Dynamic Features of the Ethylenediaminetetraacetate Complexes of Ca, Sr, Ba, and Co(II) in Aqueous Solutions Studied by the Ultrasonic Absorption Method

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Abstract: Ultrasonic absorption was measured in aqueous solutions of ethylenediaminetetraacetate (EDTA) complexes of Ca, Sr, Ba, and Co(II) (1:1 complex). The absorption was ascribed to the configuration change reaction of the complex, i.e., pentacoordinated structure $\rightleftharpoons$ hexacoordinated structure (k_f, k_b). Rate constants k_f, k_b and the volume change of the reaction ΔV were obtained. The rate constant was discussed in relation to the coordinated water substitution rate constants of the metal ions with use of a step-by-step mechanism. Supplementary work is reported for the Co(II) complex solutions of EDTA-related ligands.

Although EDTA is a hexadentate ligand, there is a considerable body of evidence to indicate that less than six of the coordination sites will bind to metal ions. For example, Jorgensen[1] has proposed, on the basis of the electronic spectra, that only five of the six EDTA sites are bound to metal ions; water presumably occupied the sixth site. The same conclusion has been advanced by Higginson[2] from proton dissociation data, by Margerum et al.[3] from temperature-jump studies, and by Everhart et al.[4] from nuclear magnetic resonance spectra. On the other hand, a hexacoordinated structure has been proposed by Krishnan et al.[5] from Raman spectra and by Matwiyoff et al.[6] from nuclear magnetic resonance spectra. Coexistence of pentacoordinated and hexacoordinated EDTA complexes has been suggested by Bhat et al.[7] from electronic spectra, by Brunetti et al.[8] from thermodynamic studies, by Wilkins et al.[9] from oxidation rate measurements, by Higginson et al.[10] from electronic spectra, and by Grant et al.[11] from nuclear magnetic resonance spectra. These literature data suggest that the two possible structural forms may exist. They may be represented by the equilibrium expression pentacoordinated structure $\rightleftharpoons$ hexacoordinated structure. In the study described here we used ultrasonic absorption as a probe to study the foregoing equilibrium and aimed to obtain the kinetic parameters concerned with the reaction.

Experimental Section

Materials. Wako reagent grade nitrates of magnesium, calcium, strontium, barium, and cobalt(II), as well as EDTA dipotassium salt, 1,2-diaminopropanetetraacetate (PDTA), and *trans*-1,2-diaminocyclohexanetetraacetate (CyDTA), were used without further purification. Solutions were prepared by mixing the desired amounts of metal nitrates and EDTA with the mole ratio of 1:1. Final pH was adjusted to 12.0 by dropwise addition of KOH solution. No supporting electrolytes were added.

Measurements and Treatment of the Data. Ultrasonic absorption was measured by the pulse method in the frequency range 4.5-95 MHz. Details of the apparatus have been described elsewhere.[12] The velocity of sound was measured at 5.00 MHz by an interferometer. The temperature was controlled at 25.0 ± 0.1 °C. The absorptions were represented by the single relaxation equation

$$\alpha/f^2 = \frac{A}{1 + (f/f_r)^2} + B \qquad (1)$$

where α is the absorption coefficient, f is the frequency, f_r is the relaxation frequency, and A and B are the relaxing and nonrelaxing absorptions, respectively. The absorption parameters f_r, A, and B were determined by fitting the data to eq 1 by means of a computer. The above equation can be converted into a more convenient form, describing an excess absorption per wavelength ($\alpha'\lambda$):

$$\alpha'\lambda = fv(\alpha/f^2 - B) = 2(\alpha'\lambda)_{\max}\frac{f/f_r}{1 + (f/f_r)^2} \qquad (2)$$

where α' is the excess absorption coefficient, λ is the wavelength, v is the velocity of sound, and the subscript max indicates the maximum value.

Results and Discussion

Representative absorption spectra of Ca, Sr, and Ba EDTA complexes are shown in Figure 1. The concentration dependence of the absorption for Sr complex is shown in Figure 2. The experimental conditions and the results are summarized in Table I. In these figures and the table, the following features can be recognized as important: (1) The value of f_r depends on the metal species in the order of Ba > Sr > Ca. (2) The value of f_r is independent of the complex concentration. (3) The value of relaxation absorption $(\alpha'\lambda)_{\max}$ increases with the complex concentration.

