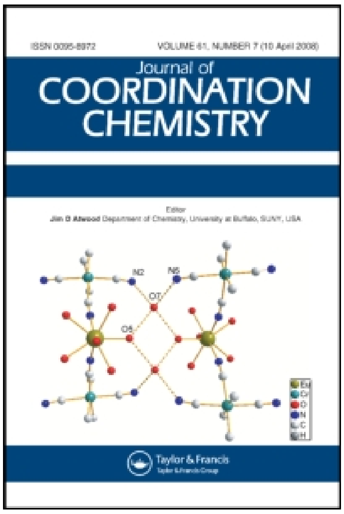

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SYNTHESES OF MANY-MEMBERED CHELATE RING COMPOUNDS

Hiroshi Ogino[a]
[a] Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan

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SYNTHESES OF MANY-MEMBERED CHELATE RING COMPOUNDS

HIROSHI OGINO
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

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The synthetic methods for many-membered chelate ring compounds can be classified into three categories: (i) direct reaction of a metal complex with a bidentate ligand, (ii) utilization of template reaction, (iii) expulsion of central donor atom(s) in coordinated ter- or quadri-dentate ligand. Examples of formation of the compounds are discussed. The following nomenclature is proposed for the various sizes of chelate rings; "Medium-sized chelate ring" refers to eight- to 11-membered rings, and "large chelate rings" are those with more than 11 members. Many-membered chelate rings mean both medium-sized and large chelate rings.

Key words: Many-membered ring, large chelate ring, medium-sized ring, ring strain, entropy effect, high-dilution method

1. INTRODUCTION

Chelate rings containing more than six atoms have been very scarce until recently, whereas numerous examples of five- and six-membered chelate rings are known. O'Brien surveyed the papers which attempted to prepare many-membered chelate ring compounds up to 1950. His conclusion was thus: "It is evident that the proposed structures of complexes with chelate rings containing more than six atoms are not firmly established. Lack of x-ray and other conclusive data, the several possible linkages, and the possibility of polymerization, all tend to make the proposed structures highly speculative."[1]

The literature which appears in his review will not be referred to here.

Today, the existence of many-membered chelate ring compounds is well established. As the number of ring members increases from five, the stability of the chelates decreases generally. The cyclic voltammograms (CV) given in Figures 1 and 2 illustrate the situation. The CV of $[Co(en)_3]^{3+}$ which contains only five-membered rings is reversible in the 0.1 mol dm^{-3} en solution and quasi-reversible in the neutral solution, indicating the occurrence of the following redox reaction:†

$$[Co(en)_3]^{3+} + e^- \rightleftharpoons [Co(en)_3]^{2+}$$

When $HClO_4$ is added to the solution (curve 1 in Figure 1), the anodic peak disappears due to the occurrence of the following chemical reaction:

$$[Co(en)_3]^{2+} + 6H^+ \longrightarrow Co^{2+} + 3enH_2^{2+}$$

---

†The following abbreviations are used: en = $H_2N(CH_2)_2NH_2$; tn = $H_2N(CH_2)_3NH_2$; tmd = $H_2N(CH_2)_4NH_2$

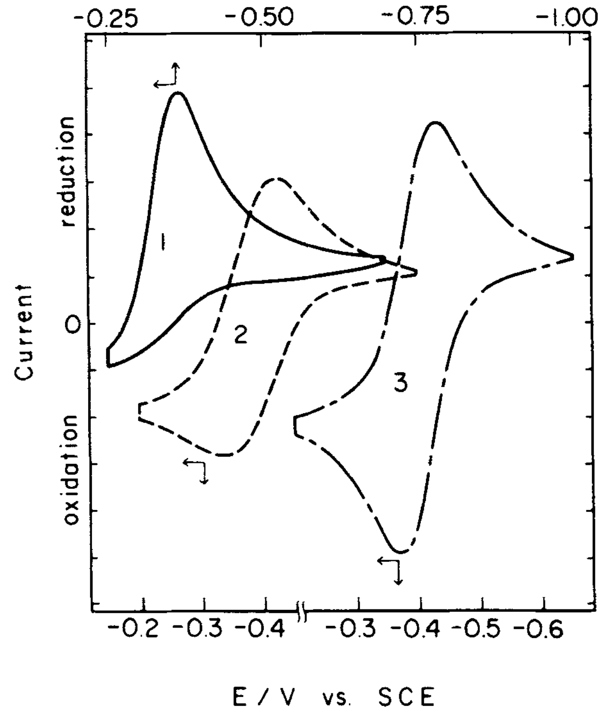


FIGURE 1 Cyclic voltammograms of $[Co(en)_3]^{3+}$ at $I = 1$ ($NaClO_4$). Solutions for curves 1 and 3 contain 0.1 mol dm^{-3} $HClO_4$ and 0.1 mol dm^{-3} en, respectively.

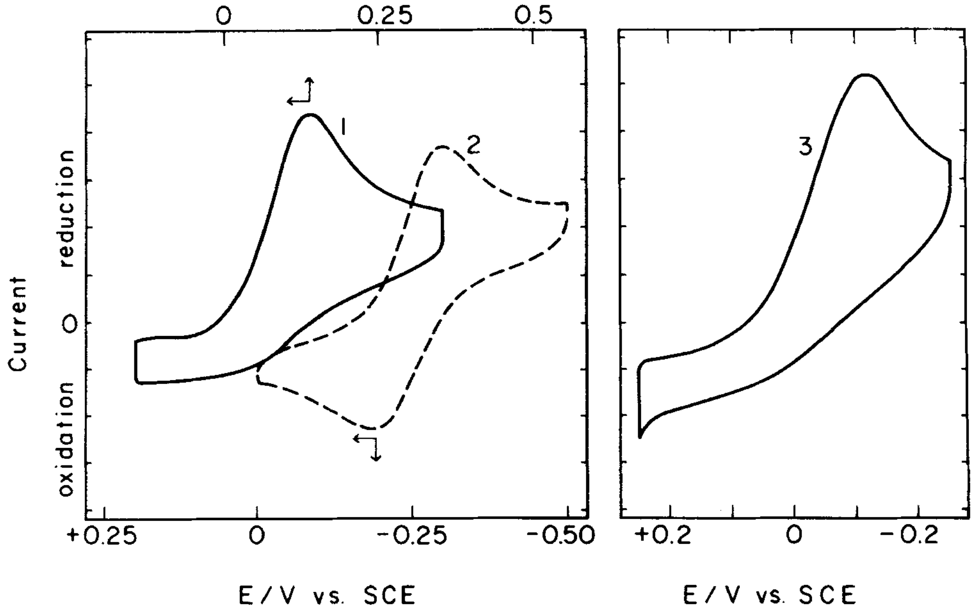
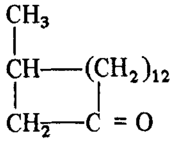
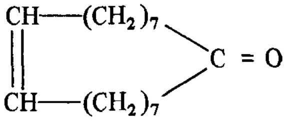


FIGURE 2 Cyclic voltammograms of $[Co(tn)_3]^{3+}$ (curves 1 and 2) at $I = 1$ ($LiClO_4$) and $[Co(tmd)_3]^{3+}$ (curve 3) at $I = 0.4$ ($LiClO_4$). Solution for curve 2 contains 0.2 mol dm^{-3} tn.

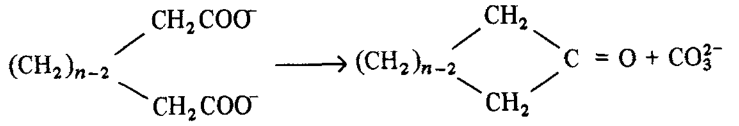
The CV of the neutral solution of $[Co(tn)_3]^{3+}$ which contains three six-membered rings shows a pattern similar to that of $[Co(en)_3]^{3+}$ in the 0.1 mol dm^{-3} $HClO_4$ solution, indicating that $[Co(tn)_3]^{2+}$ decomposes rapidly even in the neutral solution. However, an anodic peak can be observed in the presence of a large amount of tn (curve 2 in Figure 2). It was unequivocally verified that $[Co(tmd)_3]^{3+}$ contains three seven-membered rings.[2,3] The CV of the compound indicates that $[Co(tmd)_3]^{2+}$ is not stable in the neutral solution. The addition of tmd into the solution leads to the immediate decomposition of $[Co(tmd)_3]^{3+}$ itself. The stability of the five- to seven-membered chelate rings decreases dramatically in this order. This reflects increase of ring strains with increase of ring members. In medium sized rings, more severe strains may result due to unfavourable bond angle deformation and transannular interactions (the steric interactions between nonbonded groups attached to the rings). However, bidentate ligands having a very long flexible chelate backbone are expected to be stable because the strains which exist in medium-sized rings will be removed. The chemistry of organic cyclic compounds provides good examples.

In 1926, Ruzicka proved that the active fragrant principles, muscone and civetone, are many-membered cyclic ketones.[4,5]

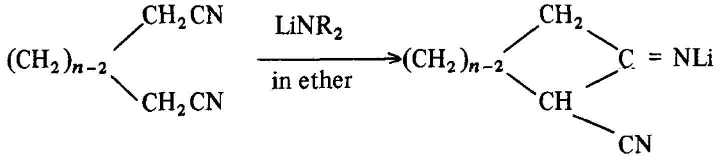

muscone

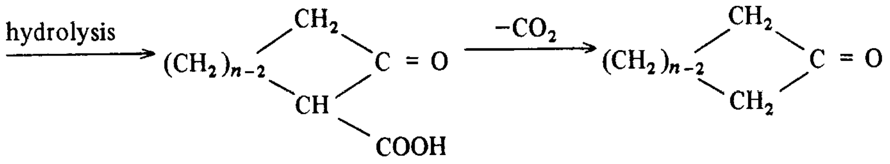

civetone

He and his school then succeeded in preparing various sized cyclic ketones by the pyrolysis of metal salts of dicarboxylic acids:[6,7]

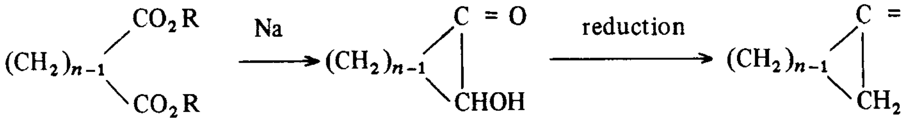


The yields of the cyclic ketones *vs* the number of ring members are shown in Figure 3. The five- and six-membered cyclic ketones are obtained in high yields, but the ketones in the range C_9 to C_{11}, yield no more than 0.5%. However, the yields increase from the C_{12} ketone and a second maximum is observed at about C_{17}. This behavior has been interpreted in terms of ring strain and entropy factors in the ring closure process.[10–13] The first decrease in the yields comes from the ring strains existing in the medium sized rings. As larger ring compounds with more than 11 members are relieved of such strains, the formation of the ring compounds is again observed. The second decrease in the yields reflects that the probability of encounter decreases between two functional groups in the same molecule. Ziegler improved Ruzicka's method greatly by using the following steps (see Figure 3 for the yields):[8,9]





As cyclization is conducted in homogeneous solutions, the high-dilution technique can be applied, so that bimolecular condensation is retarded. Even by this method, the medium-sized ring compounds containing eight to 11 members could only be prepared in very low yields. The introduction of the acyloin condensation method gave a dramatic result in the synthesis of the ring ketones (see Figure 3):[14,15]



With this method, there is no need to employ the high-dilution technique. The reaction is considered to occur only for the ester molecules adsorbed on the surface of sodium metal. The adsorbed ester molecules are far enough apart so that intermolecular coupling does not compete with the desired cyclization.

The nomenclature adopted in this paper for the various sizes of chelate rings is based on that of organic ring compounds: thus "medium-sized chelate rings" refer to eight- to 11-membered rings and "large chelate rings" are those with more than 11 members. The term, "many-membered chelate ring", will be used for both medium-sized and large chelate rings.

