(Tertiary phosphinomacrocycle)cobalt(II) Halide Coordination Chemistry. Identification and Interconversion of Four Types of Complexes[†,1]

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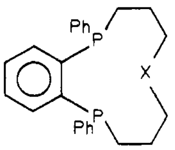
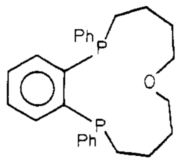
The cobalt(II) halide coordination chemistry of six macrocyclic (11-, 13-, and 14-membered) ligands (MC) containing the 1,2-bis(phenylphosphino)benzene moiety and, with one exception, at least one other potential ligating site (oxygen or nitrogen) has been studied. Four different types of complexes have been isolated, depending on the reaction conditions and the MC. If the stoichiometry 1:0.5 (MC:$CoHal_2$) is used, type I complexes are formed kinetically, which are trans octahedral $(MC)_2CoHal_2$ species with elongated Co–Hal bonds (shown by single-crystal X-ray crystallography for the bromide), as would be expected for a 19-electron system. The thermodynamic product (type II) with the 1:0.5 stoichiometry is either $[(MC)_2Co]2Hal$ or $[(MC)_2CoHal]Hal$, with the evidence favoring the former, since the ^{31}P NMR and electronic spectra are independent of the halogen. The type I and II materials are formed if the additional ligating site in the MC is ineffectual, e.g., aryl N, aryl O, or ether O, which forms seven-membered chelates. If 1:1 stoichiometries are utilized, type III species are produced that are $[(MC)_2Co][CoHal_4]$, which feature UV absorptions identical with those for type II species but which differ in the visible region. When the MC is 11-membered and contains either NMe ($11\text{-}P_2NMe$) or O ($11\text{-}P_2O$), type IV complexes are formed, with the stoichiometry $(MC)CoHal_2$ and electronic spectra similar to those for known (tridentate ligand)$CoHal_2$ complexes. The type IV species may be transformed into type I complexes at rates which depend on MC ($11\text{-}P_2O$ > $11\text{-}P_2NMe$), halogen (Cl > Br ≃ I), and solvent (CH_2Cl_2 > THF).

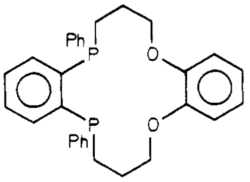
The synthesis of a number of tertiary phosphine-containing macrocycles has been described by several groups in recent years.[2] Some reports of transition-metal complexes of these species have also appeared.[3] We now report detailed studies of the complexation of cobalt(II) halides by several members of this type of macrocyclic ligand in which we show the effect of ligand structure as well as ligand nucleophilicity on complexing ability.



1, X = CH_2 ($11\text{-}P_2$)
2a, X = NPh ($11\text{-}P_2NPh$)
2b, X = $NC_6H_4Br\text{-}p$
3, X = O ($11\text{-}P_2O$)
4, X = NMe ($11\text{-}P_2NMe$)



5 ($13\text{-}P_2O$)



6 ($14\text{-}P_2O_2$)

All of the ligands described here contain the *cis*-1,2-bis(alkylphenylphosphino)benzene moiety, which is quite rare in transition-metal coordination chemistry.[4] The known chelating diphosphine–$CoCl_2$ complexes fall into four general classes: (a) tetrahedral 1:1 complexes, $(P_2)CoCl_2$;[5] (b) 5-coordinate 2:1 complexes, $[(P_2)_2CoCl]^+Cl^-$;[5a,6] (c) square-planar 2:2 complexes, $[(P_2)_2Co]^{2+}[CoCl_4]^{2-}$;[7,8] and (d) 5-coordinate 1:1 complexes, when the diphosphine ligand contains a third coordination site, $(P_2L)CoCl_2$.[5b] For example, the ligand 1,2-bis(diphenylphosphino)ethane gives complexes of the types a–c[5a,6] while 1,2-bis(diphenylphosphino)benzene forms only complexes of type c.[7a] With diphosphine ligands of the type $(Ph_2PCH_2CH_2)X$, type a complexes are formed when X = O, while type d complexes are formed when X = NH or NMe.[5c] With one exception,[2c] there are no known octahedral complexes of Co(II) which involve four phosphine ligands, and the unique case involves a macrocycle containing four phosphino and two ether sites highly favorably disposed for an octahedral complex. This paper presents evidence for the formation of metastable octahedral complexes of the type $(P_2)_2CoHal_2$ and their thermally acti-

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[†] Dedicated to the memory of Professor Rowland (Rolly) Pettit, a close friend and valued colleague.