The origin of the relaxation absorption was investigated as follows. Under the present experimental conditions, the concentrations of free metal ion and free EDTA ion are extremely low (10^{-5}–10^{-6} M) because of the very large stability constants K_{MY} of the alkaline earth–EDTA complexes MY^{2-} (log K_{MY} of Mg, 8.69; Ca, 10.59; Sr, 8.63; Ba, 7.76),[13] and the predominant reactants are MY^{2-}, OH^-, and K^+. To determine the effects of OH^-, the pH dependence of the absorption was studied. The absorption spectrum is independent of pH in the range of ≥5 for Ca, ≥7 for Sr, and ≥10 for Ba systems. These results indicate that OH^- is not involved in the present relaxation absorption. Next, the ionic association reaction between K^+ and MY^{2-} was examined.

$$K^+ + MY^{2-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (K \cdot MY)^- \qquad (3)$$

The relaxation equation for this reaction is given by

$$2\pi f_r = k_f(C_K + C_{MY}) + k_b$$

where C_i is the concentration of the ith species. This equation means that f_r increases with an increase of the ionic concentrations. The concentration independence of f_r in Table I cannot be interpreted by this mechanism.

Finally, the intramolecular configuration change of the complex was considered:

$$MY^{2-}{}_{*} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} MY^{2-}{}_{**} \qquad (4)$$

where the subscripts * and ** mean two different configurations of the same complex. For this reaction, f_r is related to the rate constants by the equation

$$2\pi f_r = k_f + k_b \qquad (5)$$

which has no concentration term. It satisfies the experimental result showing that f_r is independent of the complex concen-

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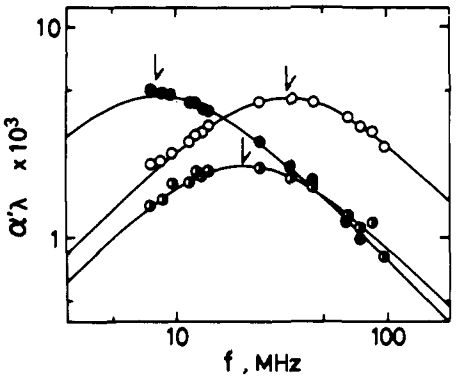


Figure 1. Ultrasonic absorption spectra of alkaline earth-EDTA systems at pH 12.0, 25 °C, and $\sum C_{MY} = 0.40$ M; ●, Ca; ◑, Sr; ○, Ba. The arrows indicate the relaxation frequency.

Table I. Ultrasonic Absorption Parameters of Alkaline Earth-EDTA Systems at pH 12.0 and 25 °C

	$\sum C_{MY}$, M	ρ, g cm^{-3}	$v \times 10^{-5}$, cm s^{-1}	f_r, MHz	$(\alpha'\lambda)_{max} \times 10^3$
Ca	0.20	1.067	1.550	8.3	1.4
	0.40	1.134	1.602	8.0	4.8
	0.60	1.164	1.620	8.0	8.3
Sr	0.20	1.075	1.548	20.3	0.9
	0.40	1.151	1.592	21.2	2.2
	0.60	1.223	1.643	21.2	3.0
Ba	0.20	1.089	1.541	35.4	2.5
	0.40	1.175	1.583	32.8	4.5
	0.60	1.251	1.621	31.1	6.5

tration. The relaxation absorption $(\alpha'\lambda)_{max}$ is given by

$$(\alpha'\lambda)_{max} = \frac{\pi(\Delta V)^2}{2\beta_0 RT} \frac{K}{(K+1)^2} \sum C_{MY} \tag{6}$$

where K is the equilibrium constant and ΣC_{MY} is the total complex concentration $(= C_{MY*} + C_{MY**})$. If the relaxation absorption observed is based on reaction 4, $\beta_0(\alpha'\lambda)_{max}$ vs. ΣC_{MY} plots will give a straight line which cuts through the origin of the coordinates. These plots are shown in Figure 3. Linear relationships are found within the limits of experimental error. Some deviation from the linearity may probably be due to the difference of the ionic strength.[14] The above discussions on f_r and $(\alpha'\lambda)_{max}$ lead to the conclusion that the absorption observed is based on the intramolecular configuration change reaction 4.