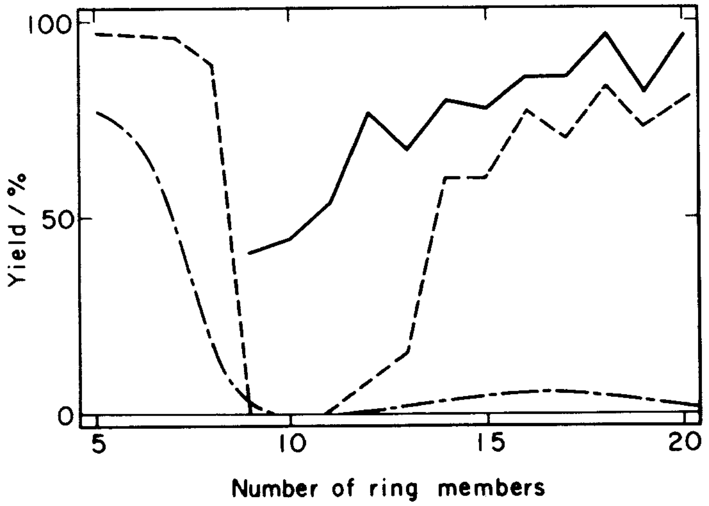
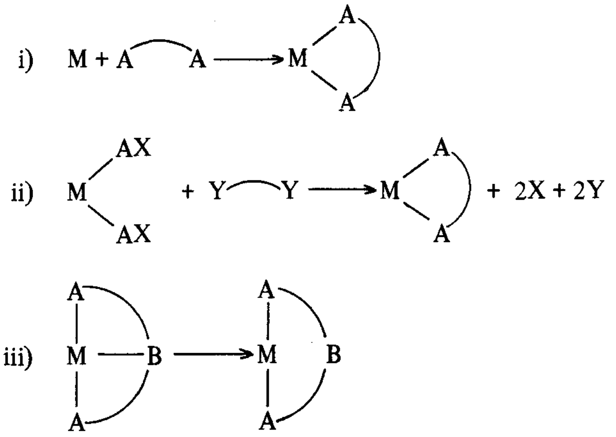
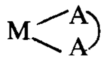


FIGURE 3 Yields of organic ring compounds as the function of the number of ring members. Ruzicka's method (— - —); Ziegler's method (- - - -); Acyloin condensation method (——).

2. SYNTHETIC METHODS FOR MANY-MEMBERED CHELATE RING COMPOUNDS

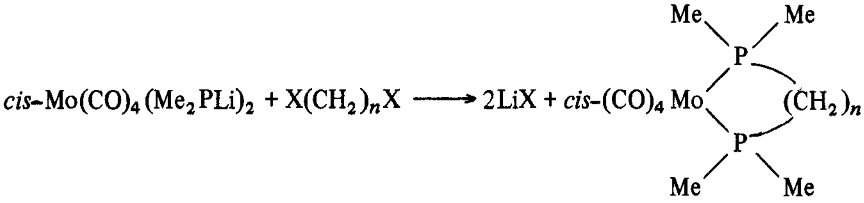
The many-membered chelate ring compounds may be synthesized in the following ways:



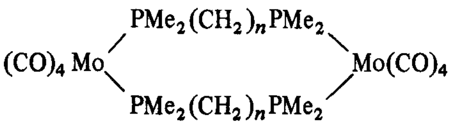
M and  denote respectively the starting complex and the many-membered chelate ring compound. Other coordinated ligands are omitted for simplicity. A and B denote donor atoms, and X and Y, functional groups to give A⌒A upon reactions. Almost all complexes containing many-membered chelate ring(s) have been prepared by the method i). More details on this method will be given in the following sections.

There have been several examples of complexes prepared by either method ii) or iii).

Stelzer and Unger prepared *cis*-[Mo(CO)$_4${PMe$_2$(CH$_2$)$_n$PMe$_2$}] (n = 3-6) by utilizing the template reaction of the coordinated ligands in *cis*-[Mo(CO)$_4$(Me$_2$PLi)$_2$] with dihaloalkanes. This corresponds to method ii),[16]



where X = Cl for n = 2 and X = Br for n = 3-6. Mass spectral measurements give evidence that the complexes are monomeric. When the number of methylene groups is five or six, small amount of dimer containing a 16- or 18-membered chelate ring is also formed:



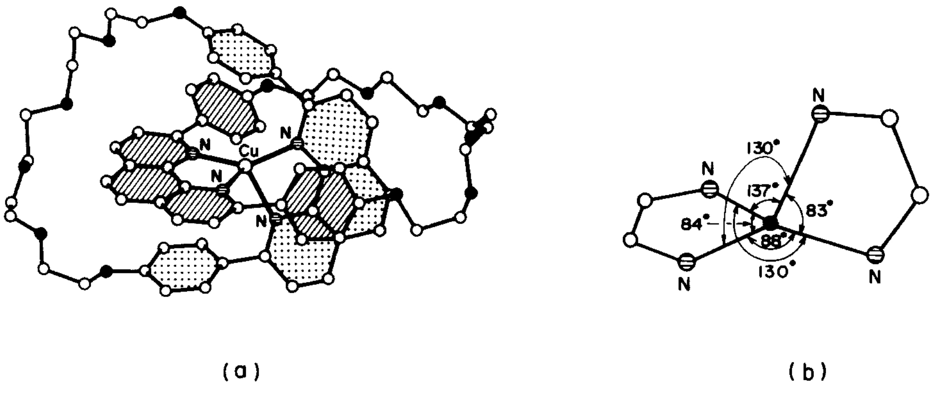
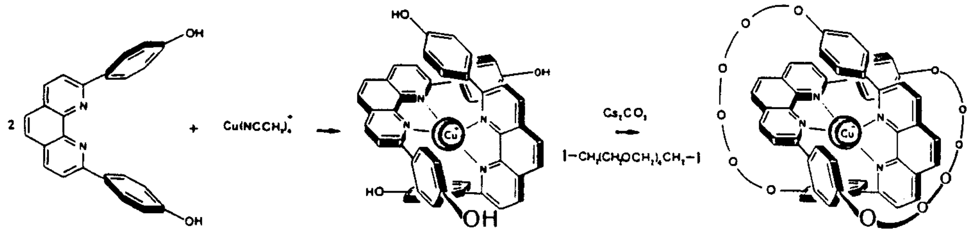


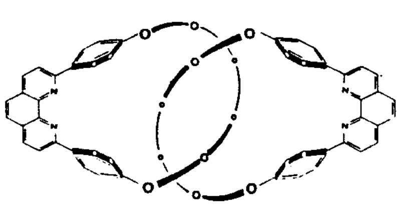
FIGURE 4 Structure of **1** (a) and the coordination polyhedron of copper(I) (b).

In connection with method ii) a very interesting compound, metallo-catenane, was prepared recently by Sauvage *et al.* via the following route:[17–20]



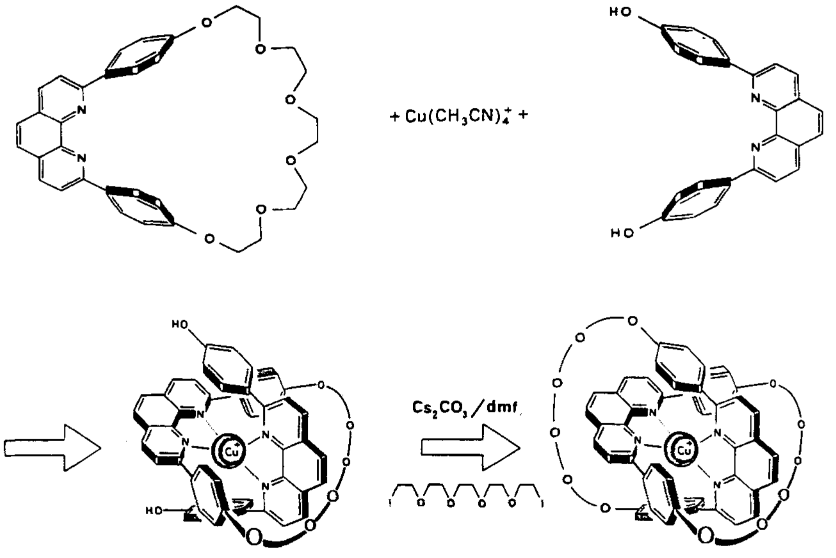
1

The crystal structure of **1** was determined by single crystal X-ray method for $[1]BF_4$ (Figure 4). The coordination polyhedron around copper(I) is highly distorted with respect to tetrahedral geometry as shown in Figure 4(b). Treatment of **1** (metallo-catenane) with tetramethylammonium cyanide in acetonitrile-water affords the catenane[20,21] in which two macrocycles are interlocked. The crystal structure of the catenane **2** was also determined. The molecular arrangement of the free ligand **2** is strikingly different from that of the metallo-catenane **1**. In **1** the two diphenyl phenanthroline fragments interpenetrate, but they are fully disentangled in **2**.

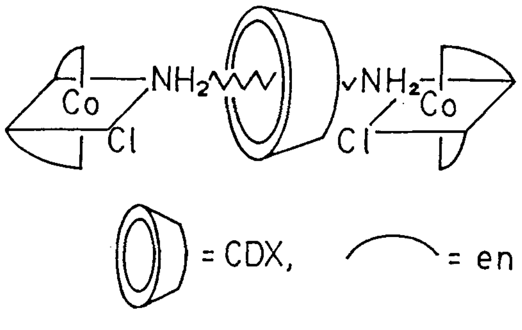


2

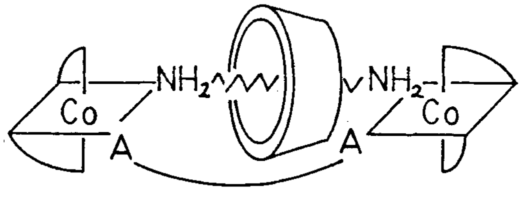
The metallo-catenane 1 was also prepared by the following route:[17]



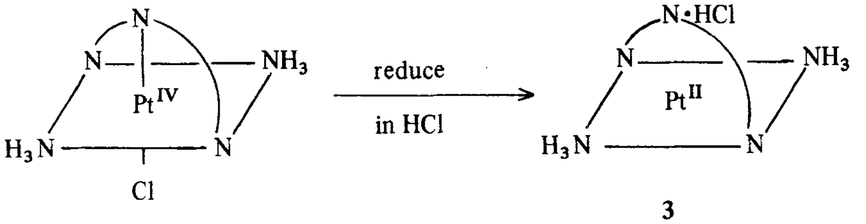
Catenane is closely related to rotaxane.[22] The rotaxane is a compound consisting of a ring threaded by chain-bearing end groups that are so bulky that the chain cannot be extruded from the ring. The syntheses of rotaxanes containing metal complexes were also reported, where the ring was α- or β-cyclodextrin (CDX) and the chain was a dimeric cobalt(III) complex.[23–25] One example of such compounds is shown below, where the chain is α, ω-diaminoalkane:



If two chloro ligands in the rotaxane are replaced by a diamine molecule or an appropriate bidentate ligand, the resulted compound corresponds to the catenane, though this is not yet achieved:

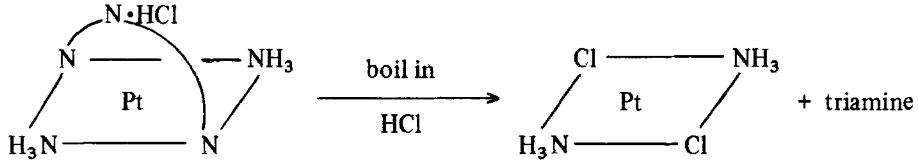


There are several examples which belong to method iii). By utilizing a reductive elimination reaction, Mochida *et al.*, prepared a square planar platinum(II) complex which contains a novel eight-membered chelate ring.[26] An octahedral platinum(IV) complex, *mer*-$[PtCl(NH_3)_2\{NH_2(CH_2)_2NH(CH_2)_2NH_2\}]Cl_3$ was used as the starting material. Upon the electrolytic reduction of this compound in HCl solution, the eight-membered chelate ring compound is formed:



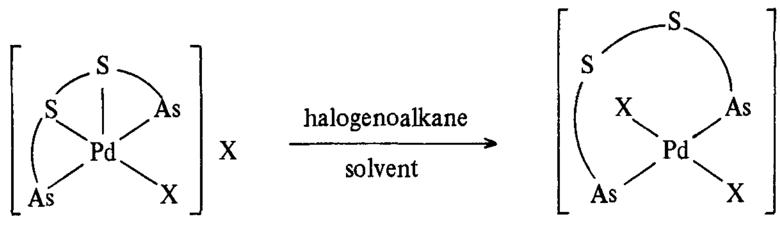
3

In this complex, the central nitrogen atom of the triamine is not attached to the platinum and the ligand acts as the *trans*-spanning ligand. This conclusion was derived as follows: when compound **3** was boiled in hydrochloric acid, the triamine was eliminated to give *trans*-$[PtCl_2(NH_3)_2]$.



