mathrm{O_{25}}$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{28}})$	3.55
LP $\mathrm{O_{26}}$	$\sigma^*\ (\mathrm{Ge_{27}{-}C_{28}})$	10.75
LP $\mathrm{O_{26}}$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	7.11

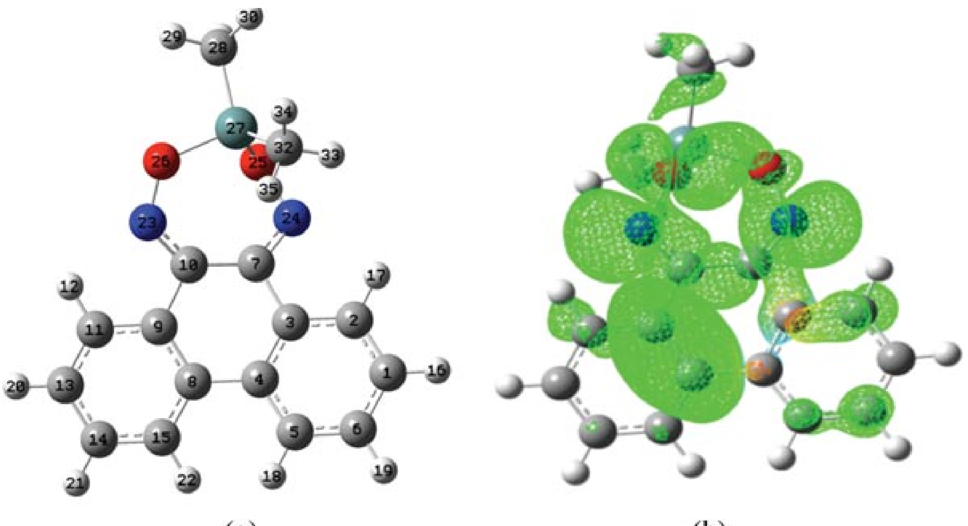
TABLE 6 Important Delocalization Effects in 1:1 Molar Complexes

Compound	*Donor*	*Acceptor*	*E(2) (Kcal/mol)*
1	LP $\mathrm{O_{25}}$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	24.49
	LP $\mathrm{O_{26}}$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	7.11
	$\sigma\ (\mathrm{Ge_{27}{-}C_{28}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	7.46
	$\sigma\ (\mathrm{Ge_{27}{-}C_{28}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	6.75
	$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	4.77
	$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	3.53
2	LP $\mathrm{O_{25}}$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	25.05
	LP $\mathrm{O_{26}}$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	5.14
	$\sigma\ (\mathrm{Ge_{27}{-}C_{28}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	7.98
	$\sigma\ (\mathrm{Ge_{27}{-}C_{28}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	6.53
	$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	4.92
	$\sigma\ (\mathrm{Ge_{27}{-}C_{32}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	3.53
3	LP $\mathrm{O_{25}}$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{27}})$	14.50
	LP $\mathrm{O_{26}}$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{27}})$	14.50
	$\sigma\ (\mathrm{Ge_{49}{-}C_{27}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{49}})$	4.59
	$\sigma\ (\mathrm{Ge_{49}{-}C_{27}})$	$\sigma^*\ (\mathrm{O_{26}{-}Ge_{49}})$	7.22
	$\sigma\ (\mathrm{Ge_{49}{-}C_{38}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{49}})$	7.22
	$\sigma\ (\mathrm{Ge_{49}{-}C_{38}})$	$\sigma^*\ (\mathrm{O_{25}{-}Ge_{49}})$	4.59

2.201% of electrons are delocalized, leading to slight departures from a localized Lewis structure model. The donor–acceptor interactions in the NBO provide qualitative information about the delocalization of electron leading to the hyperconjugative effect. Possible hyperconjugative interactions in dimethylgermanium dioximate are presented in Table 5.

The highest interaction takes place between the lone pair of oxygen with antibonding orbital (σ^*) of the other Ge—O bond, which is visualized in Fig. 2. In all the complexes, the value of these interactions varied depending upon the nature of the substituent. The main interactions involved in 1:1 complexes are listed in Table 6. In the case of the diphenyl complex (**3**), the lone pairs of both the oxygen atoms are symmetrically oriented, hence it gave same magnitude of interaction with both the Ge—O bonds as compared to other complexes where these interactions are different.

The bond pair electrons of Ge—C also interact with σ^* orbitals of the Ge—O bond. These interactions are also same and slightly larger for the diphenyl complex. In the case of dimethyl- and diethylgermanium complexes, these interactions are different leading to the fact that there are stereoelectronic and structural differences between the complexes.



(a) (b)

FIGURE 2 (a) Atomic labeling and (b) lone pair interaction with Ge—O bond for **1**.