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Table I. Elemental Analyses for the Various (Macrocycle)cobalt(II) Halide Complexes

	% C		% H		% halogen[a]	
	calcd	found	calcd	found	calcd	found
		Type I				
$(1)_2CoCl_2{\cdot}(H_2O)_{2.5}$[b]	63.50	63.48	6.50	6.49		
$(2a)_2CoCl_2{\cdot}(H_2O)_{2.5}$[b]	65.51	65.71	6.05	6.52		
$(3)_2CoCl_2{\cdot}(H_2O)_{1.5}$[b]	61.22	61.20	5.89	6.41	7.53	7.18
$(5)_2CoCl_2{\cdot}(H_2O)_{1.5}$[b]	62.59	62.68	6.36	6.28		
$(6)_2CoCl_2{\cdot}(H_2O)_{3.5}$[b]	62.00	61.98	5.81	5.91		
$(1)_2CoBr_2{\cdot}(H_2O)_{4.5}$[b]	55.56	55.44	6.06	5.89	14.79	14.62
$(2b)_2CoBr_2$	54.94	54.87	4.61	4.77	24.37	24.10
$(1)_2CoI_2$	54.91	54.81	5.16	5.24	23.21	23.48
$(5)_2CoI_2$	54.14	54.05	5.24	5.33	22.00	22.02
		Type II				
$(1)_2CoCl_2{\cdot}(CHCl_3)$[c]	59.46	59.38	5.57	5.94		
$(2b)_2CoCl_2{\cdot}(CHCl_3)$[c]	54.58	55.10	4.58	4.80		
		Type III				
$[(1)_2Co][CoCl_4]$	57.71	57.47	5.42	5.64		
$[(6)_2Co][CoCl_4]{\cdot}(CHCl_3)_{0.4}$[c]	56.79	56.84	4.76	5.32	14.51	14.45
		Type IV				
$(3)CoBr_2{\cdot}(CHCl_3)$[c]	41.09	40.57	3.72	3.69	21.87	22.48
$(3)CoI_2{\cdot}(CHCl_3)$[c]	36.41	36.98	3.30	3.40		
$(4)CoCl_2{\cdot}(CHCl_3)$[c]	47.70	47.08	4.62	4.64	27.08	27.23
$(4)CoBr_2{\cdot}(CHCl_3)$[c]	42.00	42.48	4.07	4.15	21.49	22.34
$(4)CoI_2$	41.81	41.71	4.07	4.16	35.34	35.22

[a] Halogen analysis is for that associated with the metal. [b] Presence of water was confirmed by IR spectroscopy. [c] Presence of chloroform was confirmed by ^1H NMR spectroscopy.

vated conversions into several other species.

Results

Complexations by Macrocycles Exhibiting Only Bidentate Behavior. The reactions described below have led to the isolation of three different complexes, depending on the reaction conditions. Reaction of ligands **1**–**3**, **5**, or **6** with 0.5 equiv of $CoCl_2{\cdot}6H_2O$ in tetrahydrofuran or tetrahydrofuran–ethanol solutions gave yellow complexes (type I, λ_{max} 325 nm (ϵ 1.7 × 10^4 M^{-1} cm^{-1})) which precipitated as amorphous powders. A similar reaction with anhydrous cobalt(II) chloride gave microcrystalline yellow precipitates with the same UV spectra. Dissolution of either material in dichloromethane led to its transformation into a complex with λ_{max} 356 nm (ϵ 1.7 × 10^4 M^{-1} cm^{-1}), and an isosbestic point was observed at 337 nm. Evaporation of dichloromethane from the latter complex gave brown glasses, which upon crystallization from hot chloroform–hexane gave green crystals (type II complex) with λ_{max} 356 (ϵ 1.7 × 10^4 M^{-1} cm^{-1}) and 600 nm (ϵ 1.4 × 10^2 M^{-1} cm^{-1}).