The two ammonia molecules must occupy their original *trans* positions, because *cis-trans* isomerizations are very rare in platinum(II) chemistry. This leads to the conclusion that the triamine must be attached to the other two *trans* positions. Repeated recrystallization of compound 3 gives $[Pt(NH_3)\{H_2N(CH_2)_2NH(CH_2)_2NH_2\}]Cl_2$, and hence the eight-membered chelate ring is not stable and tends to revert to a complex with two fused five-membered rings. A complex was also prepared, *trans* spanning-$[Pt(NH_3)_2\{CH_3N(CH_2CH_2NH_2)_2 \cdot HCl\}]Cl_2$.

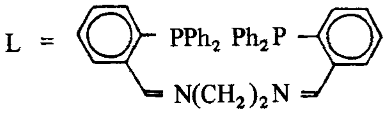
McAuliffe *et al.* prepared $[PdX_2L]$ complexes (X = Cl, Br, and I), where L denotes the potentially quadridentate diarsine-dithioether ligand $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$.[27,28] The choice of solvents controls the coordination mode of L to palladium(II). In nitromethane solution, the complexes are 1-1 electrolytes and have electronic spectra characteristic of pentacoordinate palladium(II). Therefore the complexes have As_2S_2X donor sets. However, in dichloromethane or 1,2-dichloroethane, the complexes are non-electrolytes and show spectra which are characteristic of planar palladium(II). Molecular weight measurements in chloroform solution show that the $[PdX_2L]$ species are monomeric. ^1H NMR spectra provide indications that the terminal $AsMe_2$ groups are coordinated to the metal. The solution infrared spectra of the $[PdBr_2L]$ complex provide evidence for a *trans* structure. These facts suggest that the following transformation occurs by changing the solvent from nitromethane to halogenoalkanes:



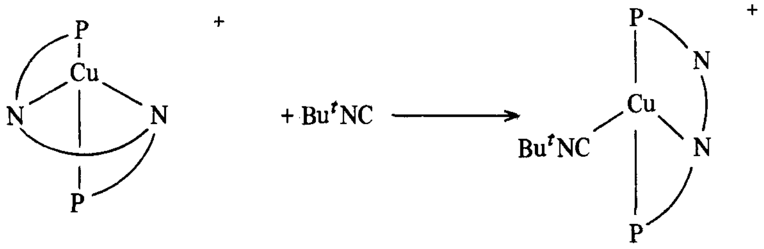
4 **5**

The complex **5** in halogenoalkane solvents must contain a 14-membered chelate ring. The more polar nitromethane will stabilize the ionic form **4**, whereas in a halogenoalkane, the ions will not be stabilized by solvation and the halide displaces the thioether donors. The corresponding [PtX$_2$L] complexes show analogous behavior.

Nickel, copper, and silver complexes of the following ligand (L) were prepared by Rauchfuss *et al.*[29] Among the complexes, [CuL](ClO$_4$), which contains the quadridentate ligand is a unique example of a large chelate ring. The complex has



severely distorted tetrahedral geometry. Addition of Bu^tNC to the CH_2Cl_2 solution of the complex results in the formation of [CuL(Bu^tNC)](ClO$_4$), isolated as crystals. The structure determined by single crystal X-ray methods reveals that the isocyanide displaces one of the internal imine nitrogen atoms in $[CuL]^+$ to give a nine-membered chelate ring:



The $[CuL(Bu^tNC)]^+$ ion in CD_2Cl_2 undergoes imine site exchange on the NMR time scale.

Zubieta *et al.* prepared [$Mo_2^VO_3L_2$] which contains the quadridentate ligand (L), $^-S(CH_2)_2NMe(CH_2)_3NMe(CH_2)_2S^-$.[30–32] This compound is extremely moisture-sensitive and readily reacts upon exposure to moist air to give [$Mo_2O_4(HL)_2$]. The structural study confirms that the latter compound contains large chelate rings formed by the coordination of only the two sulfur atoms of L to the $Mo_2O_4^{2+}$ core (Figure 5). The two amine nitrogens are not coordinated to the molybdenum and are protonated to form a six-membered H-N-C-C-C-N ring with a chair conformation as shown in Figure 4. A similar coordination mode of L was also found in [$Fe(NO)_2(HL)$].[33]

TABLE 1
Many-membered chelate ring compounds

Case	$L^\dagger$	Complex	ref.
	A. N–N ligand		

1	$H_2N(CH_2)_nNH_2$	*cis*-$[Co(en)_2L]^{3+}$ (n = 4, 9, 10, 12, 14);
		cis-$[(en)_2CoL_2Co(en)_2]^{6+}$ (n = 4-10, 12, 14);
		$[Co(NH_3)_4L]^{3+}$ (n = 4, 12, 14);
		$[(NH_3)_4CoL_2Co(NH_3)_4]^{6+}$ (n = 10)
			34–38

2	$Me_2N(CH_2)_nNMe_2$ (n = 5, 7, 10)	*trans*-$[PdCl_2L]_2$	39
3	$Me_2NN{=}CH(CH_2)_3CH{=}NNMe_2$	*trans*-$[PdCl_2L]_2$	40
4	$[NH_2CH_2CH_2\overset{+}{\underset{H}{N}}RCH_2CH_2NH_2]Cl^-$ (R = H, CH_3)	*trans*-$[Pt(NH_3)_2L]^{2+}$	26
	B. P–P ligand		
5	$Ph_2P(CH_2)_2O(CH_2)_2PPh_2$	$[NiX_2L]$ (X = Cl, Br, I; pseudo-tetrahedral); *trans*-$[RhCl(CO)L]$; *trans*-$[RhCl(CO)L]_2$; $[RhCl(SO_2)(CO)L]$	41–44
6	$Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$	$[NiX_2L]$(X = Cl, Br; pseudo-tetrahedral); *trans*-$[NiI_2L]$ (distorted square planar); *trans*-$[Ni(NCS)_2L]$; *trans*-$[Ni(H_2O)_2L]$ $(BF_4)_2$;	43–47
7	$Ph_2P(CH_2)O(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$	*trans*-$[Rh(EtOH)(CO)L](PF_6)$; *trans*-$[RhCl(CO)L]$ *trans*-$[Rh(H_2O)(CO)L](PF_6)$; *trans*-$[RhCl(CO)L]$	43, 48
8	$Me_2P(CH_2)_nPMe_2$	*cis*-$[Mo(CO)_4L]$ (n = 4–6); *cis*-$[Mo(CO)_4L]_2$ (n = 5, 6)	16
9	$Ph_2P(CH_2)_3PPh_2$	*cis*-$[PdCl_2L]$; *cis*-$[PtCl_2L]_2$; *trans*-$[RhCl(CO)L]_2$; *trans*-$[IrCl(CO)L]_2$	49, 50
10	$Ph_2P(CH_2)_4PPh_2$	*cis*-$[PdCl_2L]_3$; *cis*-$[PtCl_2L]_3$; *trans*-$[RhCl(CO)L]_2$; *trans*-$[IrCl(CO)L]_3$	49, 50
11	$Ph_2P(CH_2)_6PPh_2$	*trans*-$[RhCl(CO)L]_2$; *trans*-$[IrCl(CO)L]_2$	51
12	$Ph_2P(CH_2)_8PPh_2$	$[NiI_2L]_2$ (pseudo-tetrahedral)	52
13	$Ph_2P(CH_2)_nPPh_2$	$[PdX_2L]_2$ (n = 8; X = Cl, Br, I, NCS); $[PdX_2L]_{1\ \mathrm{and}\ 2}$ (n = 10; X = Cl, Br, I); $[Pd(NCS)_2L]$ (n = 10); *trans*-$[PdX_2L]$ (n = 12; X = Cl, Br, I, NCS)	53

Table I continued

14	$Ph_2P(CH_2)_nPPh_2$	*cis*-$[PtCl_2L]$ (n = 9–11, 16); *cis*-$[PtCl_2L]_2$ (n = 8–12, 16); *trans*-$[PtCl_2L]$ (n = 7–12); *trans*-$[PtCl_2L]_2$ (n = 7–12, 16)	54
15	(o-$Ph_2PC_6H_4CH_2)_2$	*cis*-$[Pt(CH_3)_2L]$; *trans*-$[RhCl(CO)L]$; *trans*-$[Rh(CO)_2L](BF_4)$; *trans*-$[IrCl(CO)L]$	55
16	$Ph_2PCH_2NHMe(CH_2)_2NHMeCH_2PPh_2$	*cis*-$[Mo(CO)_4L]$	56
17	$Ph_2P(CH_2)_6P(Et)Ph$	*trans*-$[PtCl_2L]_2$	57
18	$(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2$	*trans*-$[NiCl_2L]$; $[CoI_2L]$ (tetrahedral)	58
19	$Bu^t_2P(CH_2)_5PBu^t_2$	*trans*-$[IrCl_2HL]_2$	59, 60

20	$Bu^t_2P(CH_2)_nPBu^t_2$	*trans*-$[PtCl_2L]$ (n = 9, 10, 12);
		trans-$[PtCl_2L]_2$ (n = 9, 10, 12);
		trans-$[PtCl_2L]_3$ (n = 8, 12)
			61–63

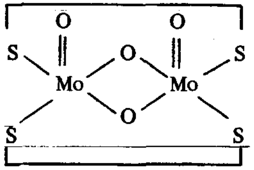
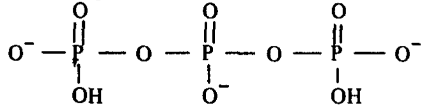
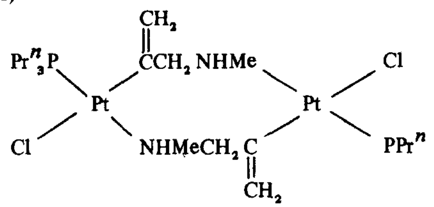
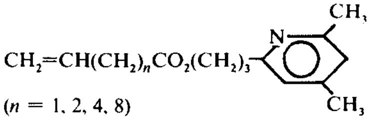
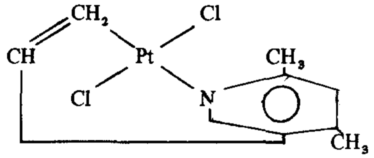
21	$Bu^t_2P(CH_2)_nPBu^t_2$	*trans*-$[RhCl(CO)L]_2$ (n = 5, 10); *trans*-$[RhHCl_2L]_2$ (n = 5), *trans*-$[RhCl(NCR)L]_2$ (R = Me, Bu^t; n = 5)	61, 64–66
22	$Bu^t_2P(CH_2)PBu^t_2$	*trans*-$PdCl_2L$(n = 10, 12); *trans*-$[PdCl_2L]_2$ (n = 5, 7 10, 12)	63, 67–69
23	$Bu^t_2P(CH_2)_nPBu^t_2$ (n = 9, 10)	*trans*-$[IrCl(CO)L]$; *trans*-$[IrCl(CO)L]_2$	61, 62, 67
24	$Bu^t_2P(CH_2)_2CHMe(CH_2)_2PBu^t_2$	*trans*-$[MCl_2L]_2$ (M = Pd, Pt); *trans*-$[MCl_2HL]_2$ (M = Rh, Ir)	60, 64, 65, 70
25	$Bu^t_2PCH_2CHMe(CH_2)_3PBu^t_2$	*trans*-$[PtCl_2L]_2$	71
26	$Bu^t_2P(CH_2)_4C{\equiv}C(CH_2)_4PBu^t_2$	*trans*-$[RhCl(CO)L]$	72, 73
27	$Bu^t_2P(CH_2)_nC_6H_4(CH_2)_nPBu^t_2$	*trans*-$[PdL]$ (n = 3, 4)	74
28	$Bu^t_2P(CH_2)_4C_6H_4(CH_2)_4PBu^t_2$	*trans*-$[PdCl_2L]$; *trans*-$[PtCl_2L]$	74
29	$Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2$	*trans*-$[PdCl_2L]_7$; *trans*-$[PtCl_2L]_6$; *trans*-$[IrCl_2H(CO)L]$; *trans*-$[IrCl(CO)L]$; $[IrBr_2HL]_2$; $[IrBr(CO)L]_2$	75
	C. S–S ligand		
30	$PhS(CH_2)_{12}SPh$	*trans*-$[PdX_2L]$ (X = Cl, Br); *trans*-$[PtCl_2L]$	76, 77
31	$Bu^tS(CH_2)_5SBu^t$	*trans*-$[MCl_2L]_2$ (M = Pd, Pt)	78
32	 $^-S(CH_2)_2NMe(CH_2)_3NMe(CH_2)_2S^-$ H^+	$[Fe(NO)_2L]$ (pseudo-tetrahedral);  (square pyramid)	30–33