The value of f_r has the order Ba > Sr > Ca, which is in accord with that of the coordinated water substitution rate constants k_{H_2O} of these metal ions,[15] i.e., Ba^{2+} $(k_{H_2O} = 7.2 \times 10^8)$ $> Sr^{2+}$ $(3.5 \times 10^8) > Ca^{2+}$ $(3.0 \times 10^8) \gg Mg^{2+}$ (1.4×10^5). This agreement implies that the water substitution process is related to the present relaxation absorption. Since the value of k_{H_2O} of Mg^{2+} is three orders of magnitude smaller than those of Ca^{2+}, Sr^{2+}, and Ba^{2+} the relaxation absorption should be located in the lower frequency range; this is the reason why no relaxation absorption was observed for the Mg-EDTA system in the present experiment.

Spectroscopic investigations of Higginson et al.[10] have indicated that the labile transition metal-EDTA complexes take two configurations in aqueous solution, i.e., the pentacoordinated structure and the hexacoordinated structure. To investigate the relationship between the sound absorption and reaction 7, ultrasonic absorptions were measured for Co(II) complexes of EDTA and its related ligands for which the equilibrium constants are known.[10] The results are shown in Figure 4. As can be seen from eq 6, if the absorption is based on reaction 7, the relaxation absorption should vary with K (or

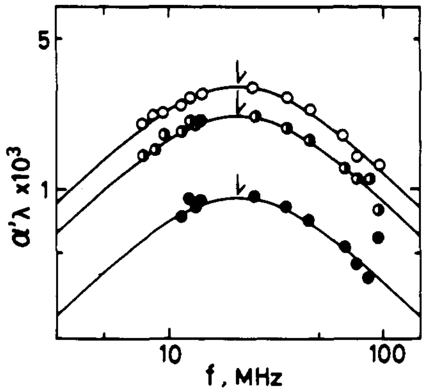


Figure 2. Concentration dependence of the ultrasonic absorption for Sr-EDTA system at pH 12.0 and 25 °C: $\sum C_{MY}$ = ●, 0.20 M; ◑, 0.40 M; ○, 0.60 M.

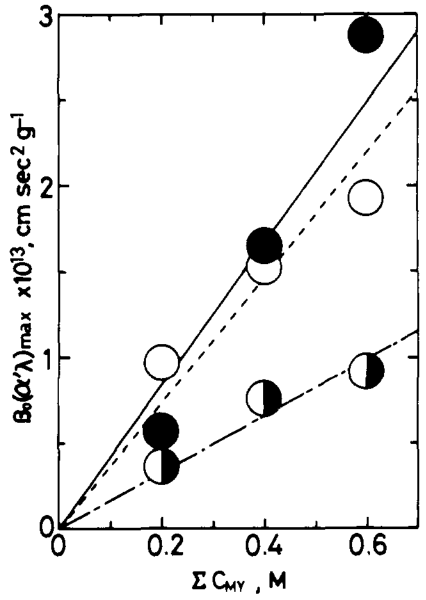
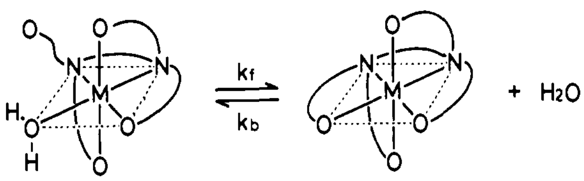


Figure 3. The plots of $\beta_0(\alpha'\lambda)_{max}$ vs. $\sum C_{MY}$ for alkaline earth-EDTA systems: (—●—), Ca; (---◑---), Sr; (- - - -○- - - -), Ba.

the proportion of a pentacoordinated structure) and reach a maximum value at $K = 1$, i.e., proportion of each structure is