The rate of the 325 → 350 nm transformation was found to be a function of the macrocycle: 14-P_2O_2 > 13-P_2O_2 ≈ 11-P_2NPh > 11-P_2 ≈ 11-P_2O. The half-lives for the reactions, as crudely determined by the time required for the two peaks to reach equal intensity, ranged from less than 1 min for the 14-P_2O_2 complex to about 30 min for the 11-P_2 species. The solvent also plays a role in this transformation; for example, the 11-P_2 species has half-lives of about 15 h in methanol or acetonitrile, as compared to 15 min in dichloromethane.

When anhydrous cobalt(II) bromide (0.5 equiv) was reacted with the above-described macrocycles, analogous results were obtained, except with **3** (11-P_2O), which gave a purple complex (vide infra). The initially formed yellow-green (type I) complexes exhibited absorption maxima at 310 nm (ϵ 5.4 × 10^2 M^{-1} cm^{-1}). These complexes underwent transformation into materials with λ_{max} 356 nm (ϵ 1.7 × 10^4 M^{-1} cm^{-1}) but at much reduced rates relative to the chlorides; the $(1)_2CoBr_2$ species had a half-life of 12 h in boiling dichloromethane as opposed to 30 min at room temperature for the corresponding chloride. As with the chlorides, the bromide complexes were isolated as brown glasses upon removal of dichloromethane and crystallization from hot chloroform–hexane gave green crystalline (type II) materials with UV–vis spectra essentially the same as those described for the chloride complexes.

The complexation with cobalt(II) iodide hexahydrate as described above for the bromide gave initially orange microcrystalline species [λ_{max} at 312 (ϵ 2.9 × 10^3 M^{-1} cm^{-1}) and 725 nm (ϵ 1.0 × 10^3 M^{-1} cm^{-1})]. A purple complex was obtained with 11-P_2O (vide infra). The subsequent behavior of the orange complex was essentially identical with the corresponding bromide complexes.

The combustion analytical data (Table I) for the type I complexes are in accord with the formulation $(MC)_2CoX_2{\cdot}(H_2O)_n$, where MC = macrocycle and n is the range 0–4.5, and the green type II complexes were in agreement with the $(MC)_2CoCl_2{\cdot}(CHCl_3)_n$ formulation.

The reaction in tetrahydrofuran of the above-described macrocycles with 1.0 equiv of cobalt(II) chloride or bromide gave green crystalline materials after removal of solvent and recrystallization from chloroform–hexane. The UV absorption spectra were identical for all the halides, λ_{max} 356 nm (ϵ 1.7 × 10^4 M^{-1} cm^{-1}) but differed in the visible region (Table II). The combustion analyses were consistent with the formulation $[(MC)_2Co][CoHal_4]{\cdot}(CHCl_3)_n$ (Table I).

Complexations by Macrocycles Exhibiting Tridentate Behavior. The reactions of **3** and **4** with the cobalt(II) halides in THF led to the isolation of burgundy to purple powders or microcrystalline materials (type IV) which after recrystallization from chloroform–hexane had elemental compositions (Table I) consistent with the formulation $(MC)CoHal_2{\cdot}(CHCl_3)_n$. The electronic spectra of these complexes were quite different from those of type I–III complexes, with a major absorption in the 510–535-nm region (ϵ ~10^3 M^{-1} cm^{-1}).

The type IV materials may be transformed into type I species in the presence of excess ligands, and the process

Table II. Ultraviolet-Visible Absorptions and Effective Magnetic Moments for Various (Macrocycle)cobalt(II) Halide Complexes