Table I continued

	D. As-As ligand		
33	$Me_2As(CH_2)_{12}AsMe_2$	*trans*-$[PdCl_2L]$	79
34	$Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$	*trans*-$[MX_2L]$ in dichloromethane or dichloroethane (M = Pd, Pt; X = Cl, Br, I, NCS, SCN)	27, 28
35	$Ph_2As(CH_2)_nAsPh_2$ (n = 12, 16)	*trans*-$[PdX_2L]$ (X = Cl, Br, I, NCS, SCN)	80
36	$Ph_2As(CH_2)_nAsPh_2$ (n = 6, 7, 9, 11)	*cis*-$[PtCl_2L]_2$; *trans*-$[PtCl_2L]$	81
37	$Ph_2As(CH_2)_6AsPh_2$	*trans*-$[MCl(CO)L]_2$ (M = Rh, Ir)	51
38	(o-$Ph_2AsC_6H_4CH_2)_2$	*trans*-$[RhCl(CO)L]$; *trans*-$[IrCl(CO)L]$; *trans*-$[Ir(CO)_2L]^+$	55
	E. O-O ligand		
39		*cis*-$[Co(NH_3)_4(H_2P_3O_{10})]$	82, 83
	F. A-B ligand (bidentate ligand containing heterodonor atoms)		
40	$CH_2{=}C$-CH_2-NHMe		84
41	 (n = 1, 2, 4, 8)		85
42	$NH_2(CH_2)_{11}COO^-$	*cis*-$[Co(NH_3)_4L]^{2+}$; *cis*-$[Co(en)_2L]^{2+}$; $[(en)_2CoL_2Co(en)_2]^{4+}$	86

†Ligand which forms a many-membered chelate ring.

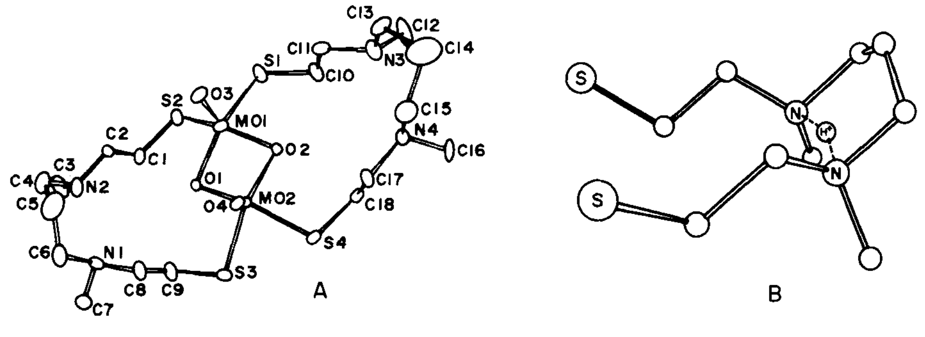


FIGURE 5[32] Structure of $[Mo_2O_4(HL)_2]$ (A) and schematic view of the ligand folding in the complex, illustrating the six-membered $\overline{\text{H-N-C-C-C-N}}$ ring (B).

3. EXAMPLES OF MANY-MEMBERED CHELATE RING COMPOUNDS

In Table I, examples of many-membered chelate ring compounds are summarized and classified into several categories according to the kind of donor atoms involved. Some interpretations will be given below for selected examples and this may explain implicitly the factors controlling the formation of many-membered chelate ring compounds.

3.1 Cobalt(III) Complexes Containing α,ω-Diaminoalkanes

When a Me_2SO solution containing equimolar amounts of *cis*- or *trans*-$[CoCl_2(en)_2]Cl$ and α,ω-diaminoalkanes ($H_2N(CH_2)_nNH_2$ will hereafter be referred to as N-N) is kept at 40-80°C for an appropriate period, various cobalt(III) species are formed.[34,35] When N-N = tmd, the main products obtained from the acidified reaction mixture are $[Co(en)_2(tmd)]^{3+}$, $[CoCl(en)_2(tmdH)]^{3+}$, $[(en)_2ClCo(tmd)CoCl(en)_2]^{4+}$, $[(en)_2Co(tmd)_2Co(en)_2]^{6+}$, and a small amount of other higher charged species. The yield of $[Co(en)_2(tmd)]^{3+}$ which contains a seven-membered ring, markedly depends on the concentration of the reactants; this amounts to only a few percent when the concentrations of N-N and $[CoCl_2(en)_2]Cl$ are both 0.3 mol dm^{-3}. When the concentrations of both reactants are 0.025 mol dm^{-3} however, the yield increases to 70%. Under the latter condition, similar preparations were attempted by use of various N-N (n = 2-10, 12, 14) in place of tmd. When the number of the methylene groups of the N-N is more than four, products similar to those observed in the tmd system are obtained: $[Co(en)_2(N\text{-}N)]^{3+}$, $[CoCl(en)_2(N\text{-}NH)]^{3+}$, $[(en)_2ClCo(N\text{-}N)CoCl(en)_2]^{5+}$, $[(en)_2Co(N\text{-}N)_2(Co(en)_2]^{6+}$, and some other higher charged species. When en is used as N-N only $[Co(en)_3]^{3+}$ is formed and no dimeric complex is detected. The reaction of $[CoCl_2(en)_2]Cl$ with tn leads to the occurrence of disproportionation reactions which gives not only $[Co(en)_2(tn)]^{3+}$ but also $[Co(en)_3]^{3+}$, $[Co(en)(tn)_2]^{3+}$, and $[Co(tn)_3]^{3+}$. Again, no dimeric complex is detected. Therefore, as the methylenic chain becomes longer, the diamines tend to coordinate with a metal ion as a unidentate ligand and with two metal ions as a bridging ligand.

The yields of monomeric $[Co(en)_2(N\text{-}N)]^{3+}$ are strongly dependent on the methylenic chain length. The yields of $[Co(en)_2(N\text{-}N)]^{3+}$ *vs* the number of ring

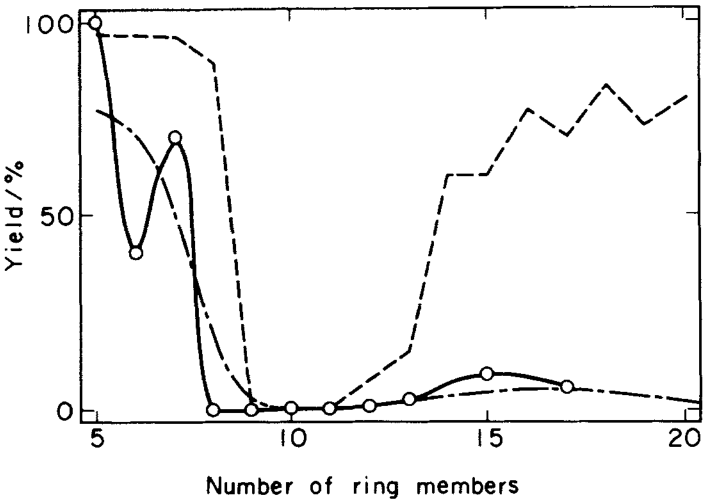


FIGURE 6 Yields of $[Co(en)_2(N\text{-}N)]^{2+}$ (——) and organic ring compounds (Ruzicka's method — - —; Ziegler's method - - - -) as the function of the number of ring members.

members are shown in Figure 6. The yields of the monomer decrease sharply for the eight-membered ring and virtually become zero for eight- to eleven-membered ring systems. The 12-membered chelate ring complex was obtained in 1% yield after which the yields increase with the increase of the ring member. The second maximum is observed at the 15-membered ring. The trend is strikingly similar to that obtained in the

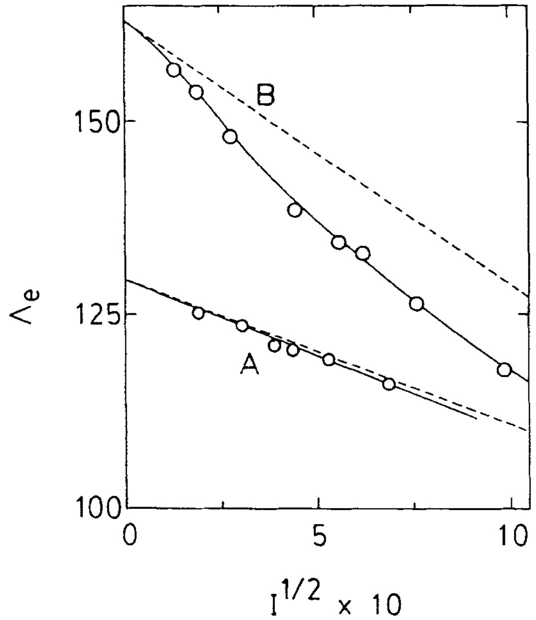
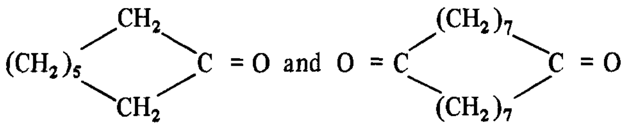


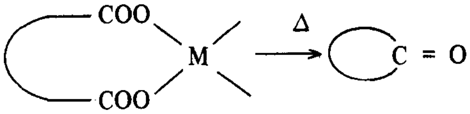
FIGURE 7[38] Equivalent conductance as the function of $I^{1/2}$. A: $[Co(en)_2\{NH_2(CH_2)_{12}NH_2\}]Br_3 \cdot H_2O$. B: $[Co_2(en)_4\{NH_2(CH_2)_{12}NH_2\}_2]Cl_6 \cdot 6.5H_2O$. Dotted lines are theoretical ones calculated by Onsager equation.

synthesis of the organic ring ketones which is also shown in Figure 6. The ring closure processes of both the dicarboxylates and the complexes are thus controlled by the same factors (*i.e.* ring strain and entropy effects). Parallelism between the chelate ring compounds and the ring ketones provides support for the formulation of monomeric complexes containing a many-membered ring. Further supports for the monomeric form of $[Co(en)_2(N\text{-}N)]^{3+}$ are: i) SP-Sephadex cation exchange chromatography shows that the complexes $[Co(en)_2(N\text{-}N)]^{3+}$ are monomeric tripositive ions as judged from the flow rates. ii) Conductometric measurements also support the formulation. In Figure 7 are plotted Λ_e values of $[Co(en)_2\{NH_2(CH_2)_{12}NH_2\}]Br_3 \cdot H_2O$ and $[(en)_2Co\{NH_2(CH_2)_{12}NH_2\}_2Co(en)_2]Cl_6 \cdot 6.5H_2O$, against $\sqrt{I}$ (I = ionic strength). The curves of the former and latter species are consistent respectively with a 3-1 electrolyte and a 6-1 electrolyte.[87,88] iii) Crystallographic analysis by X-ray methods has been made for $[Co(en)_2\{NH_2(CH_2)_{14}NH_2\}]Br_3 \cdot 3H_2O$.[89] The crystals are triclinic, space group $P\bar{1}$, $a = 14.021(2)$, $b = 28.709(4)$, $c = 8.339(1)$ Å, $\alpha = 98.71(1)$, $\beta = 97.80(1)$, $\gamma = 102.01(1)°$, $U = 3196.3(7)$ Å^3, $Z = 4$, $R = 0.11$. There are two independent molecules in the unit cell. A perspective view of one of the molecules is shown in Figure 8. It is evident that the large chelate ring is formed, though the central part of the diamine is omitted due to the uncertainties with respect to accurate atomic positions.