(7)

equal to 50%. Higginson et al.[10] have reported the proportion of a pentacoordinated structure: Co(II)-EDTA, 24%; Co(II)-PDTA, 12%; Co(II)-CyDTA, <5%. Then the magnitude of the relaxation absorption as predicted from these values should be in the order of EDTA > PDTA ≫ CyDTA. For Co(II)-EDTA system, f_r and $(\alpha'\lambda)_{max}$ were obtained to be 1.9 MHz and 4.2×10^{-3}, respectively. Through the use of these values and the composition data, the rate constants of reaction 7 were obtained from eq 5; $k_f = 9.1 \times 10^6$ s^{-1} and $k_b = 2.9 \times 10^6$ s^{-1}, and ΔV was obtained from eq 6 to be 4.9 cm^3 mol^{-1}. Assuming that the values of k_f and ΔV are constant independent of the ligand, the relaxation absorption curves can be calculated for Co(II)-PDTA and CyDTA systems with the above-mentioned composition; these are also shown in Figure 4. Relatively good coincidences of the theory with the experi-

Table II. Kinetic Parameters for Reactions 7 and 9 at 25 °C

	$k_f \times 10^{-7}$,[a] s^{-1}	$k_b \times 10^{-7}$,[a] s^{-1}	$k_{23} \times 10^{-8}$,[a] s^{-1}	$k_{H_2O} \times 10^{8}$,[b] s^{-1}	ΔV,[a] $cm^3\ mol^{-1}$
Mg				0.0014	
Ca	3.6	1.5	2.3	3.0	5.3
Sr	9.2	3.9	6.5	3.5	3.6
Ba	14.5	6.2	10.1	7.2	5.4
Co(II)	0.9	0.3	0.65[c]	0.65[c]	4.9

[a] Reference 16. [b] Reference 15. [c] The value of k_{H_2O} of $Co(H_2O)_4(NH_3)_2^{2+}$. Reference 19.

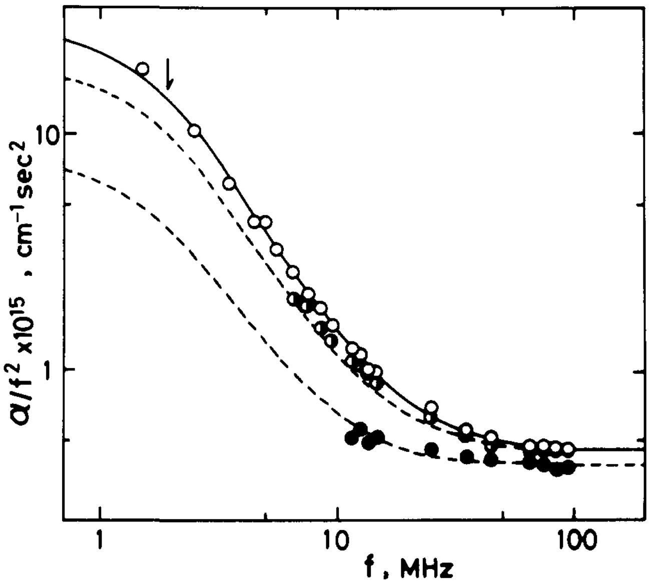


Figure 4. Ultrasonic absorption spectra of Co(II) complexes at pH 7.0, 25 °C, and $\sum C_{MY}$ = 0.50 M: ○, Co(II)-EDTA; ◐, Co(II)-PDTA; ●, Co(II)-CyDTA. The dotted lines are theoretical curves calculated with the proportion of pentacoordinated structure in reaction 7 and the kinetic values for Co(II)-EDTA system.

mental data suggest that the assignment of the absorption and the values obtained are satisfactory.

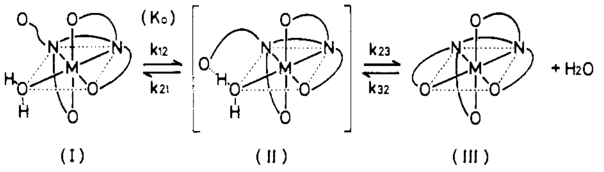
Similarities of the absorption of the alkaline earth-EDTA systems to those for the Co(II)-EDTA lead us to view reaction 7 as the source of the absorption. Assuming the proportion for the alkaline earth-EDTA systems to be equal to the mean values of those for the transition metal-EDTA systems, the equilibrium constant of reaction 7 is

$$K = \frac{k_f}{k_b} = \frac{C_6}{C_5} = 7/3 \qquad (8)$$

where C_6 and C_5 are the concentrations of hexacoordinated and pentacoordinated structures, respectively. With the help of this value, k_f, k_b, and ΔV were calculated[16] using the data in Table I and eq 5 and 6, and are listed in Table II.