	UV-vis λ_{max} nm (ϵ, M^{-1} cm^{-1})[a]	μ_{eff}, μ_B
	Type I	
$(MC)_2CoCl_2$[b]	320 (1.7×10^4)	2.1 (MC = 7)
$(MC)_2CoBr_2$[b]	310 (1.8×10^4), 410 (1.8×10^3), 710 (5.4×10^2)	
$(MC)_2CoI_2$[b]	312 (1.9×10^4), 456 (2.9×10^3), 725 (1.0×10^3)	2.3 (MC = 1)
	Type II	
$(MC)_2CoX_2$[b,c]	356 (1.7×10^4), 600 (1.4×10^2)	2.9,[d] 3.3[e]
	Type III	
$[(MC)_2Co][CoCl_4]$[b]	356 (1.7×10^4), 575 (2.4×10^2), 675 (4.0×10^2)	4.0 (MC = 1), 3.4 (MC = 7)[f]
$[(MC)_2Co][CoBr_4]$[b]	356 (1.7×10^4), 605 (2.8×10^2), 690 (4.6×10^2)	
$[(MC)_2Co][CoI_4]$[b]	356 (1.7×10^4), 645 (3.0×10^2), 725 (5.1×10^2)	
	Type IV	
$(3)CoCl_2$	510 (8.9×10^2), 280 sh (3.7×10^3)	3.5
$(3)CoBr_2$	520 (6.5×10^2), 330 sh (1.4×10^3)	2.9
$(3)CoI_2$	535 (1.0×10^3), 465 sh (7.6×10^2), 350 sh (3.0×10^3)	2.7
$(4)CoCl_2$	520 (5.5×10^2), 340 sh (8.7×10^2)	2.3
$(4)CoBr_2$	525 (9.0×10^2), 330 sh (2.0×10^3)	3.0
$(4)CoI_2$	530 (1.1×10^3), 460 sh (7.0×10^2), 340 sh (3.7×10^3)	2.8

[a] Carried out in CH_2Cl_2 solutions. [b] Spectra are independent of macrocycle (MC). [c] Spectra are independent of halogen. [d] $(\mathbf{2b})_2CoCl_2$. [e] $(\mathbf{1})_2CoBr_2$. [f] Value given is per cobalt atom.

is quite facile with (**3**)$CoCl_2$. With 1:1 ligand to metal salt stoichiometry, yellow type I complex was formed along with purple type IV; the corresponding type IV bromides and iodides were formed exclusively with 1:1 stoichiometry. Similarly, only type IV species were formed with **4** utilizing any of the three cobalt(II) halides. Although all of the type IV complexes could be converted into type I, widely varying rates were observed, depending on the ligand, halogen, and solvent. Crude rate comparisons showed that under identical conditions (5.0×10^{-4} M complex, 1.5×10^{-3} M MC in $CHCl_3$ at 25 °C), (**3**)$CoBr_2$ was about thirty times more labile than (**4**)$CoBr_2$. The reactions are much slower in THF, but lack of solubility of the complexes precluded any meaningful rate comparisons.

Discussion

The reaction of ligands **1**, **2**, **5**, **6**, and under proper conditions **3** with the cobalt(II) halides (2:1 molar ratio) in THF gives type I complexes, which given sufficient time and activation energy are transformed cleanly (isosbestic point in the UV spectrum) to species of type II. The nature of the type I complexes remained problematic until we were able to isolate X-ray quality crystals of the complex $(\mathbf{1})_2CoBr_2$, the structure of which is depicted in an ORTEP plot (Figure 1).[9] This centrosymmetric structure has normal cobalt–phosphorus bond lengths (2.25 and 2.29 Å), but the cobalt–bromide bond lengths are very long (2.84 Å). A search of the Cambridge Crystallographic Data Center Structural Database[10] revealed only four structures of cobalt(II)–phosphine complexes which contain bromine with Co–Br bond lengths in the range of 2.03–2.54 Å). The long Co–Br bonds in $(\mathbf{1})_2CoBr_2$ are a consequence of a d_{z^2} ground state for the unpaired spin,[11] in which a tetragonal distortion lowers the energy of the d_{z^2} orbital. The observed effective magnetic moments for two of the type I complexes are consistent with a spin-paired ground state[8,12] (see Table II, entries for $(\mathbf{1})_2CoI_2$ and $(\mathbf{6})_2CoCl_2$).[13]

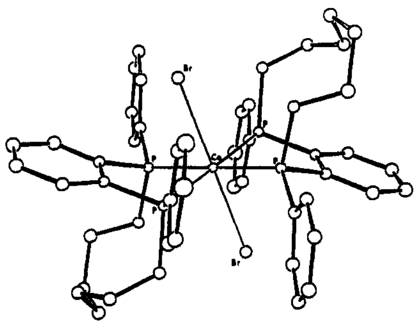
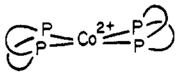