Returning to Figure 6, the parallelism between the chelates and the ring ketones suggests that Ruzicka's method is based on the pyrolytic reactions of metal chelates formed by dicarboxylates. By this, cyclic ketones as well as cyclic diketones are formed. For example, thorium salt of azelaic acid gives



The cyclic ketone may be derived from the species having a chelate structure:



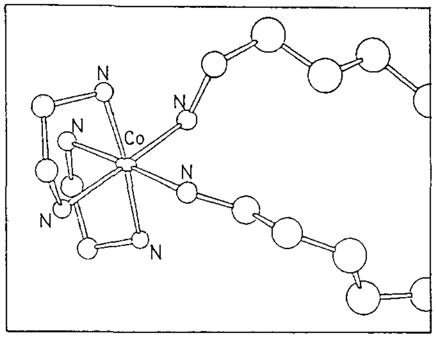
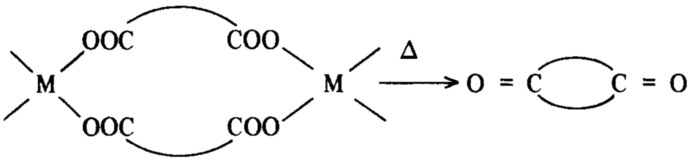
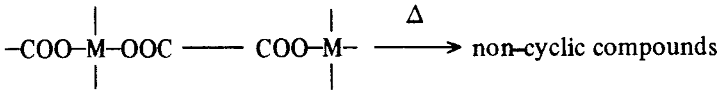


FIGURE 8[89] Structure of $[Co(en)_2\{NH_2(CH_2)_{14}NH_2\}]Br_3 \cdot 3H_2O$.

The cyclic diketone may be formed by the pyrolytic reaction of the dimeric species in which two bridging azelaates make a cyclic structure:

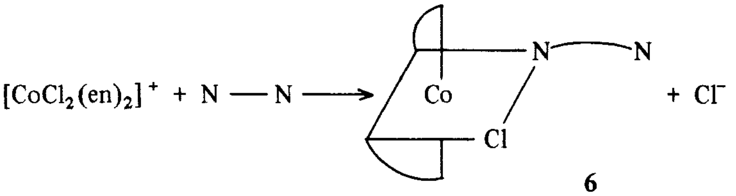


Other products may be derived from the salts having non-cyclic structures.



$$-\text{COO}-\overset{|}{\underset{|}{\text{M}}}-\text{OOC}\text{———}\text{COO}-\overset{|}{\underset{|}{\text{M}}}-\xrightarrow{\Delta}\text{non-cyclic compounds}$$

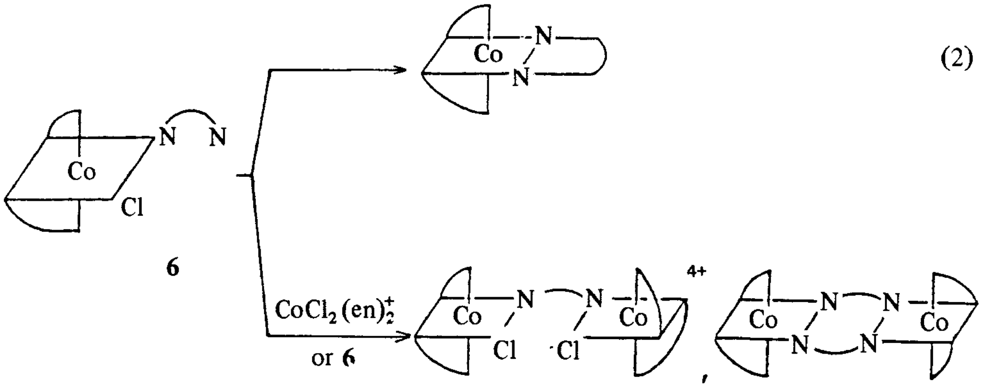
The products found in the reactions between $[CoCl_2(en)_2]Cl$ and N–N give a clue for the mechanism. The first step of the reaction would be as follows:



6

(1)

This is a sort of "Meisenheimer reaction" in which $[CoCl_2(en)_2]Cl$ reacts with various amines to give *cis*-$[CoCl(amine)(en)_2]^{2+}$.[90] Indeed, the species of the general formula $[CoCl(en)_2(N\text{-}NH)]^{3+}$ are obtained from the acidified solutions and contain unidentate N-N. An intramolecular ring closure of **6** leads to the monomer $[Co(en)_2(N\text{-}N)]^{3+}$, while a bimolecular reaction of **6** and an intermolecular reaction of **6** with $[CoCl_2(en)_2]^+$ result in the formation of the dimers:



(2)

(3)

The simultaneous occurrence of reactions (2) and (3) reasonably explains the observed products and the concentration dependence of the yield of the monomer. Reaction (2) may be first order, whereas reaction (3) may be second order. Therefore, the reaction in

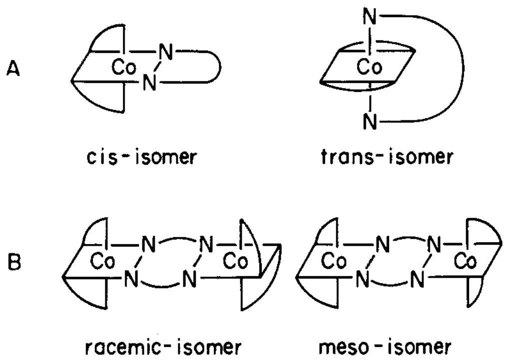


FIGURE 9 Possible structures for the monomer ($[Co(en)_2(N\text{-}N)]^{3+}$ and the dimer ($[Co_2(en)_2(N\text{-}N)_2]^{6+}$) ⁀ and N⁀N denote en and N-N, respectively. A: Possible structure of the monomer. B: Most probable structures of the dimer.

a dilute solution favors the formation of the monomer. This constitutes the principle of the high dilution method.

For $[Co(en)_2(N\text{-}N)]^{3+}$, two geometric isomers are possible, as shown in Figure 9, if the methylenic chain of N-N is long enough. However, molecular models reveal that the non-bonding interaction between the en and the N-N chelates makes *trans* spanning difficult even in the case of $NH_2(CH_2)_{14}NH_2$. Through the optical resolution of $[Co(en)_2\{NH_2(CH_2)_{12}NH_2\}]^{3+}$ it was verified that the N-N occupies cis positions in the complex.

The most probable structures of the dimeric complexes, $[Co_2(en)_4(N\text{-}N)_2]^{6+}$, are also shown in Figure 9. Catenane structures with two interlocking N-N chelate rings are also possible, if the methylenic chain of the N-N becomes long enough.

The introduction of oxygen atoms into N-N improves the yield of $[Co(en)_2(N\text{-}N)]^{3+}$: The reaction of $[CoCl_2(en)_2]^+$ with $NH_2(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$ gives $[Co(en)_2(N\text{-}N)]^{3+}$ in a good yield even under the conventional concentration condition.[38] Such effects have been suggested by Shaw *et al*:[68] Factors which stabilize large organic rings such as the suitably positioned sterically demanding substituents, heteroatoms (-O-, -NH-, or -S-), double and triple bonds should also stabilize large chelate rings.

3.2 *Complexes Containing α,ω-Bis(disubstituted phosphino)alkanes.*

The first example of a monomeric eight-membered chelate ring compound evidenced by X-ray analysis was the paramagnetic complex $[NiCl_2\{Ph_2P(CH_2)_2O(CH_2)_2PPh_2\}]$.[42] A perspective view of the structure is shown in Figure 10. The complex has a distorted tetrahedron with a P_2Cl_2 donor set. The oxygen atom of the chelate ring is 3.74 Å apart from the nickel ion and is not coordinated to the metal. But the same ligand (L) acts as a terdentate one in $[Rh(CO)L](PF_6)$; the central oxygen atom in L is coordinated to the metal.[48]

A structural study of another complex $[NiI_2\{Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2\}]$ was then made.[45,46] The ligand has a longer chain containing two oxygen atoms. The complex is low-spin in contrast to the complex mentioned above. The donor set has been shown to be P_2I_2, the diphosphine ligand forming an 11-membered ring. The

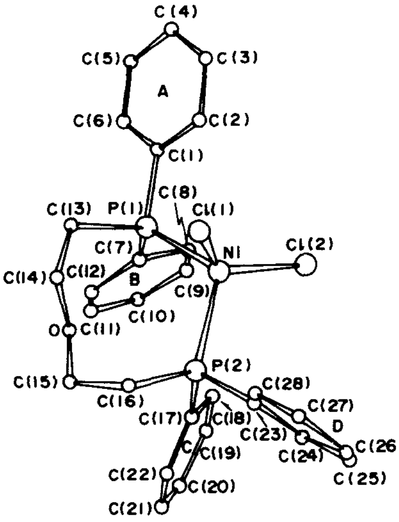


FIGURE 10[42] Structure of $[NiCl_2\{Ph_2P(CH_2)_2O(CH_2)_2PPh_2\}]$.

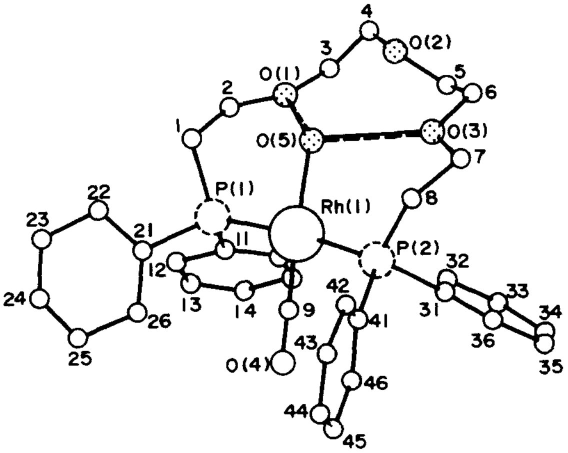


FIGURE 11[48] Structure of $\{Rh(H_2O)(CO)\{Ph_2P(CH_2)_2(OCH_2CH_2)_3PPh_2\}\}^+$.

complex is distorted considerably toward a tetrahedron. Later, Alcock *et al.* prepared a rhodium(I) complex $[Rh(H_2O)(CO)L](PF_6)$ containing the ligand $Ph_2P(CH_2)_2(OCH_2CH_2)_3PPh_2$ as L.[48] The geometry of the coordination sphere about the rhodium is very close to square planar with a P_2OC donor set (Figure 11). The oxygen donor is provided by a water molecule. Two oxygen atoms in the 14-membered chelate ring interact with the water molecule through hydrogen bonds. In *trans*-$[Rh(EtOH)(CO)L]^+$ ($L = Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$), a similar hydrogen bond is formed between the coordinated EtOH and L.

In 1973, Shaw *et al.* prepared large chelate ring compounds, $[PtCl_2L]_{1\text{ and }2}$ and $[IrCl(CO)L]_{1\text{ and }2}$, containing *trans*-spanning diphosphine ligands $Bu^t_2P(CH_2)_nPBu^t_2$

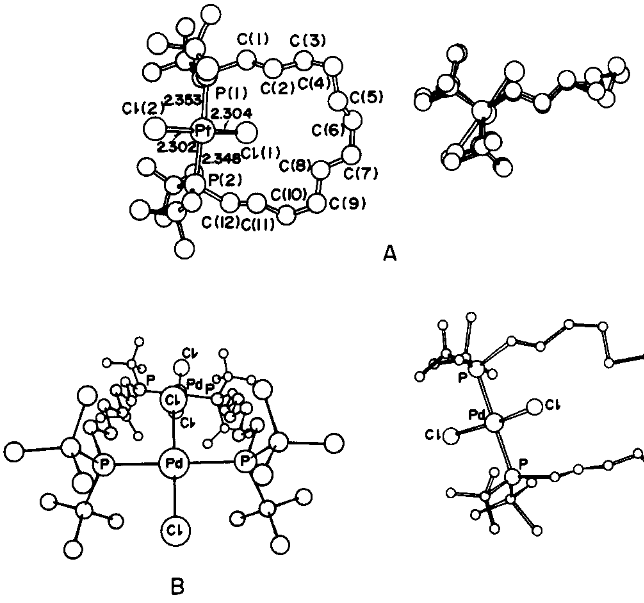


FIGURE 12 Structures of $[PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}]$ (A),[62] $[PdCl_2\{Bu^t_2P(CH_2)_7PBu^t_2\}]_2$ (B),[69] and $[PdCl_2\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]_2$ (C).[67]

(n = 9 or 10).[61] Next, a number of *trans*-$[MCl_2L]_x$ (M = Pd, Pt; $x = 1 - 3$), *trans*-$[MCl(CO)L]_x$ (M = Rh, Ir; x = 1 or 2), and some other related complexes were prepared and investigated with the ligands of the type, $Bu^t_2P(CH_2)_nPBu^t_2$. The structures of some of them are shown in Figure 12. One example of monomeric 15-membered chelate ring compounds is shown in A of Figure 12. The *tert*-butyl groups are eclipsed and the Pt-Cl bond axis is inclined toward the chelate ring plane. The structure of the 20-membered ring compound is shown in B of Figure 12. The polymethylene chains are in the extended conformation and the torsion angles of Pd-P-CH_2-CH_2 groups are very close to 60°. Because of steric interaction between the Pd-Cl and PBu^t_2 groups which are eclipsed, the chelate ring takes a barge (elongated boat) conformation. The barge conformation is also found in $[Pd_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$[68] and $[Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2]$.[78] It is interesting that the 16- or 20-membered chelate ring compound containing an N,N,N′,N′-tetramethyldiaminoalkane of the type $[Pd_2Cl_4\{Me_2N(CH_2)_nNMe_2\}_2]$ (n = 5 or 7) takes a sofa (elongated chair conformation as shown in Figure 13. The Pd-N-CH_2-CH_2 torsion angles are also close to 60°. Each Cl-Pd-Cl group is approximately vertical to the plane of the four nitrogens. Repulsion between the chlorines and the hydrogens of the methyl groups seems to be less important and each chlorine is eclipsed with one methyl group.