The values of ΔV are in agreement with that of the Co(II)-EDTA system. Furthermore, comparison with the values of ΔV of bivalent metal carboxylate complex formation reactions would be helpful; these are reported to be 7 $cm^3\ mol^{-1}$ for the Ca-acetate system[17] and 7.5 $cm^3\ mol^{-1}$ for the Zn-glycine system.[18] Taking into account the difference in the coordination site, i.e., one is free metal ion and the other a pentacoordinated complex ion, the ΔV values in Table II seem to be reasonable.

The rate constants of the hexacoordinated complex formation reaction, k_f, can be compared with k_{H_2O} of the corresponding metal ions. k_f is proportional to, but about one order of magnitude smaller than, k_{H_2O} of the corresponding metal ions. These differences, however, can be understood by the following step-by-step mechanism where an intermediate complex with intramolecular hydrogen bond between the carboxyl group and the coordinated water molecule is assumed.



(9)

Since the reaction I ⇌ II is much faster than the reaction II ⇌ III, the relaxation equation is

$$2\pi f_r = K_0 k_{23} + k_{32} = k_f + k_b \qquad (10)$$

where $K_0 = k_{12}/k_{21}$. For the Co(II)-EDTA system, k_{23} will be around 6.5 × $10^7\ s^{-1}$;[19] by comparison with k_f (=$K_0 k_{23}$), K_0 is estimated to be $^1/_7$. Since K_0 will be constant independent of the central metals, k_{23} for the alkaline earth-EDTA systems can be calculated from k_f with the above K_0; the result is listed in Table II. k_{23} values are in orderly agreement with k_{H_2O} of the corresponding metals;[20] the fact suggests that the water substitution process is the rate-determining process of the hexacoordinated complex formation reaction.

Although incidental with the main theme of the present research, some additional relaxation absorptions were found during the experiments.

In the low pH region, a small relaxation absorption was superposed on the main large absorption. The pH ranges observed were ≤4 for Ca, ≤6 for Sr, and ≤7 for Ba systems. The apparent stability of the complex decreases with decrease of pH and the concentration of free metal ion exceeds 10^{-2} M at the above-mentioned pH ranges. Then, the new relaxation absorption will be attributed to the reaction

$$M^{2+} + MY^{2-} \rightleftharpoons (M \cdot MY) \qquad (11)$$

In the case of the solution of excess alkaline earth ion over EDTA ion, the same kind of additive relaxation absorption was observed. This absorption will also be due to reaction 11.

When the Na salt was used instead of the K salt, a small relaxation absorption overlapped with the main relaxation absorption. This new relaxation absorption became marked when Na salt was added. Compared with K^+, Na^+ has higher charge density and an interaction with the complex anion may be stronger. Accordingly the following reaction is believed to be attributable to this absorption:

$$Na^+ + MY^{2-} \rightleftharpoons (Na \cdot MY)^- \qquad (12)$$

Further detailed studies were not developed for the above absorptions since the amplitudes are very small, they are located in a low frequency range, and they overlap with the main large absorption.

The same kinds of relaxation absorption as those observed in the alkaline earth and Co(II)-EDTA systems were also found in some other bivalent metal-EDTA systems. Studies on these systems are now in progress and the results will be reported in due course.

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(19) It is well known that the coordination of nitrogen atom accelerates the water substitution rate. Here, the value of k_{H_2O} was estimated to be equal to that of $Co(H_2O)_4(NH_3)_2^{2+}$ (J. P. Hunt, *Coord. Chem. Rev.*, **7**, 1 (1971); P. Hoggard, Ph.D. Thesis, Washington State University, 1970).