TABLE 7 Physical and Analytical Data of Organogermanium(1V) Complexes

				Elemental Analysis			
Compound	*Physical Appearance*	*Yield (%)*	*mp (°C)*	*C*	*H*	*N*	*Ge*
1	Brown, solid	57	170(d)	56.07 (56.21)	4.16 (4.55)	8.27 (8.22)	21.42 (21.03)
2	Brown, solid	72	139	58.91 (58.11)	4.94 (4.61)	7.63 (7.05)	19.79 (19.01)
3	Green, solid	55	120	67.44 (67.84)	3.92 (3.89)	6.05 (6.55)	15.68 (15.18)
4	Yellowish green, solid	48	182	50.93 (50.21)	5.56 (5.45)	5.94 (5.14)	30.79 (30.13)
5	Dark green, solid	63	212(d)	56.18 (56.02)	6.89 (6.18)	5.04 (5.42)	26.13 (26.71)
6	Yellow, solid	58	235(d)	71.15 (71.03)	4.54 (3.98)	3.32 (3.13)	17.20 (17.11)

Values given without parenthesis refer to elemental analysis found (%) and within parenthesis refer to elemental analysis calculated (%). d = decomposed.

CONCLUSIONS

A convenient synthesis of novel germanium complexes of the general formula R_2GeL and $(R_3Ge)_2L$ (R=Me, Et, Ph) has been accomplished. The stability of complexes has been evaluated by different computational parameters.

EXPERIMENTAL

General Procedures

All the chemicals were purchased from Merck (India) and Aldrich (Germany) and used without further purification. All the reactions were carried out in the presence of nitrogen atmosphere. Solvents were dried by standard methods [19]. The melting points are recorded on a Perfit apparatus and are uncorrected. The IR spectra from 4000–400 cm^{-1} were recorded on Nicolet Shimandzu spectrometer (Japan) in KBr pellets and CCl_4 solution. The ^1H ($CDCl_3$, DMSO, 300 MHz) and ^{13}C ($CDCl_3$, DMSO, 75.5 MHz) NMR spectra of complexes were recorded at room temperature on a JEOL 300 ALFT NMR (Japan) spectrometer using TMS as an internal standard. Germanium was estimated as germanium oxide using platinum crucible, and nitrogen was estimated as reported in the literature method [20].

Computational Details

To reveal the local minimum on the Potential Energy Surface of each germanium derivatives, we carried out geometry optimization using restricted density functional calculations in Gaussian 03 suite of programs [21], with using the B3LYP hybrid method that employs the Becke three parameters exchange functional and the Lee–Yang–Parr correlation functional and 6-31G level of theory. The normal mode analysis on the preferred structure yielded no imaginary frequency on vibrational study using the same level of theory, which is used for optimization. To study the intramolecular interactions and hyperconjugative effects, NBO analysis was carried out and each compound was modeled with a Gauss View visualizer.

General Procedure for Synthesis

Preparation of Ligand. The desired ligand 9,10-phenathrenequinone dioxime was prepared by the reaction of 9,10-phenanthrenequinone (0.8328 g, 4 mmol) and hydroxylamine hydrochloride (1.042 g, 15 mmol) in ethanol (25 mL) with sodium acetate (0.8203 g, 10 mmol). The shining yellowish green compound was crystallized from methanol (83%); mp 197–202°C (lit mp 202°C) [22].

Preparation of Dimethylgermanium(IV)-9,10-Phenanthrenequinone Dioximate. To the freshly prepared methanolic solution (5 mL) of sodium methoxide [prepared in situ by taking sodium (0.1279 g, 5.1 mmol) in methanol], a solution of phenanthrenequinone dioxime (0.5955 g, 2.5 mmol) in benzene (15 mL) was added dropwise. The yellowish green color of the solution changed to dark brown during the addition. Subsequently, the mixture was refluxed for 5 h. To the methanolic–benzene solution (10 mL) of the sodium salt of ligand H_2L, the benzene solution of dimethylgermanium dichloride (0.4339 g, 2.5 mmol) was added slowly through a dropping funnel at room temperature under the nitrogen atmosphere. The color of the reaction mixture changed to brown, and a precipitate of NaCl started to form. It was then refluxed for 6 h to ensure completion of the reaction. The precipitated NaCl was filtered off, and the solvent was dried in vacuum. A brown-colored compound obtained was washed with hexane and dried (0.481 g, 57%).

Diethyl- and diphenylgermanium derivatives of the type R_2GeL were also prepared using the above procedure. For the preparation of complexes **4**–**6**, to the sodium salt of ligand, trialkyl/triaryl germanium halides were added in a 1:2 molar ratio to form corresponding products without changing the above procedure. The physical and analytical data of complexes are described in Table 7.

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