With a $Bu^t_2P(CH_2)_nPBu^t_2$ having an even number of methylene groups, a chelate with a strain-free conformation cannot be formed. In C of Figure 12, the structure of the complex $[Pd_2Cl_4\{Bu^t_2P(CH_2)_{10}PBu^t_2\}_2]$ which contains a 26-membered ring is shown.[60] There is a twist in the middle of the methylenic chain, although the conformation of the two Pd moieties are quite similar to that found in B of Figure 12.

The preparative procedure of *trans*-$[MCl_2L]_x$ (x = 1-3; M = Pd and Pt) is generally as follows: equimolar amounts of $[PdCl_2(NCPh)_2]$ or *trans*-$[PtCl_2(NCPh)_2]$ and $Bu^t_2P(CH_2)_nPBu^t_2$ are mixed in ethanol or 2-methoxyethanol. The concentration of

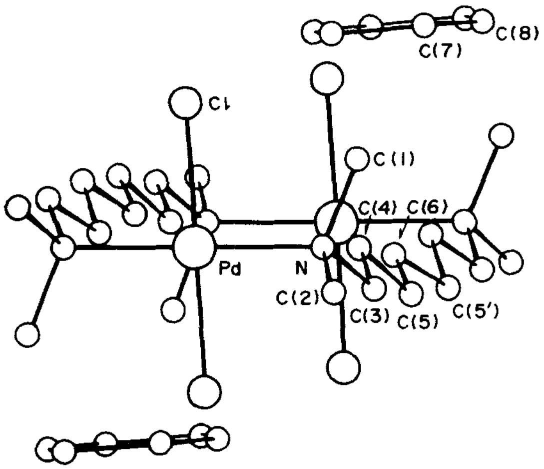


FIGURE 13[39] Structure of $[PdCl_2\{Me_2N(CH_2)_7NMe_2\}]_2 \cdot C_6H_6$.

each reactant is approximately 0.03 - 0.1 mol dm^{-3}. After the mixture is heated under reflux for ~20 h, the products are separaed by fractional crystallization and/or chromatography. Complexes containing the monodentate diphosphine ligand do not appear to be formed. The sterically demanding substituents on phosphorus atoms (*i.e.* *t*-butyl groups) are therefore very effective in stabilizing large chelate rings relative to unidentate structures. The yields of *trans*-$[PdCl_2L]_x$ and *trans*-$[PtCl_2L]_x$ reported in the papers are summarized in Table II.

TABLE II
Products obtained upon the reaction of $[MCl_2(NCPh)_2$ (M = Pd or Pt) with $Bu^t_2P(CH_2)_nPBu^t_2$(L).[63,68,91] Yield is given in parenthesis.

M	Number of methylene groups, *n*	Main products
Pd	5	$[PdCl_2L]_2$ (62%)
	6	$[PdCl_2L]_x$* (76%)
	7	$[PdCl_2L]_2$ (36%)
	8	$[PdCl_2L]_2$ (56%)
	9	$[PdCl_2L]_2$ (70%)
	10	$[PdCl_2L]$ (20%), $[PdCl_2L]_2$ (62%)
	12	$[PdCl_2L]$, $[PdCl_2L]_2$
Pt	5	$[PtCl_2L]_2$ (45%), $[PtCl_2L]_3$ $[PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$, $[PtCl(Bu^t_2PCH_2CH_2C{=}CHCH_2PBu^t_2)]$
	6	$[PtCl_2L]_x^*$, $[PtCl(Bu^t_2PCH_2CH_2CHCH_2CH_2CH_2PBu^t_2)]$
	8	$[PtCl_2L]_3$
	9	$[PtCl_2L]$, $[PtCl_2L]_2$, probably $[PtCl_2L]_3$
	10	$[PtCl_2L]$ (28%), $[PtCl_2L]_2$ (54%), probably $[PtCl_2L]_3$
	12	$[PtCl_2L]$ (18%), $[PtCl_2L]_2$ (15%), $[PtCl_2L]_3$ (33%)

*The value of *x* is unknown.

Table II indicates that when the number of the methylene groups "*n*" is less than 9 or 10, monomers are not formed, but dimers or sometimes trimers are formed. The monomers are formed at $n \geq 9$. This trend is the same as that observed for the reactions of $[CoCl_2(en)_2]Cl$ and N-N. However, the yields of the complexes containing the chelating diphosphine are better than those of the cobalt(III) complexes containing α,ω-diaminoalkanes, though the diphosphine complexes are prepared in rather higher concentrations than those used for the cobalt(III) complexes. In other words, the large chelate rings of $Bu^t_2P(CH_2)_nPBu^t_2$ are preferentially formed in the absence of a dilution technique. Shaw has pointed out the importance of an unusually small internal entropy of a complex containing a unidentate diphosphine and so it follows that the unusually small internal entropy loss on chelation is important.[92] This comes from the very bulky *tert*-butyl substituents. When a diphosphine is coordinated to a metal, the *tert*-butyl substituents will restrict the rotation around $M-P-CH_2$ bonds severely. Space-filling molecular models reveal that the preferred orientation around $MPCH_2CH_2CH_2$ bonds in the open-chain intermediate is the same as that found for the structures of the complexes such as *trans*-$[MCl_2L]_2$ determined by X-ray diffraction. Shaw called this effect the "*gem*-*tert*-butyl" effect. This is the extension of the "*gem*-dimethyl" effect (Thorpe-Ingold effect) observed for the cyclization of organic compounds. The latter effect has been used to explain the phenomenon that *gem*-dimethyl or similar groups make the formation of small ($\leq$ seven-membered) rings easy.

Treatment of *trans*-$[PtCl_2(NCPh)_2]$ with $Bu^t_2P(CH_2)_5Bu^t_2$ or $Bu^t_2P(CH_2)_6PBu^t_2$ gives rise to cyclometallated products as well as the large chelate ring compounds under mild conditions.[68,91] The complex *trans*-$[Pd_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ can also be converted into the cyclometallated complex $[PdCl_2(Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2)]$, though heating above 260°C is required.

Various large chelate ring compounds of rhodium and irridium have been prepared by the reactions of $Bu^t_2P(CH_2)_nPBu^t_2$ with rhodium(I), rhodium(III), iridium(I), and iridium(III) salts or complexes (Table I). When $Bu^t_2P(CH_2)_5PBu^t_2$ and $Bu^t_2P(CH_2)_6PBu^t_2$ are used as the ligands, cyclometallated complexes as well as the large chelate ring compounds are formed.[60,66,71,72,93] It is interesting that when one of such complexes $[RhHCl(Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2)]$ is treated with MeNC in the presence of $NaBPh_4$, a 16-membered chelate ring compound $[Rh_2(CNMe)\{Bu^t_2P(CH_2)_5PBu^t_2\}_2](BPh_4)$ is formed. The latter species can also be prepared by treating $[Rh(CNMe)_4](BPh_4)$ with $Bu^t_2P(CH_2)_5PBu^t_2$.[66]

When *tert*-butyl groups in $Bu^t_2P(CH_2)_nPBu^t_2$ are replaced by phenyl groups which are sterically less demanding, the ligands do not necessarily occupy trans positions of a metal center.[50,54,68] Treatment of *trans*-$[PtCl_2(NCBu^t)_2]$ with $Ph_2P(CH_2)_5PPh_2$ (L) in refluxing 2-methoxyethanol gave *cis*-$[PtCl_2L]_2$.[68]

McAuliffe *et al.* prepared platinum(II) complexes of a series of $Ph_2P(CH_2)_nPPh_2$ (L; $n = 7$–$12, 16$) as shown in case 14 of Table I.[54] They pointed out that the formation of the *cis* or *trans* isomer is critically dependent on the choice of starting materials. The use of $K_2[PtCl_4]$ gives *cis*-$[PtCl_2L]_x$ ($x = 1$ and/or 2), while the use of Zeise's salt $K[PtCl_3(C_2H_4)]$ gives *trans*-$[PtCl_2L]_x$ ($x = 1$ and/or 2). The *cis* isomer is thermodynamically more stable than *trans* isomer, because the *trans* isomer in acetone changes to *cis* isomer upon heating or the addition of excess L.

When $[Mo(CO)_6]$ or $[Mo(CO)_4(\text{norbornadiene})]$ reacts with $Ph_2PCH_2NHMe(CH_2)_2NHMeCH_2PPh_2$ (L), *cis*-$[Mo(CO)_4L]$ is formed where two phosphorus atoms are coordinated and the nitrogen atoms are uncoordinated.[56] This is a novel example of nine-membered chelate ring compounds evidenced by X-ray analysis.

Treatment of $[MCl(cod)]_2$ (M = Rh or Ir; cod = cyclooctadiene) in benzene with $Ph_2P(CH_2)_6PPh_2$(L) in the presence of CO gives *trans*-$[MCl(CO)L]_2$.[51] Upon refluxing $[MCl(cod)]_2$ (M = Rh or Ir) with the same ligand in mesitylene under nitrogen however, *trans*-$[MCl(Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2)]$ is obtained in a good yield.[51,94] The