Figure 1. ORTEP representation of $(\mathbf{1})_2CoBr_2$.[9]

The ORTEP plot shown in Figure 1 also shows that the halogen atoms are relatively shielded by the organic superstructure attached to the phosphine ligand sites. If solvation of the halide ions is important in the type I → type II transformation, then the inhibition of this process by the "loop" between phosphino sites may account for the observation of type I complexes with the macrocyclic ligands but not with many other chelating diphosphines.[5a,6,7,11,14] Consistent with this notion also is the reactivity order as a function of MC, where the type I → type II transformation is fastest with the largest loop (**6**) and slowest with the smallest (**1** and **3**).



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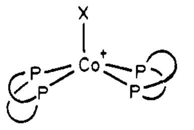

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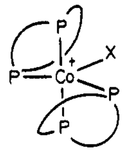

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The structure of the type II complexes may be either planar tetracoordinate (**7**) or pentacoordinate square pyramidal (**8**) or trigonal bipyramidal (**9**), the latter two having been shown in at least one case to be quite similar in energy.[15] We favor structure **7** for the type II species since their electronic spectra match those of the tetrahalocobaltate type III complexes, which have the dicationic **8** moiety.[7a,b] Considerable effort was expended on attempts

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[9] We thank Professor R. E. Davis for the structure determination, which was refined to R = 0.055. The details of this structure will be published elsewhere.

[10] The Structural Database is maintained by the Cambridge Crystallographic Data Center, Department of Chemistry, Cambridge CB21EW, England. Our searches were carried out by Professor Davis[9] on a local copy of the October 1980 issue of the Database, using programs originating at the Data Center.

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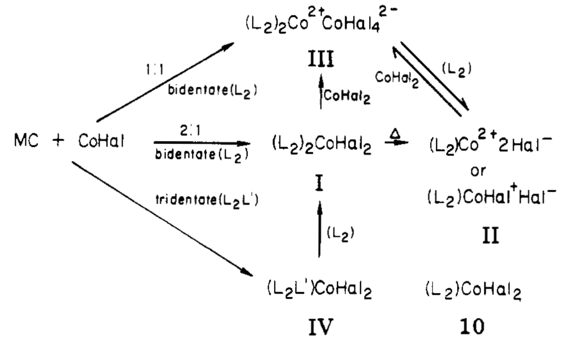
to prepare X-ray quality crystals of type II materials, to no avail. The effective magnetic moments of two of the type II materials are consistent with either the 7 or 8/9 structure in a spin-paired state.[7a,12] The ^{31}P NMR spectra of $(1)_2CoCl_2$ and $(1)_2CoBr_2$ are also consistent with type II species having structure 7; both exhibit a broadened singlet at δ 43.9 (coordination chemical shift = 69.3 ppm)[16] in $CDCl_3$. Presumably, if the structures were 8 or 9, the nature of the halogen attached to cobalt would affect the observed ^{31}P NMR chemical shift, as well as the UV spectrum, neither of which happens. We noted also that addition of 1 to a solution of $(1)_2CoCl_2$ did not change the ^{31}P NMR absorption of the metal complex and the chemical shift of 1 was sharp and where it was expected for the free ligand (−25.4 ppm[2a]).

In contrast to the above reactions, when ligands **3** and **4** are reacted in THF with the cobalt(II) halides in a 1:1 molar ratio, burgundy to purple powders or microcrystals precipitated (type IV). The elemental analysis of these species indicated a 1:1 stoichiometry and the spectral properties were similar to complexes formed from cobalt(II) halides and open-chain PNP tridentate ligands.[5,17] The trend from high to low effective magnetic moments of the species $(\mathbf{3})CoCl_2 \rightarrow (\mathbf{3})CoI_2$ is similar to that for 2,6-bis((diphenylphosphino)ethyl)pyridine,[17b] but the complexes from **4** appear not to follow the same trend. The magnetic moments are indicative of a ground ^2E state with a thermally accessible ^4A state.[17] The structure of the type IV materials (P_2X)CoHal may be either trigonal bipyramidal or square pyramidal in the extreme, and the similarity in the energies of the two had been noted in at least one case, albeit with cationic species.[15] We tend to favor the latter structure based on the study of Dreiding molecular models, with the square-pyramidal case being modeled after a structure that we have recently determined for $(11\text{-}P_2NH)NiCl_2$.[18]