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Triligating 11-Membered Rings Containing *tert*-Phosphino Sites. Synthesis and Structure

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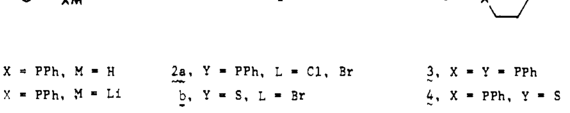
Abstract: The synthesis and characterization of seven 11-membered triheteromacrocycles, of the type 2,6,10-triheterobicyclo[9.4.0]pentadeca-11(1),12,14-triene, are described. The compounds include **3** [2,6,10-$(PPh)_3$], **4** [2,10-$(PPh)_2$-6-S], **5** [2,10-$(PPh)_2$-6-O], **6** [2,10-$(PPh)_2$-6-NMe], **7** [2,10-$(PPh)_2$-6-NPh], **8** [2,10-$(PPh)_2$], **9** [2,10-S_2-6-PPh], and **12** [2,6,10-S_3]. These macrocycles are obtained as crystalline solids using high-dilution techniques in yields ranging from 32 to 56%. Results of crystal structure determinations of five of these are reported and conformational features of the cycloundecene-type macrocycle are described. Crystal structure data follow. **3:** a = 10.823 Å, b = 17.934 Å, c = 13.122 Å, β = 93.15°, $P2_1/n$, Z = 4, R = 0.103, 4175 reflections with $I > 2\sigma_I$. **9:** a = 15.805 Å, b = 8.862 Å, c = 13.083 Å, β = 113.79°, $P2_1/c$, Z = 4, R = 0.048, 2754 reflections with $I > 2\sigma_I$. **7** · acetone: a = 9.243 Å, b = 16.441 Å, c = 18.963 Å, β = 93.13°, $P2_1/c$, Z = 4, R = 0.058, 3879 reflections with $I > 2\sigma_I$. **6:** a = 9.690 Å, b = 15.576 Å, c = 16.436 Å, β = 117.60°, $P2_1/c$, Z = 4, R = 0.079, 3782 reflections with $I > 2\sigma_I$. **12:** a = 5.419 Å, b = 16.090 Å, c = 13.664 Å, β = 98.03°, $P2_1/c$, Z = 4, R = 0.028, 2430 reflections with $I > 2.5\sigma_I$. X-ray data were collected on a Syntex $P2_1$ autodiffractometer with monochromated Mo Kα radiation at −35 °C, except for **9**, which was studied at room temperature with monochromated Cu Kα radiation. The three macrocycles bearing phenyl rings at the 6 position, **3**, **9**, and **7**, all display the same conformation of approximate $m(C_s)$ symmetry. In all five structures, the ring system adopts an L-shaped arrangement, with angles between the plane of the benzo ring and that of the three heteroatoms ranging from 97.2° in **12** to 113.9° in **6**. In all cases, the phenyl substituents on the *o*-phenylenediphospha unit are cis, and occupy pseudoequatorial positions in the conformations observed in the crystalline state.

Interest in macrocyclic polyhetero ligand systems has been and continues to be quite intense.[1] Thus far the majority of such systems have been used for the ligation of the relatively hard[2] alkali and alkaline earth metal cations, although some nitrogen- and sulfur-containing cyclic ligands have been used for transition metals.[1a] We,[3] along with others,[4,5] recently communicated the synthesis and properties of several *tert*-phosphino-containing macrocyles which are much more appropriate for ligation of the softer[2] transition metals. We now describe our efforts concerning the synthesis of a number of 11-membered multiheteromacrocycles which, with one exception, contain at least one *tert*-phosphino site.

Results and Discussion

Synthesis. The macrocyclizations described here involve the reaction of a bis(nucleophile) (**1**) and a bis(electrophile) (**2**), with the formation of two bonds, under high-dilution conditions, to give **3–9** and **12** in yields of 30–60% (eq 1). The high-dilution reaction involves the dropwise (8–12 drops/min) addition of separate THF solutions (ca. 0.1 M) of **1** and **2** to separate dilution chambers continuously charged with hot THF by distillation. The diluted solutions of **1** and **2** then add



(1)

1a, X = PPh, M = H
b, X = PPh, M = Li
c, X = S, M = H
d, X = S, M = Li

2a, Y = PPh, L = Cl, Br
b, Y = S, L = Br
c, Y = O, L = Cl
d, Y = NMe, L = Cl
e, Y = NPh, L = Cl
f, Y = CH_2, L = Br

3, X = Y = PPh
4, X = PPh, Y = S
5, X = PPh, Y = O
6, X = PPh, Y = NMe
7, X = PPh, Y = NPh
8, X = PPh, Y = CH_2
9, X = S, Y = PPh
[10, X = O, Y = PPh]
[11, X = NMe, Y = PPh]
12, X = Y = S