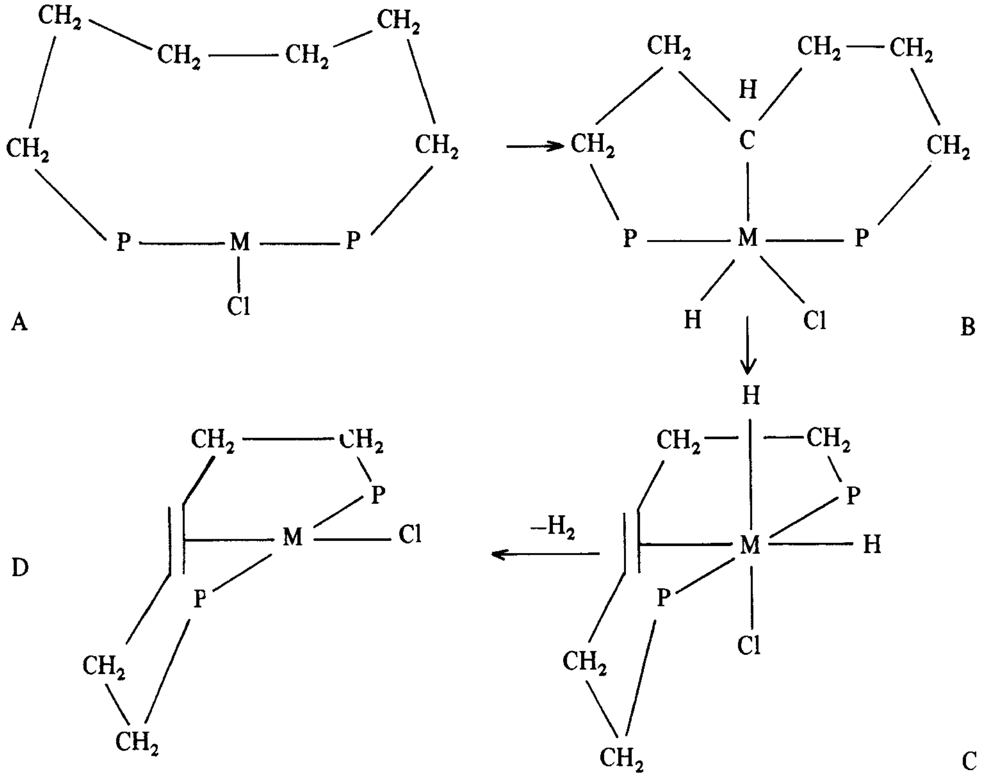
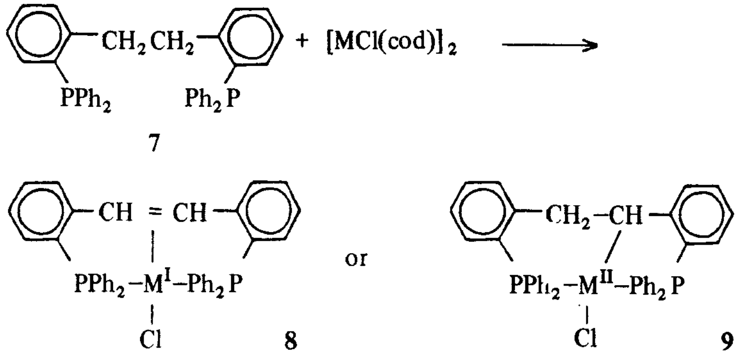


FIGURE 14[51] Proposed mechanism for the dehydrogenation of $Ph_2P(CH_2)_6PPh_2$ with rhodium(I) and iridium(I) complexes.

mechanism for this reaction has been presented by Clark (Figure 14):[51] The reaction most probably proceeds through the formation of *trans*-spanning diphosphine complex A in Figure 14. The abstraction of one proton from the methylenic chain occurs to give rise to complex B and then the olefin-dihydride complex C. The complex C loses molecular H_2 to give the final complex D.

It has been shown that similar reactions occur for 2,2′-bis(diphenylphosphino) bibenzyl:[95,96]



7

8

9

(4)

The rhodium(I) complex of **8**, $[\overline{\text{RhCl}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}{=}\text{CHC}_6\text{H}_4\text{PPh}_2\text{-}o)}]$ can also be prepared by the reaction of $\text{PPh}_2(\text{o-MeC}_6\text{H}_4)$ with $\text{RhCl}_3\cdot3\text{H}_2\text{O}$.[97] Again, the formation of a nine-membered chelate ring compound as the intermediate was postulated for reaction (4).[98] In fact, several nine-membered chelate ring compounds containing **7** were isolated later (case 15 in Table I).[55]

3.3 Complexes Containing 2,11-Bis(diphenylphosphinomethyl)benzo[c]phenanthrene and Derivatives

The above complexes have been prepared extensively by Venanzi and his colleagues. In Table III are summarized the complexes of this class. The ligand 2,11-bis(biphenylphosphinomethyl)benzo[c]phenanthrene (L^1) was originally designed to form square planar complexes of the type *trans*-$[\text{MX}_2\text{L}^1]$ in which the diphosphine ligand spans *trans*-positions.[101] In fact, a number of such complexes have been prepared. The *trans* structures were confirmed for some of them by X-ray methods. However, complexes having cis geometry *cis*-$[\text{PtCl}_2\text{L}^1]$ and *cis*-$[\text{PtH}(\text{PPh}_3)\text{L}^1]$ (BF_4) were also prepared recently.[107] As is expected from the size and rigidity of the ligand, the complex is severely distorted (Figure 15). Three to six coordinate complexes are now known. Three coordinate complexes $[\text{CuClL}^1]$, $[\text{AgClL}^1]$, and $[\text{AuClL}^1]$ are the first complete set of compounds of copper(I), silver(I), and gold(I) of the type $[\text{MXL}_2]$.[99,100] The PMP bond angles increase from 132°(Cu) to 141°(Ag) to 176°(Au). The five coordinate complexes have distorted trigonal bipyramidal structures with the two phosphorus atoms in axial positions. Even in six coordinate complexes prepared so far, the *trans*-spanning structures of the ligand are retained.

Complexes containing derivatives of L^1 have also been prepared. These are summarized in Table III.

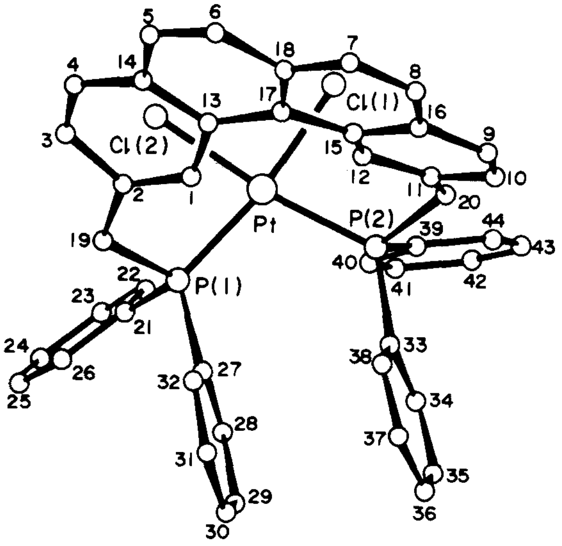
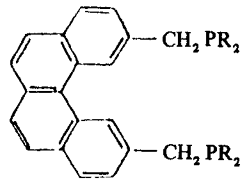


FIGURE 15[107] Structure of cis-$[\text{PtCl}_2\text{L}^1]$. L^1 = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene.

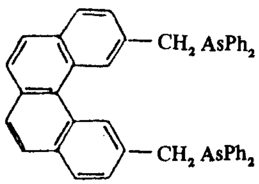
TABLE III

Complexes containing 2,11-bis(diphenylphosphinomethyl)-benzo[c]phenanthrene and derivatives

L =

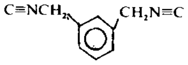
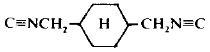
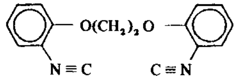
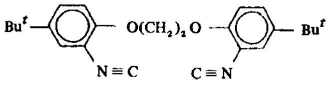
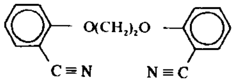
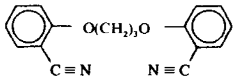
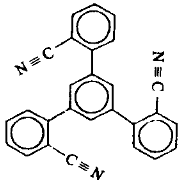


L_{As} =



Ligand	Complex	ref
	Three coordinate complex	
	$[MXL^1]$ ($M = Cu, Ag, Au$; $X = Cl, I, NO_3$); $[Ag(BF_4)L^1]$	99, 100
	Four coordinate complex	
	trans-$[NiX_2L^1]$ ($X = Cl, Br, I, NCS$); *trans*-$[MX_2L^1]$ ($M = Pd, Pt$; $X = Cl, Br, I$); *trans*-$[RuCl(NO)L^1]$;	
	trans-$[PtHXL^1]$ (BF_4) (X = acetone, PPh_3);	101–108
L^1:R = Ph	*trans*-$[Pt(Et)(CO)L^1](BF_4)$; *trans*-$[PtClXL^1]$ ($X = H, Et$); *cis*-$[PtCl_2L^1]$; *cis*-$[PtH(PPh_3)L^1](BF_4)$;	
	trans-$[MX(CO)L^1]$ ($M = Rh, Ir$; $X = Cl, Br, I, NCS$); *trans*-$[M(CO)(CH_3CN)L^1](BF_4)$ ($M = Rh, Ir$)	
	Five coordinate complex	
	$[M(CO)_3L^1]$ ($M = Fe, Ru$); $[RuCl(CO)XL^1]$ ($X = NO, P(OCH_2)_3CEt$)	106, 109
	Six coordinate complex	
	$[IrHX_2(CO)L^1]$ ($X = Cl, Br, I$); $[IrH_2I(CO)L^1]$; $[IrH_2(CO)(CH_3CN)L^1](BF_4)$; $[IrH_2(CO)_2L^1]$ (BF_4);	104, 108
	trans-$[IrCl_3(CO)L^1]$	
L^2:R = m-MeC_6H_4	*trans*-$[MCl_2L^2]$ ($M = Ni, Pd, Pt$); *trans*-$[Ni(NCS)_2L^2]$	110
L^3: R = p-$CH_3OC_6H_4$	*trans*-$[MCl_2L^3]$ ($M = Ni, Pd, Pt$); *trans*-$[Ni(NCS)_2L^3]$	110
L^4: R = m-$CF_3C_6H_4$	*trans*-$[MCl_2L^4]$ ($M = Ni, Pd, Pt$); *trans*-$[Ni(NCS)_2L^4]$; *trans*-$[PtXClL^4]$ ($X = H, Me$);	110, 111
	trans-$[PtX(\text{pyridine derivative})L^4]$ ($X = H, Me$)	
L^5: R = C_6H_{11}	*trans*-$[MCl_2L^5]$ ($M = Ni, Pd, Pt$); *trans*-$[Ni(NCS)_2L^5]$	110
L^6: R = Bu^t	*trans*-$[MCl_2L^6]$ ($M = Ni, Pd, Pt$); *trans*-$[Ni(NCS)_2L^6]$; *trans*-$[PtHClL^6]$	110
L_{As}	*trans*-$[MX_2L_{As}]$ ($M = Pd, Pt$; $X = Cl, Br, I$); *trans*-$[MCl(CO)L_{As}]$ ($M = Rh, Ir$);	112
	trans-$[IrCl(CO)L_{As}]_2$	

TABLE IV
Many-membered chelate ring compounds containing diisonitrile or dinitrile

Case		Complex	ref
1	diisonitrile ligand $C{\equiv}N(CH_2)_3N{\equiv}C$	$[Rh_2L_4]X_2$($X = Cl, BF_4$); $[Rh_2Cl_2L_4]Cl_2$; $[Rh_2Br_2L_4](Br_3)_2$; $[Rh_2I_2L_4](I_3)_2$; $[Rh_2(Me)IL_4]^{2+}$	113, 114
2	$C{\equiv}N(CH_2)_nN{\equiv}C$ ($n = 4, 6–8$)	$[Rh_2L_4](PF_6)_2$ ($n = 4, 6$); $[RhL_2](PF_6)$ ($n = 7, 8$)	115
3	$C{\equiv}N(CH_2)_nN{\equiv}C$ ($n = 3–6, 8$)	$[Rh_2L_4]^{2+}$ ($n = 3–6$); *trans*-$[Rh_2(Ph_2PCH_2PPh_2)_2L_2]^{2+}$ ($n = 3–6, 8$); $[RhL_2]^+$ ($n = 8$); $[Rh_2(PPh_3)_4L_2]^{2+}$ ($n = 3–6$); *cis*-$[Rh(PPh_3)_2L]^+$; *cis*-$[Rh(Ph_2PCH_2CH_2PPh_2)L]^+$	116
4		$[Rh_2L_4]^{2+}$; *trans*-$[Rh_2(Ph_2PCH_2PPh_2)_2L_2]^{2+}$	116
5		$[Rh_2L_4]^{2+}$; *trans*-$[Rh_2(Ph_2PCH_2PPh_2)_2L_2]^{2+}$	116
6		$[Cr(CO)_4L]$; $[Mo(CO)_4L]$; $[W(CO)_4L]$; *fac*-$[MnBr(CO)_3L]$; $[CpFe(CO)L](PF_6)$; $[CpFe(CS)L](PF_6)$; *cis*-$[FeClXL_2]$ ($X = Cl, SnCl_3, CNMe, CO$); *cis*-$[Fe(SnCl_3)_2L]$; *trans*-$[FeCl_2L_2]$; $[RhL_2]^+$; $[Rh_2I_2L_4]^{2+}$; $[Ni(CO)_2L]$	117–121
7		$[M(CO)_4L]$ ($M = Cr, Mo$); $[CrL_3](PF_6)_x$ ($x = 0, 1, 2$); $[MnL_3](PF_6)_x$ ($x = 1, 2$); $[CpFe(CS)L](PF)_6$; $[FeL_3](PF_6)_2$; $[CoL_3](PF_6)_3$; $[L_2CoLCoL_2](PF_6)_2$; *trans*-$[CoBr_2L_2]$; *trans*-$[CoBr_2L_2](Br_3)$; $[RhL_2]^+$; $[Ni(CO)_2L]$; $[NiL_2]$; $[CuL_2](BF_4)$	118, 120
	dinitrile ligand		
8		*fac*-$[MnBr(CO)_3L]$; $[CpFe(CS)L](PF_6)$; $[PtCl_2L]$	117, 118
9		*fac*-$[MnBr(CO)_3L]$	122
10		*fac*-$[MnBr(CO)_3L]$; *fac*-$[ReBr(CO)_3L]$; *fac*-$[Mn(CO)_3L](PF_6)$; *fac*-$[Re(CO)_3L](PF_6)$	122