In the presence of excess MC, type IV materials are transformed into type I species at rates which are dependent on the nature of MC, the halogens attached to the metal, and the solvent. Presumably, this transformation is initiated by deligation of either the oxygen or nitrogen site, which opens up a coordination site for the phosphine of another MC. The rate difference between $(\mathbf{3})CoBr_2$ and $(\mathbf{4})CoBr_2$ is thus a reflection of the superior ligating ability of R_2NMe over R_2O toward the Co(II) center. The fact that the reactions are slower in THF than CH_2Cl_2 is a measure of the competition of MC for the open coordination site with solvent, where THF is a much better donor than CH_2Cl_2.

All of the observations concerning the coordination chemistry of the macrocycles (MC) in this study of the cobalt halides are summarized in Scheme I. The nucleophilicity of the ligating sites in addition to the phosphines, as well as the size of the chelate ring formed, determine whether or not the MC will behave in a bidentate or tridentate fashion. Ligand **1**, of course, must behave only as a bidentate, and we have noted earlier that **2a** did not utilize the anilino nitrogen center as a ligand in the coordination of group 6 metal carbonyls, whereas the trialkyl nitrogen atom was so used.[3b] It might be argued that the oxygen atoms in **6** are inappropriately situated to ligate the metal center, but we have determined the structure of a species which exhibits *fac* coordination of the $Mo(CO)_3$ moiety by the sulfur analogue of **6** $(14\text{-}P_2S_2)$ and the ligand appears to be relatively strain-free in the complex.[19] Thus, conjugation of the oxygen atoms with the aryl ring which reduces nucleophilicity is a more likely explanation for the lack of involvement in coordination by the oxygen atoms in **6**. The comparison of **3** and **5** is interesting; the former behaves as a tridentate ligand but the latter does not. Examination of Dreiding molecular models of a hypothetical octahedral complex with **5** reveals it to be angle strain-free but with torsional strain problems. With **3** in an octahedral complex, the ligand appears to be relatively torsion strain-free, but angle strain is present. Apparently, the formation of two seven-membered chelates is sufficiently disfavored relative to coordination by the phosphino site of another MC, that it is simply not competitive.

Scheme I



It is useful to recognize the number of valence electrons at cobalt in the four species identified with Roman numerals in Scheme I: I, 19; II, 17 or 15; III, 15; IV, 17. Presumably, the reaction of MC with $CoHal_2$ is initiated when one of the phosphino sites in MC replaces a weaker ligand (solvent or water) at cobalt, followed by rapid chelation to give **10** (a 15-electron system), a species we have not been able to observe. If the coordinated MC possesses a third, viable ligand, then **10** would give IV. If not, then **10** would be attacked by another MC to give I after chelation. Depending on how proficient is the third ligating site of MC in IV, species I is formed from IV, at widely varying rates (vide supra). Complex I is a 19-electron system and thus is labile; apparently, there is a steric kinetic stabilization as discussed above. With sufficient time and activation energy, either one or both halogens are lost to give II. Treatment of I with $CoHal_2$ rapidly transforms I into III, presumably with the cobalt halide acting as a Lewis acid to promote heterolysis. Complex III can also be formed rapidly from II and cobalt halide, and the reaction can be reversed, possibly via I, by addition of MC to III.

In summary, we have shown the interconnection of four macrocyclic phosphine-ligated cobalt(II) dihalide species. A number of 19-electron complexes have been isolated and characterized; the structure of these species is firmly based on a single-crystal X-ray structure determination. The stability of the octahedral 19-electron species is attributed to a steric shielding of the halogens to solvation. Pentacoordinate (tridentate MC)$CoHal_2$ are formed if the third ligand is sufficiently nucleophilic and sterically well-disposed to coordinate the metal center. Dialkyl ether oxygen will form such bonds if six-membered chelates are formed, but not seven-membered ones. Trialkylamino ligands impart much greater stability to the pentacoordinate species

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(16) The magnitude of this shift is reasonable; see: (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076.

(17) (a) Kelly, W. S. J.; Ford, G. H.; Nelson, S. M. *J. Chem. Soc. A* **1971**, 338. (b) Dalhoff, W. V.; Nelson, S. M. *Ibid.* **1971**, 2184.

(18) Kyba, E. P.; Davis, R. E.; Liu, S.-T.; Hassett, K. L., unpublished results. $11\text{-}P_2NH$ is the demethylated species corresponding to **4**.

(19) Davis, R. E.; Kyba, E. P., unpublished results.

than does the ether oxygen with the same chelate size.

Experimental Section

General Data. Proton magnetic resonance spectra were obtained on a Varian A-60, EM-390, Ft-80, or HA-100 instrument. Proton-decoupled phosphorus-31 nuclear magnetic spectra were determined on Varian FT-80[20] or Bruker WH-90 instruments. Chemical shifts are given as parts per million relative to 85% H_3PO_4 and are defined as negative for upfield shifts.

Infrared spectra were recorded on Perkin-Elmer 273B or Beckman IR7 grating spectrophotometers. Ultraviolet–visible spectra were obtained on a Cary-14 or -17 instrument.

Melting points were obtained with the use of a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The synthesis and characterization of the macrocycles used in this study have been described.[2e,g]

Synthesis of Type I Complexes. The following preparation of $(1)_2CoCl_2$ is typical of those for all the chlorides and bromides. A solution of cobalt(II) chloride hexahydrate (46 mg, 0.18 mmol) in THF (5 mL) was added to 1 (160 mg, 0.41 mmol) in THF (20 mL) at −10 °C in about 1 min. After 10 min, hexane (20 mL) was added, and after 30 min the complex $(1)_2CoCl_2{\cdot}(H_2O)_{2.5}$ (120 mg, 66%) was isolated as a yellow powder: mp 250–260 °C dec (yellow to green color change at ca. 170–180 °C).[21] Other pertinent data are given in Tables I and II.

The corresponding iodides were prepared similarly except that a solution of cobalt(II) iodide was prepared as follows. Cobalt(II) nitrate hexahydrate (50 mg, 0.31 mmol) in THF (5 mL) was added to sodium iodide (90 mg, 0.60 mmol) in THF (20 mL). The mixture was filtered, and the filtrate was purged with a gentle stream of nitrogen for 30 min prior to reaction.

Synthesis of Type II Complexes. The following procedure for $(1)_2CoCl_2$ (type II) is typical for all the chlorides. Type I $(1)CoCl_2{\cdot}(H_2O)_{2.5}$ (16 mg, 1.7×10^{-2} mmol) was dissolved in CH_2Cl_2 (5 mL) and allowed to stand at ambient temperature for 3 h, at which time the UV absorption at 320 nm had been replaced by one at 356 nm. The solvent was removed on a rotary evaporator, leaving a brown glass (16 mg, 100%), which was crystallized from hot chloroform–hexane (1:1, v/v, 6 mL) to give the type II complex as green crystals (8 mg, 50%): mp 270–280 °C dec; ^{31}P NMR ($CDCl_3$) δ 43.9 (br s). Other pertinent data are given in Tables I and II.

The corresponding bromides and iodides were obtained similarly except that the type I precursors were reacted in boiling chloroform for 24–36 h. The course of the reaction was followed by monitoring the disappearance of the UV absorption in the 300–315-nm region and the appearance of one in the 350–360-nm region.

Crude rate studies of the formation of type II complexes involved the preparation of 5.0×10^{-4} M solutions of the type I species and following the course of the reaction in the 300–320- and 350–360-nm region as described above. In CH_2Cl_2 at 25 °C the complexes $(MC)_2CoCl_2$ had $\tau_{1/2}$ as follows: **7**, <15 s; **2a**, **6**, ≃60 s; **1**, **3**, 30 min. The half-life at 25 °C of $(1)_2CoCl_2$ in THF, MeOH, and MeCN was ca. 15 h. The complexes $(1)_2CoBr_2$ and $(1)_2CoI_2$ had $\tau_{1/2}$ = 12 h in boiling CH_2Cl_2.