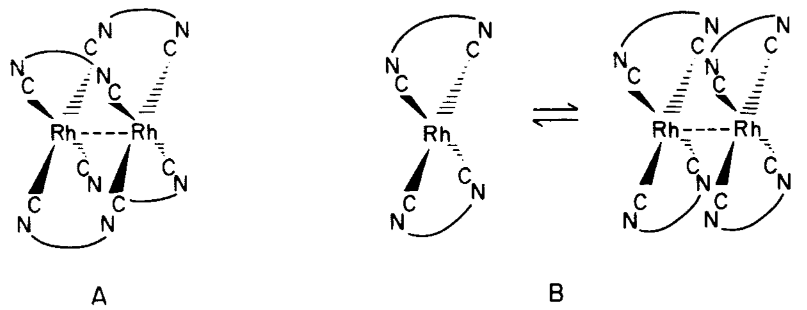
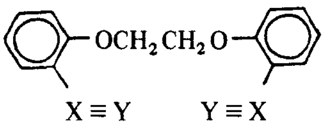


FIGURE 16 Assumed structures of rhodium(I) complexes containing $CN(CH_2)_nNC$ ligands. ⌒ denotes $(CH)_2)_n$ group. Charges on the complexes are omitted. A: $[Rh_2\{CN(CH_2)_nNC\}_4]^{2+}$ (n = 3, 4, 6) B: $[Rh\{CN(CH_2)_nNC\}_2]^+$ (n = 7, 8). The species is in equilibrium with $[Rh_2\{CN(CH_2)_nCN\}_4]^{2+}$.

3.4 Complexes Containing Diisonitriles and Dinitriles

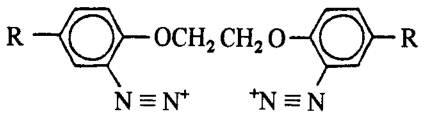
The above complexes are summarized in Table IV. The first reported complex belonging to this class was $[Rh_2\{CN(CH_2)_3NC\}_4]Cl_2$ containing a weak rhodium-rhodium interaction.[113] The structure of the species was assumed to be as shown in A of Figure 16. This was verified later by an X-ray crystal structure analysis.[114] The electronic spectrum of this dimer shows concentration dependence and suggests that the dimer aggregates further in solution to form higher oligomers. Rhodium(I) complexes containing $CN(CH_2)_nNC$ with various methylenic chain length were then prepared.[115] The reactions of $[RhCl(cod)]_2$ with the ligands followed by metathesis give complexes of the types $[Rh_2L_4](PF_6)_2$ (L = $CN(CH_2)_{4\text{ or }6}NC$) and $[RhL_2](PF_6)$ (L = $CN(CH_2)_{7\text{ or }8}NC$). The complexes of the former type are assumed to have the structure as shown in A of Figure 16, because these ligands are sterically incapable of chelation and bridge two metal centers to give cationic dimers. However, the longer ligand $CN(CH_2)_7NC$ or $CN(CH_2)_8NC$ can chelate so that the monomeric square planar complex $[RhL_2]^+$ is formed. The concentration dependence of the electronic spectra for the species indicates that $[RhL_2]^+$ forms a dimer. The proposed structures of the monomer and dimer are shown in B of Figure 16. More extensive work was carried out by Yaneff and Powell on the complexes containing $CN(CH_2)_nNC$ and its homologues.[116]

Recently, as an extension of a study of the synthesis and reactivity of chelating diisonitrile ligands, Angelici *et al.* reported the preparation of the complexes containing a less flexible ligand (Table IV):



Where -X≡Y = -N≡C and -C≡N. The ligands readily chelate to metal ions: Upon refluxing $[PtCl_2(NCPh)_2]$ with L (-X≡Y = -CN) in 1,2-dichloroethane, the ligand L displaces the monodentate NCPh to give $[PtCl_2L]$ in a good yield. This indicates the favored coordination of the chelate ligand over its monodentate analogue.[117] In special situations, the ligand L (-X≡Y = -NC) bridges two metals as in $[(CO)_5CrLCr(CO)_5]$ and $[(CO)_5WLW(CO)_5]$.[117,118]

Michelin and Angelici attempted to prepare complexes which contain chelating bis(aryldiazonium) ligands(L) of the structure:



R = H, Bu^t

However, unlike the related diisonitrile and dinitrile, the ligands L prefer to bridge two metal centers rather than form a chelate, like $[Cp(CO)_2MoLMo(CO)_2Cp]$.[123]

3.5 Other Large Chelate Ring Compounds

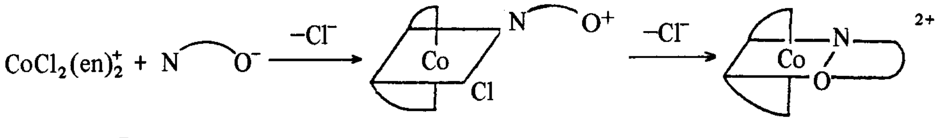
The first reported examples of large chelate ring compounds containing sulfur donors were $[MCl_2L]$ (M = Pd or Pt) containing $PhS(CH_2)_{12}SPh$ as L.[76,77] The compounds separate from solutions on long standing. Treatment of $[PdCl_4]^{2-}$ with $Me_2As(CH_2)_{12}AsMe_2$(L) in ethanol/dichloromethane gives a 15-membered chelate ring compound $[PdCl_2L]$.[79] Again, the complex takes a long time to crystallize out. These facts suggest the presence of many conformers in solutions.

Reactions of $[MCl_2(NCPh)_2]$ (M = Pd, Pt) with $Bu^tS(CH_2)_5SBu^t$ give $[MCl_2L]_2$ in good yields without resort to the dilution technique.[78]

A series of complexes of the type $[PtCl_2L]_x$ were prepared, where L denotes $Ph_2As(CH_2)_nAsPh_2$.[83] When $[PtCl_4]^{2-}$ is used as the starting material, *cis*-dimers ($x = 2$) are formed. The use of $[PtCl_3(C_2H_4)]^-$ gives rise to the *trans*-monomers ($x = 1$). This result is similar to that observed for the reactions of platinum(II) with $Ph_2P(CH_2)_nPPh_2$ as mentioned in Section 3.2.[54]

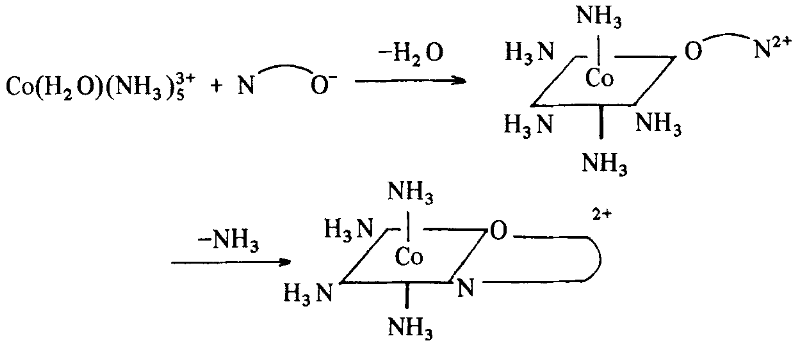
Nine-membered chelate ring compounds of rhodium(I) and iridium(I) containing 2,2′-bis(diphenylarsino)bibenzyl (L = o-$Ph_2AsC_6H_4CH_2CH_2C_6H_4AsPh_2$-$o$) were prepared (case 38 in Table I).[55] The iridium complex $[IrCl(CO)L]$ changes to $[IrHCl(CO)\{o\text{-}Ph_2AsC_6H_4CHCH_2C_6H_4AsPh_2\text{-}o\}]$ under reflux in chloroform. On the other hand, the phosphorus analogue $[IrCl(CO)\{o\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}o\}]$ changes in solution at room temperature to give $[IrHCl(CO)\{o\text{-}Ph_2PC_6H_4CHCH_2C_6H_4PPh_2\text{-}o\}]$. The cyclometallation of the complex containing the diphosphine ligand occurs more easily than that containing the arsine homologue.

The coordination with a metal ion of a bidentate ligand containing heterodonor atoms gives rise to the problem of which donor atom is coordinated first to the metal center. Upon reacting *cis*-$[CoCl_2(en)_2]Cl$ with a 12-aminoacidate $NH_2(CH_2)_{11}COO^-$ (ad$^-$) in Me_2SO and then acidifying the mixture, a 15-membered chelate ring compound $[Co(ad)(en)_2]^{2+}$, $[CoCl(N\text{-}adH)(en)_2]^{2+}$ and several higher charged species were obtained.[86] The second species is the complex containing the N-bonded $NH_2(CH_2)_{11}COOH$ which is regarded as the result of the "Meisenheimer reaction". The products indicate that $[Co(ad)(en)_2]^{2+}$ is formed by the following sequence. Coordination of the amino group in ad$^-$ precedes that of the carboxylate group:



where $N\frown O^-$ denotes the 12-aminoacidate. The yield of $[Co(ad)(en)_2]^{2+}$ amounts to 30% without the dilution technique. This may come from low solubility of adH which satisfies naturally the condition of high dilution.

On the other hand, the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with ad^- gives $[Co(ad)(NH_3)_4]^{2+}$, $[Co(O\text{-}adH)(NH_3)_5]^{3+}$, $[Co(NH_3)_6]^{3+}$, and some other species. In this case, a complex containing *O*-bonded monodentate $NH_3(CH_2)_{11}COO$ is formed. This result indicates that the coordination of the carboxylate group in ad^- precedes that of the amino group. This sequence is the reverse of the reaction of ad^- with $[CoCl_2(en)_2]^+$:



Analogous preparations by use of $NH_2(CH_2)_5COO^-$ (ah^-) afforded $[CoCl(en)_2(N\text{-}ahH)]^{2+}$ and $[Co(O\text{-}ahH)(NH_3)_5]^{3+}$. However, no formation of any complexes containing the chelated ah^- was observed. This result is consistent with the instability of the medium-sized chelate ring compounds.

Chelate ring opening of a seven-membered ring compound $[Co\{NH_2(CH_2)_3COO\}(en)_2]^{2+}$ occurs in an acidic solution:[124]

The complex $[Co\{NH_2(CH_2)_{11}COO\}(en)_2]^{2+}$ undergoes a similar reaction.[125] Kinetic study for $[Co\{NH_2(CH_2)_nCOO\}(en)_2]^{2+}$ revealed that the rate of chelate ring opening decreases in the following order:[125]

$$[Co\{NH_2(CH_2)_3COO\}(en)_2]^{2+} + H_3O^+ \longrightarrow$$
$$[Co\{\text{N-bonded } NH_2(CH_2)_3COOH\}(H_2O)(en)_2]^{3+}.$$

$n = 3$ (seven-membered ring) $>$ $n = 11$ (15-membered ring) $>$ $n = 2$ (six-membered ring)

It is interesting that the seven-membered ring opens more rapidly than the 15-membered ring.

4. EPILOGUE

Syntheses of many-membered chelate ring compounds appear to be easier than have previously been appreciated. Especially, use of properly designed ligands makes the formation of the many-membered chelate ring compounds remarkably favorable. However, medium sized chelate ring compounds are still very scarce. Continuing efforts for preparing such compounds and innovation of synthetic methods are needed.

In this review, eight-membered chelate ring compounds containing bis(diphenylphosphino)methane or its homologues are omitted, because there are already excellent reviews on the subject.[126–128]

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