To a solution of $[(1)_2Co][CoCl_4]$ (5.2 mg, 5.0×10^{-3} mmol, see below) in CH_2Cl_2 (10 mL) at room temperature was added 1 (2.0 mg, 5.0×10^{-3} mmol), and the UV spectrum was determined within 5 min; it was identical with that of $(1)_2CoCl_2$ (type II).

Synthesis of Type III Complexes. The following is typical of all of the procedures for the tetrahalocobaltates. A solution of 1 (39 mg, 0.10 mmol) in THF (10 mL) was added to cobalt(II) chloride hexahydrate (24 mg, 0.10 mmol) in THF (1 mL). The solution was concentrated to 3 mL and cooled to 0 °C. The complex $[(1)_2Co][CoCl_4]$ was isolated as green microcrystals (32 mg, 62%): mp 250–260 °C; ^{31}P NMR ($CDCl_3$) δ 43.8 (br s). Other pertinent data are given in Tables I and II.

The same complexes could be prepared by the reaction of 1 equiv of cobalt(II) halide in THF with either type I or II complexes. The reactions were over in seconds after the reagents were mixed.

Synthesis of Type IV Complexes. The following procedure for $(3)CoBr_2$ is typical of all of the type IV species except $(3)CoCl_2$, a procedure for which follows that of the bromide.

(3)CoBr$_2$. The macrocycle 3 (62 mg, 0.16 mmol) in THF (10 mL) was added to anhydrous cobalt bromide (35 mg, 0.16 mmol) in THF (2 mL). The purple solution was concentrated to 5 mL, cooled to −20 °C and filtered to give a purple powder (50 mg, 51%). This was recrystallized from chloroform–hexane (4:1, v/v) to give $(3)\ CoBr_2{\cdot}CHCl_3$ as purple needles (40 mg, 40%). No ^{31}P NMR signal was observed for any of the type IV species. Pertinent data are given in Tables I and II.

(3)CoCl$_2$. A solution of cobalt(II) chloride hexahydrate (40 mg, 0.17 mmol) in ethanol (0.5 mL) was added to macrocycle 3 (67 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) at room temperature. The burgundy solution was concentrated at room temperature in a vacuum line to 1 mL, which led to the deposition of $(3)CoCl_2$ as a reddish purple powder (5 mg, 20%). Pertinent data are given in Tables I and II.

The melting decomposition ranges of the type IV complexes are as follows: $(3)CoCl_2$, 236–242 °C; $(3)CoBr_2$, 256–266 °C; $(3)CoI_2$, 255–265 °C; $(4)CoCl_2$, 228–232 °C; $(4)CoBr_2$, 200–204 °C; $(4)CoI_2$, 240–248 °C.

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Registry No. $(1)_2CoCl_2$ (type I), 83350-21-4; $(1)_2CoBr_2$, 83350-25-8; $(1)_2CoI_2$, 83350-27-0; $(1)CoCl_2$ (type II), 83350-29-2; $[(1)_2Co][CoCl_4]$, 83378-19-2; **(2a)**$_2CoCl_2$, 83350-22-5; **(2b)**$_2CoBr_2$, 83350-26-9; **(2b)**$_2CoCl_2$, 83350-30-5; **(3)**$_2CoCl_2$, 83350-23-6; **(3)**-CoBr$_2$, 83350-33-8; **(3)**CoI$_2$, 83350-34-9; **(4)**CoCl$_2$, 83350-35-0; **(4)**CoBr$_2$, 83350-36-1; **(4)**CoI$_2$, 83350-37-2; **(5)**$_2CoCl_2$, 83363-77-3; **(5)**$_2CoI_2$, 83350-28-1; **(6)**$_2CoCl_2$, 83350-24-7; [**(6)**$_2$Co][CoCl$_4$], 83350-32-7.

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[20] We are grateful for an NSF matching grant to E.P.K. and A. H. Cowley of this department, which enabled the purchase of this instrument.

[21] The melting points of the type I–IV complexes were all in the range of 250–280 °C and were accompanied by extensive color changes and decomposition. The onset of decomposition appeared to depend on, inter alia, the heating rate, and thus this physical property is not a useful identifying characteristic of these types of complexes.